

Excess Transport Properties Of Binary Mixtures Of IBMK With FURFURALDEHYDE, N-BUTYLACETATE, BUTAN-2-ONE At 308K

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ABSTRACT

The ultrasonic velocity (u), density (ρ) and viscosity (η) have been measured in binary liquid mixtures containing **IBMk+ furfuraldehyde**, **IBMk+ n-butylacetate** **IBMk+ butan-2-one**. 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-mole molecular free length, Excess properties, internal pressure, dipole-dipole interactions, dipole-induced dipole interactions.

INTRODUCTION

The ultrasonic studies are extensively used to estimate the thermodynamic properties and predict the intermolecular interactions in pure liquid^[1], liquid mixtures^[2-5] and ionic interactions in electrolytic solutions^[6,7]. Though the molecular interactions studies can be best carried out through spectroscopic methods^[8,9] the other non spectroscopic techniques such as dielectric^[10] magnetic^[11] ultrasonic velocity and viscosity^[12-17] measurements have been widely used in field of interactions and structural aspect evaluations studies. In the present work an attempt has been made to investigate the behaviour of binary solutions of **IBMK+ Furfuraldehyde** **IBMK+ n-Butylacetate** **IBMK+ Butan-2-one** with regard to adiabatic compressibility, intermolecular free length, free volume and internal pressure from ultrasonic measurements at 308 K.

In view of the applications of these solvents and their mixtures in chemistry and modern technology three binary mixtures have been studied and reported at 308 K in this paper under THREE categories namely ,

System:1 IBMK+ Furfuraldehyde

System:2 IBMK+ n-Butylacetate

System:3 IBMK+ Butan-2-one

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

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

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 volume¹⁸. Eyring and Kincaid¹⁹ 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

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

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 4.28×10^9 for all liquids.

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^{20,21}. 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's²² 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 thermodynamics²³ 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 π_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)

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

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.

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.

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

6. Acoustic Impedance (Z)

The Specific acoustic impedance is given by

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

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

7. Gibb's Free Energy (ΔG^*)

The relaxation time for a given transition is related to the activation free energy. The variation of τ with temperature can be expressed in the form of Eyring salt process theory²⁴.

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

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.

The excess values are calculated using the formula,

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

Where, $A_{id} = \sum A_i X_{ii}$, where A_i is any acoustical parameter and X_{ii} 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,

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

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.

ρ_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

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

Where,

η_2 is the Viscosity of water

t_1 , is the time of flow of water

ρ_1 is the density of water.

η_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.

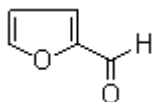
3. Velocity Measurement

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.

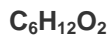
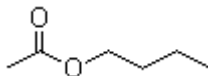
4. Results and Discussion

The experimental values of density viscosity, ultrasonic velocity for the three binary systems **Ibmk+ furfuraldehyde**, **Ibmk+ n-butylacetate** **Ibmk+ butan-2-one** at 308k are given in the tables 1, 2, 3. The parameters adiabatic compressibility (β_{ad}), free length (L_f), free volume (V_f), acoustic impedance (Z), internal pressure (π_i), relaxation time (τ) at 308k are listed in tables 4,5,6,7,8,9.

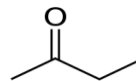
The structure of the following systems are studied at 308K.



Furfuraldehyde



N-Butylacetate



Butan-2-One

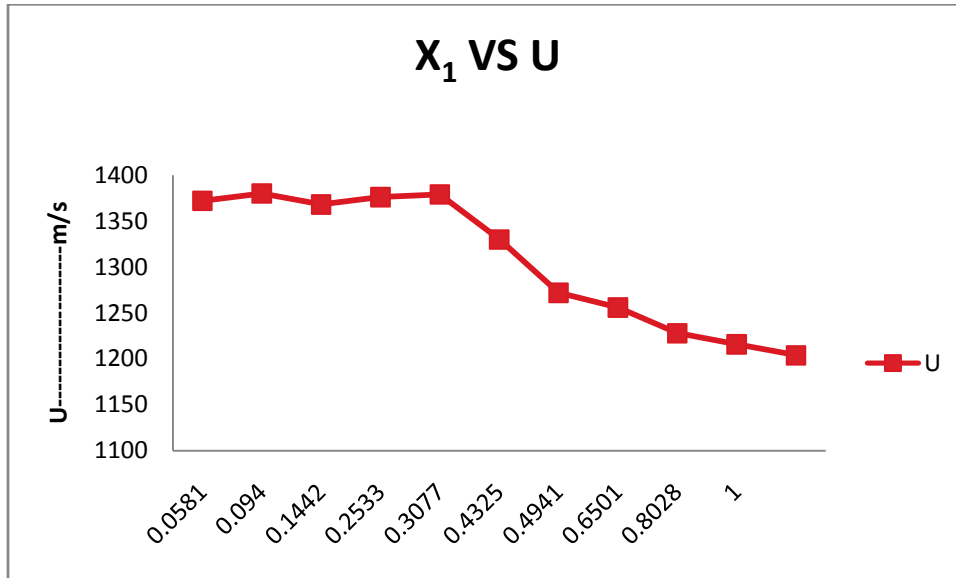
SYSTEM:-1 IBMK +Furfuraldehyde

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 +Furfuraldehyde at 308 K.

| Mole fraction | | ρ (g/cm ³) | η (cp) | U (m/s) | Z (gm ⁻² s ⁻¹) | LJP | χ_u (m/s) |
|---------------|--------|--------------------------------|----------------|------------|--|---------|-------------------|
| X1 | X2 | | | | | | |
| 0.0000 | 1.0000 | 1.1477 | 0.8247 | 1372 | 1574.6444 | 42.1053 | 0.0000 |
| 0.0581 | 0.9419 | 1.119 | 0.7186 | 1380 | 1544.22 | 43.6364 | 0.0130 |
| 0.094 | 0.906 | 1.1017 | 0.6587 | 1368 | 1507.1256 | 41.3793 | 0.0087 |
| 0.1442 | 0.8558 | 1.0782 | 0.6089 | 1376 | 1483.6032 | 42.8571 | 0.0209 |
| 0.2533 | 0.7467 | 1.0302 | 0.5297 | 1379 | 1420.6458 | 43.4389 | 0.0373 |
| 0.3077 | 0.6923 | 1.008 | 0.4924 | 1330 | 1340.64 | 35.5556 | 0.0073 |
| 0.4325 | 0.5675 | 0.9623 | 0.4366 | 1272 | 1224.0456 | 29.2683 | -0.0210 |
| 0.4941 | 0.5059 | 0.9385 | 0.3925 | 1256 | 1178.756 | 27.9070 | -0.0256 |
| 0.6501 | 0.3499 | 0.888 | 0.3474 | 1228 | 1090.464 | 25.8065 | -0.0275 |
| 0.8028 | 0.1972 | 0.8441 | 0.2991 | 1216 | 1026.4256 | 25.0000 | -0.0171 |
| 1.0000 | 0.0000 | 0.7937 | 0.3945 | 1204 | 955.6148 | 24.2424 | 0.0000 |

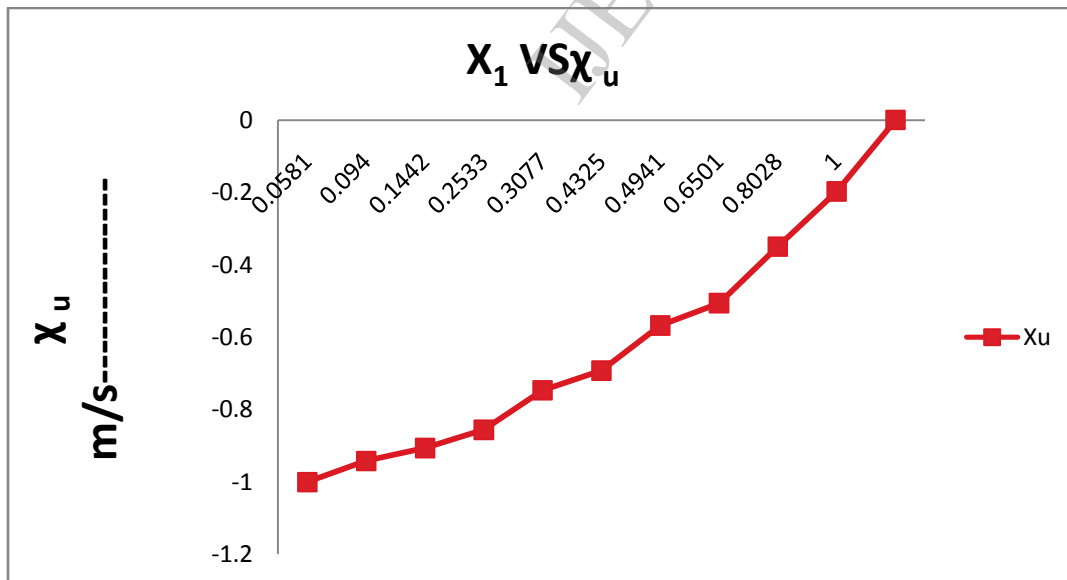
SYSTEM:-1 IBMK +Furfuraldehyde

Fig. 1 Molefraction vs U



MOLE FRACTION OF FIRST COMPONENT

Fig.2 Molefraction vs χ_u

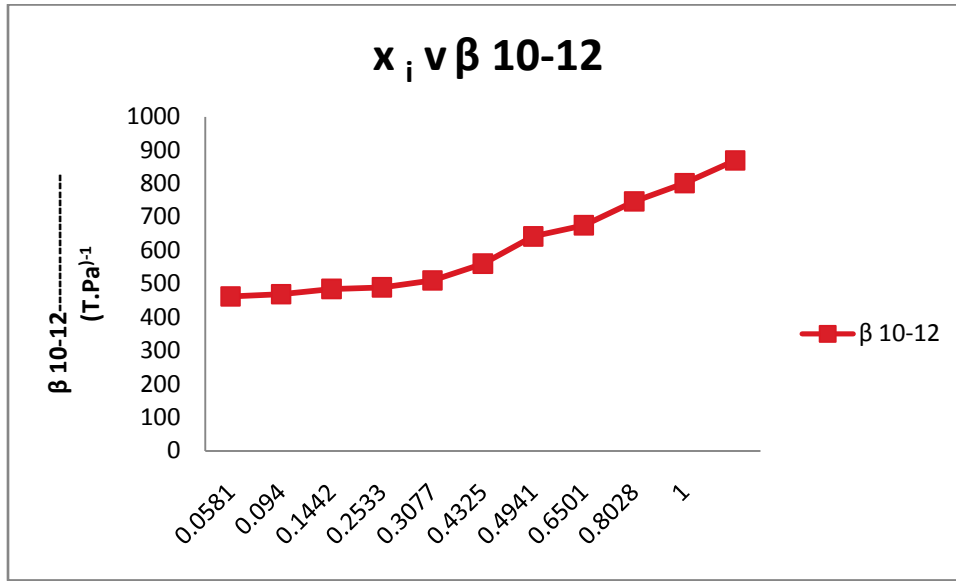


MOLE FRACTION OF FIRST COMPONENT

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+Furfuraldehyde at 308 k.

