

## Comparative Study of Molecular Interactions in Binary Liquid Mixtures of 4-Methyl-2-Pentanone with Aniline, N, N-Dimethyl Aniline and Chlorobenzene at 308 K

D. Ubagaramary\*

R & D Centre, Bharathiyar University, Coimbatore, Tamil Nadu, India

### Abstract

The ultrasonic velocity ( $u$ ), density ( $\rho$ ) and viscosity ( $\eta$ ) have been restrained for binary mixtures of 4-methyl-2-pentanone with butan-2-one, cyclohexanone and furfuraldehyde at temperature  $T=308\text{K}$  at changed mole fractions. The experimental data have been used to calculate the acoustical and thermo-dynamical parameters like adiabatic compressibility ( $\beta_{ad}$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure ( $\pi_i$ ), acoustical impedance, Gibb's free energy and their excess volumes in particular, it is seen that the response of these parameters to frequency is less prominent in to comparison to that of the binary mixtures containing 4-methyl-2-pentanone with butan-2-one, cyclohexanone and furfuraldehyde. Molecular interface studies with ultrasonic method in the binary liquid mixtures of 4-methyl-2-pentanone+butan-2-one, 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde have been conceded out at 308 K. Using the dignified values of ultrasonic velocity, density and viscosity, acoustical parameters and their additional values are estimated. The necessity of glut properties of mixture compositions were associated and discuss in terms of the intermolecular free length and other elements moving the salvation and self-association effect. From the belongings of these glut parameters the nature and strength of the interfaces in these binary systems are discussed.

**Keywords:** binary mixtures, density, viscosity, hydrogen bonding, molecular interactions

**\*Corresponding Author**

E-mail: raja\_sundaram@rocketmail.com

### INTRODUCTION

In the current year, the performance became ultrasonic powerful tool for the study of the molecular behavior of the liquid mixture. A dynamic and thermal property of pure liquids and liquid mixtures study has found various applications in the chemical, textile, pharmaceutical and many other industries. Physical in predicting and chemical properties of the liquid mixture, and no measurements of the speed of the ultrasonic waves in pure fluids and mixtures of liquid to be important.<sup>[1-4]</sup> Acoustic and thermal parameters help to understand the various types of

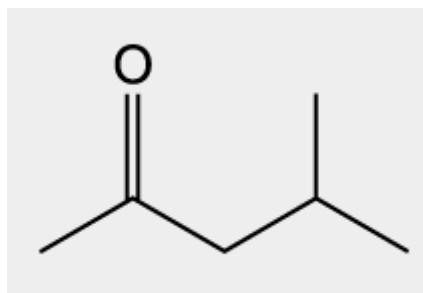
association, such as molecular packing and/or movement and different types of interactions between molecules and their strengths that are affected by the size in pure components/mixtures.<sup>[5]</sup> The study of the nature of the interactions in systems involving 4-methyl-2-pentanone, acetophenone, cyclohexanone by many researchers. However, no reports of any work in the bilateral mixtures containing 4-methyl-2-pentanone with acetophenone, cyclohexanone and buta-2-one. Fluid used in this study is important because of the different industrial applications. It is used for different purposes in the industry. 4-methyl-2-pentanone is a clear, colorless

liquid ketone. The principal end users of MIBK include industrial solvent, coatings, extraction, and chemical intermediate. And daily life without 4-methyl-2-pentanone, they cannot be manufactured.

4-methyl-2-pentanone is very flammable with a high vapor pressure. Exposure to 4-methyl-2-pentanone is possible in both industrial and consumer applications. Occupational exposure limits have been established to control the allowable amount of exposure in workplace settings. Although infrequent and for short duration, consumer exposure depends upon the conditions under which 4-methyl-2-pentanone is used. 4-methyl-2-pentanone does not cause adverse health/environmental effects at levels typically found in the workplace and/or environment.

Other names: MIBK isopropyl acetone, 2-hexanonone isobutyl methyl ketene, 4-methylpentan-2-one, and 4-methyl-2-pentanone MIK.

It is said here that the nature of the interactions in the binary liquid mixture highly of 4-methyl-2-pentanone with acetophenone, cyclohexanone and buta-2-one of speed, density and viscosity measurements of ultrasonic 308K. From these values adiabatic compressibility, and the length of the free, free size, internal pressure, acoustic resistance and enthalpy been calculated. In order to shed light on the interaction between molecules presence of the, it is necessary to study the excess parameters.<sup>[6]</sup>



Deviation physical properties of the liquid mixture of ideal behavior is a measure of the interaction between the particles, which may be due to either adhesive or cohesive forces. the sign and magnitude of these deviations depend on the strength of the interaction between unlike molecules in mixtures. The experimental values of  $U$ ,  $\rho$ ,  $\eta$  were used to compute adiabatic compressibility  $\beta$ , free length  $L_f$ , free volume  $V_f$ , internal pressure  $\pi$ , acoustic impedance  $Z$  and enthalpy  $H$  and their additional functions. Excess values mark plays an important role in assessing compactness molecular dueto rearrangement and over the molecular interactions in binary liquid mixture.

### EXPERIMENTAL DETAILS

Analytical grade chemicals were obtained from SRL chemicals used. They and purified by standard procedure<sup>[7]</sup> were examined.

