

Acoustical and Thermodynamical Studies in Ternary Mixtures of Ethylene Glycol and Glycerol with Octanol AT 303.15K

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Abstract -The ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for the ternary mixtures of Ethyleneglycol with Glycerol in Octanol at 303.15K. The observed data have been used to evaluate some of the thermo acoustical parameters such as adiabatic compressibility (β), intermolecular free length (L_f), free volume (V_f), internal pressure (π_i), acoustic impedance (Z), Bulk Modulus (K), Absorption Coefficient (α/f^2), Relaxation time (τ), Molar Sound Velocity (R) and Gibb's free energy (ΔG) to elucidate the molecular association in the mixture. The variation of these parameters with concentration of solute indicates the nature of interaction present in the ternary mixture.

Key Words: Ethyleneglycol, Ultrasonic velocity, adiabatic compressibility, acoustic impedance, molecular association.

1. INTRODUCTION

The ultrasonic study of liquids plays an important role in understanding the nature and strength of molecular interactions [1,2]. A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman effect [3], Nuclear Magnetic Resonance, ultra violet and ultrasonic method [49]. The study of thermodynamic properties of binary and ternary mixtures contributes to an understanding of the behavior of different liquids and functional groups. Number of studies on the thermodynamic properties of ternary mixtures has increased in recent years due to industrial applications [1-5]. A third component added to a mixture of two immiscible components brings about the phenomenon in certain ternary liquid mixtures has been studied earlier [6-9] by observing on the distribution of molecules of one component between the other two components and the formation of hitherto unknown compounds from a study of the change in free volume, molar volume, internal pressure and other thermodynamic parameters.

The measurement of ultrasonic velocity has been adequately employed in understanding the molecular interactions in liquid mixtures. Molecular interaction studies can be carried out by both spectroscopic and non-spectroscopic techniques. However, ultrasonic velocity and viscosity measurements have been widely used in the field of interactions and structural aspect evaluation studies.

Internal pressure has gained significant interest by chemists, physicists and chemical engineers in past, as it provides a measure of explaining molecular interactions, internal structure, clustering phenomenon and dipolar interactions. Internal pressure has been a subject of active interest among several researchers during recent past [7-10]. Several attempts have been made by a number of investigators [11-15] to calculate the internal pressure of liquids and liquid mixtures theoretically.

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. Cohesion creates pressure within the liquid. So internal pressure 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 interaction. In the present paper, we report density, viscosity, ultrasonic velocity for the ternary system consisting of Ethylene glycol +Glycerol+ Octanol at 303.15K and atmospheric pressure over the entire composition range. The experimental results are used to calculate adiabatic compressibility, inter molecular free length, relaxation time, acoustical impedance, bulk modulus, free volume, internal pressure, Gibb's free energy, classical absorption coefficient, molar sound velocity. These parameters are used to discuss the nature of intermolecular interaction of mixtures. So, in the present work emphasis has been placed on the

determination of the parameters of the organic liquid mixtures, namely, density, and speed of sound, which are industrially important.

2. EXPERIMENTAL SECTION

The mixtures of various concentrations in mole fraction were prepared by taking analytical reagent grade chemicals with minimum assay of 99.9% and obtained from E.Merck Ltd (India). All the component liquids were purified by the standard methods [23]. The density, viscosity, and ultrasonic velocity were measured as a function of concentration of the ternary liquid mixture at temperature T = 303.15K.

Ultrasonic velocity measurements were made using an ultrasonic interferometer with the accuracy of $\pm 0.1 \text{ m}\cdot\text{s}^{-1}$. An electronically operated digital constant temperature bath operating in the temperature range of -10°C to 85°C with an accuracy of $\pm 0.1^\circ\text{C}$ has been used to circulate water through the outer jacket of the double-walled measuring cell containing the experimental liquid. The densities of the mixture were measured using a 10-ml specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ kg}\cdot\text{m}^{-3}$. An Oswald viscometer (10 ml) with an accuracy of $\pm 0.001 \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$ was used for the viscosity measurement. The flow time was determined using a digital racer stopwatch with an accuracy of $\pm 0.1 \text{ s}$.