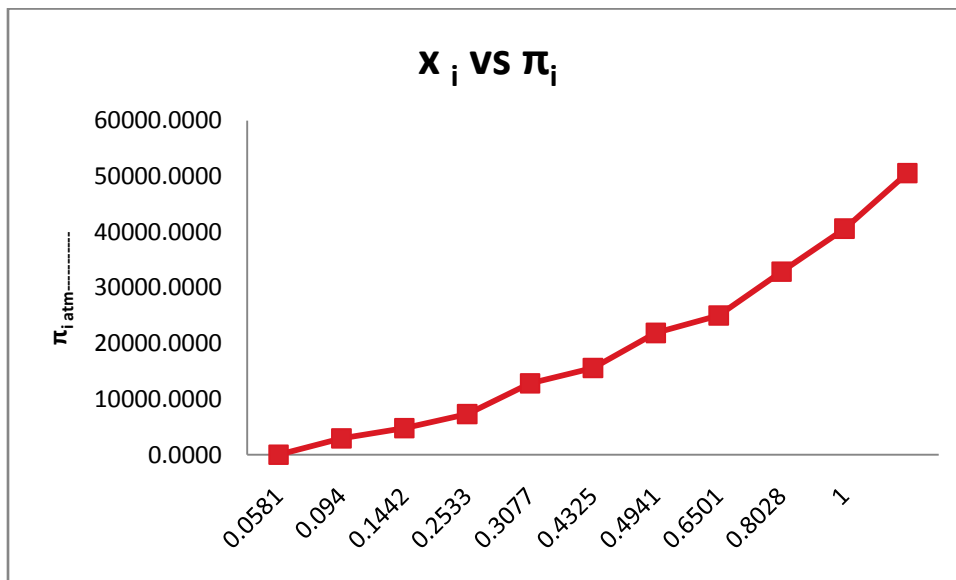
| $\beta 10^{-12}$ (T.Pa) ⁻¹ | $\tau 10^{-7}$ (s) | $V_f 10^{-5}$ (ml/mole) | π_i (atm) | CE (gJ/mole) | $\alpha/f^2 10^3$ (NPm ⁻¹ s ²) | L_f (T.Pa) ⁻¹ | $\Delta G^\# 10^{-20}$ (gj/mole) |
|--|-----------------------|----------------------------|------------------|-----------------|--|-------------------------------|-------------------------------------|
| 462.875 | 6983 | 2.60443 | 7932.7268 | 664.0903 | 64.0580 | 107.8580 | 4.1042 |
| 469.258 | 6205 | 4.03575 | 7241.9122 | 623.3419 | 47.1600 | 108.9154 | 4.08237 |
| 485.025 | 5827 | 5.12771 | 6881.4328 | 602.5299 | 40.3440 | 110.2476 | 4.07079 |
| 489.851 | 5472 | 6.64827 | 6489.0040 | 581.7856 | 33.4915 | 111.1181 | 4.05918 |
| 510.446 | 4971 | 10.3058 | 5838.0356 | 550.3318 | 24.5744 | 113.5536 | 4.04145 |
| 560.836 | 4897 | 11.5892 | 5635.9651 | 544.2252 | 23.3916 | 116.8928 | 4.03867 |
| 642.267 | 4756 | 14.7727 | 5234.0042 | 532.1823 | 20.4850 | 122.3334 | 4.03326 |
| 675.439 | 4440 | 19.7261 | 4898.8692 | 512.0502 | 16.9663 | 124.6613 | 4.02056 |
| 746.776 | 4248 | 27.1096 | 4463.3773 | 496.2613 | 13.7821 | 129.6099 | 4.0124 |
| 801.119 | 3885 | 42.0305 | 3998.3248 | 470.6258 | 10.2160 | 133.5919 | 3.99593 |
| 869.142 | 5504 | 18.2163 | 4393.5863 | 554.4432 | 17.6500 | 138.4530 | 4.06025 |

Fig.3 Molefraction vs β



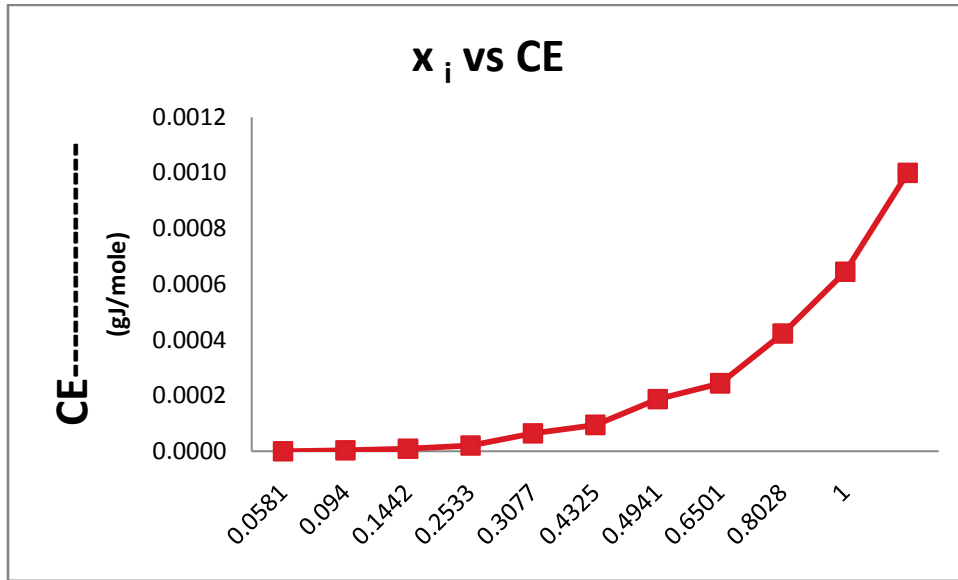
MOLE FRACTION OF FIRST COMPONENT

Fig.4 Molefraction vs π_i



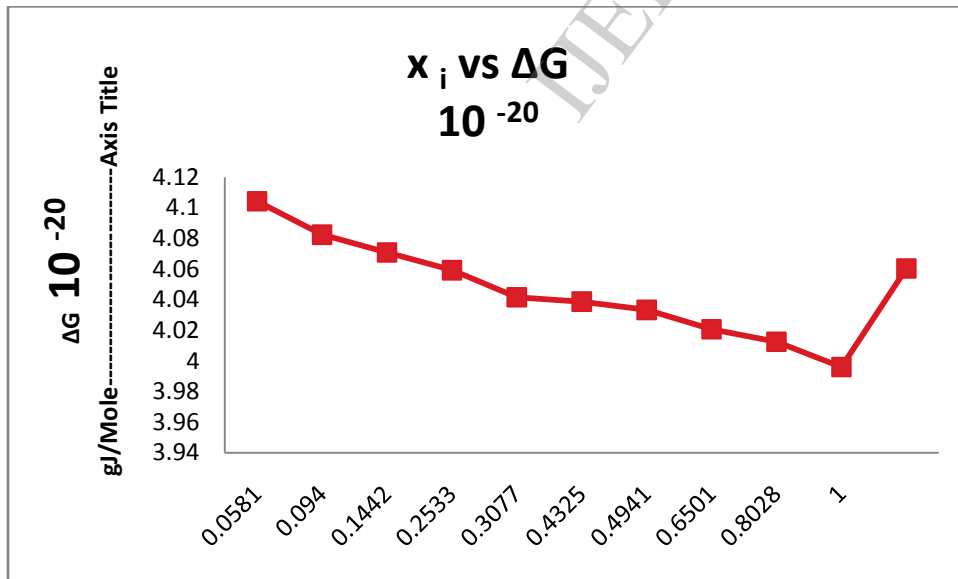
MOLE FRACTION OF FIRST COMPONENT

Fig.5 Molefraction vs CE



MOLE FRACTION OF FIRST COMPONENT

Fig.6 Mole fraction vs ΔG^\ddagger

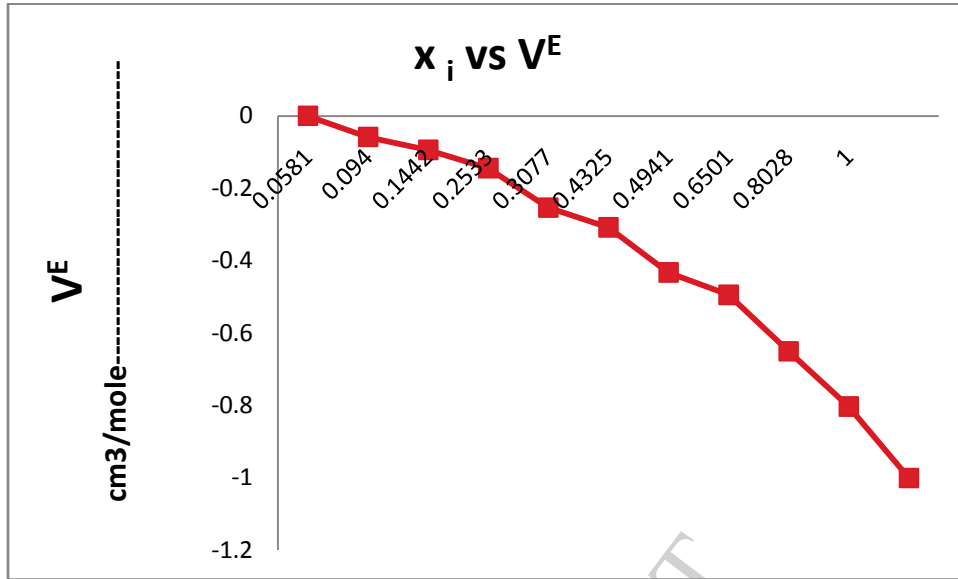


MOLE FRACTION OF FIRST COMPONENT

Table:-3 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+Furfuraldehyde at 308k

