Evaluation and study of Acoustics parameters of the Binary Liquid Mixture Containing 2-Ethoxyethanol and Ethanol at 312.15 °K

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ABSTRACT:

Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of 2-Ethoxyethanol and Ethanol were measured over entire composition range. These measurements were done at constant temperature 312.15 K and at frequency 1MHZ. These were used to evaluate various acoustic parameters such as refractive index, relative association (R_A), relaxation time (τ), free length (Lf), internal pressure (πi), real volume (Xτ), classical absorption coefficient ($\alpha/f2$). Along with these thermo-acoustic parameters excess parameters were computed. These are excess ultrasonic velocity (U^E), excess free length (L_f^E). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 312.15K.

KEY WORDS: Ethanol, relaxation time, Wada's constant, free length, adiabatic compressibility

INTRODUCTION:

The ultrasonic study of intermolecular interactions plays an important role in the development of molecular sciences. Many researchers have undertaken these studies qualitatively through ultrasonic velocity, adiabatic compressibility and viscosity measurements for liquid binary and ternary mixtures. Ultrasonic velocity measurements are useful in the field of interactions and structural aspect studies, for characterizing the Physico-chemical behavior of liquid mixtures. Ultrasonic measurements of acoustic parameters with change in mole fraction give an insight in to the molecular process. Ultrasonic waves are high frequency mechanical waves [1]. Ultrasonic wave propagation affects the physical properties of the medium and hence can provide information about molecular interactions of the pure liquids and liquid mixtures. The measured ultrasonic parameters are being extensively useful to study intermolecular processes in liquid systems [2]. The sign and magnitude of the non-linear deviations from ideal values of velocities and adiabatic compressibilities of liquid mixtures with composition are related to the difference in molecular size and strength of interaction between unlike molecules. In the present study the chemicals used are 2-Ethoxyethanol and Ethanol.

Ethanol also called ethyl alcohol is an organic compound. It is simple alcohol with formula C_2H_6O. It is volatile and flammable colorless liquid. It has wine like odor and has pungent taste. It is psychoactive drug and active ingredient in alcoholic drinks. It is naturally produced by the fermentation of sugars by yeasts of via petrochemical process such as ethylene hydration. It also has medical applications as an antiseptic and disinfectant. It is also used as chemical solvent and in the synthesis of organic compounds. It is a fuel source. It has relative polarity 0.654 and polarity index 5.2. Its dielectric constant is 24.3. It is a polar liquid.

2-Ethoxy Ethanol is a solvent used widely in commercial and industrial applications. Its chemical formula is $C_4H_{10}O_2$. It is clear, colorless, nearly odorless liquid. It is miscible with water, ethanol, diethyl ether, acetone and ethyl acetate [3]. It has an ideal property as multi-purpose cleaner. Therefore, it is used in products such as varnish removers and degreasing solutions. The chemical formula of 2-Ethoxyethanol is $C_4H_{10}O_2$ or $CH_3CH_2OCH_2CH_2OH$. It plays a role as protic solvent.

In the present work, density, viscosity and ultrasonic velocity of 2-Ethoxyethanol and ethanol binary mixture have been measured and used to compute various acoustic parameters such as refractive index, relative association (R_A), relaxation time (τ), free length (Lf), internal pressure (πi), real volume (Xτ), classical absorption coefficient (α/f2). Along with these thermo-acoustic parameters excess parameters were computed. These are excess ultrasonic velocity (U^E), excess free length (L_f^E). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 312.15K. Behavior of these parameters has been used to interpret the intermolecular interaction in this binary mixture for entire mole fraction range.

EXPERIMENTAL:

Chemicals used were 2-ethoxyethanl and ethanol obtained from SDFCL, Mumbai. Density of the pure components and their mixtures were measured by using 10 ml specific gravity bottle up to the accuracy (0.001 g) [4]. The Abbe's refractometer is very popular and owes its popularity to its convenience, its wide range (n_D = 1.3 to 1.7), and to the minimal sample is needed [5]. The accuracy of the instrument is about ±0.0002; its precision is half this figure. The improvement in accuracy is obtained by replacing the compensator with a monochromatic source and by using larger and more precise prism mounts. The former provides a much sharper critical boundary and the latter allows a more accurate determination of the prism position.