Using the experimental values, the following thermodynamic parameters were calculated:

$$\begin{aligned} \text{Adiabatic Compressibility} & : \beta = 1/U^2 \cdot \rho \\ \text{Intermolecular free length} & : L_f = K_T \beta^{1/2} \end{aligned}$$

Where K_T is the temperature dependent constant and ' β ' is the adiabatic compressibility.

$$\text{Free Volume} : V^f = (M_{\text{eff}} \cdot U / K \cdot \eta)^{3/2}$$

Where ' M_{eff} ' is the effective mass of the mixture, ' K ' is a dimensionless constant independent of temperature and liquid. Its value is 4.281×10^9 .

$$\text{Internal Pressure } (\pi_i) : \pi_i = bRT (k\eta/U)^{1/2} (\rho^{2/3}/M^{7/6})$$

Where, ' b ' stands for cubic packing, which is assumed to be '2' for all liquids, ' k ' is a dimensionless constant independent of temperature and nature of liquids. Its value is 4.281×10^9 . ' T ' is the absolute temperature, ' M_{eff} ' is the effective molecular weight, ' R ' is the Universal gas constant.

$$\text{Acoustic impedance } (Z) : Z = U \cdot \rho$$

Gibb's free energy for activation of flow (ΔG) can be calculated using relation

$$\Delta G = RT \ln(\Delta V_m)$$

where R is the Universal gas constant ($8.31432 \times 10^7 \text{ JK}$), and T is the absolute temperature

Molar Sound Velocity or Rao's Constant (R)

Rao's constant can be calculated by the relation $R = V_m U^{1/3}$

3. RESULTS AND DISCUSSION

The experimental values of density, viscosity and speed of sound for 303.15k are presented in Table 1. The thermo-acoustical parameters for 303.15k are given in table 1&2. In order to understand reaction kinetics of binary mixture, tabulated values of thermo-acoustical parameters are graphically represented in Figures 1-12

TABLE - 1: Measured Values of Density (ρ), Viscosity (η) and velocity (U) of ternary mixture at 303.15Kk

| S. | X(i) | Y(i) | Z(i) | $\rho \times 10^{-3}$ | η | U | β_a | $L_f \times 10^{-10}$ | Z |
|----|--------|--------|--------|-----------------------|--------|------|-----------|-----------------------|--------|
| 1 | 0.1000 | 0.5000 | 0.4000 | 1.1292 | 1.3820 | 1860 | 3.264 | 1.1312 | 2.1003 |
| 2 | 0.1000 | 0.6000 | 0.3000 | 1.1270 | 1.3940 | 1882 | 3.182 | 1.1168 | 2.1210 |
| 3 | 0.1000 | 0.7000 | 0.2000 | 1.1253 | 1.4000 | 1903 | 3.107 | 1.1037 | 2.1414 |
| 4 | 0.2000 | 0.5000 | 0.3000 | 1.2342 | 1.3421 | 1831 | 3.681 | 1.2013 | 2.2598 |
| 5 | 0.2000 | 0.6000 | 0.3000 | 1.2283 | 1.4010 | 1879 | 3.479 | 1.1678 | 2.3079 |
| 6 | 0.3000 | 0.4000 | 0.3000 | 1.2396 | 1.3810 | 1890 | 3.470 | 1.1663 | 2.3428 |
| 7 | 0.3000 | 0.5000 | 0.2000 | 1.2254 | 1.3920 | 1903 | 3.384 | 1.1517 | 2.3319 |
| 8 | 0.4000 | 0.4000 | 0.2000 | 1.0420 | 1.2030 | 1849 | 3.048 | 1.0931 | 1.9266 |
| 9 | 0.5000 | 0.1000 | 0.4000 | 0.9630 | 0.9320 | 1640 | 3.583 | 1.1847 | 1.5793 |
| 10 | 0.6000 | 0.1000 | 0.3000 | 0.9010 | 1.1830 | 1543 | 3.784 | 1.2180 | 1.3902 |