The purity of the samples from the density and viscosity measurements.<sup>[8]</sup> To prepare mixtures in the required ratios, mode of action of continuous variation was used and the mixtures were maintained in well-stoppard conical flasks. After mixing the liquids completely, bottles were left undisturbed to allow to achieve thermal equilibrium.

Ultrasonic pulse echo overlap Singlecrystal (Mittal, India: Model: F-80X) was used to measure velocities. it ultrasound consists of a high-frequency generator and made measurements cell. the measure the velocities of ultrasonic on a fixed frequency of 2 MHz. The equipment has been calibrated by measuring the speed in gasoline nitrate and  $\text{CCl}_4$ . The results are in good agreement with literature values.<sup>[9-15]</sup> And the speed of ultrasound has the accuracy of the temperature of  $\pm 0.1$  and was controlled by circulating water around the liquid cell control thermostatically constant temperature water bath (accuracy  $\pm 0.1$  K).

Been using bottle specific gravity of the fluid density measurements of pure and liquid mixtures. Weights was measured with an electronic balance (shimadzu AU 220) capable of measuring up to an average of 4–5 0.1 mg. An measurements taken for each sample. Ostwald viscosity was used measure of viscosity in the desired temperature, which was calibrated using a mixture of water and nitrobenzene. After have achieved bath temperature, and the flow of time may flow measurements were made with measured. The hour electronic timer with 0.01 s accuracy. Viscosity is determined using the relationship.

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

## EXPERIMENTAL TECHNIQUES

### Adiabatic Compressibility ( $\beta$ )

The adiabatic compressibility is defined as the fractional decrease of volume per unit increase of pressure, when no heat flows in/out. These changes are related to the compressibility of the medium in a thermodynamic relation expressed as:

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

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

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

### 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 neighboring molecules and is given by the relation:

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

where  $K_T$  is the temperature dependent constant.

### Free Volume ( $V_f$ )

Free volume is one of the important in explaining differences in physical and chemical properties of liquids and liquid mixtures factors. Free space and real estate affiliate to have close contact with the molecular structure and they may show interesting features about the interactions that may occur when two or more of the fluid mixing together. And influenced these molecular interactions between the molecules resemble unlike the structural arrangements along with the shape and size of the particles. Liquid can be handled as if it were composed of individual molecules each moving in Vodafone size in average due to the possibility of its neighbors. That is, not was packed in liquid molecules quite closely and there are some free spaces between the molecules of the movement and the size of Vodafone called 9. Eyring size free and Kincaid 10 definition of free size, with an effective size can be a particular molecule of the liquid can move and obedience to perfect the volume of gas laws free in terms of the speed of ultrasound ( $U$ ) and the viscosity of the fluid ( $\eta$ ) as

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

### Internal Pressure ( $\pi_i$ )

Measurement of internal pressure is important for the study of thermodynamic properties of liquids. Internal pressure, a cohesive force, is the resultant of force of attraction and/or repulsion between the molecules.<sup>[11,12]</sup> Cohesion creates a pressure within the liquid in the range of 103–104 atmospheres. Internal pressure also gives an idea about the solubility characteristics. Dissolved solutes exist under the internal pressure of the medium and their interactions with the solvent that arise through hydrogen bonding, charge transfer, Columbic (or) Vander Waal's interaction. The term  $a/v^2$  in van der

Waal's 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 is based on the Maxwell's equation of thermodynamics,<sup>[13]</sup> given as follows:

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

Based on statistical thermodynamics and based on the concept of free volume, internal pressure can be determined as follows:

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

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

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

Combining the Equations (6) and (7), the final equation for the evaluation of internal pressure is:

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

where  $K$  is constant,  $T$  the absolute temperature,  $\eta$  the viscosity ( $\text{NS/m}^2$ ),  $U$  the ultrasonic velocity ( $\text{m/s}$ ),  $\rho$  is the density ( $\text{kg/m}^3$ ) of the liquid.

### Relaxation Time ( $\tau$ )

Relaxation time is the time taken by excitation energy to convert into translational energy, depending on the temperature and impurities. Dispersion of

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

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

### Acoustic Impedance ( $Z$ )

The specific acoustic impedance is given by

$$Z = U \cdot \rho \quad \text{Eq. (10)}$$

where  $U$  and  $\rho$  are velocity and density of the liquid, respectively.

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

The relaxation time for a given transition is related to the activation free energy. The variation of  $\Delta G$  with temperature can be expressed in the form of Eyring salt process theory.<sup>[14]</sup>

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

The above equation can be rearranged as:

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

where  $K$  is Boltzmann constant and  $h$  is Plank's constant.

The excess values are calculated using the formula

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

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

System 1: 4-Methyl-2-Pentanone+Chlorobenzene (Tables 1 and 2).