The viscosity of pure liquids and their mixtures [6] were measured using Ostwald's viscometer with an accuracy of ± 0.001 Nsm^{-2}. Ultrasonic sound velocities were measured using multifrequency ultrasonic interferometer MX–3 (H. C. Memorial Scientific Corporation, Ambala Cantonment) with working frequencies 1MHZ, 3MHZ & 5MHZ. From the measured values of Density (ρ), viscosity (η) and Ultrasonic velocity various acoustic parameters such as refractive index, relative association (R_A), relaxation time (τ), free length (Lf), internal pressure (πi), real volume (Xτ), classical absorption coefficient (α/f2) were evaluated. Along with these thermo-acoustic parameters excess parameters were computed. These are excess ultrasonic velocity (U^E), excess free length (L_f^E). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 312.15K.

THEORATICAL BACKGROUND:

For the measurement of ultrasonic absorption by interferometer technique, the experimental liquid is placed in the cell of the ultrasonic interferometer. Then the distance between the crystal and the reflector is slowly varied by the micrometer screw. The current in the anode circuit of the oscillator undergoes cyclic variation giving rise to alternate maxima and minima. The distance between consecutive alternate maxima and minima corresponds to half wavelength in the liquid medium. The ultrasonic velocity is found using the average values of minima and maxima. The standard equations utilized for computation of different thermo-acoustic parameters are explained below.

1. RELATIVE ASSOCIATION: it is a parameter used to assess the association in any solution relative to association existing in water at 0 °C. it is influenced by two factors 1)the breaking up of solvent molecules on addition of electrolyte to it & 2)the salvation of ions that is simultaneously present.

$$R_A = \frac{ds}{do}\left[\frac{Uo}{Us}\right]^{1/3} \qquad (1)$$

Uo & Us are ultrasonic velocities in solvent & solution respectively and ds & do respective densities.

2. RELAXATION TIME: The general formula is

$$\tau = (4/3)\, \beta_{ad}\, \eta \quad \text{second} \qquad (2)$$

It is closely related with viscosity and classical absorption ultrasonic energy. Increase in relaxation time increases the ultrasonic absorption and vice versa. The dispersion of sound velocity in a binary mixture reveals information about the characteristic time of relaxation process.

3. INTERMOLECULAR FREE LENGTH: It is the distance covered by sound wave between the surfaces of the neighboring molecules. It is measure of intermolecular attractions between the components in a binary liquid mixture.

$$L_f = k\, \beta_{ad}^{1/2} \quad m \qquad (3)$$

K is a constant known as Jacobson's constant given by

$K = (93.875 + 0.375\ T \text{ in degree Kelvin}) \times 10^{-8}$

4. INTERNAL PRESSURE: It is also known as molar compressibility of the given liquid mixture. This is very large pressure. It gives idea about the solubility characteristics.

$$\pi_i = bRT\ \left(\frac{k\,\eta}{u}\right)^{1/2} \left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad Pa \qquad (4)$$

$b = 2$, $R = 8.314$ J/ mol. °K, k is a constant equal to 4.28×10^9

U is the velocity of the ultrasonic wave and ρ is the density of the binary mixture

5. REAL VOLUME: It is associated with molecular interaction between the constituents of a liquid mixture. It is inversely proportional to Vanderwaal's constant and density of the liquid mixture. It is directly related with effective molar mass of the binary liquid mixture.

$$X_\Gamma = M_{eff} / \rho\, b \quad m^3/mol \qquad (5)$$

6. CLASSICAL ABSORPTION: it is also known as attenuation coefficient. It is measure of spatial rate of decrease in intensity level of the ultrasonic wave.

$$(\alpha/f^2) = (8\pi^2\eta) / 3\rho U^3 \quad NPS^2m^{-1} \qquad (6)$$

η is the viscosity of the binary mixture, U is the velocity of the ultrasonic wave and ρ is the density of the binary mixture

7. EXCESS PARAMETERS: The general relation for evaluating various excess parameters is

$$A^E = A_{expt} - A_{id} \qquad (8)$$

where A_{expt} is the experimentally determined values of any acoustical parameters and $A_{id} = \sum A_i X_i$, Ai is any acoustical parameters & X_i the mole fraction of that liquid component. The nature and degree of molecular interaction between the component molecules of the liquid mixture have been speculated through the size and extent of deviation of the excess parameters. There will be positive deviation if size of the solvent molecule is increased and if it is decreased then the deviation is negative. A stronger molecular interaction may be due to charge transfer, dipole-induced dipole and dipole- dipole interactions. It leads to more compact structure of binary or ternary liquid mixtures. Weak molecular interactions may cause expansion in the volume of the liquid mixture.