TABLE - II: Thermodynamical parameters of ternary mixture at 303.15Kk

| S.No | X(i) | Y(i) | Z(i) | R | $\tau \times 10^{-10}$ | $K \times 10^9$ | $V_f \times 10^{-3}$ | $\pi_i \times 10^6$ | $\alpha/P^2 \times 10^{-12}$ | (- |
|------|--------|--------|--------|-------|------------------------|-----------------|----------------------|---------------------|------------------------------|--------|
| 1 | 0.1000 | 0.5000 | 0.4000 | 1.133 | 6.0143 | 3.0637 | 1.8795 | 0.4366 | 5.0006 | 3.8651 |
| 2 | 0.1000 | 0.6000 | 0.3000 | 1.140 | 5.9140 | 3.1427 | 1.7857 | 0.4547 | 4.8787 | 3.8661 |
| 3 | 0.1000 | 0.7000 | 0.2000 | 1.146 | 5.8003 | 3.2181 | 1.7023 | 0.4736 | 4.7464 | 3.8674 |
| 4 | 0.2000 | 0.5000 | 0.3000 | 1.031 | 6.5876 | 2.7163 | 1.7333 | 0.4978 | 4.6576 | 3.8593 |
| 5 | 0.2000 | 0.6000 | 0.3000 | 1.045 | 6.4987 | 2.8744 | 1.9343 | 0.4505 | 4.5204 | 3.8602 |
| 6 | 0.3000 | 0.4000 | 0.3000 | 1.038 | 6.3898 | 2.8816 | 1.6617 | 0.5170 | 4.3386 | 3.8613 |
| 7 | 0.3000 | 0.5000 | 0.2000 | 1.052 | 6.2802 | 2.9552 | 1.5596 | 0.5386 | 4.3338 | 3.8624 |
| 8 | 0.4000 | 0.4000 | 0.2000 | 1.225 | 4.8887 | 3.2809 | 1.7677 | 0.4742 | 4.8019 | 3.8782 |
| 9 | 0.5000 | 0.1000 | 0.4000 | 1.274 | 4.4493 | 2.7929 | 2.3390 | 0.3960 | 5.7688 | 3.8841 |
| 10 | 0.6000 | 0.1000 | 0.3000 | 1.334 | 5.9692 | 2.6424 | 1.3304 | 0.4812 | 9.3970 | 3.8656 |

