

# Study of some thermo-acoustical parameters in the binary liquid mixture 1,4-dioxane with ethylamine at different temperature

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## ABSTRACT

In the binary mixture of 1,4-dioxane with ethylamine , the ultrasonic velocity ( $u$ ), density ( $\rho$ ), and viscosity ( $\eta$ ) has been measured over the entire range of composition at temperature 298.15K, 303.15K,308.15k. The measured data are used to compute the thermo-acoustical parameters such as adiabatic compressibility ( $\beta_a$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure( $\pi_i$ ), relaxation time ( $\tau$ ) acoustic impedance ( $Z$ ), Vander Waal's constant ( $b$ ), Gibb's Free energy ( $\Delta G$ ), Rao constant ( $R$ ), Wada Constant( $W$ ), classical absorption ( $\alpha/f^2$ ), Isothermal Compressibility ( $\beta_i$ ), Internal latent heat of vaporization ( $\Delta H$ ). These calculated parameters values have been used to explain the association and the dissociation present in the binary liquid mixture, which are depending on the intermolecular interaction present in this system.

**Keywords** : Thermo-acoustical, binary mixture, association, dissociation, intermolecular interaction..

## INTRODUCTION

A large number of studies have been made on the molecular interaction in liquid systems by various physical methods like, Raman Effect, Nuclear Magnetic Resonance, Ultra Violet and ultrasonic method. The ultrasonic technique is one of the good techniques for the study of molecular forces in organic liquids. [1-7]. The ultrasonic studies find extensive applications, such as characterization of the physico-chemical behaviour of the liquid and liquid mixtures.

To permit continuous adjustment of the derived properties of the medium Using a mixed solvents rather than single pure liquids are of utmost practical importance in most chemical and industrial process as they provide a wide range mixtures of two or more components at different concentrations[8-9].

The thermodynamic studies of binary solutions have attracted much attention of scientists and experimental data on a number of systems are available from review and publication. Viscosity, density measurements and the properties derived from these are excellent tools to detect solute - solute and solute - solvent interactions [10-19]. The 1,4-Dioxane have potential for use it as a solvent in the processing of crude petroleum, petroleum refining, petrochemicals, and Ethylamine is an aliphatic amine, having the biggest outlet for Ethylamine is for the production of agricultural chemicals (e.g. Atrazine)[20]. The binary mixture are indispensable for many chemical process industries e.g. petroleum petrochemicals. The present paper deals with the measurement of density, viscosity, speed of sound of the binary liquid mixture 1,4-dioxane with ethylamine over the entire range of concentrations. The measured data are used to compute the thermo-acoustical parameters such as adiabatic compressibility ( $\beta_a$ ), free length ( $L_f$ ), free volume ( $V_f$ ), internal pressure( $\Pi_i$ ), relaxation time ( $\tau$ ) acoustic impedance ( $Z$ ), Vander Waal's constant ( $b$ ), Gibb's Free energy ( $\Delta G$ ), Rao constant ( $R$ ), Wada Constant( $W$ ), classical absorption ( $\alpha/f^2$ ), Isothermal Compressibility ( $\beta_i$ ), Internal latent heat of vaporization ( $\Delta H$ ) at 298.15K, 303.15k & 308K at frequency 7MHz.

## METHODOLOGY

The liquid mixtures of 1,4-dioxane and ethylamine of various concentrations in mole fraction were prepared by taking AR grade chemicals. All the liquids used were purified by the standard methods [21]. The mixtures were preserved in well-stopper conical flasks. After the thorough mixing of the liquids, the flasks were left undisturbed to allow them to attain thermal equilibrium. In all the mixtures the mole

fractions of 1,4-dioxane has been increased from 0.0 to 1.0 in ethylamine.

