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Acoustical Studies On Molecular Interactions Inbinary Liquid Mixtures At 308 K Through Ultrasonic Measurements

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Abstract:
Molecular interaction studies using ultrasonic technique in the binary liquid mixtures of Chlorobenzene+Ibmk IBMK+Cyclohexanol,IBMK+Acetophenone at 308k have been carried out at 308k. Using the measured values of ultrasonic velocity, density and viscosity, acoustical parameters and their excess values are evaluated. From the properties of these excess parameters the nature and strength of the interactions in these binary systems are discussed.

Keywords: *Acoustical Parameters, Binary system, Molecular interactions, Ultrasonic velocity. adiabatic compressibility, inter-molecular free length, internal pressure, dipole-dipole interactions,induced dipole-induced dipole interactions.*

1.Introduction

The ultrasonic investigations of pure liquids and liquid mixtures consisting polar non polar components are considerable importance in analyzing intermolecular interaction between component molecules[1-3]. These studies find several applications in industries. Such studies as variations in concentration and temperature are useful in giving insight in to structure and various bonding of associated molecular complexes [4-6] and other related molecular processes. Ultrasonic velocity and related thermodynamic parameters helps us for characterizing thermodynamic and physico-chemical aspects of binary liquid mixtures such as molecular association and dissociation [7-8].

Thermodynamics studies of binary liquid mixtures have attracted much attention of scientists.These physico-chemical analyses are used to handle the mixtures of hydrocarbons, alcohols, aldehydes, ketenes etc.The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values [9-12]. These excess values of ultrasonic velocity, adiabatic compressibility, molar volume and viscosity in binary liquid mixture are useful in understanding the solute-solvent interactions.

The study of molecular association in binary liquid mixture having alcohol as one of component is of particular interest since alcohols are strongly self associated liquids having three dimensional network of hydrogen bonding and can be associate with any other group having some degree of polar attraction [13-16]. The variation in ultrasonic velocity gives information about the bonding between molecules and formation of complexes at various concentration and temperature through molecular interactions [17-20]. In order to have clear understanding of intermolecular interaction between component molecules of an attempt has been made to study the ultrasonic behaviors of IBMK in binary liquid mixture at 308k temperature.

In recent years ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids and solids owing to its ability of characterizing physico chemical behavior of the medium. The present investigation deals with the study of molecular interaction in 3 binary liquid mixtures are

- SYSTEM; 1 Chlorobenzene+Ibmk
- SYSTEM;2 IBMK+Cyclohexanol,,
- SYSTEM;3 IBMK+Acetophenone at 308K

Departure from linearity in the velocity versus concentration in liquid mixtures is taken as an indication of the existence of interaction between the different species. The physical and chemical properties of liquid mixtures have been studied by numbers of workers [21,22] and they correlated the non-linear variation of ultrasonic velocity, compressibility and other related parameters with structural changes occurring in a liquid as its concentration is varied in a liquid mixture.

The intermolecular forces responsible for the molecular interactions can be classified as long range forces and Short range forces. The long range forces are the electrostatic induction and dispersion forces and they arise when the molecules come close enough together causing significant overlap of electron clouds and are often highly directional.

The non-linear variation of adiabatic compressibility of the solution with concentration of the solute was qualitatively described to hydrogen bonding and their result confirms that the sign and magnitude of such deviation depends on the strength of interaction between unlike molecules.

Though spectroscopic methods play a major role in the molecular interaction studies, the non-spectral studies such as calorimetric, magnetic, ultrasonic velocity and viscosity measurements have also been widely used, in the elucidation of the formation of complexes.

In this report we have evaluated the acoustic Parameters, namely the Adiabatic Compressibility (β), Free Length (L_f), Free volume (V_f), Internal Pressure (πi), Relaxation Time(τ),Acoustic Impedance(Z)and Gibb's free energy(ΔG*) for three binary mixtures are

- SYSTEM; 1 Chlorobenzene+Ibmk
- SYSTEM;2 IBMK+Cyclohexanol,,
- SYSTEM;3 IBMK+Acetophenone at 308k

The results are discussed in terms of molecular interactions.

2.Experimental Techniques

2.1.Aspects In Theoretical

2.1.1.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.

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

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

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

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,

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

Where K_T is the temperature dependent constant.

2.3. 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 [24].Eyring and Kincaid [25] 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 (η) as

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

Where M_{eff} is the effective molecular weight –

$$= \sum \boldsymbol{M_i X_i}$$

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 4.28×10^9 for all liquids.

2.4. 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 [26].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 [27] 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 [5] is

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

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

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

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

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

The final equation for the evaluation of internal pressure can be obtained by combining and

rearranging the equations (6) and (7)

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

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.

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

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

2.6. Acoustic Impedance (Z)

The Specific acoustic impedance is given by

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

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

2.7. Gibb's Free Energy (ΔG)*

The relaxation time for a given transition is related to the activation free energy. The variation of KTwith temperature can be expressed in the form of Eyring salt process theory.

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

The above equation can be rearranged as,

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

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

2.8. Excess Parameter

The excess values are calculated by using the formula,

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

Where, Aid=$\sum$ AiX i, where Ai is any acoustical parameter and Xi is the mole fraction of liquid component.

3.Experimental

3.1. 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,

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

Where,

W_1, is the weight of the distilled water.

W_2, is the weight of the experimental liquid

ρ_1 is the density of water.

ρ_2 is the density of experimental liquid.

3.2.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 stopwatch with an accuracy of 0.1 sec. Viscosity was determined using the relation

$$\eta_2 = \eta_1 \left(\frac{t_2}{t_1}\right)\left(\frac{\rho_2}{\rho_1}\right) \qquad (14)$$

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.

3.3.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 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 0.01mmat 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(ρ), viscosity(η), ultrasonic velocity (u) for the three binary

systems chlorobenzene+IBMK,IBMK+cyclohexanol,,IBMK+Acetophenone at 308K are given in the tables 1, 2, 3.The parameters adiabatic compressibility (β_{ad}), free length (Lf), free volume (Vf), acoustic impedance (Z), internal pressure(π_i) relaxation time (τ) at 308K are listed in tables 1, 3,7.

4.1.System:-1 Chlorobenzene + Ibmk

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	0.7637	0.5428	508.40	388.2401	8.7944	0.0000
0.0506	0.9494	0.8013	0.6011	592.40	474.6707	9.5276	0.0529
0.1037	0.8963	0.8055	0.6106	628.80	506.5073	9.8847	0.0150
0.2019	0.7981	0.8418	0.6116	780.80	657.2898	11.7188	0.0773
0.3045	0.6955	0.8444	0.6202	868.80	733.6538	13.1291	0.0409
0.3991	0.6009	0.8890	0.6460	993.20	882.9930	15.8207	0.0610
0.5094	0.4906	0.9137	0.6926	1153.20	1053.6921	21.4861	0.0938
0.6059	0.3941	0.9442	0.7158	1268.00	1197.3083	28.9157	0.0953
0.7042	0.2958	0.9790	0.7191	1385.60	1356.5500	44.7761	0.0971
0.8055	0.1945	1.0154	0.7298	1442.00	1464.2605	60.7595	0.0513
0.9016	0.0984	1.0474	0.7527	1569.60	1643.9847	315.7895	0.0645
1.0000	0.0000	1.0687	0.7681	1580.00	1688.5886	480.0000	0.0000

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 Chlorobenzene+ IBMK at 308 K.