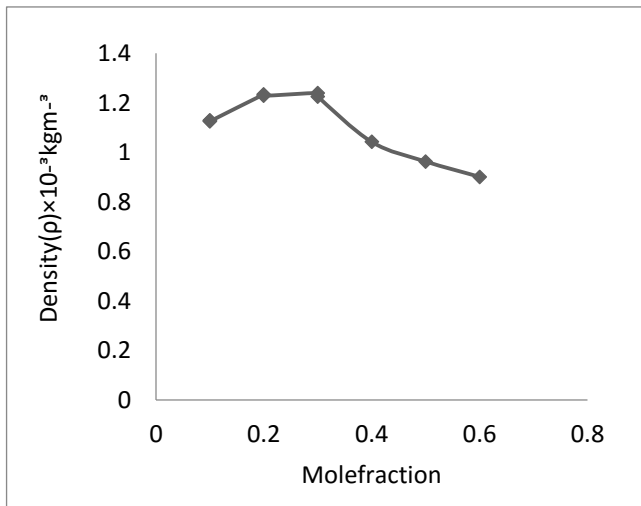


Fig-1 : Molefraction Vs Density

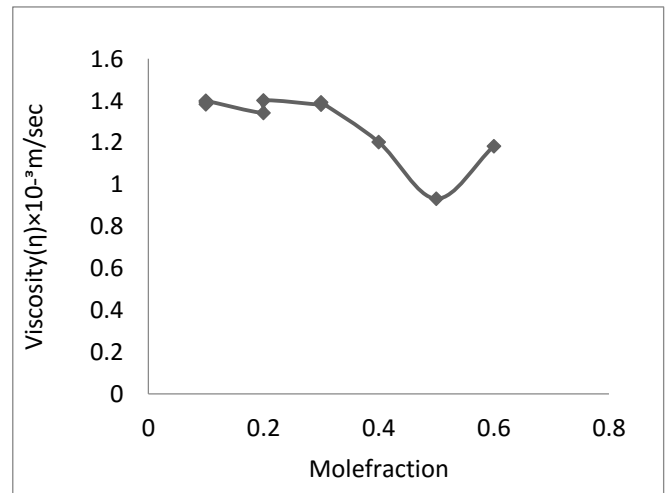


Fig - 3: Molefraction Vs viscosity

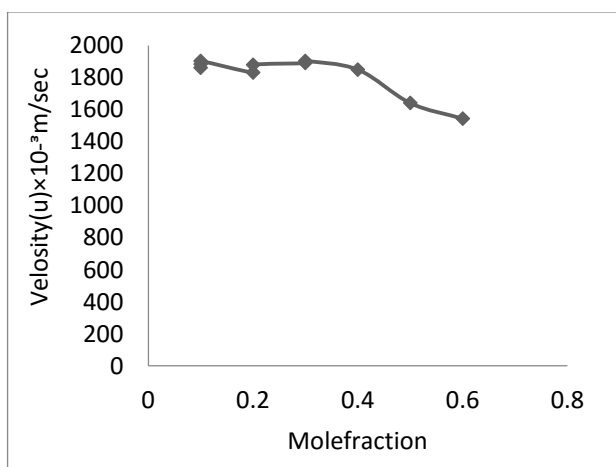


Fig - 2: Molefraction Vs Velocity

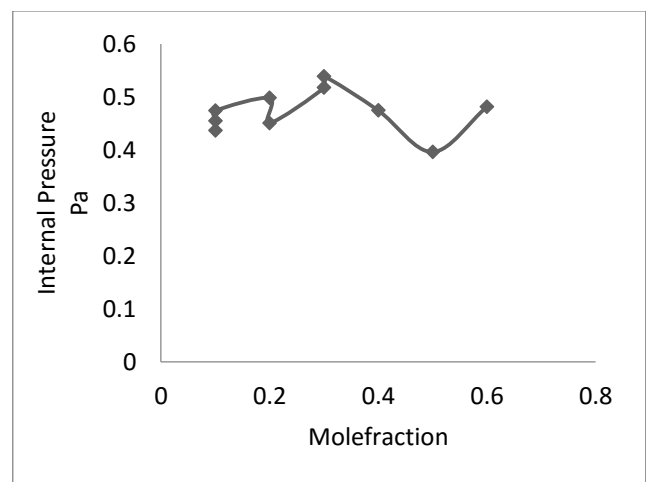


Fig - 4: Molefraction Vs Internal Pressure

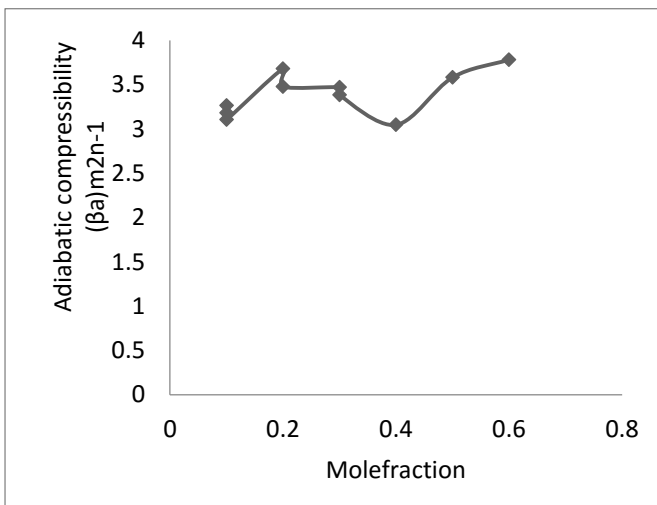


Fig - 5: Molefraction Vs Adiabatic compressibility

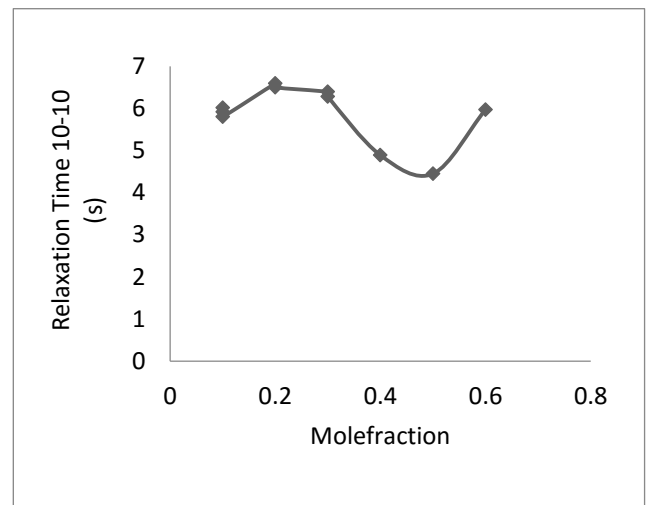


Fig - 8: Molefraction Vs Relaxation Time

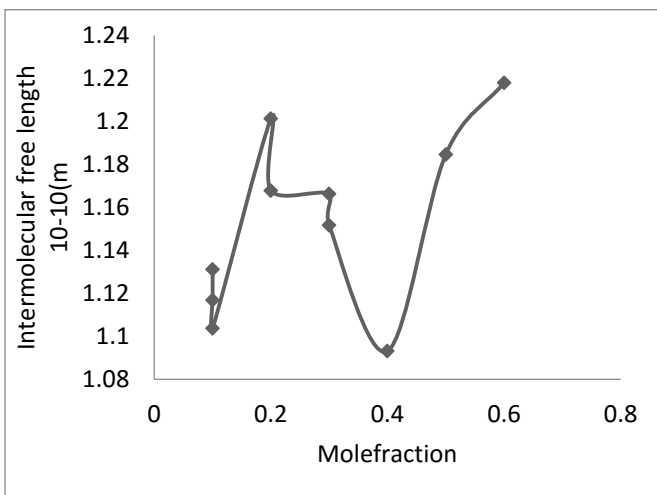


Fig - 6: Molefraction Vs Intermolecular Free length

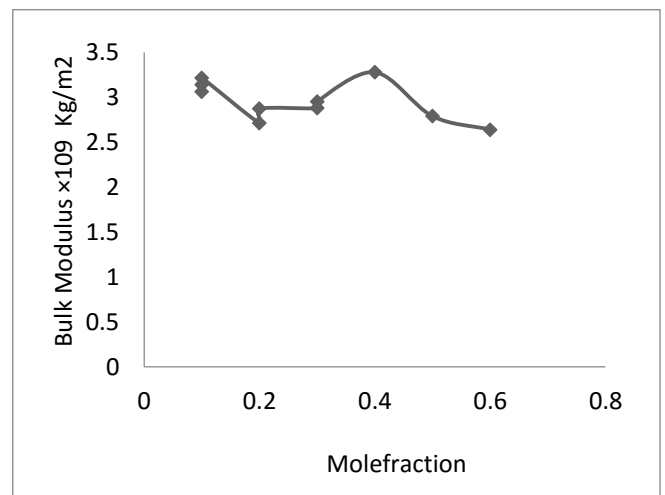