**Table 1.** Mole Fraction of First Component ( $X_1$ ), Mole Fraction of Second Component ( $X_2$ ), Density ( $\rho$ ), Viscosity ( $\eta$ ), Ultrasonic Velocity ( $U$ ), Acoustic Impedance ( $Z$ ), Leonard's Jones Potential (LJP) and Molecular Interaction Parameter ( $\chi_u$ ) Values at Different Mole Fraction of Chlorobenzene+IBMK at 308 K.

| Mole fraction |        | P (kg/m <sup>3</sup> ) | $\eta \cdot 10^{-3}$<br>(NpM <sup>-2</sup> ) | U<br>(m/s) | Z $\cdot 10^{-3}$<br>(kgm <sup>-2</sup> s <sup>-1</sup> ) | LJP      | $\chi_u \cdot 10^{-3}$<br>(m/s) |
|---------------|--------|------------------------|----------------------------------------------|------------|-----------------------------------------------------------|----------|---------------------------------|
| $X_1$         | $X_2$  |                        |                                              |            |                                                           |          |                                 |
| 0.0000        | 1.0000 | 763.7                  | 5.428                                        | 508.40     | 38.824                                                    | 8.7944   | 0.0000                          |
| 0.0506        | 0.9494 | 801.3                  | 6.011                                        | 592.40     | 47.467                                                    | 9.5276   | 52.900                          |
| 0.1037        | 0.8963 | 805.5                  | 6.106                                        | 628.80     | 50.651                                                    | 9.8847   | 15.000                          |
| 0.2019        | 0.7981 | 841.8                  | 6.116                                        | 780.80     | 65.729                                                    | 11.7188  | 77.300                          |
| 0.3045        | 0.6955 | 844.4                  | 6.202                                        | 868.80     | 73.365                                                    | 13.1291  | 40.900                          |
| 0.3991        | 0.6009 | 889                    | 6.46                                         | 993.20     | 88.299                                                    | 15.8207  | 61.000                          |
| 0.5094        | 0.4906 | 913.7                  | 6.926                                        | 1153.20    | 105.369                                                   | 21.4861  | 93.800                          |
| 0.6059        | 0.3941 | 944.2                  | 7.158                                        | 1268.00    | 119.731                                                   | 28.9157  | 95.300                          |
| 0.7042        | 0.2958 | 979                    | 7.191                                        | 1385.60    | 135.655                                                   | 44.7761  | 97.100                          |
| 0.8055        | 0.1945 | 1015.4                 | 7.298                                        | 1442.00    | 146.426                                                   | 60.7595  | 51.300                          |
| 0.9016        | 0.0984 | 1047.4                 | 7.527                                        | 1569.60    | 164.398                                                   | 315.7895 | 64.500                          |
| 1.0000        | 0.0000 | 1068.7                 | 7.681                                        | 1580.00    | 168.859                                                   | 480.0000 | 0.0000                          |

**Table 2.** Adiabatic Compressibility ( $\beta$ ), Relaxation Time ( $\tau$ ), Free Volume ( $V_f$ ), Internal Pressure ( $\pi_i$ ), Cohesive Force (CE), Absorption Co-efficient ( $\alpha/f^2$ ), Free Length ( $L_f$ ) and Activation Energy ( $\Delta G^\#$ ) Values at Different Mole Fraction of 4-Methyl-2-Pentanone +Chlorobenzene at 308 K.

| $\beta_s \cdot 10^{-10}$<br>(T/Pa) | $\tau \cdot 10^{-4}$<br>(s) | $V_f$<br>(mL/mole) | $\pi_i$<br>(atm) | CE $\cdot 10^{-2}$<br>(kJ/mole) | $\alpha/f^2 \cdot 10^3$<br>(NpM <sup>-1</sup> s <sup>2</sup> ) | $L_f$<br>A <sup>0</sup> | $\Delta G^\# \cdot 10^{-20}$<br>(kJ/mole) |
|------------------------------------|-----------------------------|--------------------|------------------|---------------------------------|----------------------------------------------------------------|-------------------------|-------------------------------------------|
| 50.7                               | 3.6664                      | 0.1118             | 0.0000           | 0.0000                          | 0.0000                                                         | 2.17                    | 0.0000                                    |
| 35.6                               | 2.8502                      | 0.1206             | 4181.7276        | 52.600                          | 1.683                                                          | 1.96                    | 0.003                                     |
| 31.4                               | 2.5562                      | 0.1694             | 4074.2113        | 51.310                          | 1.35                                                           | 1.90                    | 0.003                                     |
| 19.5                               | 1.5891                      | 0.1984             | 3716.3508        | 45.323                          | 5.62                                                           | 1.67                    | 0.003                                     |
| 15.7                               | 1.2974                      | 0.2320             | 3504.3769        | 43.133                          | 3.67                                                           | 1.58                    | 0.003                                     |
| 11.4                               | 0.98208                     | 0.2666             | 3416.6108        | 40.394                          | 2.31                                                           | 1.44                    | 0.003                                     |
| 8.23                               | 0.7600                      | 0.2975             | 3293.6937        | 38.382                          | 1.43                                                           | 1.32                    | 0.003                                     |
| 6.59                               | 0.62861                     | 0.3433             | 3221.5940        | 36.736                          | 1.03                                                           | 1.24                    | 0.003                                     |
| 5.32                               | 0.5101                      | 0.3626             | 3123.0564        | 34.736                          | 0.72                                                           | 1.16                    | 0.003                                     |
| 4.74                               | 0.4608                      | 0.3995             | 3118.0487        | 33.823                          | 0.62                                                           | 1.12                    | 0.003                                     |
| 3.88                               | 0.3890                      | 0.3979             | 3059.9708        | 32.528                          | 0.46                                                           | 1.06                    | 0.003                                     |
| 3.75                               | 0.3838                      | 0.1118             | 3083.0352        | 32.471                          | 0.46                                                           | 1.04                    | 0.003                                     |

System 2: 4-Methyl-2-Pentanone + Aniline (Tables 3 and 4).