4.2.SYSTEM:-1 Chlorobenzene - IBMK

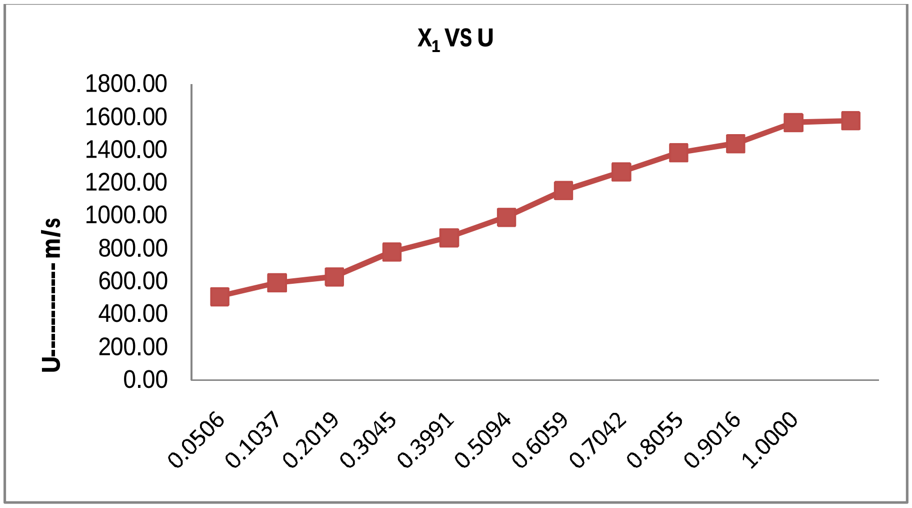

Figure 1: Molefraction vs U
Mole fraction of first component

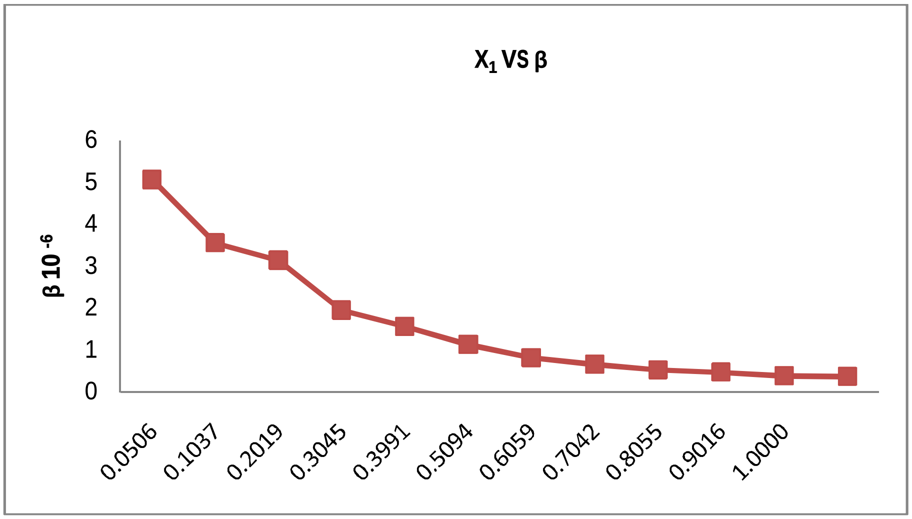

Figure 2: Molefraction Vs B
Mole Fraction Of First Component

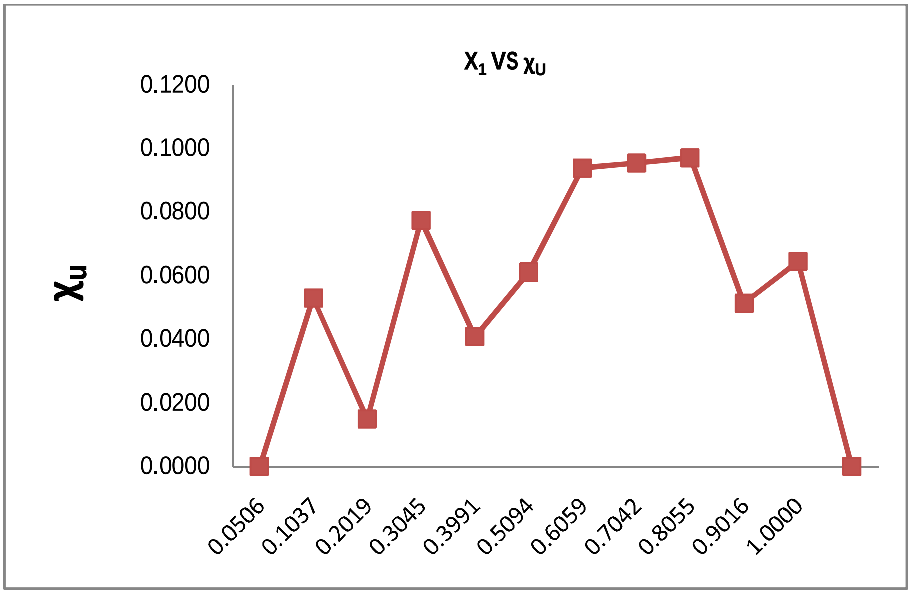

Figure 2: Molefraction vs χ_u
Mole fraction of first component

4.3.SYSTEM:-1 Chlorobenzene – IBMK

$\beta_s 10^{-10}$ $(T.Pa)^{-1}$	$\tau 10^{-6}$ (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)
35.56	2.8502	0.1118	0.0000	0.0000	0.0000	217.2169	0.0000
31.4	2.5562	0.1206	4181.7276	525.9989	0.1683	196.4480	3.0882
19.5	1.5891	0.1694	4074.2113	513.1033	0.1350	190.1739	3.0681
15.7	1.2974	0.1984	3716.3508	453.2271	0.0562	166.9419	2.9803
11.4	.9821	0.2320	3504.3769	431.3250	0.0367	158.0150	2.9428
0.823	.7600	0.2666	3416.6108	403.9375	0.0231	144.0340	2.8915
0.658	.6286	0.2975	3293.6937	383.8205	0.0143	131.8521	2.8441
0.532	.5101	0.3433	3221.5940	367.3597	0.0103	123.6918	2.8091
0.473	.4608	0.3626	3123.0564	347.3587	0.0072	116.2053	2.7705
0.388	.388947	0.3995	3118.0487	338.2262	0.0062	111.8496	2.7517
0.375	.3838	0.3979	3059.9708	325.2813	0.0046	105.5589	2.7204
35.5	2.8502	0.1118	3083.0352	324.7101	0.0046	104.1554	2.7180

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 chlorobenzene+ IBMK at 308 k.