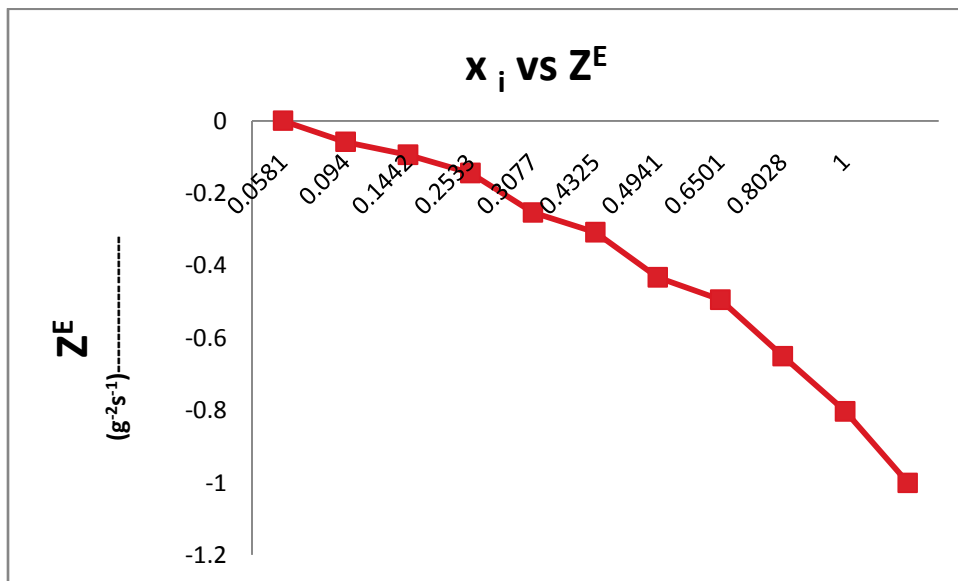
| U^E (m/s) | η^E (NS/cm ²) | VA^E (cm ³) | Z^E (g ⁻² s ⁻¹) | V^E (cm ³ /mole) | $\beta^E 10^{-08}$ (g ⁻¹ ms ²) | $V_F^E 10^{-05}$ (cm ³) | L_F^E (cm) |
|----------------|-----------------------------------|------------------------------|---|----------------------------------|--|--|-----------------|
| -55.0 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | -0.00035112 | -0.00000395 | -0.0009 |
| -3.2 | -0.0173 | -3.3573 | 44.0648 | -0.10904 | -1.72211 | .524266 | -0.7210 |
| -18.8 | -0.0646 | -2.2693 | 25.0522 | -0.14945 | -1.60387 | 1.05576 | -0.4872 |
| -27.8 | -0.0955 | -1.5578 | 10.7011 | -0.18351 | -3.16079 | 1.79261 | -1.1524 |
| -30.7 | -0.1188 | -1.0978 | -0.6754 | -0.20845 | -5.53363 | 3.74684 | -2.0548 |
| -39.2 | -0.1444 | -0.3196 | -12.2659 | -0.22298 | -2.7047E | 4.18096 | -0.3799 |
| -26.7 | -0.1410 | -0.7666 | -8.3378 | -0.40936 | .368105 | 5.41612 | 1.2425 |
| -35.0 | -0.1672 | 0.0930 | -18.6844 | -0.17973 | 1.1828E | 9.40786 | 1.6859 |
| -21.2 | -0.1382 | -0.2357 | -11.9439 | -0.1454 | 1.97867 | 14.3559 | 1.8618 |
| -14.0 | -0.1208 | 0.0396 | -9.2206 | -0.11126 | 1.21702 | 26.8929 | 1.1720 |
| -1.8 | -0.1205 | -0.2511 | -6.5086 | 0.0000 | -0.0000826 | -0.00000365 | 0.0000 |

Fig.7 Molefraction vs V^E



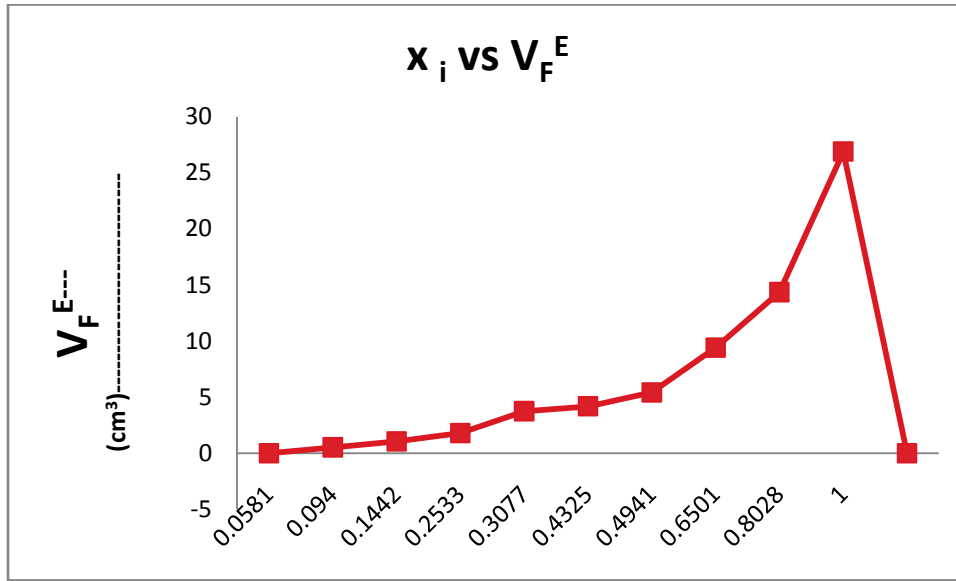
MOLE FRACTION OF FIRST COMPONENT

Fig.8 Mole fraction vs Z^E



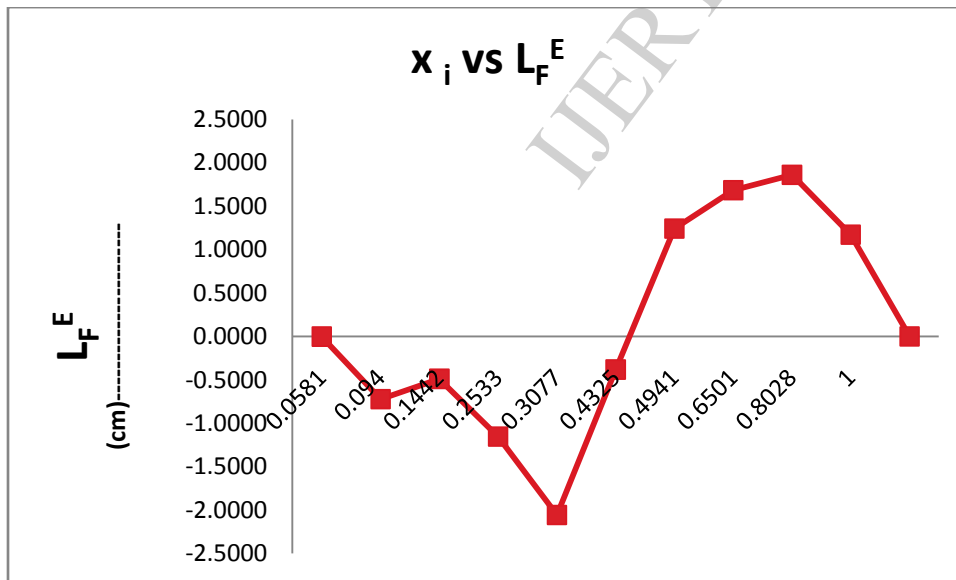
MOLE FRACTION OF FIRST COMPONENT

Fig.9 Mole fraction vs V_F^E



MOLE FRACTION OF FIRST COMPONENT

Fig.10 Mole fraction vs L_F^E



MOLE FRACTION OF FIRST COMPONENT

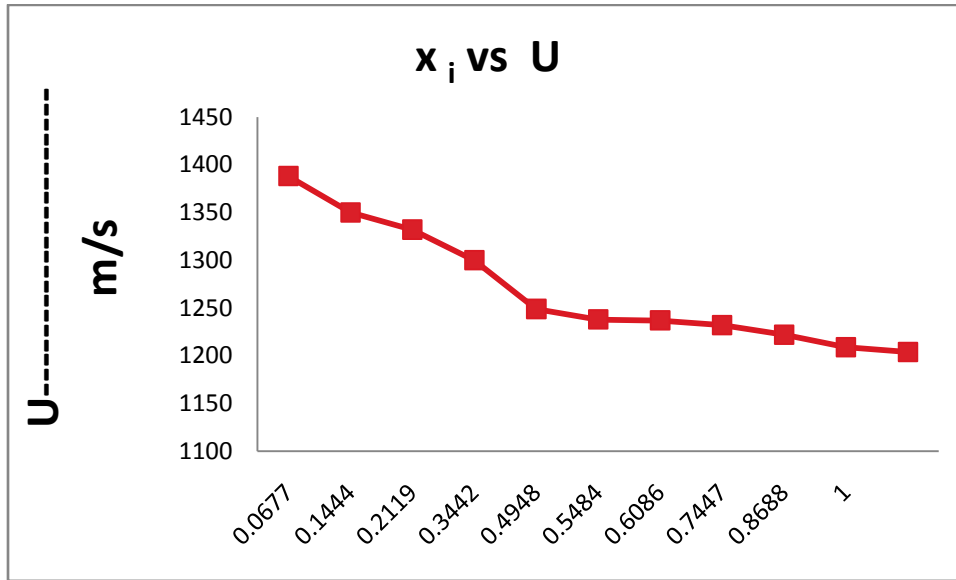
SYSTEM: 2 IBMK+n-BUTYLACETATE

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+n-BUTYLACETATE** at 308 K

| MOLE FRACTION | | ρ (g/cm ³) | η (cp) | U (m/s) | Z (gm ⁻² s ⁻¹) | LJP | χ_u (m/s) |
|---------------|--------|--------------------------------|----------------|------------|--|---------|-------------------|
| X_1 | X_2 | | | | | | |
| 0.0000 | 1.0000 | 0.87 | 0.3561 | 1388 | 1207.56 | 45.2830 | 0.0000 |
| 0.0677 | 0.9323 | 0.864 | 0.338 | 1350 | 1166.4 | 38.4 | -0.0186 |
| 0.1444 | 0.8556 | 0.8576 | 0.3039 | 1332 | 1142.3232 | 35.8209 | -0.0216 |
| 0.2119 | 0.7881 | 0.852 | 0.2777 | 1300 | 1107.6 | 32 | -0.0363 |
| 0.3442 | 0.6558 | 0.8413 | 0.2499 | 1249 | 1050.7837 | 27.3504 | -0.0571 |
| 0.4948 | 0.5052 | 0.8287 | 0.2298 | 1238 | 1025.9306 | 26.5193 | -0.0455 |
| 0.5484 | 0.4516 | 0.8247 | 0.2123 | 1237 | 1020.1539 | 26.4463 | -0.0389 |
| 0.6086 | 0.3914 | 0.8198 | 0.2027 | 1232 | 1009.9936 | 26.0870 | -0.0345 |
| 0.7447 | 0.2553 | 0.8086 | 0.1578 | 1222 | 988.1092 | 25.3968 | -0.0232 |
| 0.8688 | 0.1312 | 0.7984 | 0.1208 | 1209 | 965.2656 | 24.5524 | -0.0156 |
| 1.0000 | 0.0000 | 0.7878 | 0.3916 | 1204 | 948.5112 | 24.2424 | 0.0000 |