The ultrasonic velocities were measured by using a Multifrequency (1-10MHz) ultrasonic pulse interferometer (Model No. F-83, Mittal Enterprises, New Delhi). It consists of a high Multirange frequency generator (1 to 10MHz) and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 5 MHz Temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath. The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of  $\pm 0.5\%$ . For the viscosity measurement of pure liquids and liquid mixtures, an Ostwald's viscometer was used with an accuracy of  $\pm 0.001 \text{ NSm}^{-2}$ .

## THEORY

**Adiabatic compressibility ( $\beta_a$ )** has been calculated from the ultrasonic velocity ( $U$ ) and the density ( $\rho$ ) of the medium using the equation as:

$$\beta_a = 1 / U^2 \rho \dots\dots\dots (1)$$

**Intermolecular free length ( $L_f$ )** has been determined as:

$$L_f = K_T (\beta_a)^{1/2} \dots\dots\dots (2)$$

Where  $K_T$  - is a Jacobson's constant.

**Free volume( $V_f$ )** in terms of ultrasonic velocity ( $U$ ) and viscosity of the liquid ( $\eta$ ) as :

$$V_f = [ M_{eff.} U / K \eta ]^{3/2} \dots\dots\dots (3)$$

Where,  $M_{eff.}$  is the effective molecular weight ( $M_{eff.} = \sum m_i X_i$ , in which  $m_i$  and  $X_i$  are the molecular weights and the mole fraction of the individual constituents respectively).  $K$  is a temperature independent constant which is equal to  $4.28 \times 10^9$  for all liquids.

**Internal pressure ( $\Pi_i$ )** is calculated by

$$\Pi_i = bRT (K \eta / U)^{1/2} (\rho^{2/3} / M^{7/6}) \dots\dots\dots (4)$$

Where,  $b$  stands for cubic packing which is assumed to be 2 for all liquids and  $K$  is a dimension less constant, independent of temperature and the nature of liquids and its value is  $4.28 \times 10^9$ ,  $T$  is the absolute temperature and  $M_{eff.}$  is the effective molecular weight.

**Relaxation time ( $\tau$ )** in terms of adiabatic compressibility ( $\beta_a$ ) and viscosity of the liquid ( $\eta$ ) as:

$$\tau = 4/3 \beta_a \eta \dots\dots\dots (5)$$

**Acoustic impedance (Z)** in terms of ultrasonic velocity (U) and density of the liquid ( $\rho$ ) as:

$$Z = U.\rho \dots\dots\dots (6)$$

**Vander Waal's constant (b)**

$$b = (M/\rho).[1-(RT/MU^2)\{(1 + MU^2/3RT)^{1/2} - 1\}] \dots\dots (7)$$

Where, M = molecular weight, R = 8.3143 JK<sup>-1</sup>mol<sup>-1</sup>, is the gas constant,  $\rho$  = density.

**Gibb's free energy ( $\Delta G$ )** can be calculated from the following relation:

$$\Delta G = KT \log (KT\tau / h) \dots\dots\dots (8)$$

Where,  $\tau$  is the relaxation time, K the Boltzmann constant, T the absolute temperature and h is the Planks constant.

**Rao's Constant (R)** can be calculated from the following relation:

$$R = (M/\rho)v^{1/3} \dots\dots\dots (9)$$

Where,  $\rho$  is the density, V is the molar volume and M is Molecular Weight.

**Wada Constant or Molar compressibility (W)** can be calculated from the following relation:

$$W=(M/\rho)\beta^{-1/7} \dots\dots\dots (10)$$

Where,  $M=(m_1x_1 + m_2x_2)$

**Internal latent heat of vaporization ( $\Delta H_i$ )** calculated

by a formula,

$$\Delta H_i = (\pi_i V_m) / M_{eff} \dots\dots\dots (11)$$

Where,  $V_m$  is the molar volume,  $\pi_i$  be the internal pressure and  $M_{eff} = x_i M_i$ , where  $x_i$  is the mole fraction and  $M_i$  is the molecular weight of the component.