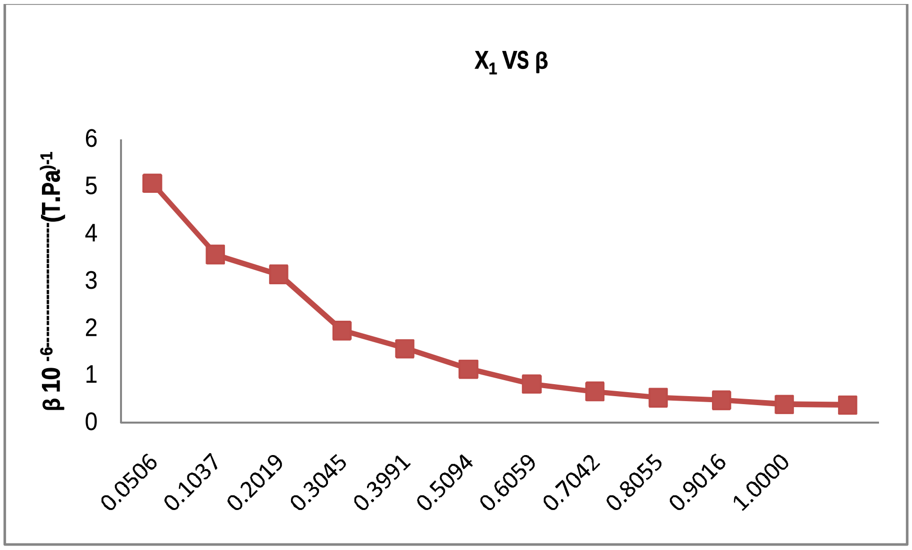

Figure 3: Molefraction vs β

Mole fraction of first component

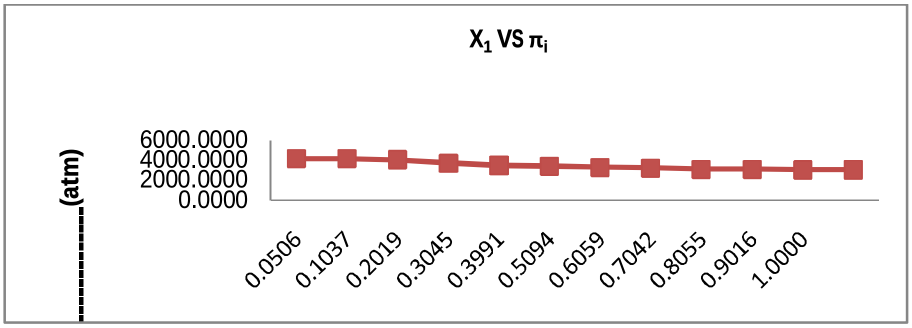

Figure 4: Molefraction vs π_i
Mole fraction of first component

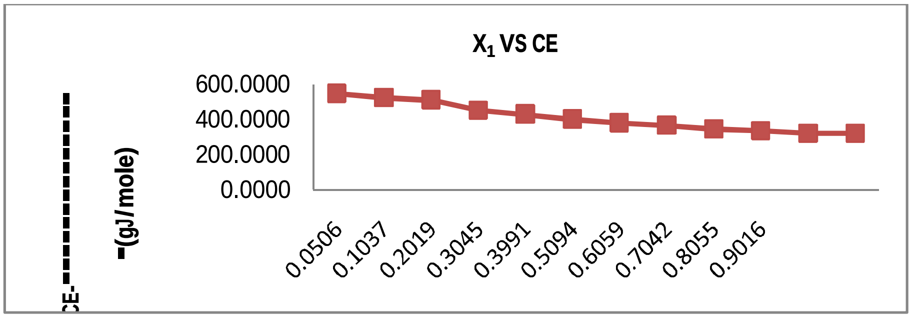

Figure 5:Molefraction vs CE

Mole fraction of first component

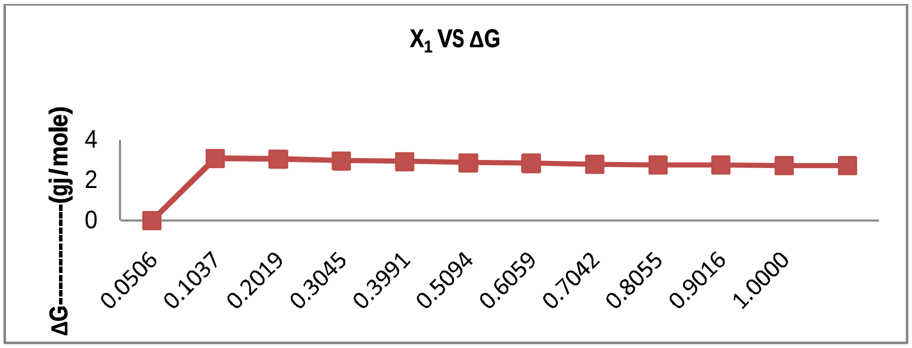

Figure 6: Mole fraction vs $\Delta G^{\neq}$
chlorobenzene+ IBMK
Mole fraction of first component

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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^{-6} ($g\text{-}^1ms^2$)**	**V_F^E (cm^3)**	**LF^E (cm)**
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
29.8	0.0469	-10.2703	20.6329	-0.8814	3.56	-201.3230	-15.0480
9.3	0.0444	-13.0383	-16.5789	0.4664	3.14	-412.5937	-15.3185
56.0	0.0234	-27.0426	6.5094	-1.3104	1.95	-803.2725	-27.4479
34.1	0.0088	-33.2351	-50.5424	2.1228	1.57	-1211.4785	-24.7747
57.1	0.0132	-44.6457	-24.2162	-0.6047	1.14	-1587.8485	-28.0600
98.9	0.0350	-56.9419	3.0545	0.1791	0.823	-2026.6864	-27.7713
110.3	0.0365	-65.8222	21.1870	-0.1530	0.659	-2410.6190	-25.0212
122.6	0.0176	-74.5795	52.6045	-0.7497	.532	-2801.6989	-21.3937
70.4	0.0055	-78.7717	28.5897	-1.2228	0.474	-3204.7418	-14.2962
95.0	0.0068	-87.4637	83.3504	-1.2341	0.388	-3587.0770	-9.7217
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

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 (LF^E)and Excess free volume (VF^E) Values at various mole fractions of chlorobenzene+ IBMK at 308K

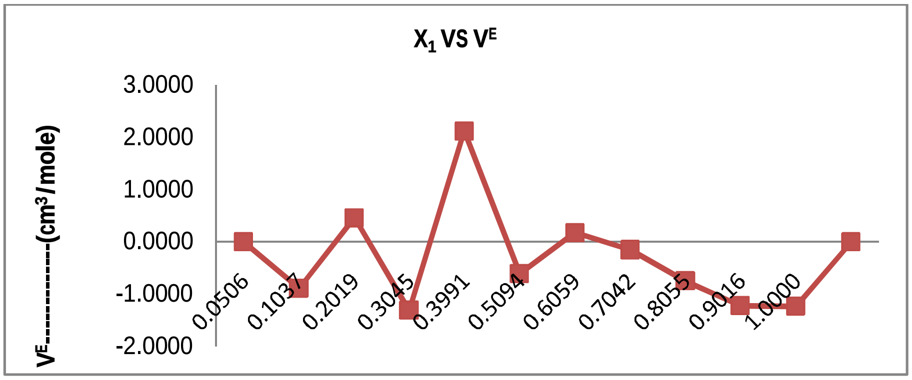


Figure 7: Molefraction vs V^E

Mole fraction of first component

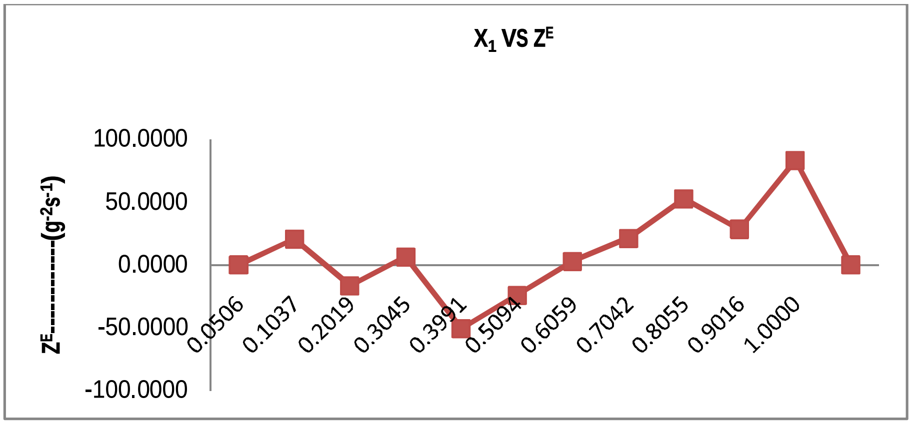


Figure 8: Mole fraction vs Z^E

Mole fraction of first component

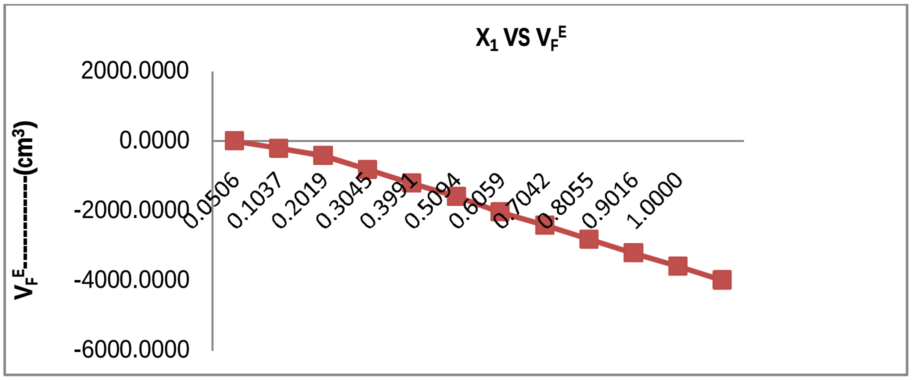


Figure 9: Mole fraction vs V_F^E

chlorobenzene+ IBMK

Mole fraction of first component

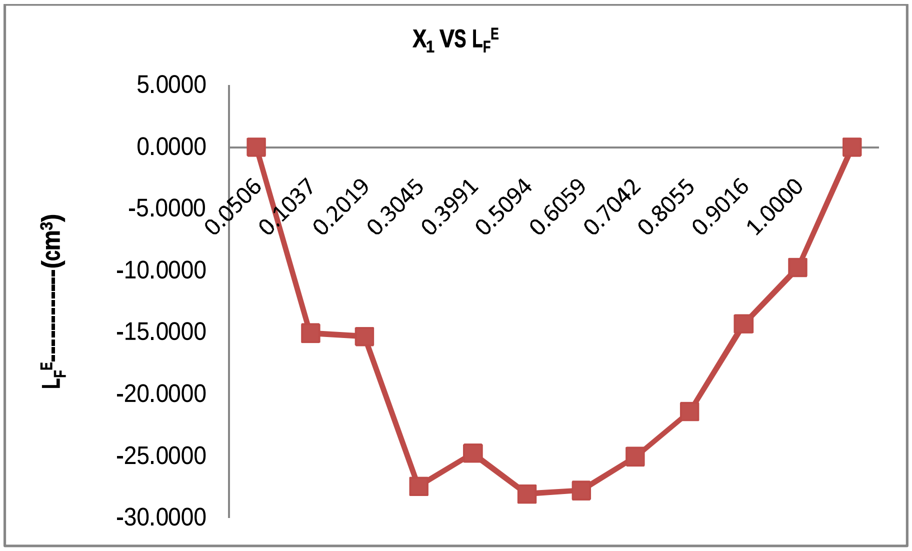


Fig.10 Mole fraction vs L_F^E
chlorobenzene+ IBMK
Mole fraction of first component