Fig - 9: Bulk Modulus Vs Molefraction

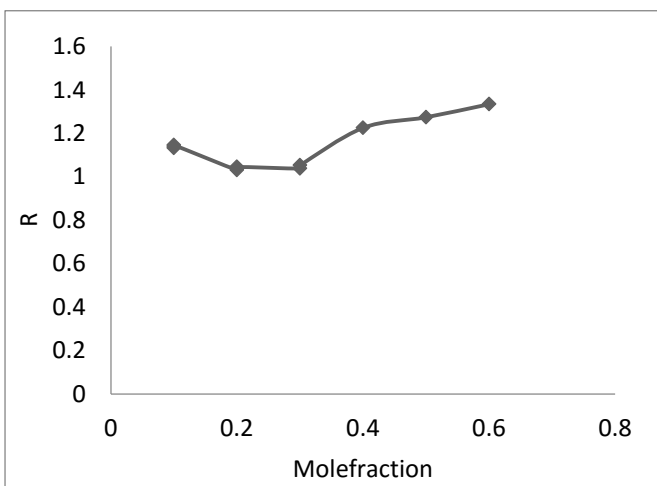


Fig - 7: Molar sound velocity Vs Molefraction

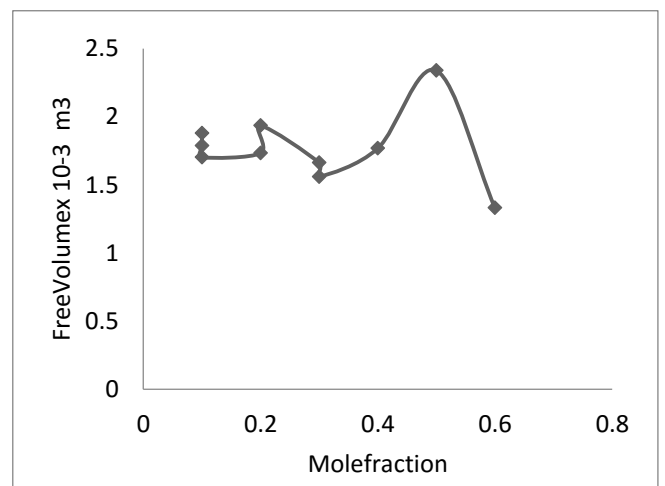


Fig - 10: Molefraction Vs Free Volume

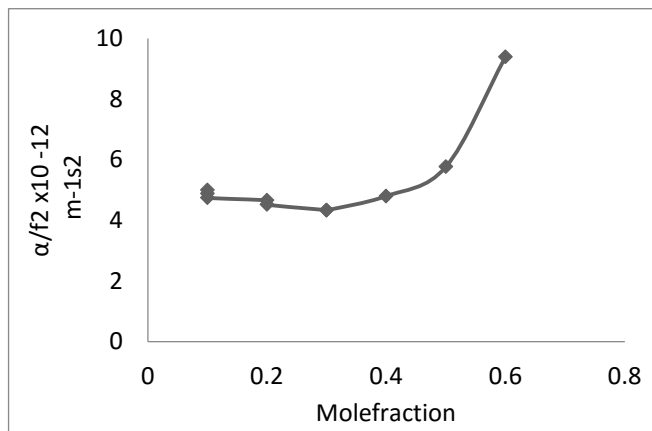


Fig - 11: Attenuation Coefficient Vs Molefraction

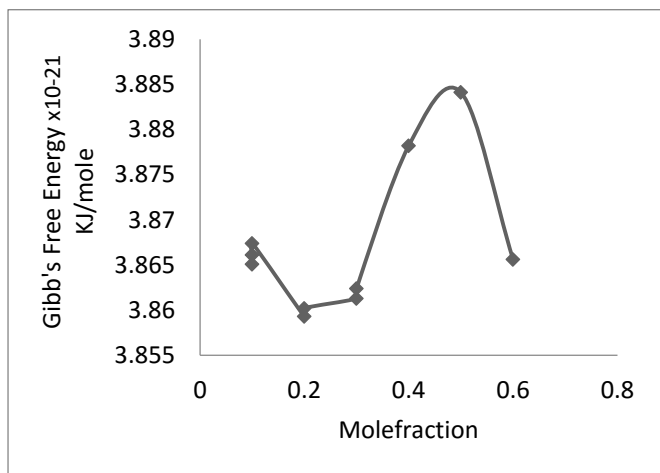


Fig - 12: Molefraction Vs Gibbs's Free ENergy

In the present investigation the ultrasonic velocity is used to access molecular interaction between Ethylene Glycol with Octanol in glycerol. Table shows the values of density, viscosity and velocity decreases with increase in molefraction. The pronounced increase or decrease in these parameters with composition of mixtures indicates the presence of interaction between the components of mixtures. Further the increase in the number of particles in solution is responsible for increasing the cohesive force between the liquid layers, thereby increasing the coefficient of viscosity. As ultrasonic velocity increases with increase in concentration, and the compressibility and intermolecular free length show reverse trend. The decrease in compressibility and L_f shows the considerable molecular interaction between the ternary mixtures, forming hydrogen bonding through dipole-dipole interaction.