**Classical absorption ( $\alpha/f^2$ )**, Absorption may be taken as being proportional from the viscosity ( $\eta$ ) using the relation,

$$(\alpha/f^2) = 8\pi^2\eta/3\rho U^3 \dots\dots\dots (12)$$

Where,  $\rho$  is the density of the liquid,  $\eta$  is the viscosity and U is the ultrasonic velocity.

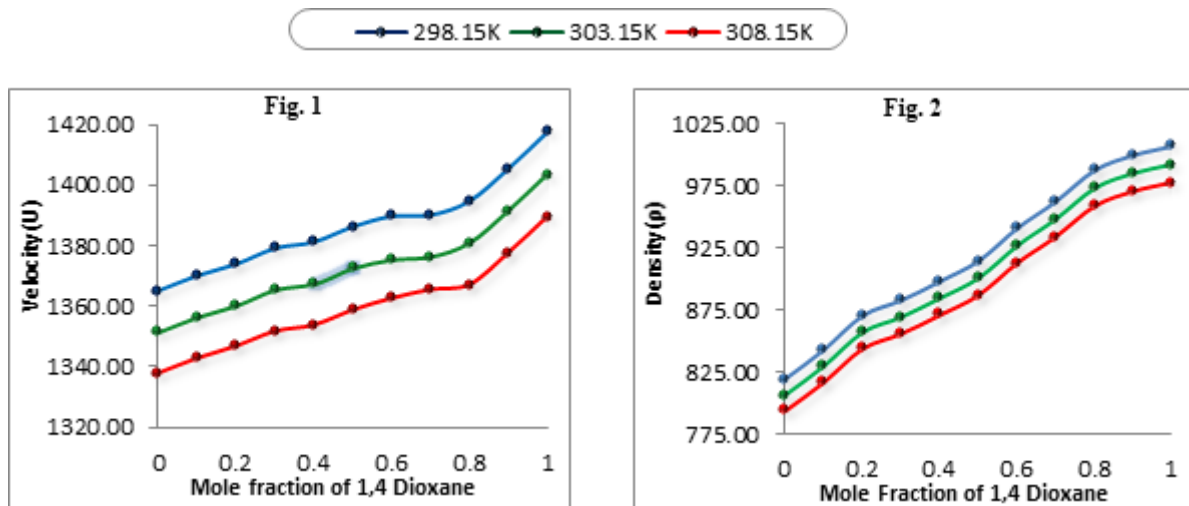
**Isothermal compressibility ( $\beta_i$ )** Isothermal compressibility is given as,

$$\beta_i = \gamma\beta_a \dots\dots\dots (13)$$

Where,  $\gamma = C_p/C_v$ ,  $\beta_a$  is the adiabatic compressibility and  $\beta_i$  is the isothermal compressibility.