4.3.SYSTEM-2 IBMK+CYCLOHEXANOL

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	0.9400	9.1057	1376.00	1293.4434	42.8571	0.0000
0.0646	0.9354	0.9298	8.9112	1404.00	1305.4385	48.9796	0.0287
0.1259	0.8741	0.9200	8.0596	1368.00	1258.5615	41.3793	0.0101
0.1741	0.8259	0.9123	7.2280	1347.00	1228.8625	37.9447	0.0007
0.3015	0.6985	0.8921	6.3076	1324.00	1181.1301	34.7826	-0.0001
0.3649	0.6351	0.8827	5.5262	1302.00	1149.2732	32.2148	-0.0086
0.4968	0.5032	0.8626	4.6885	1278.00	1102.3975	29.8137	0.0950
0.5916	0.4084	0.8489	3.7197	1256.00	1066.2238	27.9070	-0.0143
0.7127	0.2873	0.8319	2.2121	1237.00	1029.0555	26.4463	-0.0131
0.8478	0.1522	0.8139	1.1315	1225.00	997.0237	25.6000	-0.0042
0.9245	0.0755	0.8000	1.0806	1212.00	969.5425	24.7423	-0.0041
1.0000	0.0000	0.7937	0.3945	1204.00	955.6189	24.2424	0.0000

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+_CYCLOHEXANOl at 308 K

4.4.SYSTEM-2 IBMK+CYCLOHEXANOL

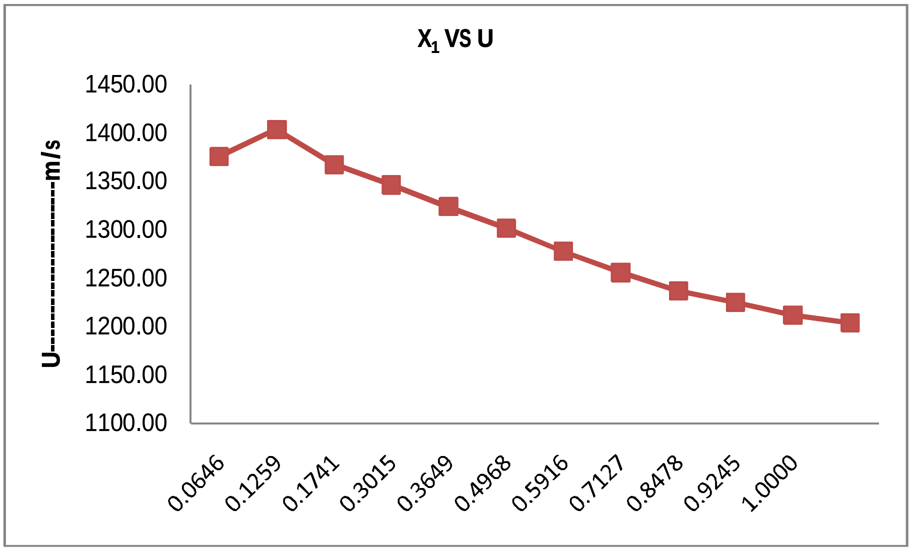


Figure 12: Mole fraction vs U

Mole fraction of first componet

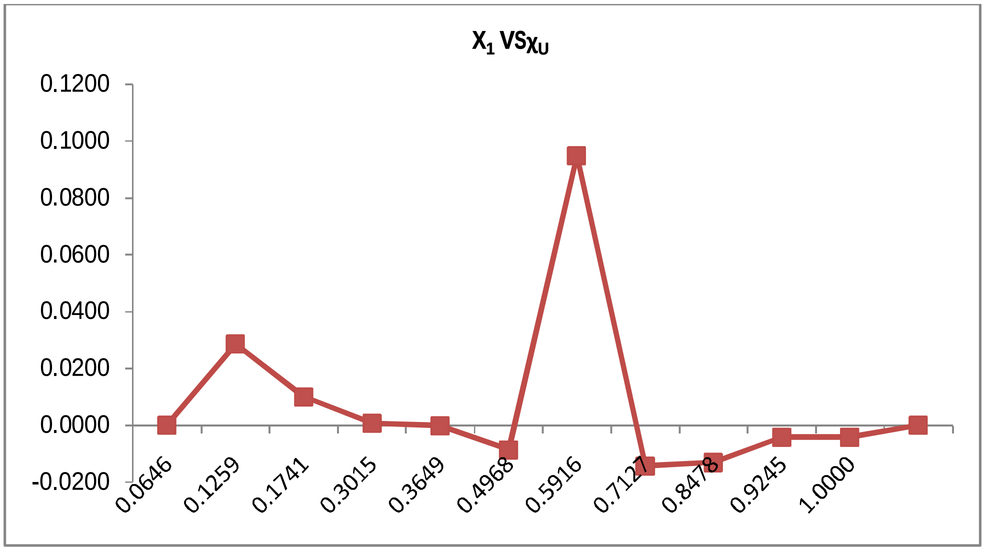


Figure 13: Mole fraction vs χ_U

Mole fraction of first component

β_{10}^{-12} $(T.Pa)^{-1}$	$\tau 10^{-6}$ (s)	V_f (ml/mole)	π_i (atm)	CE (gJ/mole)	$\alpha/f^2 10^{3}$ (NPm^1s^2)	L_f $(T.Pa)^{-1}$	$\Delta G^{\#}10^{-20}$ (Gj/mole)
56.18	6.8216	0.0066	11965.9158	1274.9777	1.4197	119.0063	3.2493
54.56	6.4826	0.0071	11633.8271	1253.1974	1.2499	118.4583	3.2399
58.08	6.2415	0.0079	11129.7093	1211.6640	1.1303	120.6442	3.2329
60.41	5.8221	0.0091	10562.3319	1159.6082	0.9644	122.0934	3.2201
63.94	5.3779	0.0109	9804.7692	1100.8189	0.7810	124.5360	3.2054
66.83	4.9241	0.0129	9189.4914	1042.7207	0.6388	126.2502	3.1892
70.98	4.4371	0.0161	8413.2523	976.8919	0.4915	128.9065	3.1699
74.67	3.7034	0.0222	7478.9073	882.4095	0.3299	131.0749	3.1365
78.56	2.3170	0.0473	5733.7076	690.3324	0.1232	133.4211	3.0499
81.88	1.2352	0.1275	4061.0914	499.7656	0.0333	135.5473	2.9338
85.10	1.2261	0.1345	3944.2142	493.8441	0.0315	137.4549	2.9324
86.91	.45716	0.6036	0.0000	0.0000	0.0000	138.4527	2.7502

Table 5: adiabatic compressibility(β), relaxation time(τ), free volume(V_f), internal pressure(π_i), cohessive force(CE), absorption co-efficient(α/f^2), free length(L_f)& activation energy($\Delta G^{\#}$) values at different molefraction of IBMK+ CYCLOHEXANOl at 308 K.

