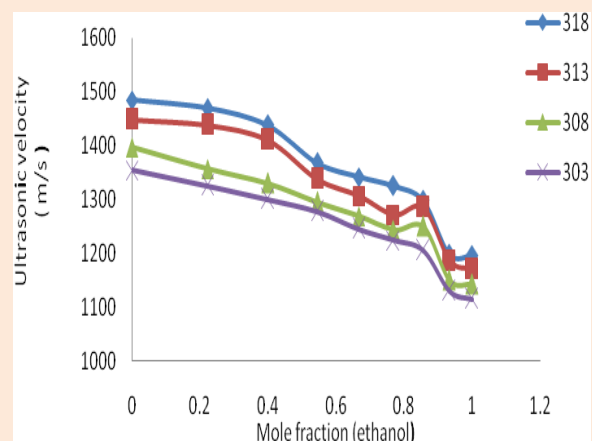


## Research Article

## Ultrasonic Study of Molecular Interaction in Binary Mixture at Different Temperatures (303 K – 318 K)

Hina Chhabra<sup>1</sup> and G C Joshi<sup>2\*</sup><sup>1</sup>Department of physics, G B Pant University of Ag. & Technology, Pantnagar-263145, Uttarakhand<sup>2</sup>Radiations and Isotopic Tracers Laboratory G B Pant University of Ag. & Technology, Pantnagar-263145, Uttarakhand**Abstract**

The study of molecular interaction using ultrasonic technique in the binary liquid mixture of Ethanol + Glycerol as a function of the composition has been carried out at four different temperatures 303<sup>o</sup>K, 308<sup>o</sup>K, 313<sup>o</sup>K and 318<sup>o</sup>K and a fixed frequency 5MHz. The thermo-acoustic parameters such as Adiabatic compressibility ( $\beta$ ), Intermolecular free length ( $L_f$ ), Free volume ( $V_f$ ), Internal pressure ( $\pi_i$ ), Relaxation time ( $\tau$ ) and Gibb's free energy( $\Delta G^*$ ), and their excess values are evaluated from the measured values of Ultrasonic velocity (U), Density ( $\rho$ ) and Viscosity ( $\eta$ ). The molecular interaction present in the liquid mixtures such as hydrogen- bonding, dipole-dipole association, acceptor-donor and electrostriction are analyzed on the basis of these parameters. The negative values of these excess parameters suggest the presence of dipolar and dispersive interaction between the components of the molecule in the mixture while the positive values of excess thermo-acoustic parameters suggest the presence of weak interactions between the unlike molecules in the liquid mixtures.



**Keywords:** Ultrasonic velocity, Thermo-acoustic parameters, Molecular interaction, Excess parameters

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**Introduction**

In the estimation of structural properties of molecules, the study of molecular interaction in liquid mixtures is of considerable importance. The knowledge of physio-chemical properties of non-aqueous binary liquid mixtures has relevance in theoretical and applied areas of research, and such results are frequently used in design process such as flow, mass transfer or heat transfer calculations in many chemical and industrial processes. Mixed solvents, rather than pure solvents find practical applications in most of the chemical processes and their properties are less known. On mixing the different solvents, the deviation from ideality of binary mixture is believed to be arising from the nature of solvent-solvent interaction and have been expressed by many acoustic as well as excess acoustic parameters. Speed of sound is fundamentally related to the binding process between the constituents of the medium and is highly sensitive to the structure and interactions present in the liquid mixtures. In recent years, ultrasonic technique has become powerful and reliable tools for the study of molecular interactions in pure liquids as well as liquid mixtures [1-3]. Derived parameters from ultrasonic velocity measurements and the corresponding excess functions provide qualitative information regarding the nature and strength of molecular interactions in liquid mixtures [4]. The determination of ultrasound velocity, density, viscosity, thermo-acoustic and their excess parameters derives wide applications in characterizing the behavior and the qualitative estimation of the molecular interactions in solutions of binary liquid mixtures. Glycerol is a chemical, which has multitude of uses in pharmaceutical, cosmetic and food industries. Due to its various applications in pharmaceutical, health care and food industries, it is important to understand the structure and molecular interaction of glycerol. Similarly alcohols are strongly self-associated liquids having a three dimensional network of hydrogen bond and can be associated with any

group [5-6], so it is interesting to study the molecular association in binary/ternary mixtures having alcohol as a one of the components. The ultrasonic measurements on solutions of alcohols and glycerol have been found to be highly useful in understanding the structure of molecular interaction.