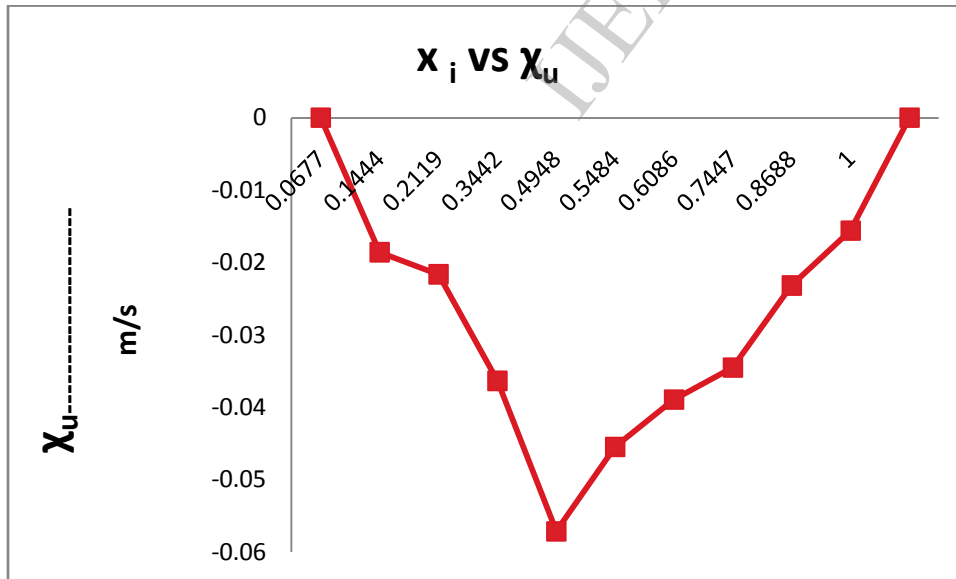
SYSTEM: 2 IBMK+n-BUTYLACETATE

Fig.1 1 Molefraction vs U



MOLE FRACTION OF FIRST COMPONENT

Fig.12 Mole fraction vs χ



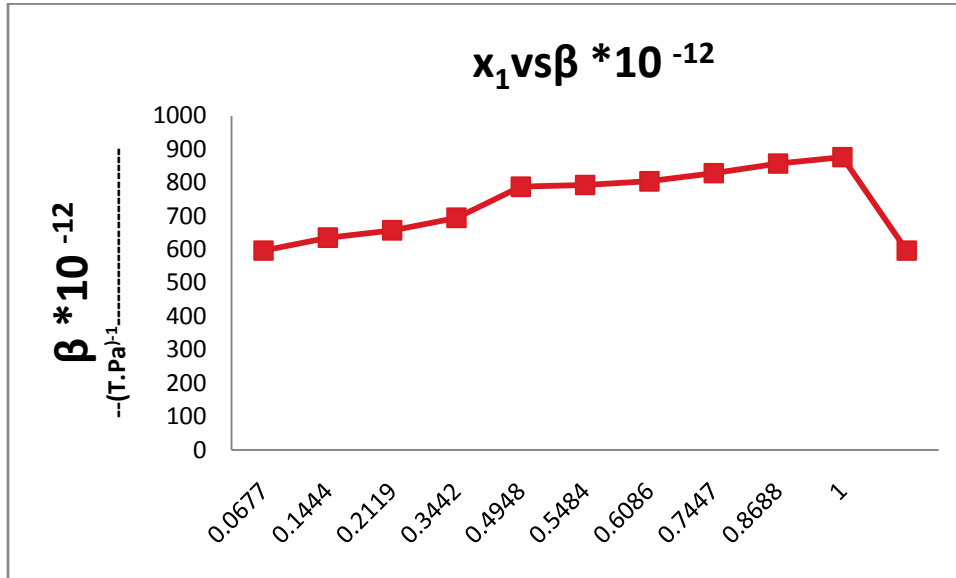
MOLE FRACTION OF FIRST COMPONENT

Table:-5

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(ΔG^\ddagger) values at different mole fraction of IBMK+ n-BUTYLACETATE at 308K.

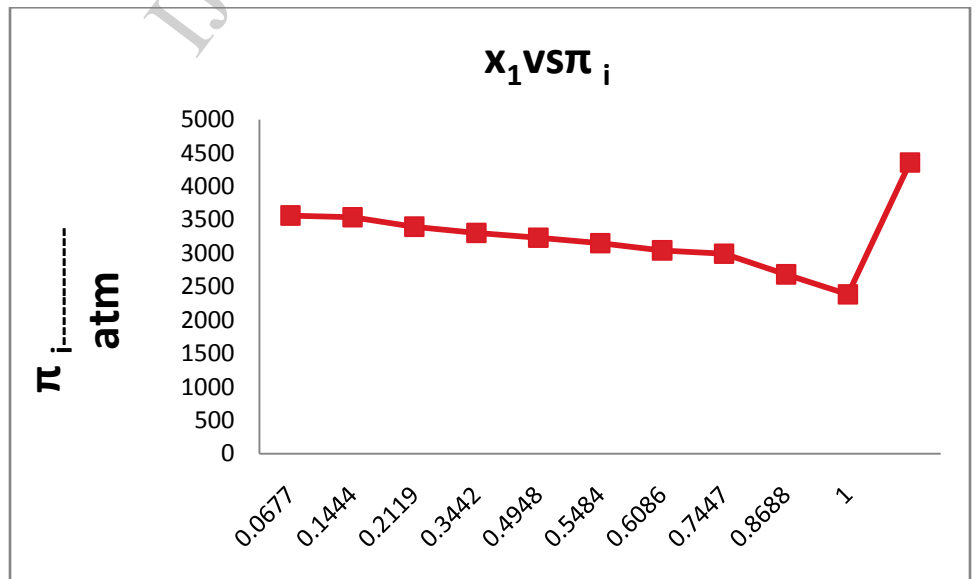
| $\beta * 10^{-12}$ (T.Pa) ⁻¹ | $\tau * 10^{-7}$ (s) | V_f (ml/mole) | π_i (atm) | CE (gJ/mole) | $\alpha/f^2 * 10^3$ (NPm ⁻¹ s ²) | L_f (T.Pa) ⁻¹ | $\Delta G^\ddagger * 10^{-20}$ (Gj/mole) |
|--|-------------------------|--------------------|------------------|-----------------|--|-------------------------------|---|
| 596.6 | 0.5457 | 0.0006 | 3563.7983 | 4303.5003 | 9987.5328 | 123.1656 | 5.3344 |
| 635.1 | 0.5216 | 0.0006 | 3537.3537 | 4125.9693 | 9669.2967 | 125.3199 | 5.3260 |
| 657.2 | 0.4725 | 0.0008 | 3396.283 | 3879.6529 | 8183.1061 | 126.6337 | 5.3077 |
| 694.5 | 0.4346 | 0.0009 | 3303.3119 | 3658.7483 | 7295.5970 | 128.6034 | 5.2923 |
| 787.3 | 0.3697 | 0.0013 | 3230.7676 | 3230.9426 | 5924.1124 | 133.6241 | 5.2625 |
| 792.4 | 0.3432 | 0.0016 | 3149.2799 | 3103.8883 | 5137.2869 | 134.0019 | 5.2487 |
| 803.7 | 0.3297 | 0.0017 | 3042.5687 | 3023.9736 | 4797.5843 | 134.6742 | 5.2413 |
| 828.2 | 0.2602 | 0.0034 | 2994.0523 | 2651.2859 | 3066.0132 | 136.1574 | 5.1976 |
| 856.9 | 0.2017 | 0.0068 | 2683.1912 | 2302.9123 | 1899.5468 | 137.7591 | 5.1506 |
| 875.7 | 0.6628 | 0.0002 | 2385.781 | 4131.4185 | 20887.3052 | 138.9705 | 5.3702 |