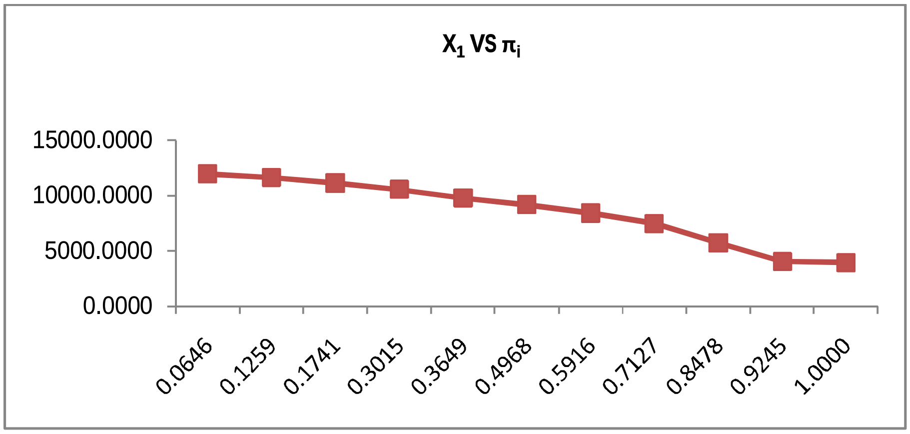


Figure 14: Mole fraction vs π

Mole fraction of first component

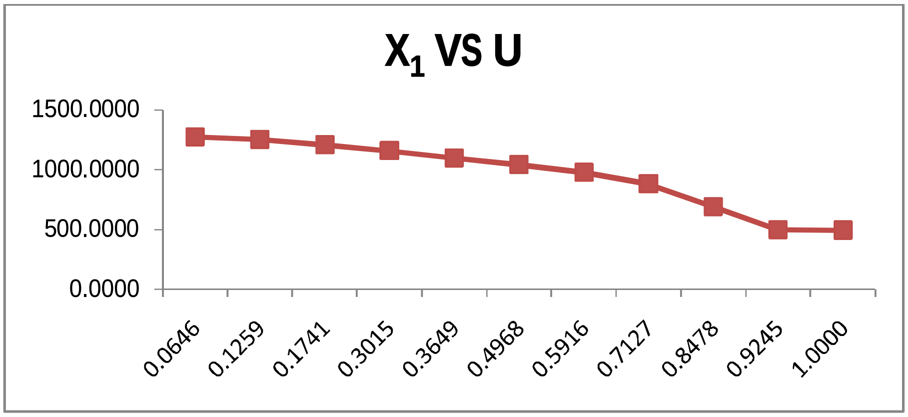
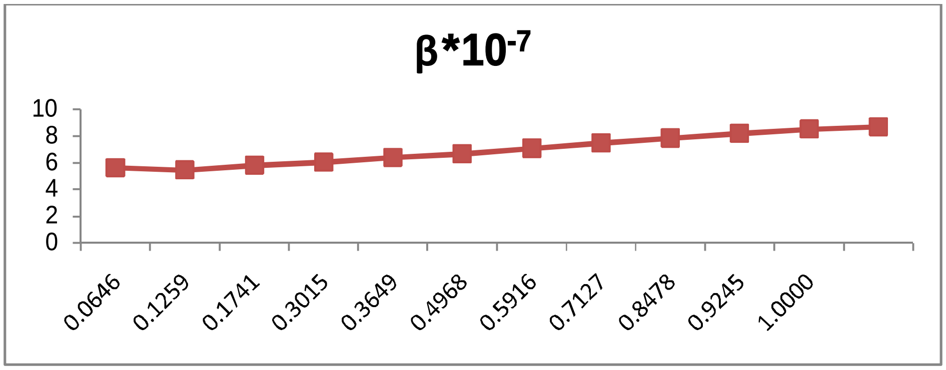


Figure 15: Mole fraction vs CE

Mole fraction of first component



Figur 16: Mole fraction vs β

Mole fraction of first component

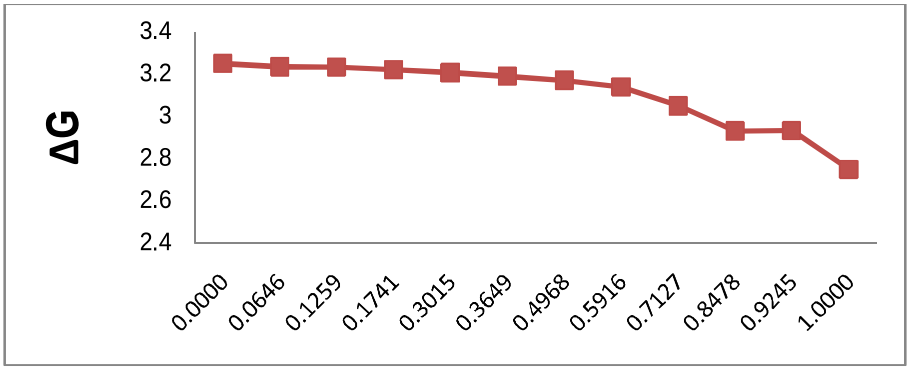


Figure 17: Mole fraction vs ΔG

Mole fraction of first component

U^E (m/s)	η^E (NS/cm^2)	VA^E (cm^3)	Z^E $(g^{-2}s^{-1})$	V^E $(cm^3/mole)$	$\beta^E 10^{-9}$ $(g^{-1}ms^2)$	V_F^E (cm^3)	LF^E (cm)
0.0000	0.0000	0.0000	0.0000	0.0000	.0678	0.0000	0.0000
39.1112	-7.6132	-2.7754	33.8186	-0.0999	-.360	-0.0381	-1.8042
13.6548	-7.0890	-1.1855	7.6502	-0.1565	-.197	-0.0738	-0.8104
0.9452	-6.6768	-0.3976	-5.7657	-0.1837	-.112	-0.1014	-0.2985
-0.1420	-5.5872	-0.4690	-10.4592	-0.1995	-.150	-0.1757	-0.3334
-11.2372	-5.0443	0.2629	-20.8981	-0.2499	-5.64	-0.2115	0.1479
110.8453	-3.9154	0.3451	-23.2147	-0.1961	-4.67	-0.2871	0.2392
-18.2448	-3.1032	0.7976	-27.3626	-0.1853	3.13	-0.3376	0.5641
-16.4156	-2.0653	0.7702	-23.6204	-0.1515	4.77	-0.3847	0.5553
-5.1784	-0.9064	0.0931	-10.0121	-0.1423	-3.57	-0.3852	0.0544
-4.9860	-0.2522	0.3618	-11.5821	0.4965	5.10	-0.4241	0.4704
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

Table 6: *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 (LF^E)and Excess free volume (VF^E) values at various mole fractions of IBMK+ CYCLOHEXANOl at 308K.*