The intermolecular free length is the distance covered by a sound wave between the surface of the neighbouring molecules and it depends upon the intermolecular attractive and repulsive forces. The

increase in value L_f implies that the mean distance between the molecules increases thereby decreasing the potential energy of interaction between them leading to decrease in the values of velocity and density. The decrease in density is mainly due to decrease of intermolecular forces because of thermal agitation. The decrease in velocity indicates the presence of weak interactions between the components of mixture. A continuous decrease in β_a , L_f and increase of acoustic impedance are the clear evidence for the existence of strong interactions like dipole-dipole, dipole-induced dipole interaction because of the fact that polar solvent ethylene glycol mixed with nonpolar solvents like glycerol and octanol tends to break dipolar association releasing overall EG dipoles consequently the free dipoles of EG cause induced dipole moments in the neighbouring molecules resulting in dipolar induced dipole interaction leading to contraction in the volume. Table 2 shows that the value of free volume which reflects the close packing of the solvent molecules decreases with the increase in mole fraction of EG.

The bulk modulus increases with increasing concentration this may be due to contraction governed by compressibility, which depends on intermolecular forces resulting in increases in bulk modulus with increases in concentration. The molar sound velocity increases with increasing concentration and it shows there is strong interaction between molecules.

Further the decrease in free volume and increase in internal pressure with rise in concentration of EG clearly shows the increasing magnitude of interactions. The Gibbs's free energy indicates the need for shorter time for the cooperative process or the rearrangement of the molecule in the mixtures. Rao's constant shows a decreasing trend with increase of mole fraction of EG. This non-linear trends may be attributed to possibility of molecular interactions that are taking place.

3. CONCLUSION

The above discussion reveals that the existence of molecular interactions in the ternary mixtures. The present investigation shows that greater molecular interaction exists in the mixtures which may be due to hydrogen bonding formation. Also the weak molecular interaction that exists which may be due to dominance of dispersion forces and dipolar interaction between the unlike molecule in this manner all the parameters which have been evaluated from the measured values support one another to give a conclusion that the interactions becoming strong starting from weak interactions among the component molecule of the mixtures.

4. REFERENCES

- [1]. VA Tabhane, Indian J. Pure & Applied Physics, 1983, 23, 155.
- [2]. VA Tabhane; BA Patki, Indian J. Pure & Applied Physics, 1985, 23, 58.
- [3]. M Ramamurthy; OS Sastry, Indian J. Pure & Applied Physics, 1983, 21, 579. [4] EJ Freedman, Chem. Phy., 1955, 21, 1784.
- [4]. ANKannappam; V Rajendra, Indian J. Pure & Applied Physics, 1955, 30, 176
- [5]. AA Mistry; VD Bhandakkar; O. P. Chimankar, J. of Chem. & Pharm. Res., 2012, 4(1), 170-174.
- [6]. Paul Divakar ; k Samatha, International Journal of Advanced Science and Technology, 2016, 55-70.
- [7]. Mishra Sujatha and Paikary Rita, 2013 "Research Journal of Physical Science", Vol 1(4) 15-21.
- [8]. A.N.Kannapan, S.Thirumaran and R.Palani, 2009 "Journal of Physical Science", Vol 2(20) 97-108.
- [9]. V.D.Bhandakkar, 2014 "International Journal of Advanced Research in Physical Science", Vol 1(5) pp 1-5.
- [10]. S.Thirumaran and J.Earnest Jayakumar, 2009 "Indian Journal of Pure and Applied Physics", Vol 47 pp 265-272.
- [11]. R.Palani and K.Meenakshi, 2007 "Indian journal of Chemistry", Vol 46A pp 252-257.
- [12]. M.Pushpalatha, C.H. Srinivasu and K.Narendar, 2013 "International journal of Research in Pharmacy and Chemistry", 3(1) 129-131.
- [13]. P.Kumar, S.Kumar, S.Singh and R.S.Gangwar, 2011 "Oriental Journal of Chemistry", 27(2) 639-644.
- [14]. S.Nagaraj, M.C.S Subha C.Nagamani and K.Chowdoji Rao, 2016 "World Journal of Pharmacy and Pharmaceutical Sciences", 5(1) 1423-1441.

BOOKS

1. Riddick, J.A., Bunger, W.B., Sanako, T.K., 1986, Physical properties and methods of purification, John Wiley & Sons, New York.
2. Hirschfelder, J.O., Curtio, and Byron bird R., 1950, Molecular theory of gases and Liquids, John Wiley & Sons, New York.