In the present work, an attempt has been made by investigating the temperatures dependence of different parameters to throw some light on the relative strength of the molecular interactions and their nature in the binary mixture of ethanol and glycerol at the crystal frequency of 5 MHz.

## Experimental

The Ethanol and Glycerol used were of Analytical Reagent (AR) grade with minimum assay of 99.9% from SD fine chemicals. These chemicals are used without further purification. The ultrasonic velocity in the liquids and their mixtures have been measured using a Multifrequency (1-8 MHz) ultrasonic interferometer (Model: M-82S) purchased from M/S Mittal Enterprises, New Delhi and for maintaining temperature stability ( $\pm 0.01$  K), a constant temperature water bath (Model SSI-03 spl, Mittal Enterprises, New Delhi) was used having range of  $-5$  °C to  $85$  °C with an accuracy of  $\pm 0.1$  °C. A 10 ml specific gravity bottle and electronic balance machine (Citizen CTG6C2B-600) were used for the determination of density measurements. The viscosity of the sample has been measured using Ostwald viscometer with an accuracy of  $\pm 0.0001$  Nsm<sup>-2</sup>. Triply distilled water has been used as reference liquid.

### Determination of thermo-acoustic parameters

The experimentally measured ultrasonic speed (U), density ( $\rho$ ) and viscosity ( $\eta$ ) are used to calculate the various thermo-acoustic parameters using the following standard expressions:

#### Compressibility ( $\beta$ )

The compressibility of mixtures was calculated by the following formula:

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

where,  $\rho$  is the density of solution and U is the ultrasonic velocity of solution.

#### Intermolecular free path length ( $L_f$ )

Intermolecular free path length was calculated by using the relation:

$$L_f = K_T \times \beta^{1/2}$$

Where,  $K_T$  is temperature dependent Jacobson constant having value  $(91.368 + 0.3565T) 10^{-8}$ .

#### Free Volume ( $V_f$ )

Free volume was calculated by using the formula:

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

where, U is the ultrasonic velocity of the solution, K is a constant having value  $4.28 \times 10^9$ ,  $\eta$  is viscosity and  $M_{eff}$  is the effective molecular weight.

#### Internal Pressure ( $\pi_i$ )

The internal pressure of a liquid system was calculated by using the following expression:

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

where,  $b$  is a cubical packing fraction taken as 2 for all the liquids,  $\eta$  is viscosity of the solution,  $U$  is ultrasonic velocity,  $\rho$  is density,  $R$  is universal gas constant,  $T$  is temperature and  $M_{\text{eff}}$  is effective molecular weight of the solution.

$M_{\text{eff}}$  is calculated by using the formula:

$$M_{\text{eff}} = x_1 m_1 + x_2 m_2$$

where  $x_1$ ,  $m_1$  and  $x_2$ ,  $m_2$  are mole fraction and molecular weight of the glycerol and ethanol solutions respectively.

#### Relaxation time ( $\tau$ )

The relaxation time was calculated as:

$$\tau = \frac{4}{3} \beta \eta$$

Where,  $\beta$  is the Compressibility of solution and  $\eta$  is viscosity of solution.

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

The relaxation time for a given transition is related to the activation free energy. The variation of  $\tau$  with temperature can be expressed by

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

The above equation can be rearranged as,

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

where,  $K$  is the Boltzmann constant and  $h$  is plank's constant.

#### Excess Parameters

Excess values of various acoustic and thermodynamic parameters were calculated using the relation:

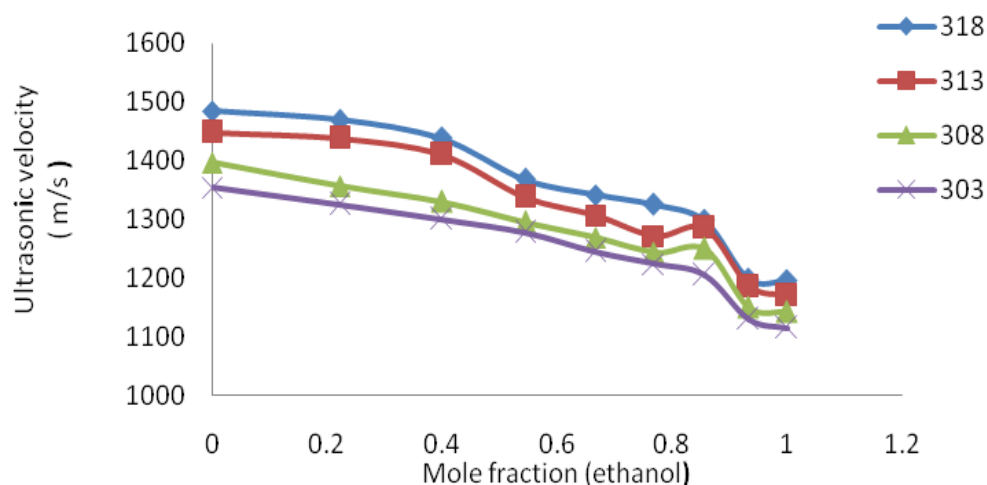
$$Y^E = Y_{\text{exp}} - Y_{\text{ideal}}$$