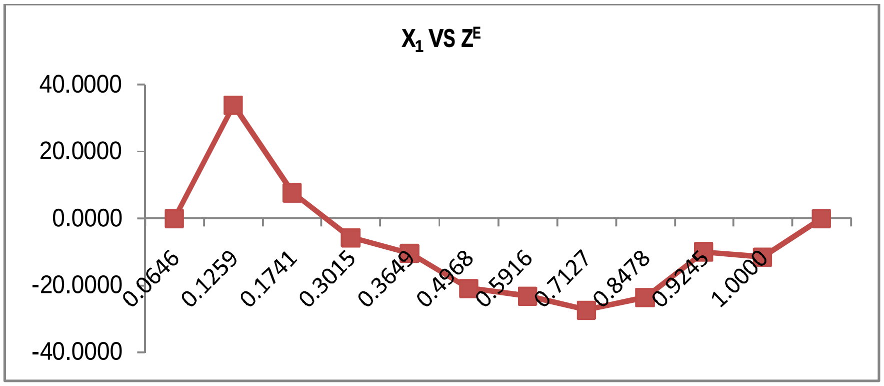


Figure 18:Mole fraction vs Z^E

Mole fraction of first component

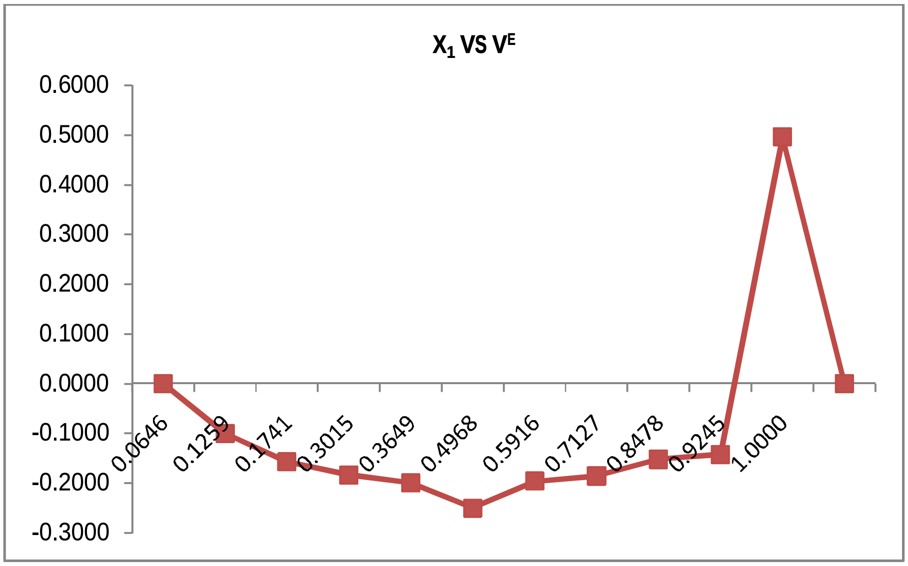


Figure 19: Mole fraction vs V^E

Mole fraction of first component

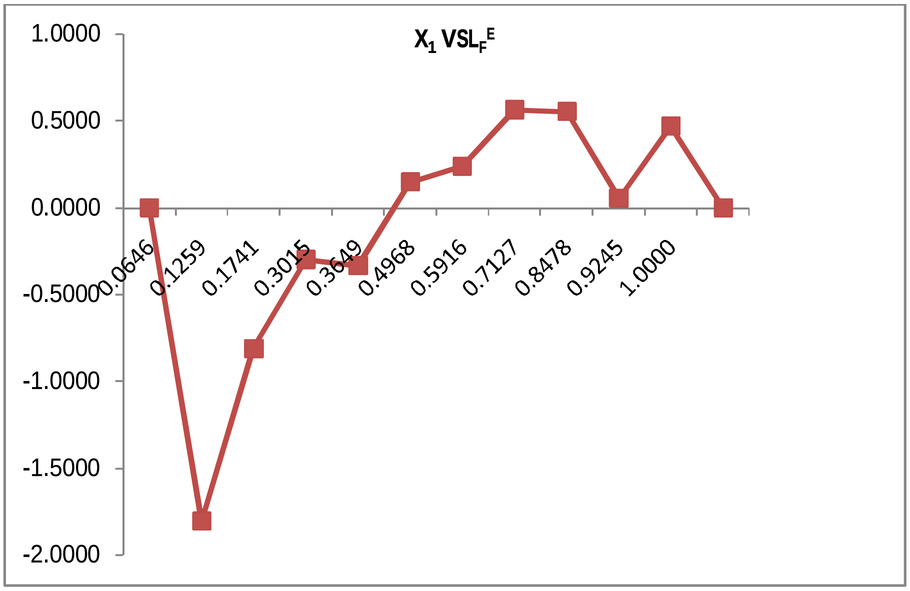


Figure 20: Mole fraction vs L_F^E

Mole fraction of first component

4.4.SYSTEM-3 IBMK+ACETOPHENONE

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	1.0040	0.7215	1444.00	1449.79	53.6313	0.0000
0.0681	0.9319	0.940	0.6986	1404.00	1395.58	61.5385	0.0268
0.1214	0.8786	0.9764	0.6706	1377.00	1344.51	48.9796	0.0066
0.1861	0.8139	0.9463	0.5889	1353.00	1280.35	43.0493	-0.00261
0.3156	0.6844	0.9306	0.5177	1333.00	1240.49	38.8664	0.00035
0.3854	0.6146	0.9014	0.4403	1309.00	1179.93	35.9551	-0.0033
0.5124	0.4876	0.8861	0.4175	1288.00	1141.29	32.9897	-0.0006
0.5797	0.4203	0.8551	0.3804	1263.00	1079.99	30.7692	-0.00556
0.7189	0.2811	0.8244	0.3522	1243.00	1024.73	28.4866	-0.0016
0.8586	0.1414	0.8102	0.3220	1220.00	988.44	26.8908	0.0067
0.9179	0.0821	0.7937	0.3945	1204.00	955.62	25.2632	-0.0014
1.0000	0.0000	1.0040	0.7215	1444.00	1449.79	24.2424	0.0000

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 IBMK+ACETOPHENONE at 308 K

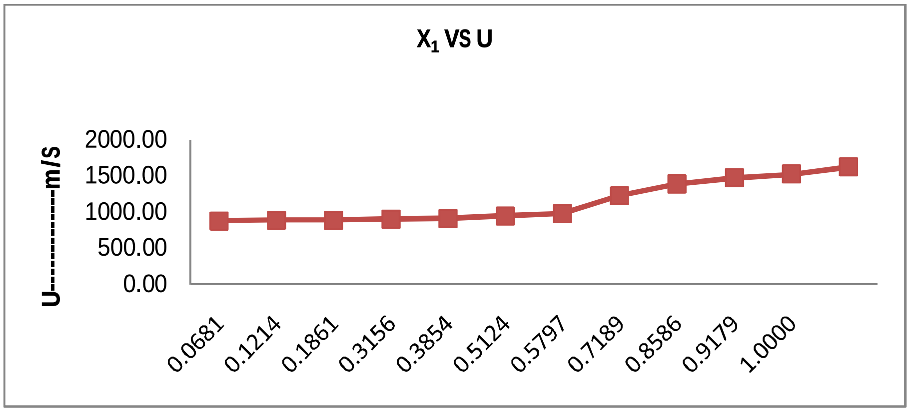


Figure 21: a) Mole fraction vs U

Mole fraction of first component

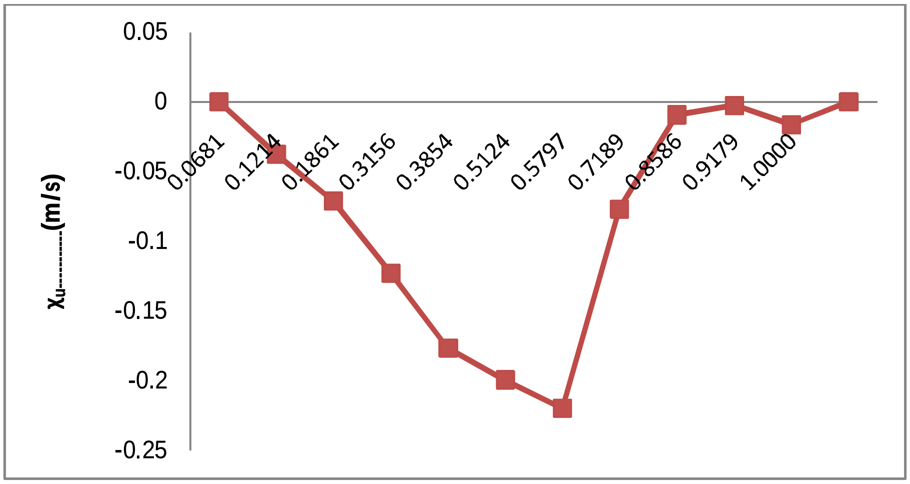


Figure 21: b) Mole fraction vs χ_u

Mole fraction of first component

β 10^{-12} $(T.Pa)^{-1}$	τ 10^{-7} (s)	V_f (ml/mole)	π_i (atm)	CE (gJ/mole)	α/f^2 10^{3} (NPm^1s^2)	L_f $(T.Pa)^{-1}$	$\Delta G^{\#}$ 10^{-20} (gj/mole)
48.59	5.4158	0.3296	3045.3442	358.9771	7.0692	112.4605	2.7815
47.77	4.5951	0.4140	2815.6019	333.1236	5.0455	112.4064	2.7511
51.03	4.7538	0.4110	2820.5481	334.0448	5.3874	114.5690	2.7574
54.01	4.8295	0.4175	2793.1674	333.0614	5.4726	116.7244	2.7603
57.73	4.5326	0.4777	2654.8239	319.3693	4.7224	119.6134	2.7486
60.48	4.1744	0.5564	2515.9073	303.9911	3.9645	121.5199	2.7334
64.75	3.8009	0.6670	2354.0765	287.0192	3.2183	124.5995	2.7161
68.02	3.7868	0.6922	2317.7882	283.9533	3.1590	126.6909	2.7154
76.43	3.7183	0.7432	2248.9377	278.1825	2.9781	130.2366	2.7120
78.51	3.6867	0.7825	2196.3225	274.3474	2.8615	133.7021	2.7105
82.93	3.5602	0.8554	2123.8372	266.8362	2.6327	136.1347	2.7040
86.91	4.5716	0.6035	2378.8592	300.1660	4.2975	138.4527	2.7502