**Table 3.** Mole Fraction of First Component ( $X_1$ ), Mole Fraction of Second Component ( $X_2$ ), Density ( $\rho$ ), Viscosity ( $\eta$ ), Ultrasonic Velocity ( $U$ ), Acoustic Impedance ( $Z$ ), Leonard's Jones Potential (LJP) and Molecular Interaction Parameter ( $\chi_u$ ) Values at Different Mole Fraction of 4-Methyl-2-Pentanone + Aniline at 308 K.

| Mole fraction |        | $\rho$<br>(kg/m <sup>3</sup> ) | $\eta \cdot 10^{-5}$<br>(Npm <sup>-2</sup> ) | U<br>(m/s) | Z $\cdot 10^{-3}$<br>(kgm <sup>-2</sup> s <sup>-1</sup> ) | LJP   | $\chi_u \cdot 10^{-3}$<br>(m/s) |
|---------------|--------|--------------------------------|----------------------------------------------|------------|-----------------------------------------------------------|-------|---------------------------------|
| $X_1$         | $X_2$  |                                |                                              |            |                                                           |       |                                 |
| 0.0000        | 1.0000 | 101.41                         | 1.5777                                       | 1380.00    | 1399                                                      | 43.64 | 0.0000                          |
| 0.0506        | 0.9494 | 100.16                         | 1.4937                                       | 1373.00    | 1375                                                      | 42.29 | 0.0007                          |
| 0.1037        | 0.8963 | 98.72                          | 1.4368                                       | 1364.00    | 1347                                                      | 40.68 | 0.0007                          |
| 0.2019        | 0.7981 | 97.31                          | 1.3814                                       | 1352.00    | 1316                                                      | 38.71 | 0.0007                          |
| 0.3045        | 0.6955 | 94.21                          | 1.2353                                       | 1324.00    | 1247                                                      | 34.78 | 0.0007                          |
| 0.3991        | 0.6009 | 92.73                          | 1.1620                                       | 1305.00    | 1210                                                      | 32.54 | 0.0007                          |
| 0.5094        | 0.4906 | 89.91                          | 1.0346                                       | 1275.00    | 1146                                                      | 29.54 | 0.0008                          |
| 0.6059        | 0.3941 | 88.42                          | 0.9783                                       | 1262.00    | 1116                                                      | 28.40 | 0.0008                          |
| 0.7042        | 0.2958 | 85.35                          | 0.9001                                       | 1241.00    | 1059                                                      | 26.74 | 0.0008                          |
| 0.8055        | 0.1945 | 82.56                          | 0.7966                                       | 1226.00    | 1012                                                      | 25.67 | 0.0008                          |
| 0.9016        | 0.0984 | 81.56                          | 0.4523                                       | 1210.00    | 987                                                       | 24.62 | 0.0008                          |
| 1.0000        | 0.0000 | 79.4                           | 0.3947                                       | 1204.00    | 956                                                       | 24.24 | 0.0000                          |

**Table 4.** Adiabatic Compressibility ( $\beta$ ), Relaxation Time ( $\tau$ ), Free Volume ( $V_f$ ), Internal Pressure ( $\pi_i$ ), Cohesive Force (CE), Absorption Co-efficient ( $\alpha/f^2$ ), Free Length ( $L_f$ ) and Activation Energy ( $\Delta G^\#$ ) Values at Different Mole Fraction of 4-Methyl-2-Pentanone+Aniline At 308 K.

| $\beta \cdot 10^{-12}$<br>(T Pa) <sup>-1</sup> | $\tau \cdot 10^{-7}$<br>(s) | $V_f \cdot 10^{-3}$<br>(L/mole) | $\pi_i$<br>(atm) | CE<br>(kJ/mole) | $\alpha/f^2 \cdot 10^3$<br>(Npm <sup>-1</sup> s <sup>2</sup> ) | $L_f$<br>Å <sup>0</sup> | $\Delta G^\# \cdot 10^{-20}$<br>(kJ/mole) |
|------------------------------------------------|-----------------------------|---------------------------------|------------------|-----------------|----------------------------------------------------------------|-------------------------|-------------------------------------------|
| 51.78                                          | 1.0892                      | 0.0830                          | 5695             | 52.3            | 5.1                                                            | 1.14                    | 0.003                                     |
| 52.96                                          | 1.0548                      | 0.0900                          | 5485             | 51.2            | 4.6                                                            | 1.15                    | 0.003                                     |
| 54.45                                          | 1.0430                      | 0.0950                          | 5322             | 50.6            | 4.3                                                            | 1.17                    | 0.003                                     |
| 56.22                                          | 1.0355                      | 0.1000                          | 5168             | 50.0            | 4.1                                                            | 1.18                    | 0.003                                     |
| 60.55                                          | 0.9973                      | 0.1161                          | 4783             | 48.3            | 3.4                                                            | 1.21                    | 0.003                                     |
| 63.32                                          | 0.9811                      | 0.1254                          | 4599             | 47.4            | 3.2                                                            | 1.23                    | 0.003                                     |
| 68.42                                          | 0.9438                      | 0.1461                          | 4257             | 45.6            | 2.7                                                            | 1.26                    | 0.003                                     |
| 71.01                                          | 0.9263                      | 0.1576                          | 4091             | 44.8            | 2.5                                                            | 1.28                    | 0.003                                     |
| 76.08                                          | 0.9130                      | 0.1770                          | 3817             | 43.8            | 2.1                                                            | 1.32                    | 0.003                                     |
| 80.58                                          | 0.8559                      | 0.2121                          | 3490             | 41.8            | 1.7                                                            | 1.35                    | 0.003                                     |
| 83.74                                          | 0.5050                      | 0.4910                          | 2605             | 31.8            | .6                                                             | 1.36                    | 0.003                                     |
| 86.88                                          | 0.4572                      | 0.6030                          | 2380             | 30.0            | .4                                                             | 1.38                    | 0.003                                     |