Where,  $Y^E$  is excess value of the parameter  $Y$  and  $Y_{\text{exp}}$  is experimental value of the parameter  $Y$

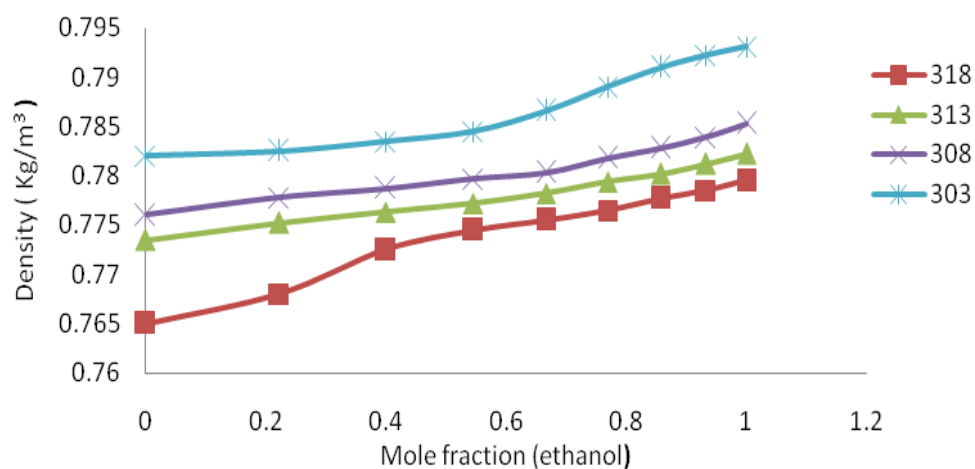
$Y_{\text{ideal}} = x_1 Y_1 + x_2 Y_2$ ;  $x_1$ ,  $x_2$  are the mole fractions and  $Y_1$ ,  $Y_2$  are the values of the parameter  $Y$  in the component liquids of the liquid mixture.

### Results and Discussions

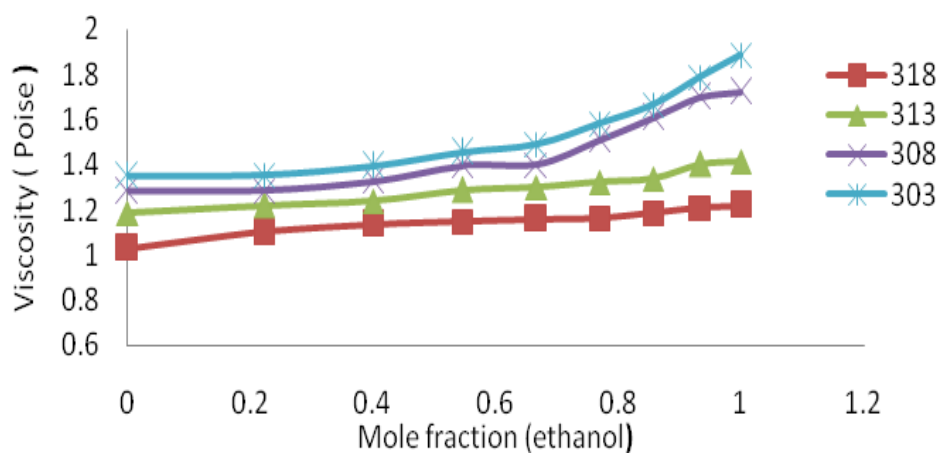
The variation of ultrasonic velocity ( $U$ ), density( $\rho$ ) and viscosity( $\eta$ ) measured at a fixed frequency of 5 MHz for the whole composition at four temperatures 303<sup>o</sup>K, 308<sup>o</sup>K, 313<sup>o</sup>K and 318<sup>o</sup>K are shown in **Figures 1–3**. The thermo-acoustic parameters such as Adiabatic compressibility ( $\beta$ ), Intermolecular free length ( $L_f$ ), Free volume ( $V_f$ ), Internal pressure ( $\pi_i$ ), Relaxation time ( $\tau$ ) and Gibb's free energy( $\Delta G^*$ ), and their excess values as a function of mole fraction at all four temperatures are represented in to **Figures 4–16**.