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

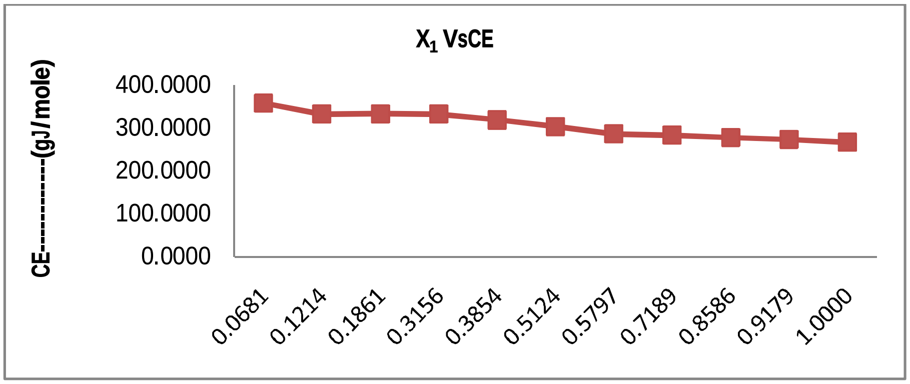


Figure 22: Mole fraction vs CE

Mole fraction of first component

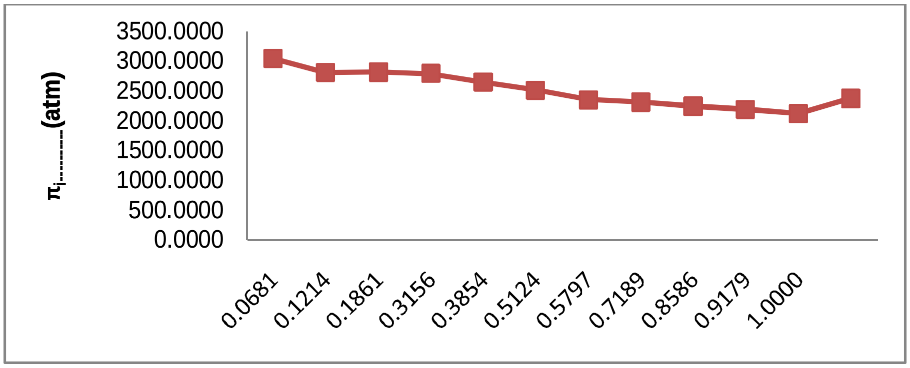


Figure 23: Mole fraction vs π_i

Mole fraction of first component

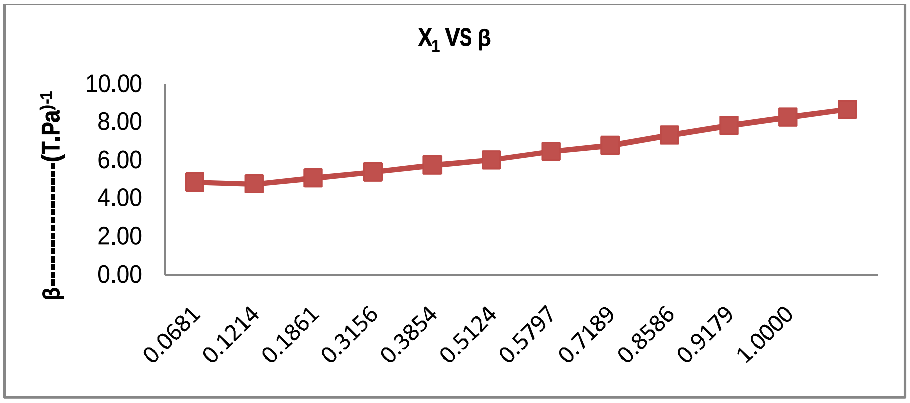


Figure 24: Mole fraction vs β

Mole fraction of first component

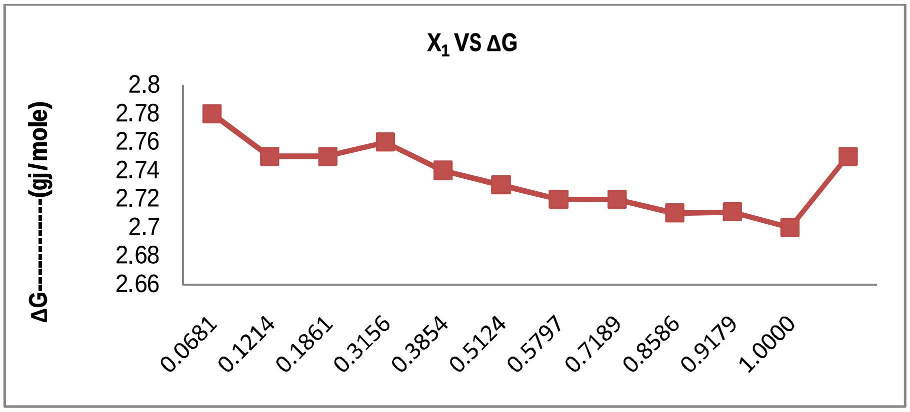


Figure 25: Mole fraction vs ΔG

Mole fraction of first component

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)
0.0000	0.0000	0.0000	0.0000	0.0000	.000817	0.0000	0.0000
37.7777	0.1981	-2.8806	34.9532	-0.1272	-3.43	0.0657	-1.8242
9.3438	0.2116	-0.8698	7.0027	-0.4508	-2.20	0.0481	-1.0470
-3.6163	0.2226	0.0741	-12.1805	-0.1793	-1.70	0.0369	-0.5732
0.4852	0.2496	-0.3107	-12.5291	-0.1987	-2.95	0.0617	-1.0502
-4.3682	0.2648	0.0221	-17.9924	-0.2486	-2.88	0.1212	-0.9580
-0.8092	0.2916	-0.2573	-15.9709	-0.2068	-3.48	0.1971	-1.1794
-7.2051	0.3060	0.2430	-21.4418	-0.1797	-2.77	0.2038	-0.8373
-1.9987	0.3365	-0.1048	-14.1437	-0.1513	-2.83	0.2167	-0.9097
8.3162	0.3675	-0.8075	-0.5645	-0.0945	-2.98	0.2177	-1.0753
-1.8157	0.3794	0.0908	-7.6369	0.1395	-.838	0.2744	-0.1840
0.0000	0.0000	0.0000	0.0000	0.0000	.00381	0.0000	0.0000

Table 9: 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 (LF^E)and Excess free volume (VF^E) values at various mole fractions of IBMK+ACETOPHENONE at 308K.