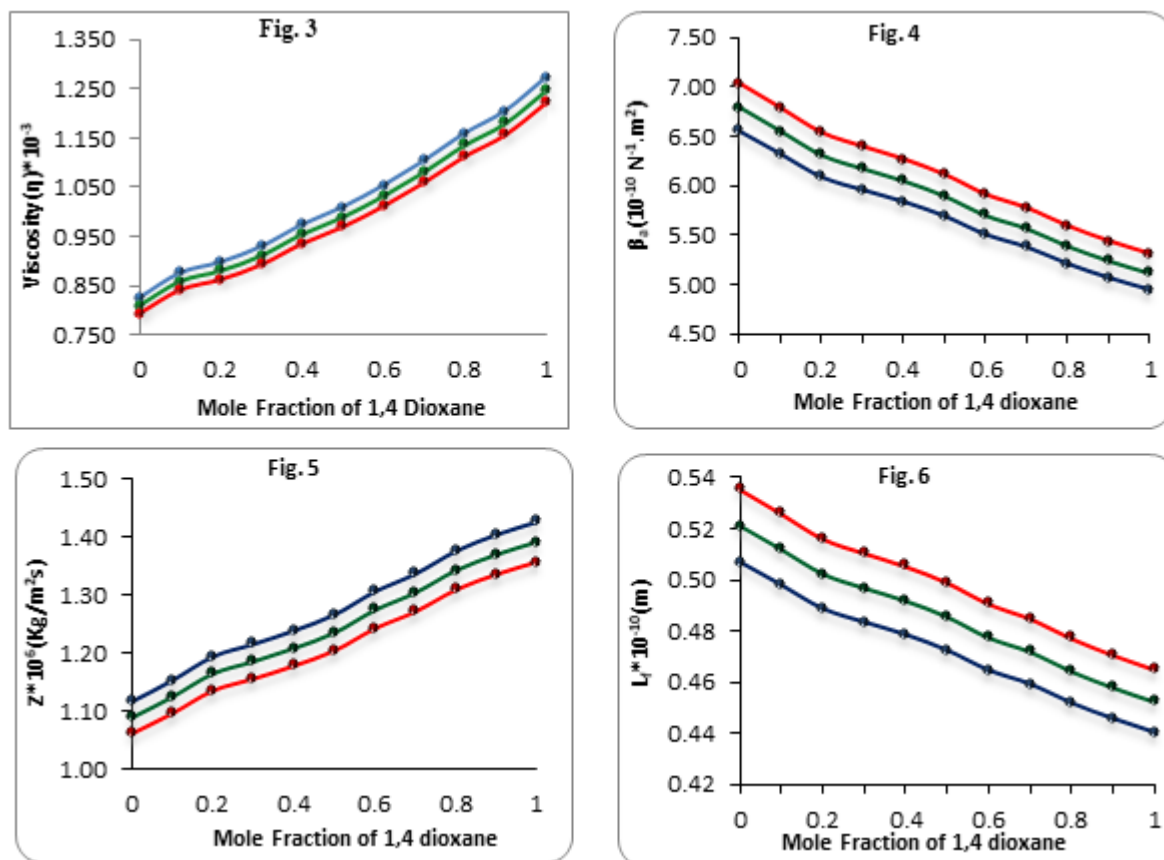
## RESULTS AND DISCUSSION

Figure shows the Graphical representation of ultrasonic thermodynamic parameters



**Fig. (1)** Contains the plot of ultrasonic velocity (U) versus molar concentration. It is observed that the ultrasonic velocity increases with increase in the concentration of 1,4-dioxane in ethylamine indicating association in the molecules of the component. The association due to stronger dipole-induced dipole interaction between 1,4-dioxane and ethylamine molecules This process may lead to strong interaction forces.

**Fig. (2)** contains the plot of density ( $\rho$ ) versus molar concentration. It is observed that density increase with increase in concentration of 1,4-dioxane in EA. Increase in density decreases the volume indicating association in component molecules. The density of the binary liquid mixture may be increase due to structural reorganization indicating the closed packed structure of molecular cluster increases. This makes the medium less compressive