RESULTS AND DISCUSSION:

The experimentally measured values of density (ρ) and ultrasonic velocity (U) & computed values specific acoustic impedance (Z) and Rao constant (R) with respect to concentrations of 2-Ethoxyethanol in ethanol are presented in the table I. Evaluation of all these parameters is done at constant temperature 312.15 K and at fixed ultrasonic frequency 1MHz. These parameters play very important role in explaining the nature and degree of association or dissociation among the constituents of the binary mixture 2-Ethoxyethanol and Ethanol. The discussion of the results obtained from these parameters is made below.

Table I: The acoustic parameters refractive index, relative association, and relaxation time are shown in table I.

Mole fraction of 2-Ethoxyethanol in Ethanol	*R I*	*RA*	τ
T=312.15°K and Frequency = 1MHZ			
0	1.3611	1	1.4178E-11
0.062715	1.363853	1.023193	1.5161E-11
0.130852	1.366844	1.029905	1.4793E-11
0.205144	1.370106	1.04528	1.5279E-11
0.286464	1.373676	1.057206	1.558E-11
0.375861	1.3776	1.063841	1.5544E-11
0.4746	1.381935	1.0773	1.6264E-11
0.584226	1.386748	1.08489	1.6644E-11
0.706644	1.392122	1.10369	1.8331E-11
0.844233	1.398162	1.116619	1.9816E-11
1	1.405	1.125923	2.1355E-11

The variation of the above mentioned parameters with rise in mole fraction of 2-Ethoxyethanol in Ethanol is illustrated in figures 1 to 4 as shown below.

The variation in refractive index with rise of mole fraction of 2-Ethoxyethanol in Ethanol is depicted in figure 1. Observation of figure 1 illustrates that the refractive index is increasing linearly with increase concentration of 2-Ethoxyethanol in Ethanol. It is the physical property of the binary mixture. It is function of temperature. As refractive index of the binary mixture is increasing linearly with increase in concentration of the solute 2-Ethoxyethanol in Ethanol, it means that the thickness of binary mixture is increasing due to contraction in the volume of the mixture [7]. It means that strong forces of attraction exists between the unlike molecules of the binary mixture. It is also helpful to find polarizability of liquids.

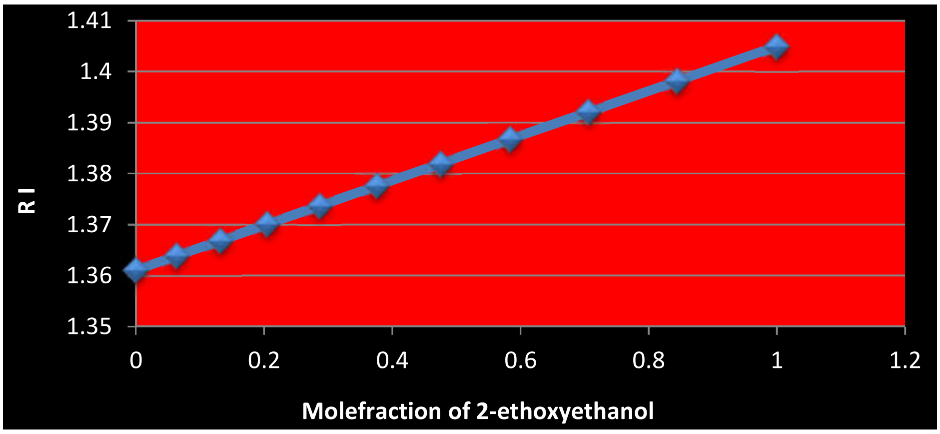

Fig 1 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and the refractive index of the binary mixture at constant temperature and fixed ultrasonic frequency