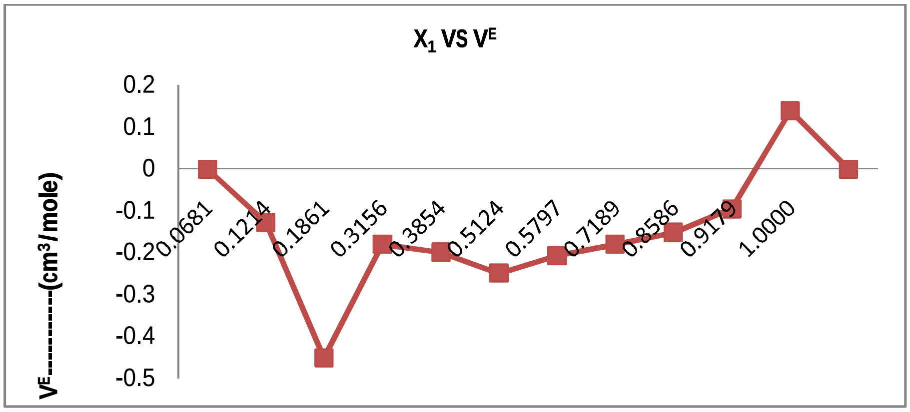


Figure 26: Mole fraction vs V^E

Mole fraction of first component

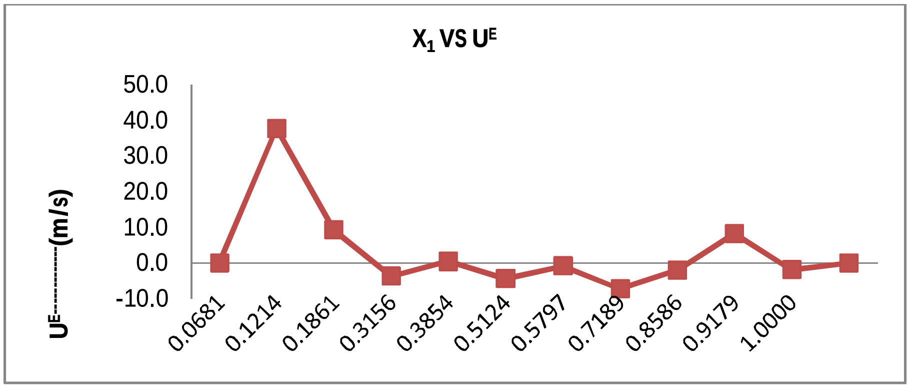


Figure 27: Mole fraction vs U^E

Mole fraction of first component

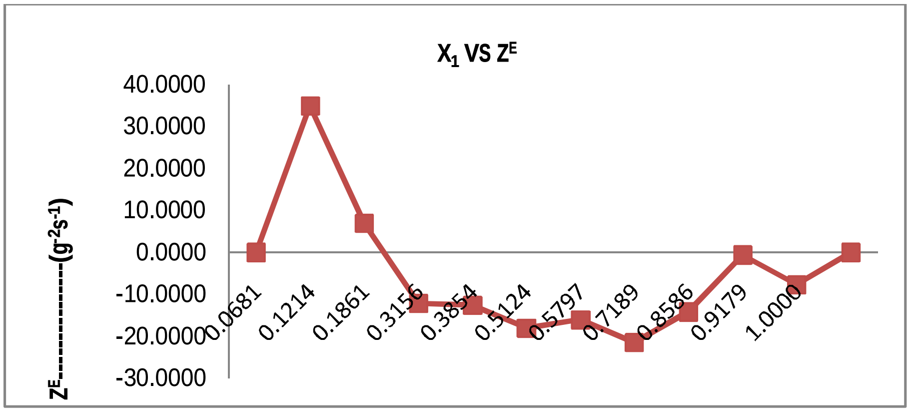


Figure 28: Mole fraction vs Z^E

Mole fraction of first component

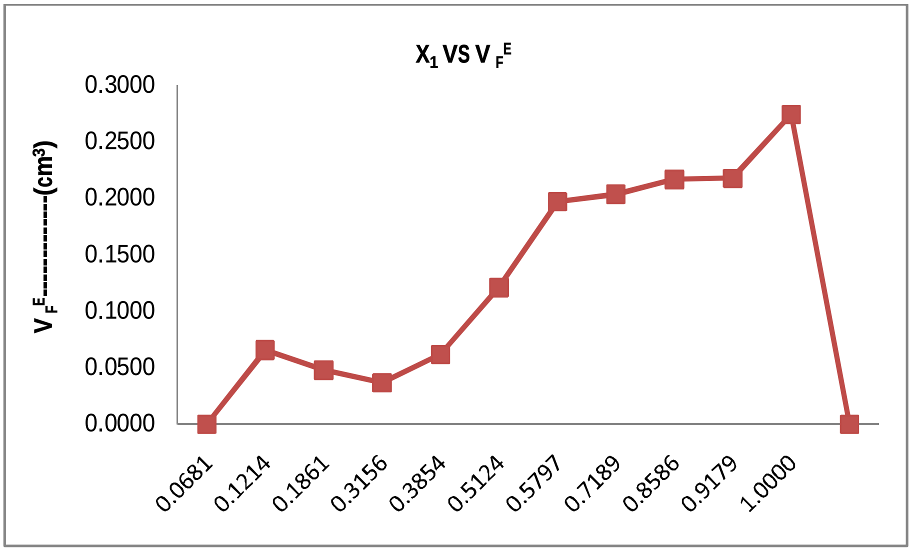


Figure 29: Mole fraction vs V_F^E

Mole fraction of first component

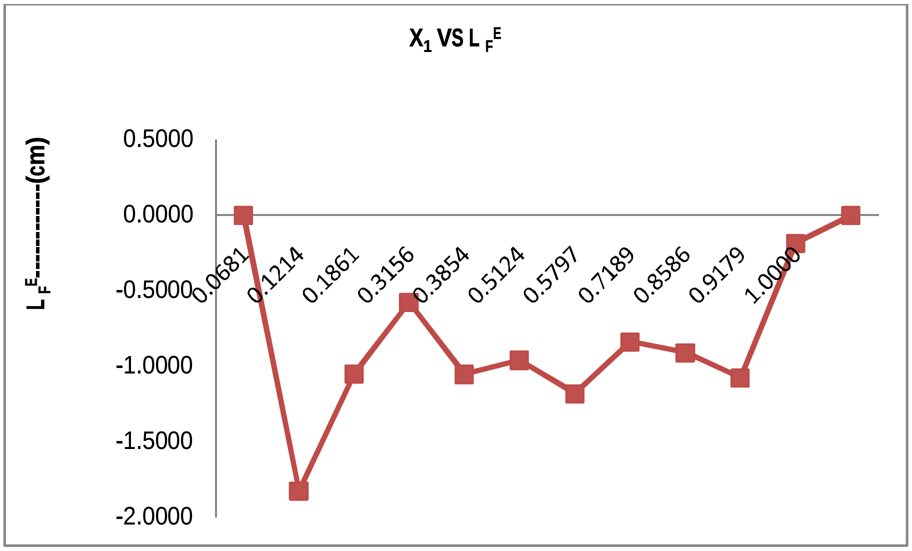


Figure 30: Mole fraction vs L_F^E

Mole fraction of first component

From the tables 1 ,4 &7,it is noted that the density decreases with increase in mole fraction for Ibmk+cyclohexanol,Ibmk+Acetophenone except chlorobenzene+Ibmk. Ultrasonic velocity and viscosity decreases with increase in mole fraction of the solute in system 1&2 except chlorobenzene+Ibmk system.

From the tables 1 ,4 &7 The corresponding plots are given in Figs-1,11,21-. ,it is noted that the

decrease in velocity is due to the increase in free length and adiabatic .The decrease in velocity is due to the increase in free length and adiabatic compressibility of the liquid mixtures system 1&system 2 except chlorobenzene+Ibmk . It is observed that for a given concentration as the number of CH group or chain length increases, the sound velocity increases.

From the tables 2 ,5 &8 , The corresponding plots are given in Figs- 2,12,22-. ,it is noted that the adiabatic compressibility and free length increases with increase of mole fraction in system 2&3 except chlorobenzene+Ibmk 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.

The internal pressure, free volume values are tabulated in 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.

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 [28] and in such a situation it is suggested that the molecules get rearranged due to co-operative process[29].

The Gibb's Free energy decreases with increasing mole fraction of all the systems.

From the table1,3&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&3 than system 1. It is suggested that dipole-dipole interactions stronger than 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. It is seen that 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 2 & 3 . This indicates that the attractive forces between the molecules of components are stronger than the intermolecular attractions in chlorobenzene+Ibmk.

FromtheTable3,6,9Showsthevaluesofexcessadiabaticcompressibility(β^E),excessfreeleng h(L_f^E)excessfreevolume(V_f^E)for crhlorobenzene+Ibmk system than Ibmk+cyclohexanol,Ibmk+Acetophene system at 308 K. From the Table 3,6,&9, it is observed that as the concentration of cyclohexanone 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 for the chlorobenzene+Ibmk system than that of Ibmk+cyclohexanol,Ibmk+Acetophenone system.

This indicates that the less interaction in the chlorobenzene+Ibmk and Ibmk+cyclohexanol than Ibmk+Acetophenone system. The possible reason may be as follows, in the chlorobenzene+Ibmk, the closeness of –CH to –C l group shows the presence of two types of effect. One is the increase of electron density in the -Cl bond and the other is the resonance effect. These two effects slightly decreasein the strength of the intermolecular hydrogen bond formation in chlorobenzene+Ibmk system than Ibmk+Acetophenone system. Hence from these factors, there is less intermolecular hydrogen bond formation and slightly less dipole-dipole interaction in chlorobenzene+Ibmk system.But in the case of cyclohexanol is non polar and more polar interaction in acetophenone+Ibmk.

5.Conclusion

The computed acoustical parameters and their values point to the specific molecular interaction in the liquid mixtures chlorobenzene+Ibmk and Ibmk+cyclohexanol lesser than Ibmk+Acetophenone. Hence it is concluded that the association in these mixtures is the result of strong Hydrogen bonding between the molecules & strong Dipole-Dipole interactions in Ibmk+Acetophenone than chlorobenzene+Ibmk and Ibmk+cyclohexanol in Binary liquid mixtures.

The order of polarity of binary liquid mixtures is given by

Ibmk+Acetophenone > chlorobenzene+Ibmk > Ibmk+cyclohexanol

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