System 3: 4-Methyl-2-Pentanone + N, N-Dimethylaniline (Tables 5 and 6)

**Table 5.** Mole Fraction of First Component ( $X_1$ ), Mole Fraction of Second Component ( $X_2$ ), Density ( $\rho$ ), Viscosity ( $\eta$ ), Ultrasonic Velocity (U), Acoustic Impedance (Z), Leonard's Jones Potential (LJP) and Molecular Interaction Parameter ( $\chi_u$ ) Values at Different Mole Fraction of 4Methyl-2-Pentanone + N,N-Dimethyl Aniline at 308 K.

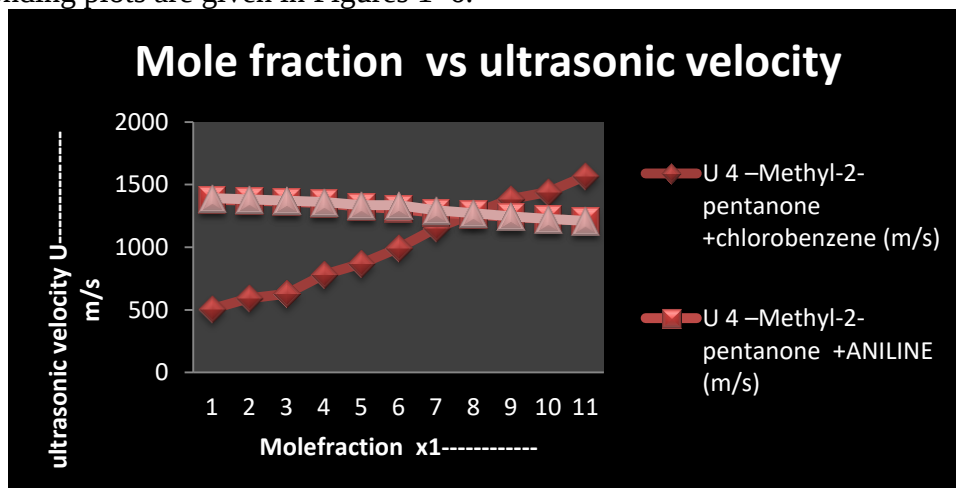
| Mole fraction |        | $\rho$<br>(kg/m <sup>3</sup> ) | $\eta \cdot 10^{-3}$<br>(Npm <sup>-2</sup> ) | U<br>(m/s) | $Z \cdot 10^{-3}$<br>(kgm <sup>-2</sup> s <sup>-1</sup> ) | LJP | $\chi_u \cdot 10^{-3}$<br>(m/s) |
|---------------|--------|--------------------------------|----------------------------------------------|------------|-----------------------------------------------------------|-----|---------------------------------|
| $X_1$         | $X_2$  |                                |                                              |            |                                                           |     |                                 |
| 0.0000        | 1.0000 | 94.08                          | 1.4368                                       | 1393.00    | 1311                                                      | 46  | 0                               |
| 0.0506        | 0.9494 | 93.38                          | 1.2987                                       | 1383.00    | 1291                                                      | 44  | 0.002                           |
| 0.1037        | 0.8963 | 92.43                          | 1.1515                                       | 1371.00    | 1267                                                      | 42  | 0.003                           |
| 0.2019        | 0.7981 | 91.56                          | 1.0334                                       | 1362.00    | 1247                                                      | 40  | 0.005                           |
| 0.3045        | 0.6955 | 89.51                          | 0.9106                                       | 1337.00    | 1197                                                      | 37  | 0.006                           |
| 0.3991        | 0.6009 | 88.54                          | 0.8206                                       | 1336.00    | 1183                                                      | 36  | 0.015                           |
| 0.5094        | 0.4906 | 86.67                          | 0.7176                                       | 1294.00    | 1122                                                      | 31  | 0.001                           |
| 0.6059        | 0.3941 | 85.52                          | 0.6683                                       | 1271.00    | 1087                                                      | 29  | -0.006                          |
| 0.7042        | 0.2958 | 85.35                          | 0.5935                                       | 1247.00    | 1064                                                      | 27  | -0.005                          |
| 0.8055        | 0.1945 | 83.51                          | 0.5287                                       | 1227.00    | 1025                                                      | 26  | -0.003                          |
| 0.9016        | 0.0984 | 81.76                          | 0.4523                                       | 1210.00    | 989                                                       | 25  | -0.009                          |
| 1.0000        | 0.0000 | 79.37                          | 0.3945                                       | 1204.00    | 956                                                       | 24  | 0                               |