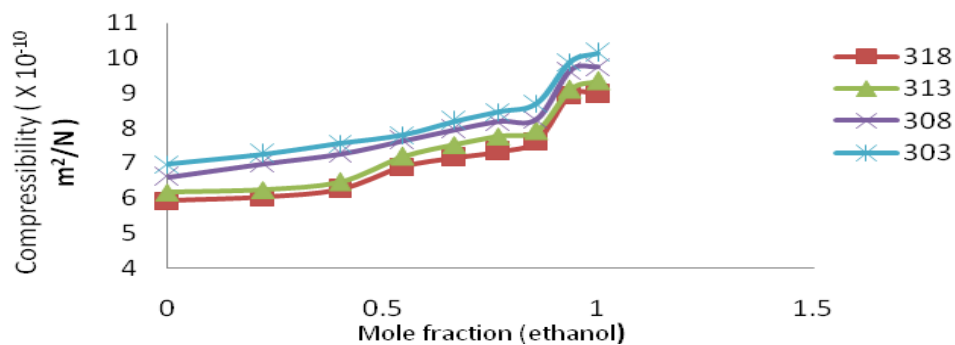
**Figure 1** Variation of Ultrasonic velocity



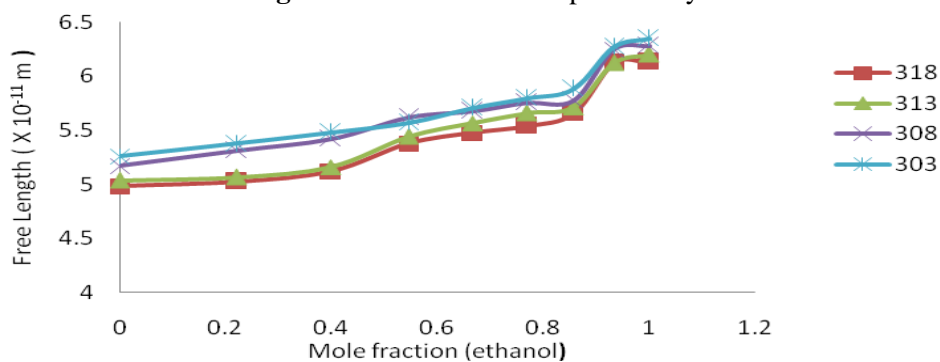
**Figure 2** Variation of Density



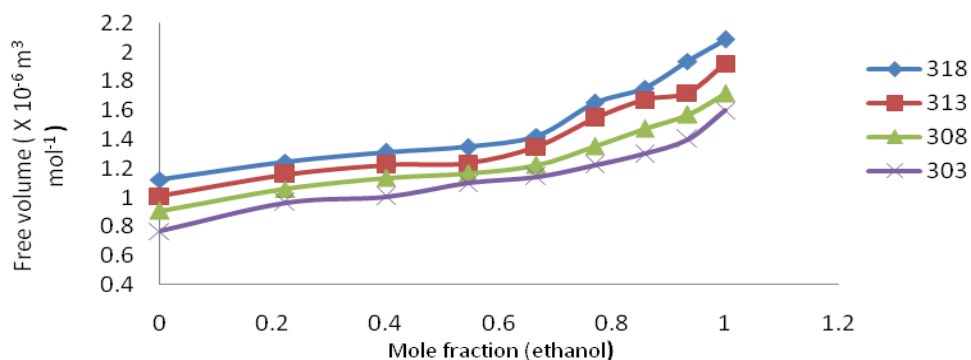
**Figure 3** Variation of Viscosity



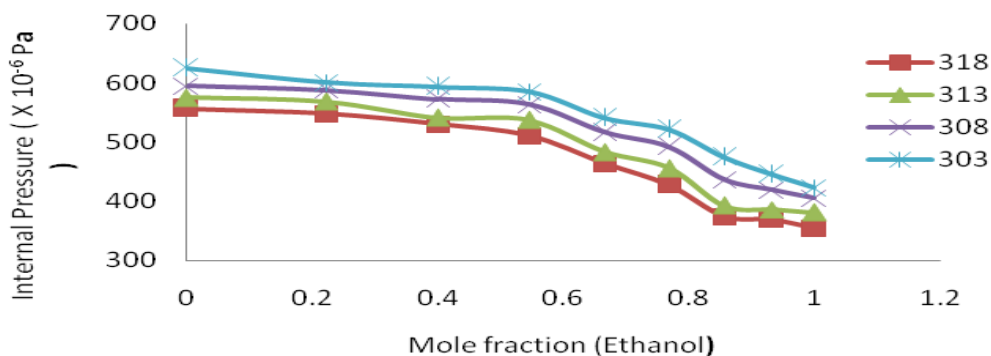