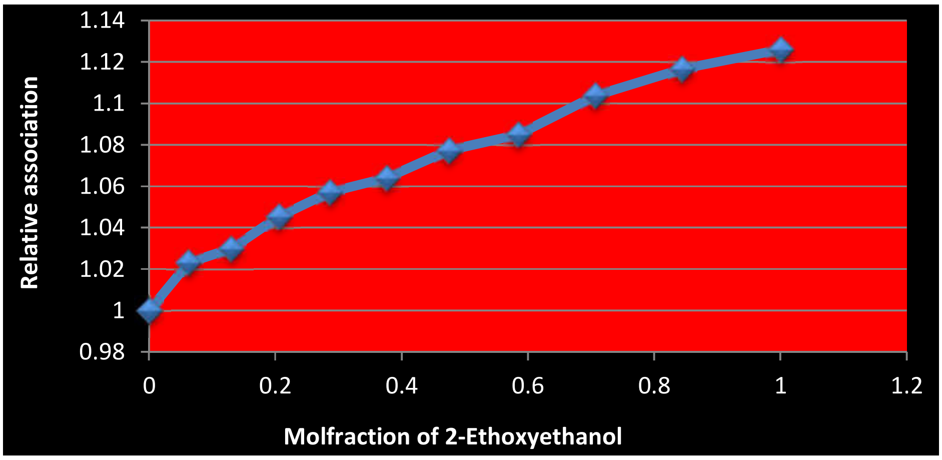

Fig 2 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and relative association of the binary mixture at constant temperature and fixed ultrasonic frequency

The nature of variations in relative association with increase in concentration of 2-Ethoxyethanol in Ethanol are illustrated in figure 2. Observation of figure 2 reveals that the relative association in the binary mixture is increasing non-linearly with increase in concentration of 2-Ethoxyethanol. The decreasing nature of relative association [8] represents dissociation and the increasing behavior represents association. The non-linear increasing values of relative association indicate complex formation and association between the components of the binary mixture. This is quite clear from figure 2.

The variation of relaxation time with mole fraction of 2-Ethoxyethanol in Ethanol is illustrated in figure 3. Perusal of figure 3 shows that the relaxation time of this binary mixture increases with the concentration of 2-Ethoxyethanol in Ethanol.

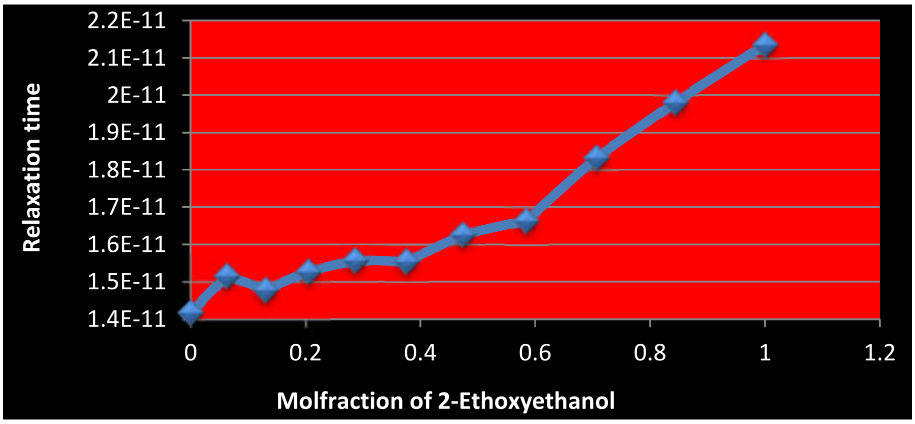

Fig 3 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and the relaxation time of the binary mixture at constant temperature and fixed ultrasonic frequency

Relaxation time is the time required for the excitation energy to appear as translational energy and it depends on temperature and impurities. In this work the relaxation time increases non-linearly with increase in concentration of 2-Ethoxyethanol in Ethanol. This behavior of relaxation time supports presence of intermolecular interaction between the constituents of this binary liquid mixture [9].

Table II: The evaluated thermo-acoustic parameters Viscosity, intermolecular free length, and Gibb's free energy are illustrated in table II.

Mole fraction of 2-Ethoxyethanol in Ethanol	η	L_F	Δ*G*
T=312.15°K and Frequency = 1MHZ			
0	0.01074	6.63709E-11	1.85306E-19
0.062715	0.011324	6.68385E-11	1.85017E-19
0.130852	0.011996	6.41486E-11	1.85123E-19
0.205144	0.012773	6.31806E-11	1.84984E-19
0.286464	0.013681	6.16438E-11	1.849E-19
0.375861	0.014754	5.92906E-11	1.8491E-19
0.4746	0.016038	5.81722E-11	1.84714E-19
0.584226	0.017595	5.61834E-11	1.84615E-19
0.706644	0.019512	5.59909E-11	1.84199E-19
0.844233	0.021917	5.4927E-11	1.83863E-19
1	0.025	5.33886E-11	1.83541E-19

The variation in these parameters with rise in mole fraction of 2-Ethoxyethanol in Ethanol is represented in figures 4 to 6 respectively.