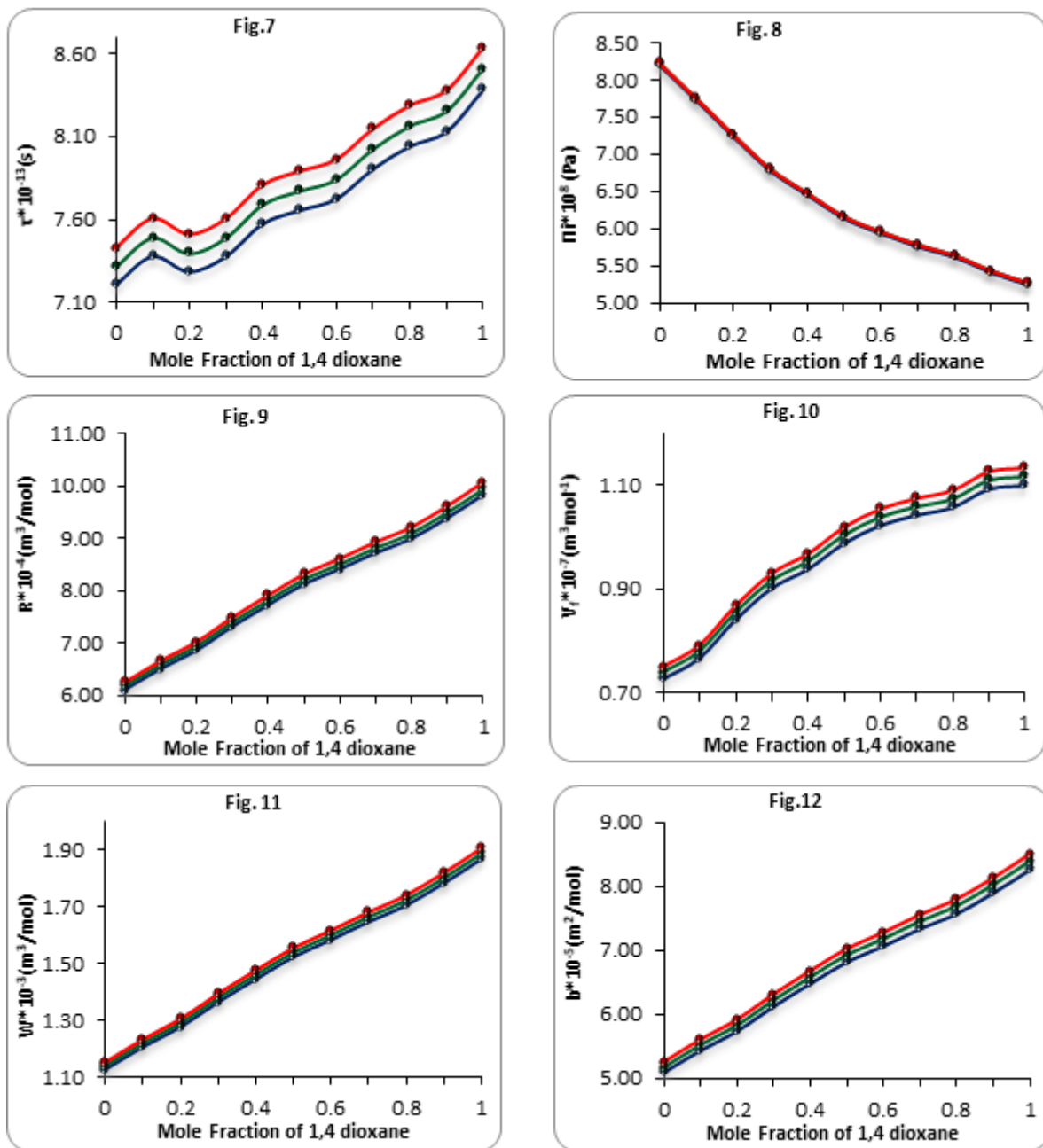


**Fig. (3)** Contains the plot of viscosity ( $\eta$ ) versus the molar concentration. It is observed that viscosity increase with increase in the concentration of 1,4-dioxane in EA. The viscosity of the mixture is depends on molecular interaction as well as on the size and shape of the molecules of component. Measurement of viscosity in binary mixture yields some reliable information in the study of molecular interaction.

**Fig.(4)** and **Fig. (15)** Represent the variation of adiabatic compressibility ( $\beta_a$ ) and isothermal compressibility ( $\beta_i$ ) versus molar concentration. It is observed that adiabatic compressibility and isothermal compressibility decrease with increase in concentration of 1,4-dioxane in EA indicating strong molecular interaction in the component molecules in binary liquid mixture associating tendency of component molecules.

**Fig. (5)** Contains the plot of acoustic impedance ( $Z$ ) versus molar concentration. It is observed that, the values of acoustic impedance increase with increase in the molar concentration of 1,4-dioxane in EA. It is in good agreement with the theoretical requirement because in acoustic impedance with molar concentration can be explained on the basis of intermolecular interactions between the component molecules, which decreases the intermolecular distance, between the component molecules, which decrease the intermolecular distance, making relative fewer gap between molecules of the binary liquid system.