**Figure 4** Variation of Compressibility



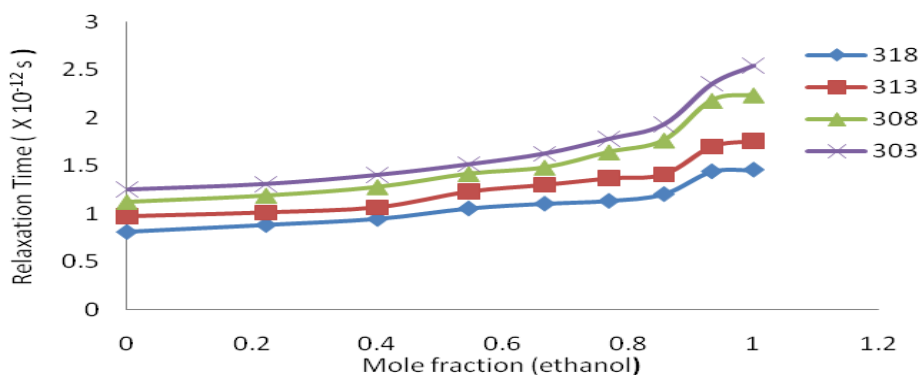
**Figure 5** Variation of Free length



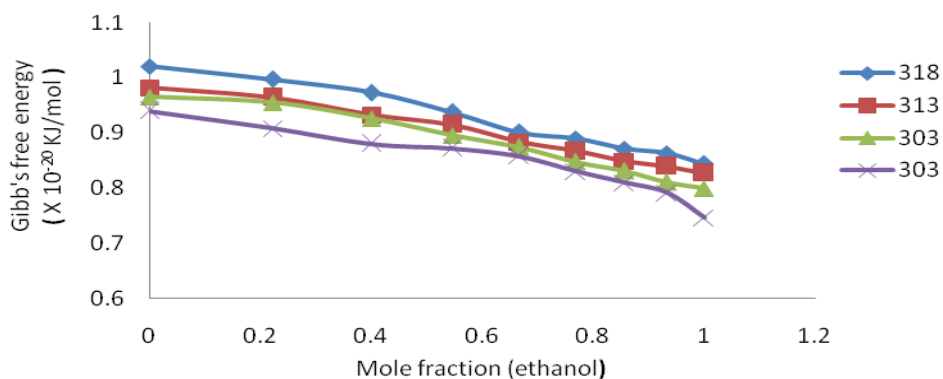
**Figure 6** Variation of Free volume



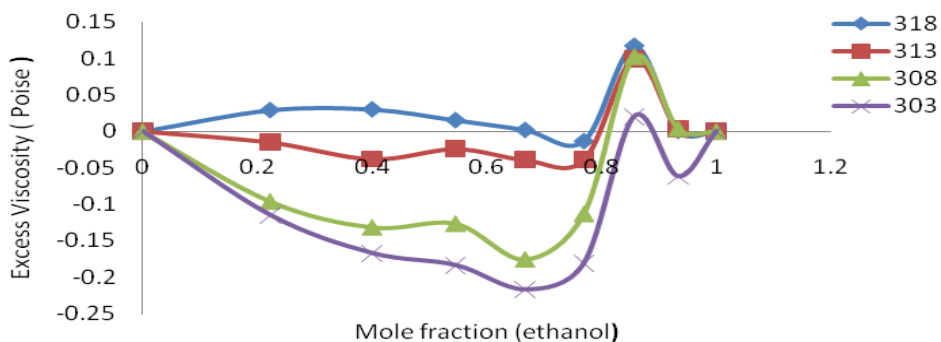
**Figure 7** Variation of Internal Pressure