Fig.14 Mole fraction vs β



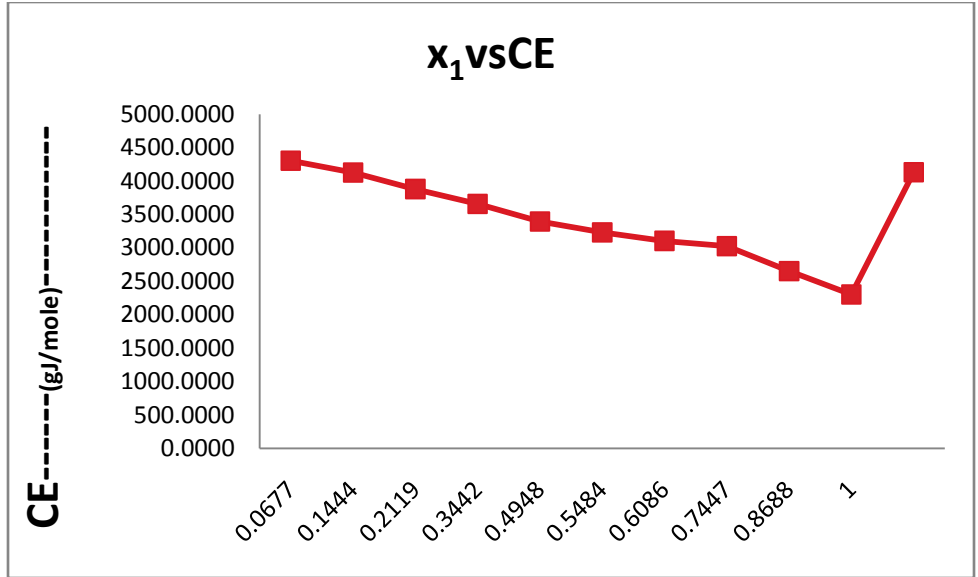
MOLE FRACTION OF FIRST COMPONENT

Fig.15 Mole fraction vs π_i



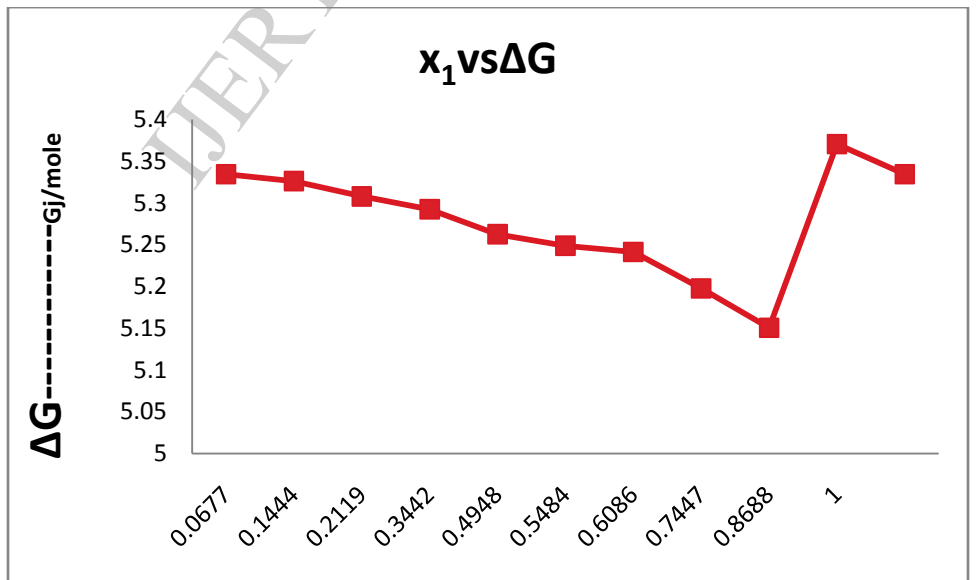
MOLE FRACTION OF FIRST COMPONENT

Fig.16 Mole fraction vs CE



MOLE FRACTION OF FIRST COMPONENT

Fig.17 Mole fraction vs ΔG

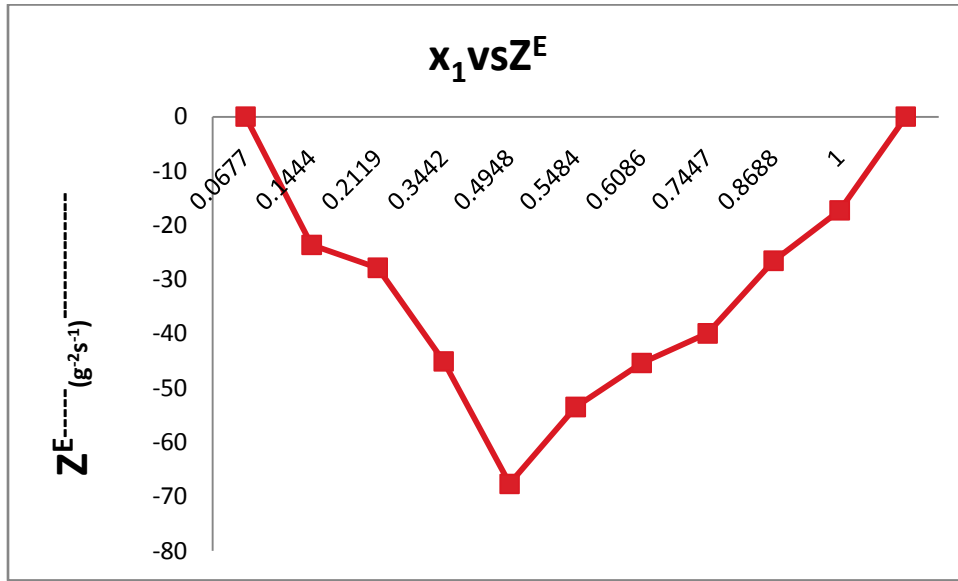


MOLE FRACTION OF FIRST COMPONENT

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 (LF^E) and EXCESS FREE VOLUME (V_F^E) VALUES AT VARIOUS MOLE FRACTIONS OF IBMK+ n-Butylacetate at 308k

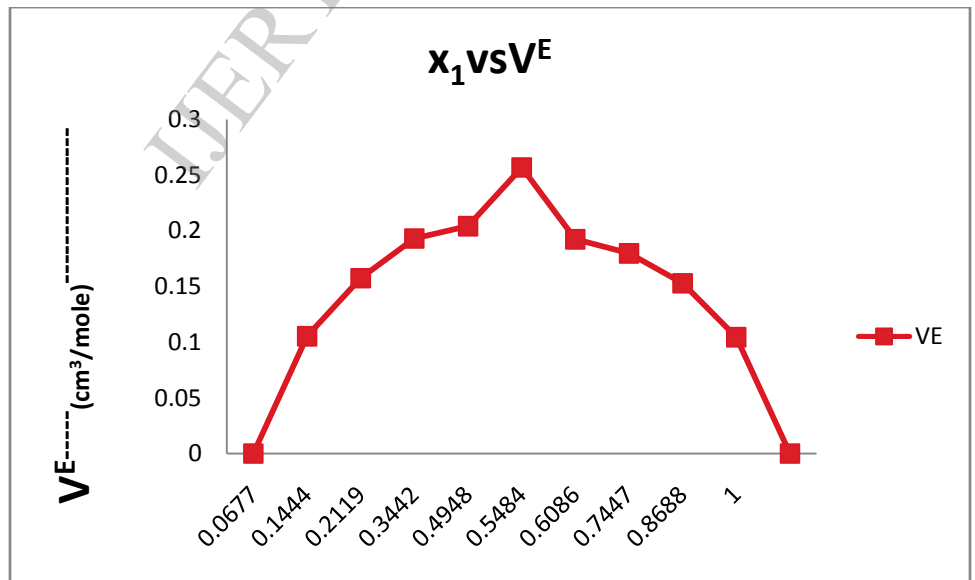
| U^E (m/s) | η^E (NS/cm ²) | VA^E (cm ³) | Z^E (g ⁻² s ⁻¹) | V^E (cm ³ /mole) | $\beta^E 10^{-8}$ (g ⁻¹ ms ²) | $V_F^E 10^{-5}$ (cm ³) | LF^E (cm) |
|----------------|-----------------------------------|------------------------------|---|----------------------------------|---|---------------------------------------|----------------|
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | .00255 | -.00827 | 8.0430 |
| -25.5432 | -0.0205 | 2.1874 | -23.6224 | 0.1053 | 1.95707 | 5.4718 | 8.6161 |
| -29.4304 | -0.0573 | 2.5560 | -27.8302 | 0.1575 | 2.03119 | 25.9043 | 8.1384 |
| -49.0104 | -0.0859 | 4.2071 | -45.0676 | 0.1930 | 3.8761 | 43.2279 | 8.5315 |
| -75.6672 | -0.1184 | 6.4208 | -67.6117 | 0.2042 | 6.92799 | 62.6479 | 8.8725 |
| -58.9568 | -0.1439 | 5.0450 | -53.4521 | 0.2569 | 5.26396 | 87.3487 | 6.9446 |
| -50.0944 | -0.1633 | 4.2961 | -45.3437 | 0.1924 | 4.27783 | 119.2848 | 6.0705 |
| -44.0176 | -0.1750 | 3.7825 | -39.9093 | 0.1797 | 3.71966 | 138.0964 | 5.3368 |
| -28.9752 | -0.2247 | 2.5075 | -26.5372 | 0.1528 | 2.37325 | 306.5364 | 3.6412 |
| -19.1408 | -0.2661 | 1.6401 | -17.2328 | 0.1044 | 1.78115 | 659.7078 | 2.3443 |
| 0.0000 | 0.0000 | 31.4669 | 0.0000 | 0.0000 | -.00490 | 0.0240 | 0.4913 |

Fig.17 Mole fraction vs Z^E



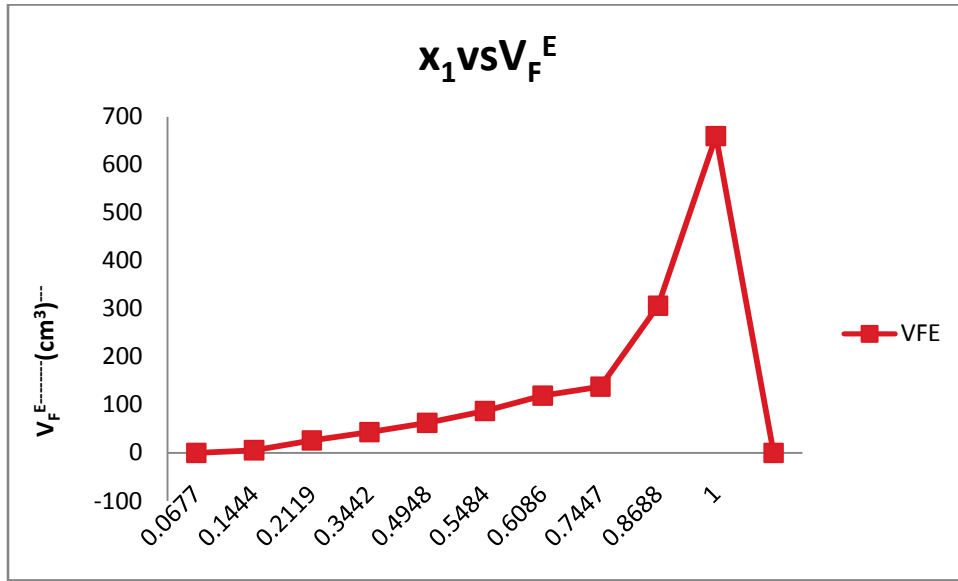
MOLE FRACTION OF FIRST COMPONENT

Fig.18 Mole fraction vs V^E



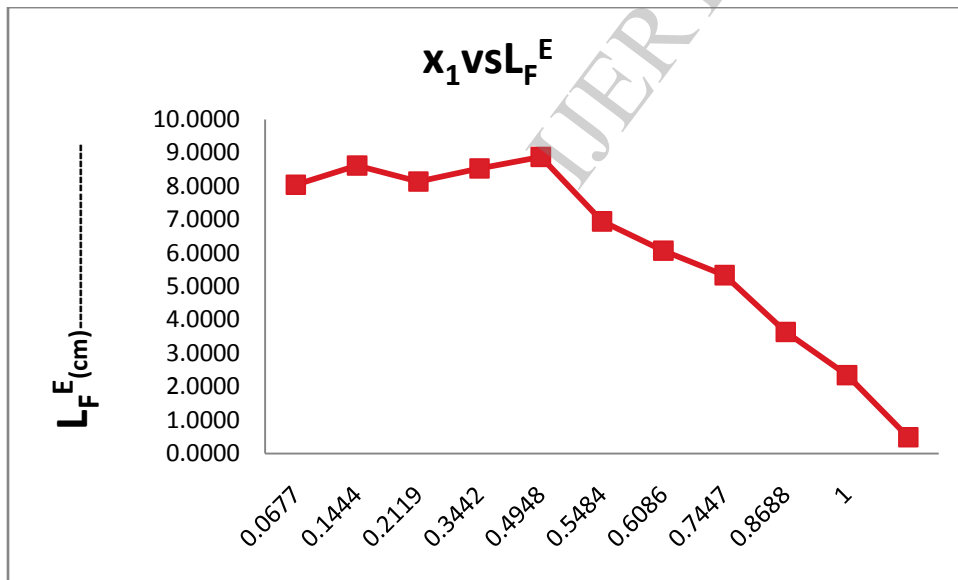
MOLE FRACTION OF FIRST COMPONENT

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 IBMK+BUTAN-2-ONE

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+BUTAN-2-ONE at 308 K

| MOLE FRACTION | | ρ (g/cm ³) | η (cp) | U (m/s) | Z (gm ⁻² s ⁻¹) | LJP | χ_u (m/s) |
|---------------|--------|--------------------------------|----------------|------------|--|-----|-------------------|
| X_1 | X_2 | | | | | | |
| 0.0000 | 1.0000 | 0.9775 | 0.5265 | 1414 | 1382.185 | 6 | 0.0000 |
| 0.0829 | 0.9171 | 0.9597 | 0.4483 | 1363 | 1308.0711 | 6 | -0.0241 |
| 0.1506 | 0.8494 | 0.9468 | 0.4346 | 1334 | 1263.0312 | 6 | -0.0350 |
| 0.2371 | 0.7629 | 0.9304 | 0.4143 | 1305 | 1214.172 | 6 | -0.0434 |
| 0.3871 | 0.6129 | 0.9025 | 0.3939 | 1268 | 1144.37 | 6 | -0.0486 |
| 0.4641 | 0.5359 | 0.8882 | 0.3522 | 1246 | 1106.6972 | 6 | -0.0536 |
| 0.6312 | 0.3688 | 0.8674 | 0.3171 | 1224 | 1061.6976 | 6 | -0.0448 |
| 0.6448 | 0.3552 | 0.8567 | 0.2808 | 1220 | 1045.174 | 6 | -0.0458 |
| 0.7789 | 0.2211 | 0.8326 | 0.2585 | 1202 | 1000.7852 | 6 | -0.0387 |
| 0.8846 | 0.1154 | 0.8132 | 0.22 | 1191 | 968.5212 | 6 | -0.0303 |
| 1.0000 | 0.0000 | 0.7934 | 0.3944 | 1204 | 955.2536 | 6 | 0.0000 |