The variation of viscosity with the mole fraction of 2-Ethoxyethanol in Ethanol is depicted in figure 4. Examination of figure 4 reveals that the viscosity increases approximately linearly with the mole fraction of 2-Ethoxyethanol in Ethanol.

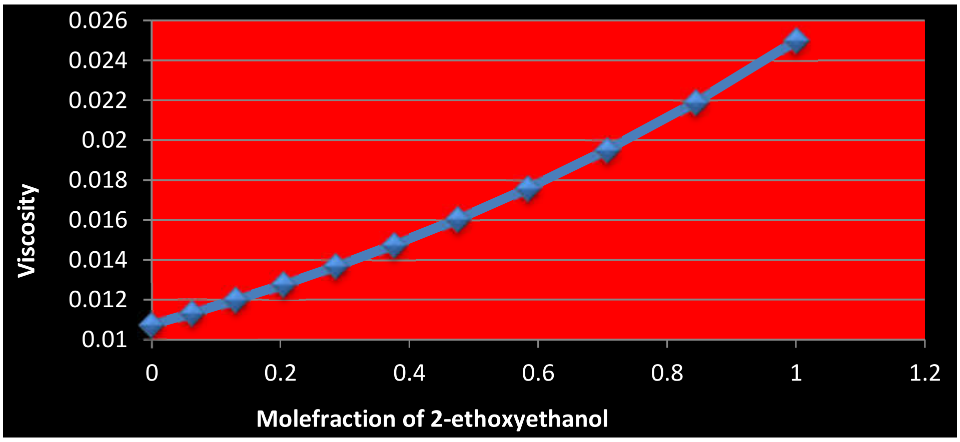

Fig 4 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and viscosity of the binary mixture at constant temperature and fixed ultrasonic frequency

The increase in viscosity with increase in concentration of 2-Ethoxyethanol in Ethanol indicates the presence of strong molecular interaction between the constituents of the binary mixture [10].

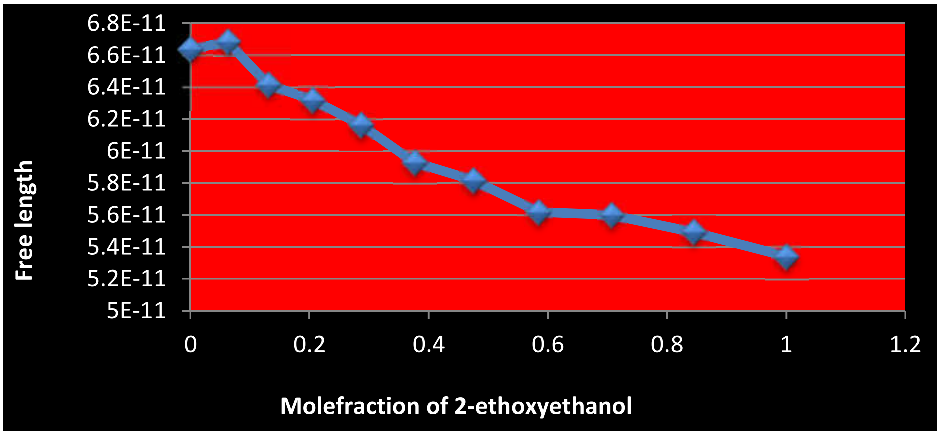

Fig 5 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of intermolecular free length of the binary mixture with rise in mole fraction of 2-Ethoxyethanol in Ethanol is depicted in figure 5. Perusal of figure 5 illustrates that the intermolecular free length is decreasing non-linearly with increase in concentration of 2-Ethoxyethanol in Ethanol. Intermolecular free length is related to ultrasonic velocity. As the ultrasonic velocity increases due to the increase in concentration, the intermolecular free length has to decrease and vice versa. Increase in concentration leads to decrease in gap between two species of the binary mixture and which is referred to as intermolecular free length. This shows that dipole induced dipole attraction increases with the concentration of 2-Ethoxyethanol in Ethanol. So this decrease in intermolecular free length with increase in concentration of the solute supports molecular interaction between the constituents of the mixture [11, 12].