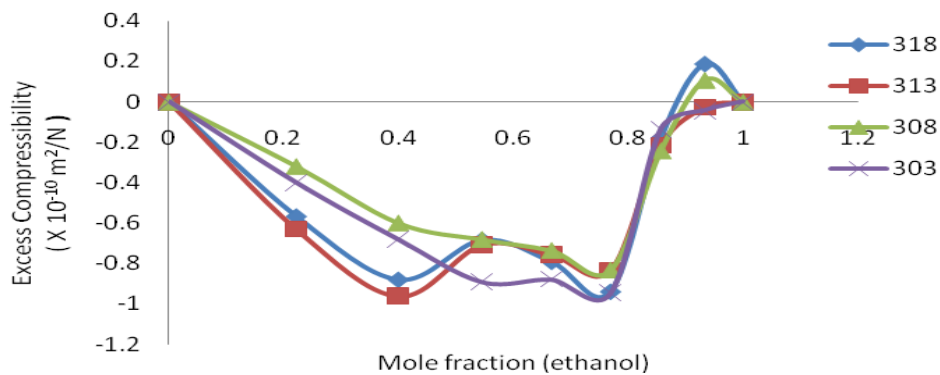
**Figure 8** Variation of Relaxation Time



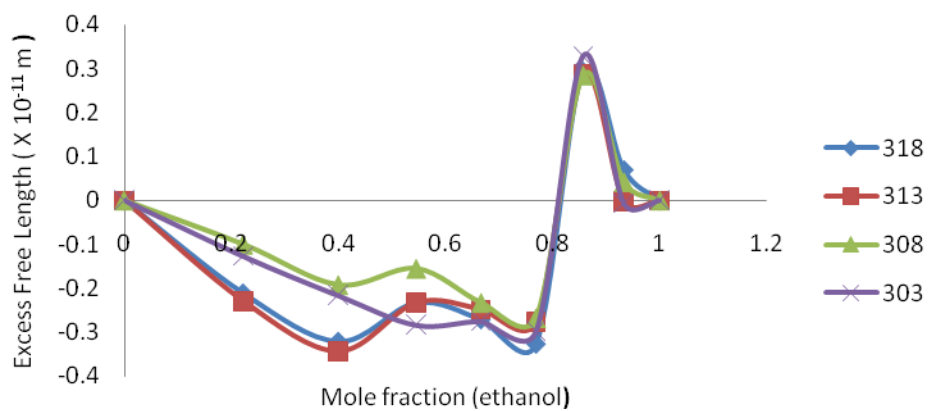
**Figure 9** Variation of Gibbs's Free Energy



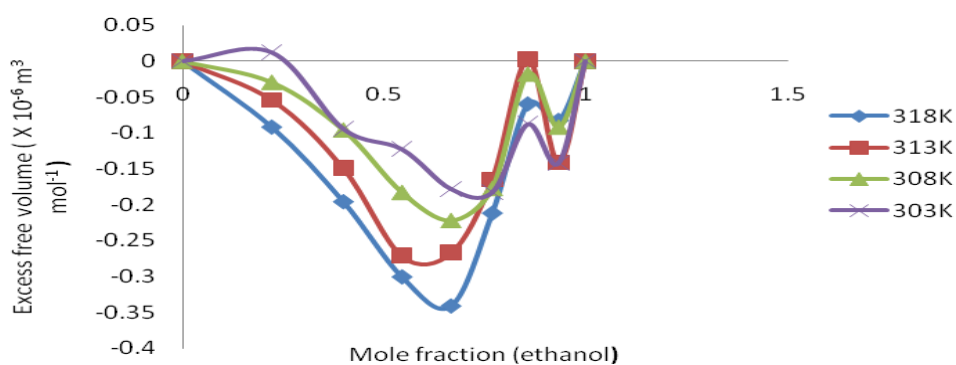
**Figure 10** Variation of Excess Viscosity