**Table 6.** Adiabatic Compressibility ( $\beta$ ), Relaxation Time ( $\tau$ ), Free Volume ( $V_f$ ), Internal Pressure ( $\pi_i$ ), Cohesive Force (CE), Absorption Co-efficient ( $\alpha/f^2$ ), Free Length ( $L_f$ ) and Activation Energy ( $\Delta G^\#$ ) Values at Different Mole Fraction of 4-Methyl-2-Pentanone + N, N-Diethyl Aniline at 308 K.

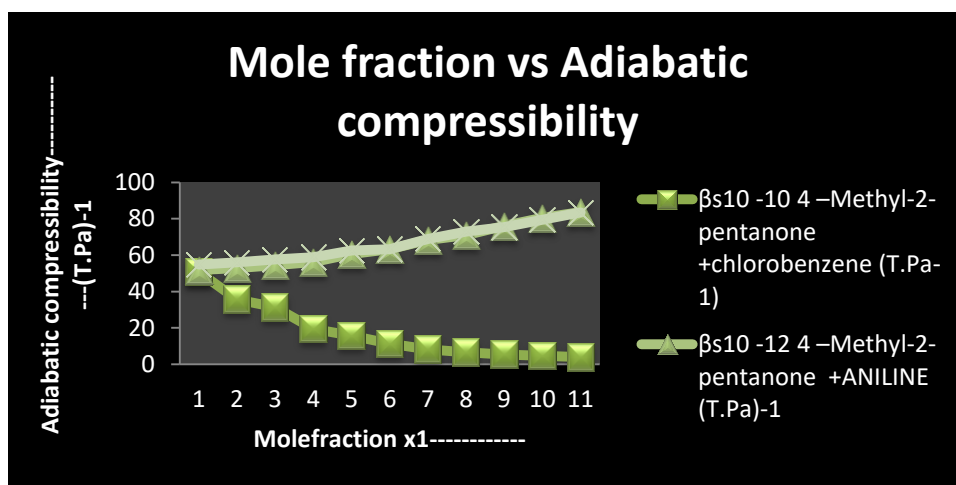
| $\beta \cdot 10^{-12}$<br>(T.Pa) <sup>-1</sup> | $\tau \cdot 10^{-6}$<br>(s) | $V_f \cdot 10^{-3}$<br>(L/mole) | $\pi_i$<br>(atm) | CE<br>(kJ/mole) | $\alpha/f^2 \cdot 10^3$<br>(Npm <sup>-1</sup> s <sup>2</sup> ) | $L_f$<br>Å <sup>0</sup> | $\Delta G^\# \cdot 10^{-20}$<br>(kJ/mole) |
|------------------------------------------------|-----------------------------|---------------------------------|------------------|-----------------|----------------------------------------------------------------|-------------------------|-------------------------------------------|
| 54.78                                          | 1.049                       | 0.1438                          | 3785             | 48.7            | 2.158                                                          | 1.18                    | 0.003                                     |
| 55.99                                          | 0.969                       | 0.1625                          | 3645             | 46.7            | 1.863                                                          | 1.19                    | 0.003                                     |
| 57.56                                          | 0.884                       | 0.1888                          | 3471             | 44.4            | 1.553                                                          | 1.20                    | 0.003                                     |
| 58.88                                          | 0.811                       | 0.2163                          | 3321             | 42.4            | 1.313                                                          | 1.21                    | 0.003                                     |
| 62.50                                          | 0.759                       | 0.2447                          | 3193             | 40.7            | 1.157                                                          | 1.24                    | 0.003                                     |
| 63.28                                          | 0.692                       | 0.2805                          | 3054             | 38.9            | 0.967                                                          | 1.24                    | 0.003                                     |
| 68.91                                          | 0.659                       | 0.3155                          | 2942             | 37.3            | 0.882                                                          | 1.28                    | 0.003                                     |
| 72.98                                          | 0.645                       | 0.3342                          | 2888             | 36.6            | 0.847                                                          | 1.30                    | 0.003                                     |
| 75.35                                          | 0.596                       | 0.3731                          | 2830             | 35.0            | 0.766                                                          | 1.31                    | 0.003                                     |
| 79.54                                          | 0.561                       | 0.4181                          | 2727             | 33.7            | 0.680                                                          | 1.34                    | 0.003                                     |
| 83.54                                          | 0.504                       | 0.5096                          | 2535             | 31.6            | 0.535                                                          | 1.36                    | 0.003                                     |
| 86.91                                          | 0.457                       | 0.6035                          | 2379             | 30.0            | 0.430                                                          | 1.38                    | 0.003                                     |