Fig.21 Mole fraction vs U

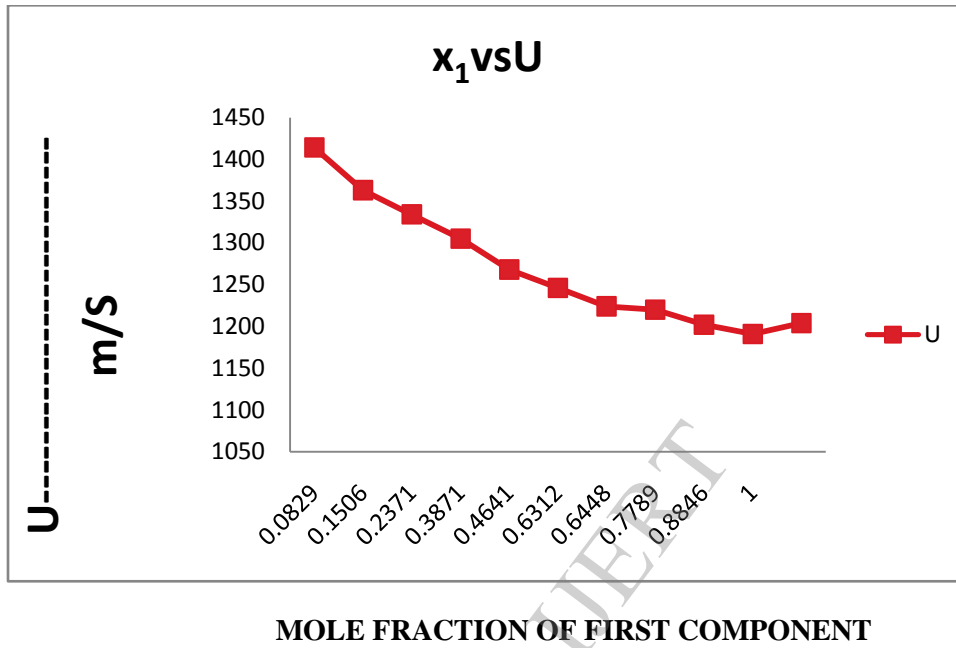


Fig.22 Mole fraction vs χ_u

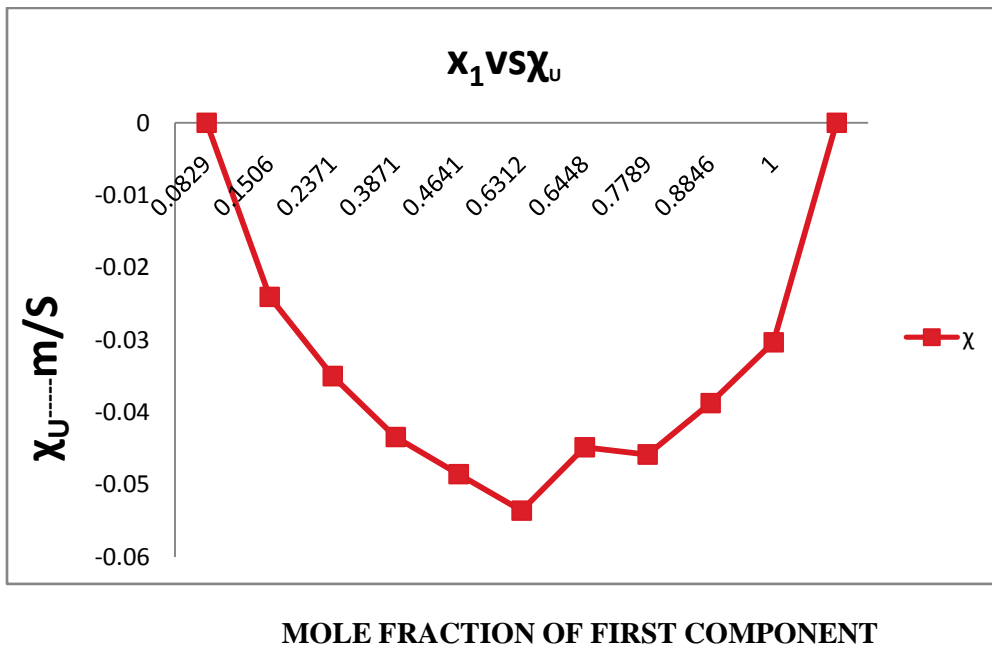


Table:-8 Adiabatic compressibility(β), relaxation time(τ), free volume(V_f), internal pressure(π_i), cohesive force(CE), absorption co-efficient(α/f^2), free length(L_f)& activation energy(ΔG^\ddagger) values at different molefraction of IBMK+BUTAN-2-ONE at 308 K.

| $\beta_s 10^{-12}$ (T.Pa) ⁻¹ | $\tau 10^{-7}$ (s) | $V_f 10^{-5}$ (ml/mole) | π_i (atm) | CE (gJ/mole) | $\alpha/f^2 10^3$ (Npm ⁻¹ s ²) | L_f (T.Pa) ⁻¹ | $\Delta G^\ddagger 10^{-20}$ (gj/mole) |
|--|-----------------------|----------------------------|------------------|-----------------|--|-------------------------------|---|
| 511.6 | 0.7182 | 4.6321 | 7474.6202 | 10331.3079 | 56751.7412 | 115.1226 | 5.38511 |
| 560.884 | 0.6228 | 7.39193 | 6722.7433 | 8793.8263 | 41304.6722 | 118.3391 | 5.3588 |
| 593.513 | 0.6120 | 8.20345 | 6465.7391 | 8166.4303 | 38360.1885 | 120.4306 | 5.35557 |
| 631.116 | 0.5937 | 9.73763 | 6114.4161 | 7423.9528 | 34018.3647 | 122.8298 | 5.34996 |
| 689.151 | 0.5819 | 12.1499 | 5626.2501 | 6438.5119 | 29055.3640 | 126.5204 | 5.34626 |
| 725.192 | 0.5287 | 17.4198 | 5175.3057 | 5727.4963 | 22730.0971 | 128.6558 | 5.32855 |
| 769.516 | 0.4874 | 26.5732 | 4622.4229 | 4907.6153 | 17017.8028 | 131.3540 | 5.31354 |
| 784.245 | 0.4370 | 38.3794 | 4302.753 | 4497.1256 | 13263.8645 | 132.3883 | 5.29337 |
| 831.294 | 0.4140 | 53.1831 | 3917.4203 | 3920.4963 | 10570.3351 | 135.2924 | 5.28336 |
| 866.92 | 0.3607 | 92.127 | 3464.6472 | 3355.5843 | 7271.1035 | 137.5274 | 5.25793 |
| 869.47 | 0.6628 | 18.2302 | 4391.9224 | 4195.3997 | 21237.1516 | 138.4792 | 5.37029 |