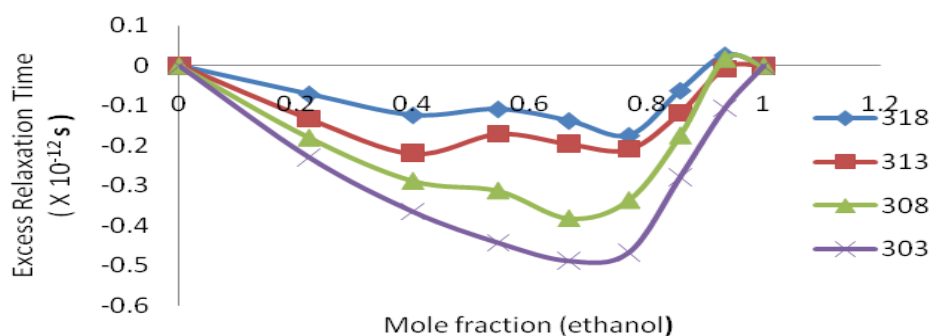
**Figure 11** Variation of Excess Compressibility



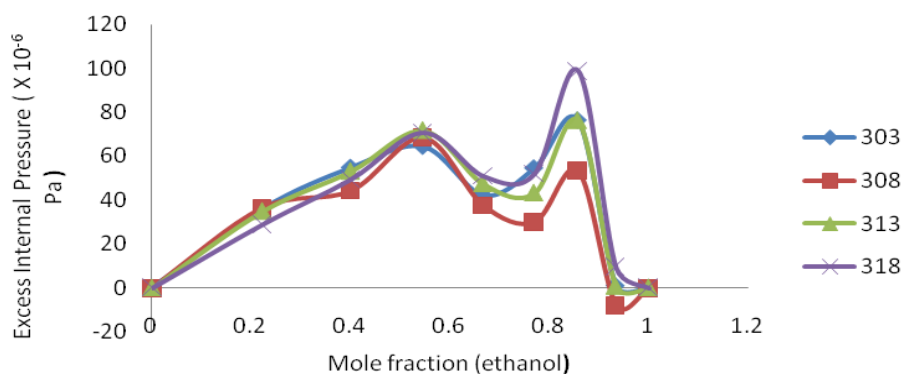
**Figure 12** Variation of Excess Free Length.



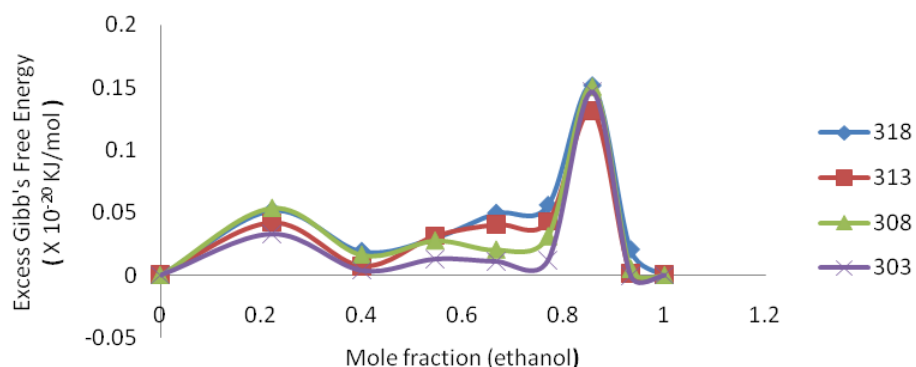
**Figure 13** Variation of Excess Free volume.



**Figure 14** Variation of Excess Relaxation Time



**Figure 15** Variation of Excess Internal Pressure



**Figure 16** Variation of Excess Gibbs's Free Energy.

It is observed from the Figures 1–3 that at a temperature as a mole fraction of ethanol increases the ultrasonic velocity decreases and the density and viscosity of the binary mixture increase totally. For a mole fraction of ethanol as the temperature increases the ultrasonic velocity increases but the density and viscosity of the binary mixture decreases. This suggests that the molecular dissociation is being taken place in the systems. Density ( $\rho$ ) is a measure of solvent-solvent and ion-solvent interactions. Increase in density with concentration indicates the increase in solvent-solvent and solute-solvent interactions. Usually, the values of density and viscosity of any system vary with concentration of solutions. The change in structure of solvent or solutions is a result of hydrogen bond formation or dissociation or hydrophobic (structure-breaking) or hydrophilic (structure-forming) character of solute. That is hydrogen bond forming or dissociating properties can thus be correlated with change in density and viscosity [7].

The variation of adiabatic compressibility ( $\beta$ ) and intermolecular free length ( $L_f$ ) plotted in Figure 4 and Figure 5 respectively showed decrement in the value of adiabatic compressibility and free length with increasing temperature which reveals that the interaction becomes weaker at higher temperatures [8-9]. The free volume plotted in Figure 6 increases however the internal pressure given in Figure 7 shows a reverse trend with increasing temperatures.