**Fig. (6)** Contains the plot of free length ( $L_f$ ) versus molar concentration. It is observed that free length decreases with increase in molar concentration of 1,4-dioxane in EA. Decrease in free length as a result of dipole-induced dipole interaction, hydrogen bonding association and due to interstitial accommodation of unlike molecules.



**Fig. (7)** Contains the plot of relaxation time ( $\tau$ ) versus molar concentration. It is observed that, the values of relaxation time increase with increase in the molar concentration of 1,4-dioxane in EA indicating more stability of 1,4-dioxane molecules. The relaxation is caused by the energy transfer between translational and vibration degree of freedom and all these degree take part in the process observed. Its behavior depends on viscosity and adiabatic compressibility of the binary liquid mixtures. In this system viscosity play an important role for increasing relaxation time with increase in molar concentration.

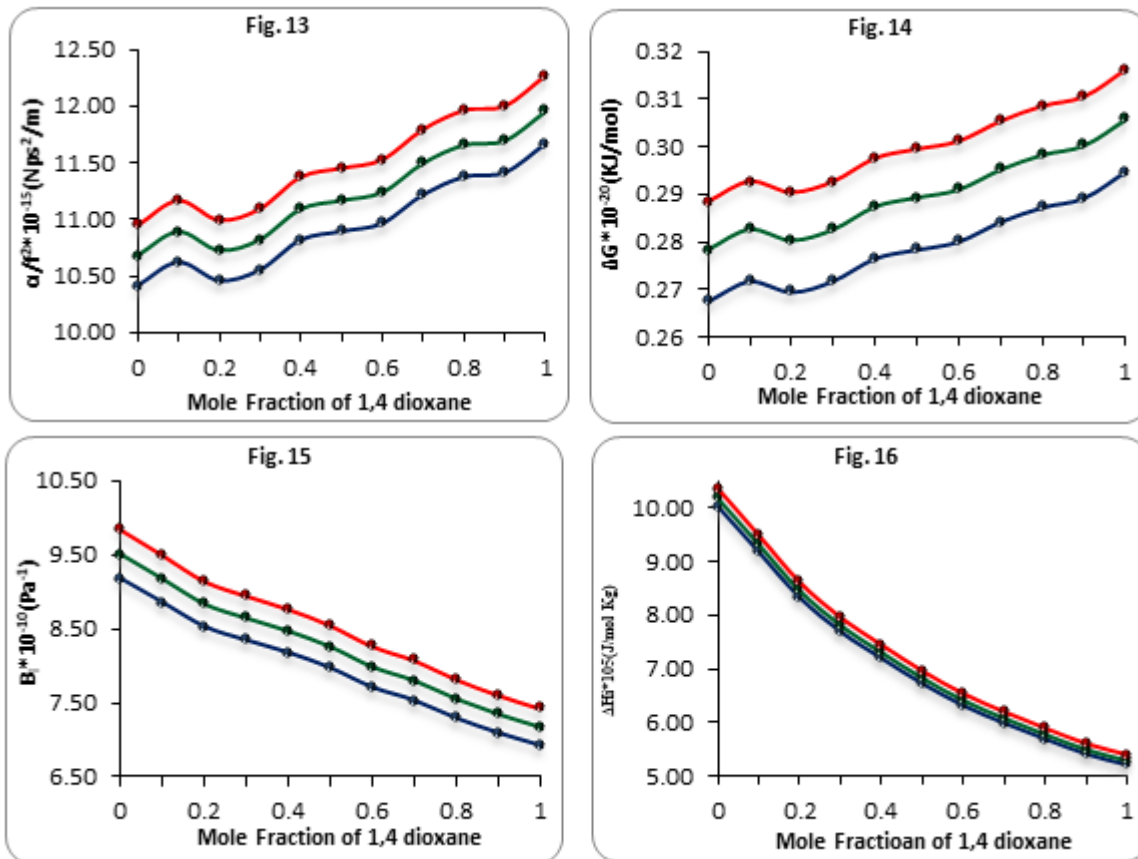
**Fig.(8) and fig. (10)** shows the plot of internal pressure and free volume versus molar concentration. It is observed that internal pressure decreases and free volume increases with increase in molar concentration of 1,4-dioxane in EA indicating increase in dipolar association in the molecules of the component.