Fig.23 Mole fraction vs β

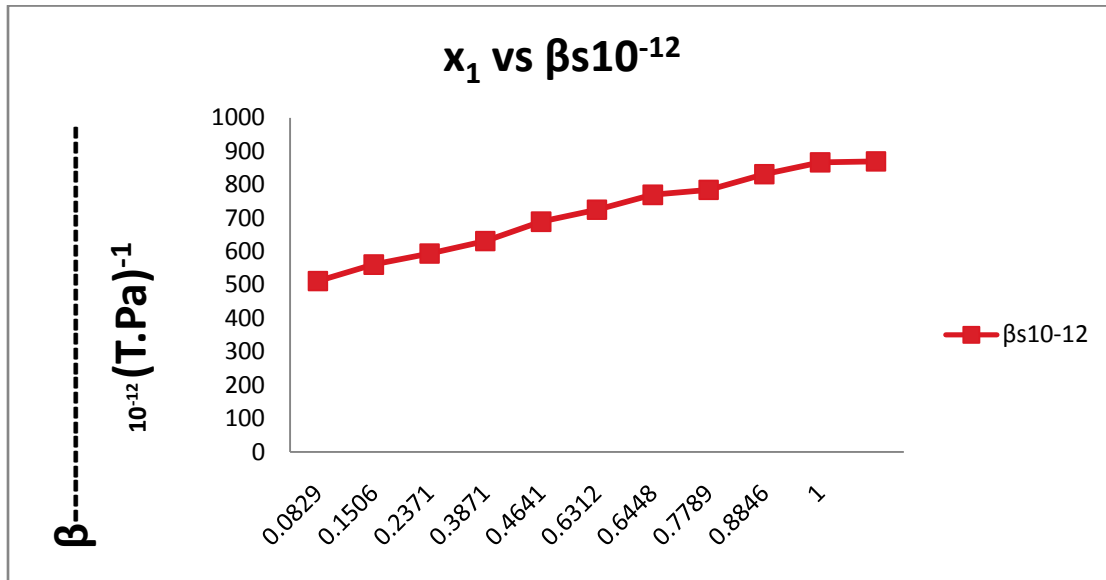
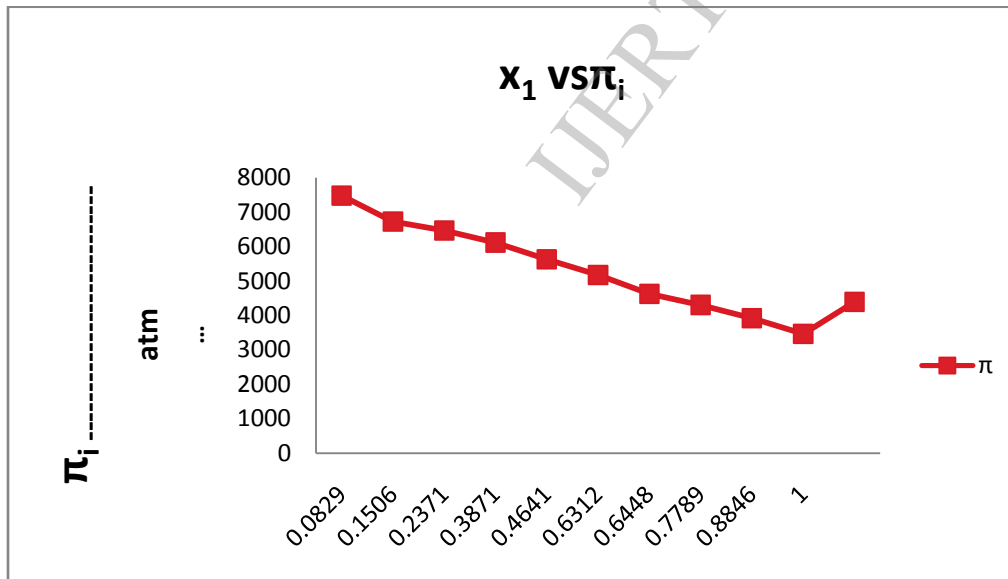
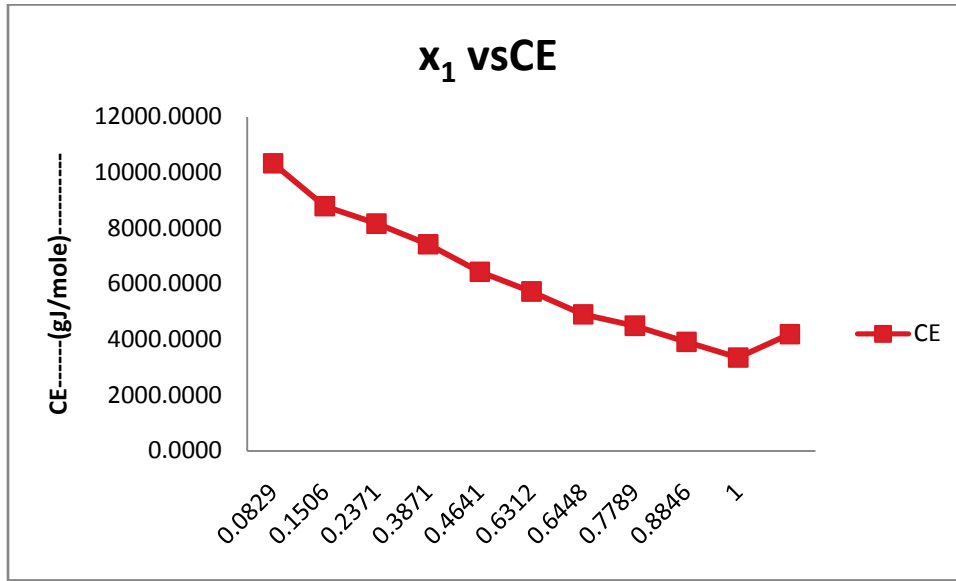


Fig.24 Mole fraction vs π_i



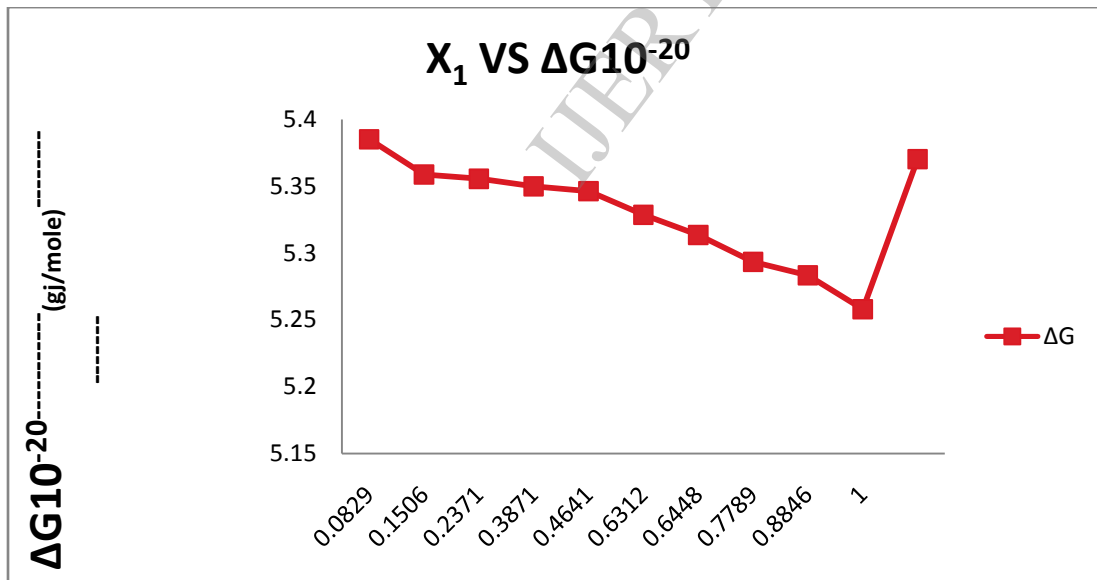
M O L E F R A C T I O N O F F I R S T C O M P O N E N T

Fig.25 Mole fraction vs CE



MOLE FRACTION OF FIRST COMPONE

Fig.26 Mole fraction vs ΔG

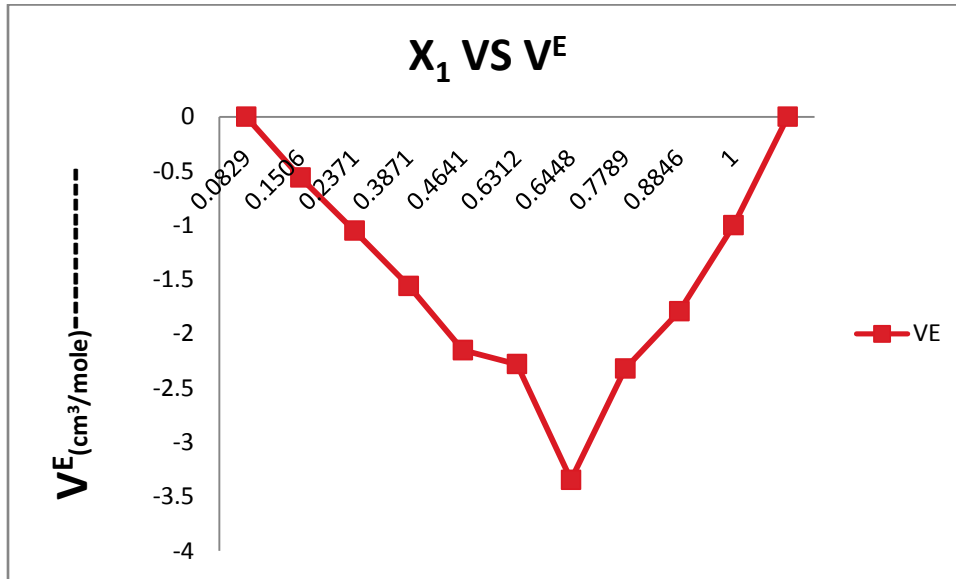


MOLE FRACTION OF FIRST COMPONENT

Table:-9 Excess ultrasonic velocity (u^E), Excess viscosity (η^E), Excess available volume (v_a^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+Butan-2-
oneat 308K.

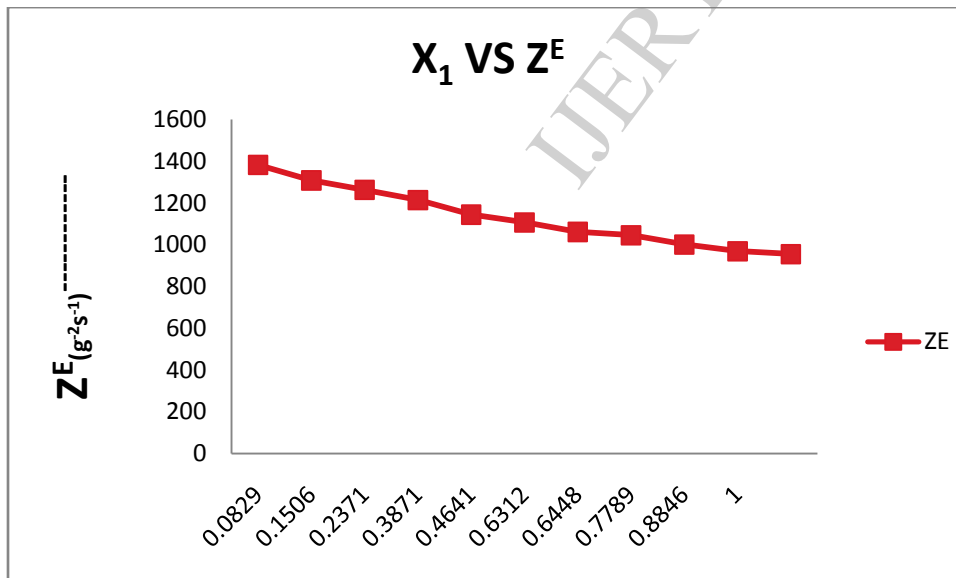
| U^E (m/s) | η^E (NS/cm ²) | VA^E (cm ³) | Z^E (g ⁻² s ⁻¹) | V^E (cm ³ /mole) | $\beta^E 10^{-8}$ (g ⁻¹ ms ²) | $V_F^E 10^{-5}$ (cm ³) | L_F^E (cm) |
|----------------|-----------------------------------|------------------------------|---|----------------------------------|---|---------------------------------------|-----------------|
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | .0000474 | 4.58578 | 0.0000 |
| -0.55867 | -0.0672 | 1.0338 | -38.7213 | -0.55867 | 1.95585 | 5.83816 | 1.2802 |
| -1.04855 | -0.0720 | 1.4140 | -54.8579 | -1.04855 | 2.79641 | 5.41864 | 1.7905 |
| -1.55839 | -0.0809 | 1.6573 | -66.7876 | -1.55839 | 3.46171 | 5.37991 | 2.1693 |
| -2.15013 | -0.0815 | 1.7249 | -72.5499 | -2.15013 | 3.89807 | 5.0646 | 2.3565 |
| -2.27864 | -0.1130 | 2.1089 | -77.3489 | -2.27864 | 4.7471 | 8.9343 | 2.6934 |
| -3.34468 | -0.1260 | 1.4487 | -51.0083 | -3.34468 | 3.20054 | 15.0492 | 1.4887 |
| -2.31974 | -0.1605 | 1.8122 | -61.7256 | -2.31974 | 4.18677 | 26.6081 | 2.2053 |
| -1.79092 | -0.1651 | 1.8385 | -48.8629 | -1.79092 | 4.09352 | 38.9734 | 1.9773 |
| -0.99906 | -0.1896 | 1.8384 | -36.0003 | -0.99906 | 3.87411 | 75.9952 | 1.7435 |
| 0.0000 | 0.0000 | 0.0000 | 0.0000 | 0.0000 | .0000457 | -0.0000439 | 0.0000 |