Further, it has been observed from Figure 8 that the relaxation time ( $\tau$ ) decreases with increasing temperature. 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.

The Gibbs's Free energy ( $\Delta G^*$ ) increases with increasing temperature as plotted in Figure 9 may be due to the dissociation of intermediate compound between binary liquids. Generally, it is observed that free energy increase favors the dissociation of products from reaction. This observation confirms the formation of hydrogen bonding in binary mixtures [10].

It can be observed from Figure 10 that excess viscosity ( $\eta^E$ ) found to be negative over the entire mole fraction range of ethanol. The negative value of excess viscosity indicates that dispersive forces arising from weak molecular interactions are operative in the system. The sign and extent of deviation of excess parameters depend on the strength of interaction between unlike molecules [11]. The variation of excess viscosity in the present study suggests that specific interactions such as formation of new hydrogen bonds, formation of charge transfer complexes, dipole-dipole interactions and other complex forming interactions are dominant in the systems investigated as the alcohols are highly polar [12].

The excess adiabatic compressibility ( $\beta^E$ ) plotted in Figure 11 found to be negative over the entire range of mole fraction of ethanol indicates that the liquid mixture is less compressible than the pure liquids and molecules in the mixture are more tightly bound in the liquid mixture than in pure liquid which reflects the strong molecular interaction and formation of H- bonds. Thus negative values of excess adiabatic compressibility indicate strong specific interactions between component molecules and interstitial accommodation of smaller molecules in the voids created by bigger molecules [13].

From Figure 12-16, it is observed that the values of excess free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ) and excess relaxation time ( $\tau^E$ ) are negatives while excess internal pressure ( $\pi_i^E$ ) and excess Gibbs's free energy ( $\Delta G^{*E}$ ) are positive over the entire range of ethanol at all temperature investigated. The negative value suggests the attractive interaction between component molecules such as hydrogen bonding, dipole-dipole interactions and other specific interactions between unlike molecules are operative in the system [14-16]. The role of internal pressure has been



found to be an important in the study of several chemical reactions and investigation of molecular interaction. The positive values of excess internal pressure ( $\pi_i^E$ ) suggest the weak intermolecular interaction occurring in the liquid mixtures [17]. The positive value of excess Gibbs free energy ( $\Delta G^{*E}$ ) suggests the presence of weak attractive interaction between the component molecules. Usually, the above computed excess parameter depends on various types of interactions that are operative between the molecules in different system such as dispersion forces, improper interstitial accommodation due to more or less same molar volume and free volumes of the unlike molecules that results in negative contribution of excess values of adiabatic compressibility ( $\beta^E$ ), excess free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), excess relaxation time ( $\tau^E$ ) and vice versa trends in excess internal pressure ( $\pi_i^E$ ) and excess Gibbs free energy ( $\Delta G^{*E}$ ).

### Conclusion

The variation in ultrasonic velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ), related thermo-acoustic parameters such as  $\beta_s$ ,  $L_f$ ,  $V_f$ ,  $\pi_i$ ,  $\tau$  and  $\Delta G^*$  and some of their excess values in the binary solution of Ethanol and Glycerol at four temperatures (303<sup>o</sup>K, 308<sup>o</sup>K, 313<sup>o</sup>K and 318<sup>o</sup>K) show the variation to be non-linear. All the experimental determinations of acoustic parameters are strongly correlated with each other. For the observed molecular interaction, hydrogen bond formations are responsible for the hetero-molecular interaction in the liquid mixture. This provides useful information about inter and intra molecular interactions of the mixture as existing in the liquid systems. In the present systems, when the temperature increases, the interaction between the component molecules decreases. The negative value of excess values of adiabatic compressibility ( $\beta^E$ ), excess free length ( $L_f^E$ ), excess free volume ( $V_f^E$ ), excess relaxation time ( $\tau^E$ ) suggests the strong attractive interaction whereas positive value excess internal pressure ( $\pi_i^E$ ) and excess Gibbs free energy ( $\Delta G^{*E}$ ) suggest the weak attractive interaction between component molecules. This further supports the view that intermolecular interaction is stronger in system I as compared to system II. In the light of the above considerations, it is concluded that ultrasonic study is reliable method and powerful probe in characterization the physio-chemical properties and molecular interaction between liquid mixture systems.

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