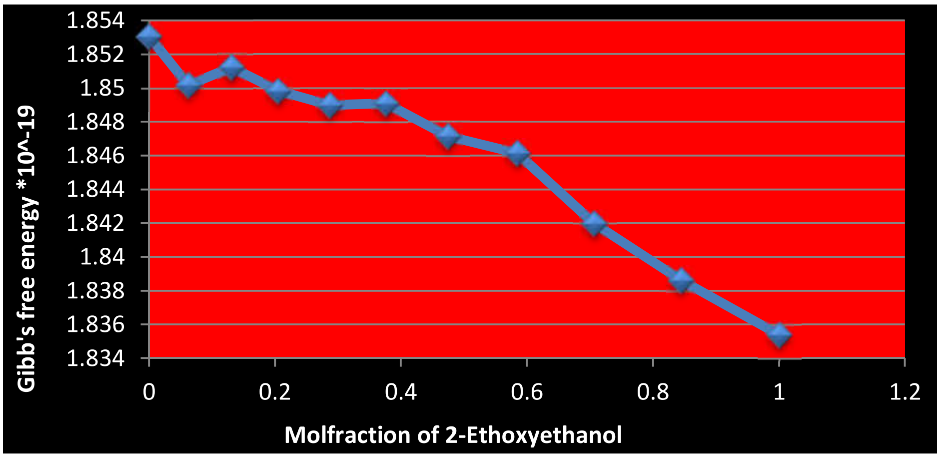

Fig 6 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and the Gibb's free energy of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of Gibb's free energy with mol fraction of 2-Ethoxyethanol in Ethanol is illustrated in figure 6. Perusal of figure 6 indicates that the Gibb's free energy decreases non-linearly with concentration of 2-Ethoxyethanol in Ethanol. This decrease in Gibb's free energy with mol fraction of 2-Ethoxyethanol in Ethanol confirms the formation of H-bond in the binary liquid mixture's components [13].

Table III. The thermo-acoustic parameters internal pressure, real volume, excess intermolecular free length and excess ultrasonic velocity are represented in table III.

Mole fraction of 2-Ethoxyethanol in Ethanol	πi	R V	L_f^E	U^E
T=312.15°K and Frequency = 1MHZ				
0	3240283645	0.278849	0	0
0.062715	3170521787	0.27581	1.28E-12	-28.0929
0.130852	3029644134	0.26199	-5.2E-13	-2.62727
0.205144	2934166839	0.254031	-5.3E-13	-7.1338
0.286464	2830207582	0.244179	-1E-12	-1.54618
0.375861	2712836302	0.231693	-2.2E-12	20.41342
0.4746	2629285812	0.22325	-2E-12	17.51682
0.584226	2532056809	0.212023	-2.6E-12	32.81995
0.706644	2481704255	0.206434	-1.2E-12	7.129444
0.844233	2419287172	0.198035	-4.8E-13	-1.04575
1	2355232194	0.188153	0	0

The variation of these parameters with rise of mole fraction is shown in figures 7 to 10 respectively. The investigation is made at 312.15 K constant temperature and at frequency 1MHz.

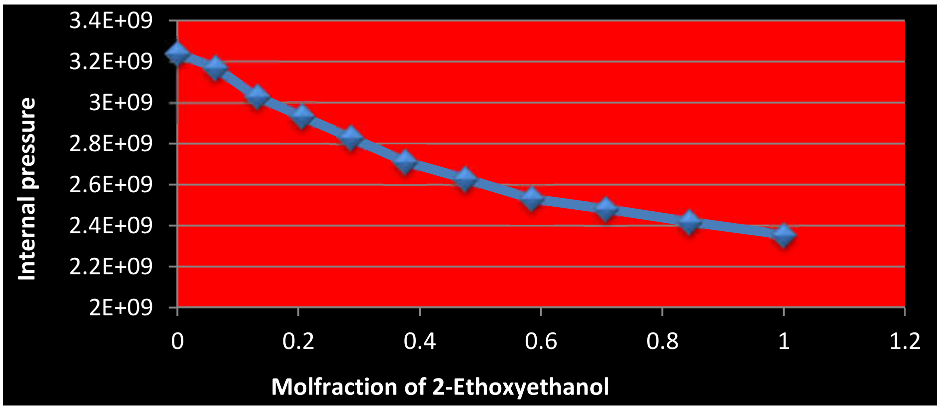

Fig 7 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and internal pressure of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of internal pressure of the binary mixture with rise in mole fraction of 2-Ethoxyethanol in Ethanol is depicted in figure 7. Perusal of figure 7 illustrates that the internal pressure is decreasing non-linearly with increase in concentration of 2-Ethoxyethanol in Ethanol. Internal pressure in a liquid system is a measure of intermolecular cohesive forces. It is used to study the nature of molecular interaction. This behavior of the internal pressure may be attributed to possibility of weak interaction. It is to be also noted that decrease of internal pressure leads to existence of ion-solvent interaction due to which the structural arrangement is affected. This suggests significant molecular interaction with increase in concentration of 2-Ethoxyethanol in Ethanol between the unlike constituents of the binary mixture [15].