Fig.27 Mole fraction vs V^E



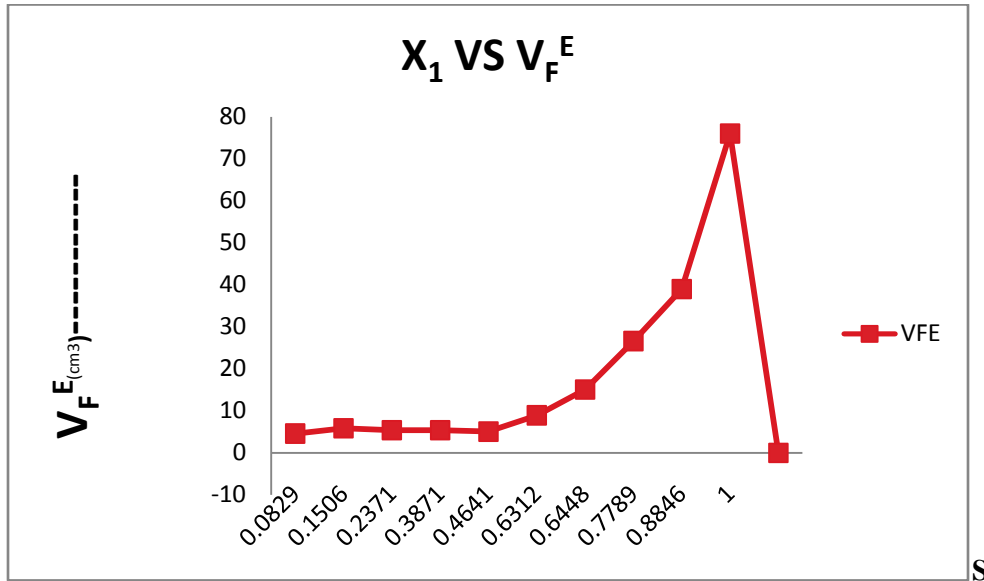
MOLE FRACTION OF FIRST COMPONENT

Fig.28 Mole fraction vs Z^E



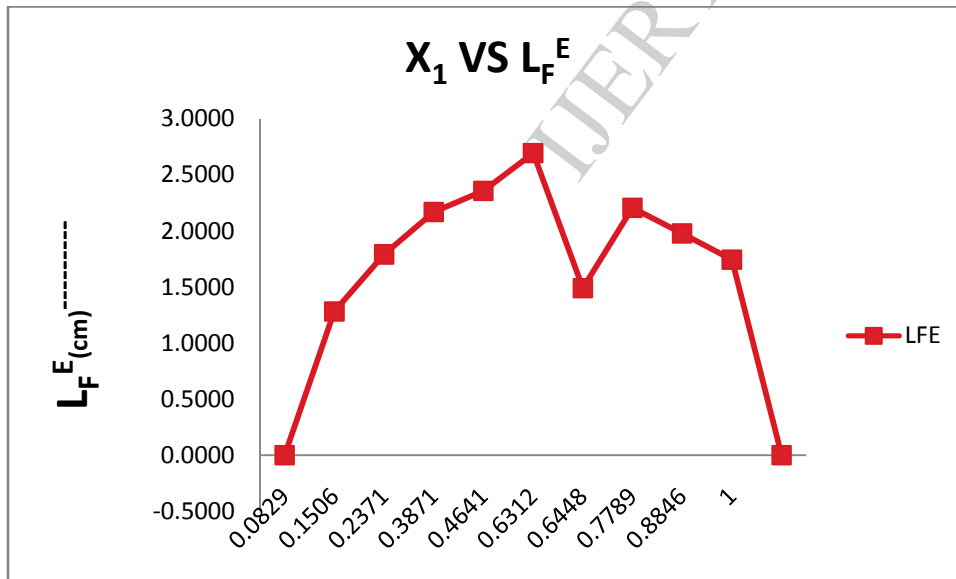
MOLE FRACTION OF FIRST COMPONENT

Fig.29 Mole fraction vs V_F^E



SSSMOLE FRACTION OF FIRST COMPONENT

Fig.30 Mole fraction vs L_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 +Furfuraldehyde, IBMK+n-Butylacetate & IBMK+Butan-2-One. Ultrasonic velocity and viscosity decreases with increase in mole fraction of the solute in For IBMK +Furfuraldehyde, IBMK+n-Butylacetate & IBMK+Butan-2-One.

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 +Furfuraldehyde, IBMK+n-Butylacetate & IBMK+Butan-2-One. 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 +Furfuraldehyde, IBMK+n-Butylacetate & IBMK+Butan-2-One 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 IBMK+n-Butylacetate except IBMK +Furfuraldehyde, IBMK+Butan-2-One 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 IBMK +Furfuraldehyde, IBMK+Butan-2-One, IBMK+n-Butylacetate 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 process²⁵ and in such a situation it is suggested that the molecules get rearranged due to co-operative process²⁶. From the tables 2,5,8. It is noted that the Gibb's Free energy decreases with increasing mole fraction of all the systems.

From the table 1,4&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+Butan-2-One, IBMK+n-Butylacetate systems than IBMK +Furfuraldehyde. It is suggested that dipole-dipole interactions stronger in IBMK+Butan-2-One, IBMK+n-Butylacetate systems than IBMK +Furfuraldehyde 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. 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 positive for almost all compositions of system IBMK+Butan-2-One, IBMK+n-Butylacetate systems than IBMK+Furfuraldehyde. This indicates that the attractive forces between the molecules of components are stronger than the intermolecular attractions in IBMK+Furfuraldehyde.

Table 3,6&9. Shows the values of excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume (V_f^E) for IBMK+Butan-2-One, IBMK+n-Butylacetate systems than IBMK+Furfuraldehyde 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 like IBMK+Furfuraldehyde. However, β^E values are positive which suggest that absence of hydrogen bonding in IBMK+Butan-2-One, IBMK+n-Butylacetate systems.

This indicates that the less interaction in the IBMK+Butan-2-One, IBMK+n-Butylacetate systems than IBMK+Furfuraldehyde system. The possible reason may be as follows, in the IBMK+Butan-2-One, IBMK+n-Butylacetate systems, 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 $-\text{CO}-\text{CH}_3$ and the other is the resonance effect.

These two effects decrease the strength of the intermolecular hydrogen bond formation in IBMK+Butan-2-One, IBMK+n-Butylacetate systems than IBMK+Furfuraldehyde system. Hence from these factors, there is less intermolecular hydrogen bond formation and less dipole-dipole interaction in IBMK+Furfuraldehyde system.

Conclusion

The computed transport parameters and their values point to the presence of specific molecular interaction in the liquid mixtures IBMK+Butan-2-One, IBMK+n-Butylacetate systems than IBMK+Furfuraldehyde system. Hence it is concluded that the association in these mixtures is the result of strong Hydrogen bonding between the molecules & less Dipole-Dipole interactions in IBMK+Furfuraldehyde, than IBMK+Butan-2-One, IBMK+n-Butylacetate systems in Binary liquid mixtures. This shows that dipole-dipole interaction present in IBMK+n-Butylacetate system because both the components are polar. Dipole-dipole interaction existing in IBMK molecule is disturbed by the addition of Butan-2-one molecule with formation dipole-induced dipole interaction between IBMK & Butan-2-one molecules.

The comparative studies of polarity in these systems are given by increasing order.



These parameters will be useful in pharma and perfuma industries for handling & mixing process.

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References

1. Ali. A., and Nain. A.K. Indian J. Pure Appl. Phys., 35 (1997) 729.
2. Jayakumar. S., Karunanidhi, N, and Kannappan. V. Indian J. Pure & Appl. Phys., 34 (1996) 761.
3. Rajendran. V. Indian J. Pure Appl. Phys. 34 (1996) 52.
4. Fort. R.J., Moore. W.R. Trans. Faraday. Soc (GB) 61 (1975) 2102
5. Sheshadri.K. and Reddy. K.C., Acustica (Germany) 29 (1973) 59
6. Kaulgud. M.V. and Patil. K.J. Indian J. Pure Appl. Phys. 13 (1975) 322.
7. Kovelenko. L.S., Ivanova. E.F. and Kransnoperova. A.P. Russ. J. Phys. Chem. 64 (1960) 184.
8. Nikam. P.S., Shirsat. L. Nano Hasan. M. J. Indian. Chem. Soc. 77(2000) 244.
9. Pimental G C and Maclellan A L, The Hydrogen Bond, (WH Freeman and Co, San Fransisco) 1960.
10. Hobbs M E and Bates WW, *J Am Chem Soc.*, 1952, 74, 746.
11. Lin W and Tsay S J, *J Phys Chem.*, 1970, **74**, 1037.
12. Kannappan A N, Kesavasamy R and Ponnuswamy V, ARPN Journal of Engineering and Applied. Sciences, 2008, 3, 41.
13. Velusamy V., Nithiyantham S. and Palaniappan L., *Main Group Chemistry*, **2007**, 6(1), 53-61.
14. Jerie K., Baranowski A., Przybylski J. & Glinski J, *J. Mol Liq.*, **2004**, 111, 25-31.
15. Bhandakkar V. D., *Adv. Appl. Sci. Res.*, 2(3) (**2011**)198-207.
16. Bhandakkar V. D., Bedare G. R., Muley V. D. and Suryavanshi B. M., *Adv. In Appl. Sci. Res.*, 2(4) (**2011**)338-347.
17. Bedare G. R., Bhandakkar V. D. and Suryavanshi B. M, *Archiv. of Appl. Sci. Res.*, **2011**, 3(5):323-338
18. Glasstone, S., Laidler, K.J., and Eyring, H., Theory of Rate Processes.
19. Mc. Graw – Hill, Newyork, 478, 479, (1950). Eyring, H. and Kincaid, J.F.J. Chem. Phy., 6,520,(1938).
20. Richards, T.W., Chem. Rev., 2,315, (1925).
21. Vanderwaals, J.d., Essay on the continuity of the gaseous and liquid States London (1873).
22. Glasstone, S., Thermodynamic for chemist, D. van Mostrand Co., Inc., Newyork, 62, (1947).
23. Ratha, D.C., Mishra, S.C. and Samal, K., J.Pure. Appl. Ultrason., 12,108, (1990).

24. Kinsler, L.E. and Rray. A.R., Fundamentals of Acoustics (Wiley Eastern, New Delhi). (1989).
25. Ali, A., Hyder, S. and Nain, A.K., Ind.J. Phys. 74 B, 63 (2000).
26. Sumathi T and Uma Maheswari, *Indian J Pure &Appl Phys*, 2009, 47, 782.

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