**Fig.(9) and Fig. (11)** contains the graph of Rao constant ( $R$ ) and Wada Constant ( $W$ ) versus molar concentration. Increase in the values of these parameters predicts weak intermolecular interaction in the interacting molecules. These parameters help



for the study of range of attractive and repulsive forces in the molecules of the components. A value of these parameters mainly depends upon the values of ultrasonic velocity and density of the binary system.

**Fig. (12)** contains the plot of Vander Waal's constant ( $b$ ) versus molar concentration. It is observed that Vander Waal's constant increases with increase in the concentration of 1,4-dioxane in EA. This is because due to change in intermolecular geometry (micro Geometry) of liquid molecules in the binary liquid mixture.



**Fig. (13)** contains the plot of classical absorption ( $\alpha/f^2$ ) versus molar concentration. It is observed that classical absorption increases with increase in concentration of 1,4-dioxane in EA indicating high stability of the solution. This is due to size 1,4-dioxane molecules is larger than EA.

**Fig. (14)** Contains the plot of Gibb's Free energy ( $\Delta G$ ) with concentration. It is observed that initially Gibb's free energy increases with increase in concentration of 1,4-dioxane in ethylamine, indicating the mobility of the molecules is low i.e. highly ordered, due to outstanding solvation. The increase in Gibb's Free energy also suggests the need of shorter time for co-operative process for the rearrangement of molecules in the mixture.

**Fig. (16)** Internal latent heat of vaporization ( $\Delta H_i$ ) decrease with increase in the concentration of 1,4-dioxane in EA. Latent heat is energy released or absorbed by thermodynamic systems, during a constant-temperature process. It is known that ( $\Delta H_i$ ) decreases with increase in temperature and increases with increase in pressure. Since the external pressure is very low, the pressure factor seems to predominate causing an increase in the values of ( $\Delta H_i$ ) with increase in temperature.

The Ultrasonic velocity( $U$ ), Density( $\rho$ ), Viscosity( $\eta$ ) and thermodynamic parameters like adiabatic compressibility ( $\beta_a$ ), Acoustical Impedance( $Z$ ), Free Length ( $L_t$ ), Relaxation time ( $\tau$ ), Internal Pressure( $\pi_i$ ), Rao's Constant( $R$ ), Free Volume( $V_f$ ), Wada's Constant ( $W$ ), Vander Waal's Constant ( $b$ ), Classical Absorption ( $\alpha/f^2$ ), Gibb's Free Energy( $\Delta G$ ), Isothermal

Compressibility ( $\beta_i$ ), and Internal Latent heat of Vaporization ( $\Delta H_i$ ) of binary liquid mixture 1,4-dioxane in ethylamine at temperature range 298.15K, 303.15K, 308.15K and frequency at 7MHz are shown in fig. (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16) respectively.

## CONCLUSION

The experimental study of ultrasonic velocity (U), density ( $\rho$ ), viscosity ( $\eta$ ) and the derived thermodynamic parameters varied with temperature and concentration in binary liquid mixture of 1,4-dioxane with ethylamine, shows that the linear behavior of the liquids at the temperature range 298.15 to 308.15. Linear behavior may be due to associative nature of the molecules. The linearity in this binary liquid mixture gives the very fruitful information about the molecular interaction. So the natures of the forces responsible for the observed heteromolecular interaction in this binary liquid mixture are dipole-induced dipole type. Graphical representation shows that, there is no complex formation of between the 1,4-dioxane and ethylamine.

**Conflicts of interest:** The authors stated that no conflicts of interest.

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