**Graph**

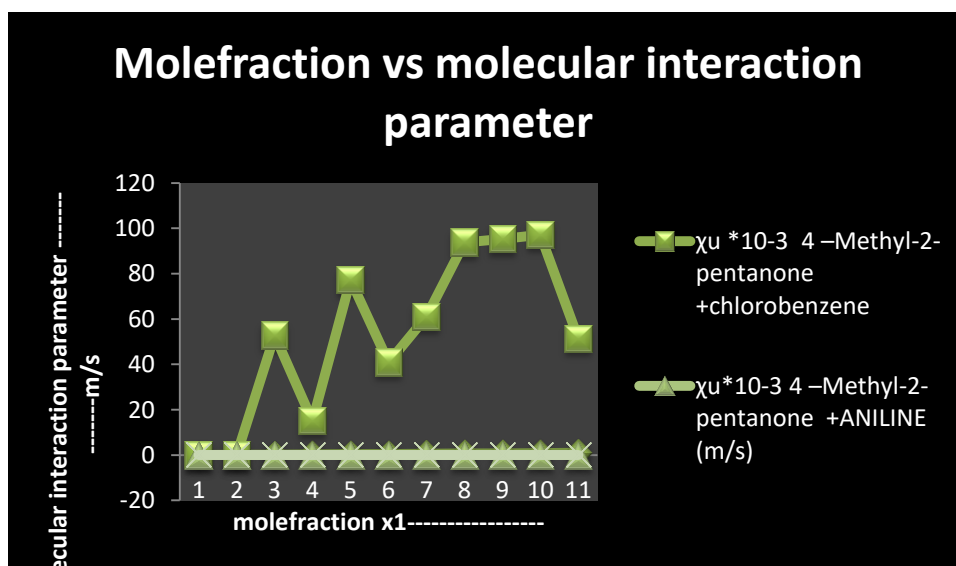
Corresponding plots are given in Figures 1–6.



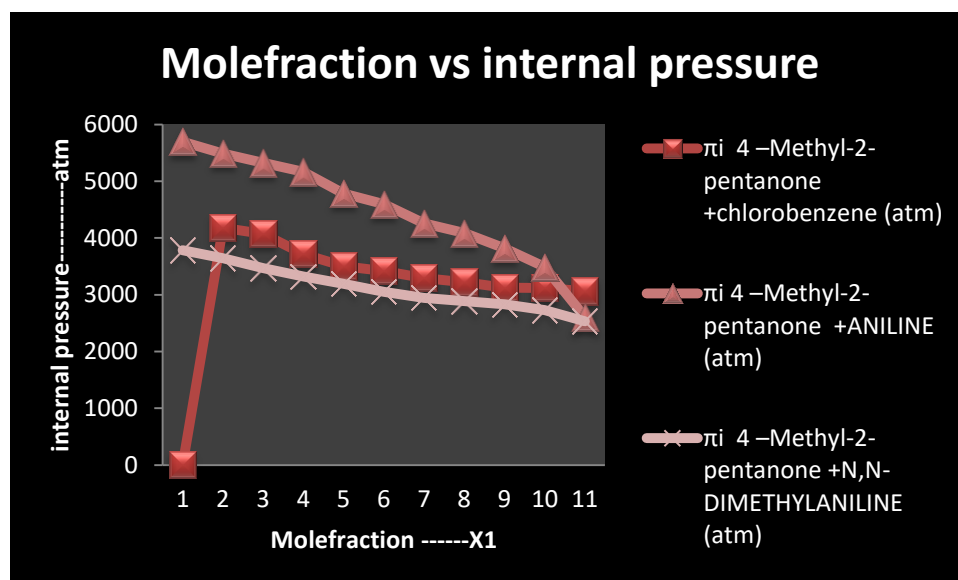
**Fig. 1.** Mole Fraction Vs Ultrasonic Velocity.



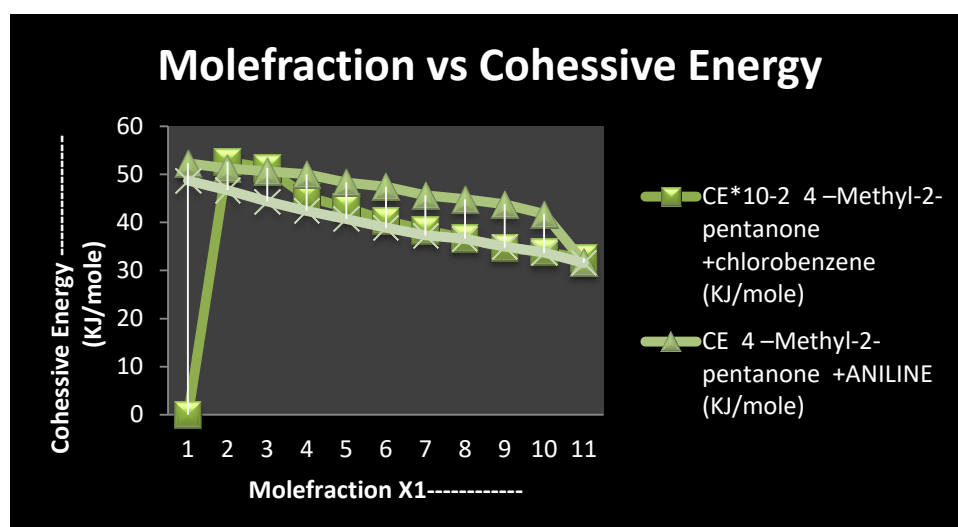
**Fig. 2.** Mole Fraction Vs Adiabatic Compressibility.



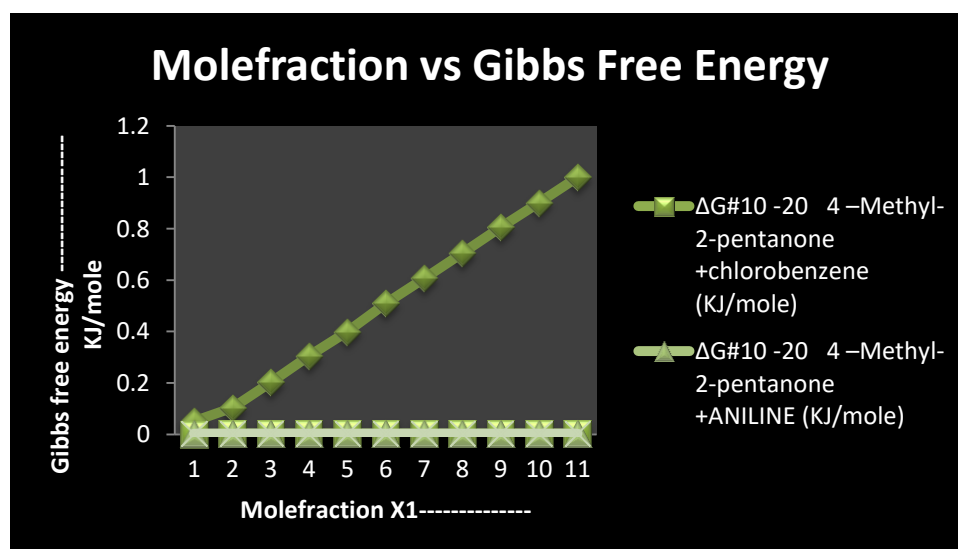
**Fig. 3.** Mole Fraction Vs Molecular Interaction Parameter.



**Fig. 4.** Mole Fraction Vs Internal Pressure.



**Fig. 5.** Mole Fraction Vs Cohesive Energy.



**Fig. 6.** Mole Fraction Vs Gibbs Free Energy.

## RESULTS AND DISCUSSION

From the Tables 1 and 4, it is noted that the density decreases with increase in mole fraction for 4-methyl-2-pentanone+butan-2-one, 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde. Ultrasonic velocity and viscosity decreases with increase in mole fraction of the solute in 4-methyl-2-pentanone+butan-2-one, 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde.

From the Tables 1, 3 and 5, the corresponding plots are given in Figures 2 and 4. 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 system 4-methyl-2-pentanone+butan-2-one, 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde. 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, 4 and 6, the corresponding plots are given in Figures 2 and 4. It is noted that the adiabatic compressibility and free length increases with increase of mole fraction in system 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde. This may lead to the presence of specific molecular interaction between the molecules of the liquid mixture. The adiabatic compressibility and free length are the deciding factors of the ultrasonic velocity in liquid systems. The internal pressure decreases and free volume increases with increasing mole fraction.

The internal pressure free volume values are tabulated in 2, 4 and 6. The corresponding plots are given in Figures 3 and 4, 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 1, 3 and 5, acoustic impedance decreases with increase of mole fraction in all the three systems. The relaxation time ( $\tau$ ) decreases with increasing concentration for all the three systems.

The dispersion of the ultrasonic velocity in the system should contain information about the characteristic time  $\tau$  of the relaxation process that causes dispersion.

The relaxation time which is in the order of  $10^{-12}$  sec is due to structural relaxation process<sup>[16-28]</sup> and in such a situation it is suggested that the molecules get rearranged due to co-operative process.<sup>[29]</sup>

The Gibb's free energy more or less same with increasing mole fraction for all the systems.

From the Tables 1, 3. The corresponding plots are given in Figures 3, 13 and 23. It is seen that the molecular interaction parameters values are more negative in system 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde than 4-

methyl-2-pentanone+butan-2-one. It is suggested that dipole-dipole interactions stronger than induced dipole-induced dipole interactions.

From the Tables 2 and 5, the corresponding plots are given in Figure 6. 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.

Hence, from these factors, there is less intermolecular hydrogen bond formation and less dipole-dipole interaction in 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde than 4-methyl-2-pentanone+butan-2-one.

## CONCLUSION

The computed acoustical parameters and their values point to the presence of specific molecular interaction in the liquid mixtures 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde than 4-methyl-2-pentanone+butan-2-one at 308 K. Hence, it is concluded that the association in these mixtures is the result of strong hydrogen bonding between the molecules and strong dipole-dipole interactions 4-methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde than 4-methyl-2-pentanone+butan-2-one in binary liquid mixtures.

The proportional studies of divergence in these systems are given by cumulative order. 4-Methyl-2-pentanone+cyclohexanone and 4-methyl-2-pentanone+furfuraldehyde than 4-methyl-2-pentanone+butan-2-one. These parameters will be useful in pharmacy and

perfumes industries for handling and mixing process.

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