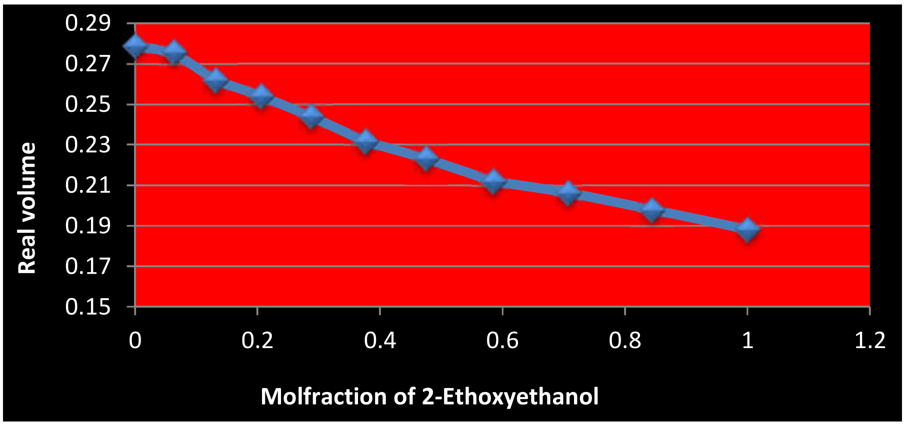

Fig 8 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and the real volume of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in real volume with rise of mole fraction of 2-Ethoxyethanol in Ethanol is depicted in figure 8. Perusal of figure 8 illustrates that the real volume is decreasing non-linearly with variable rate with the concentration of 2-Ethoxyethanol in Ethanol. The decrease in real volume with increase in concentration 2-Ethoxyethanol in Ethanol indicates that strong interaction exists between the unlike constituents of the binary mixture. It is because the volume of the binary mixture decreases as real volume decreases due to presence of strong cohesive forces between the constituents of the binary mixture. The increase in real volume with increase in concentration 2-Ethoxyethanol in Ethanol indicates that weak interaction exists between the unlike constituents of the binary mixture. It is because the volume of the binary mixture increases as real volume increases due to presence of repulsive or dissociative forces between the constituents of the binary mixture. It means that there may be complex formation due to non-linear behavior of the real volume.

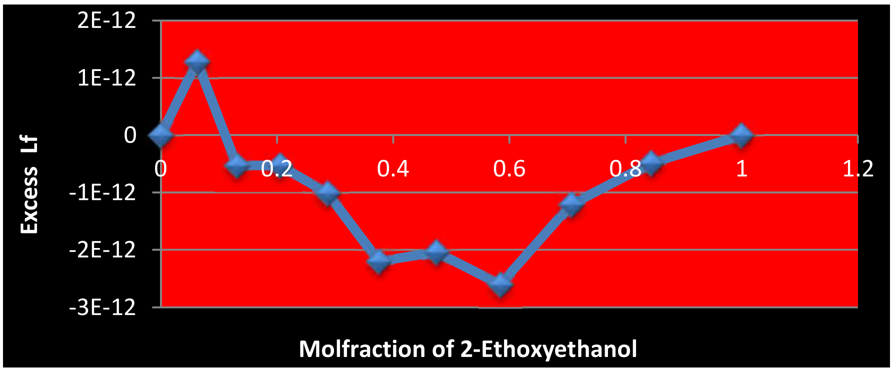

Fig 9 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and the excess intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of excess intermolecular free length of the binary mixture with rise in mole fraction of 2-Ethoxyethanol in Ethanol is shown in figure 9. Perusal of figure 9 indicates that the excess intermolecular free length is non-linearly positive and negative deviating with increase in concentration of 2-Ethoxyethanol in Ethanol. This shows significant interaction between the constituents of the binary mixture. For some portion there may be weak interaction. The non-linearity maintains interaction between the constituents of this binary system due large negative deviating portion of the graph [15].

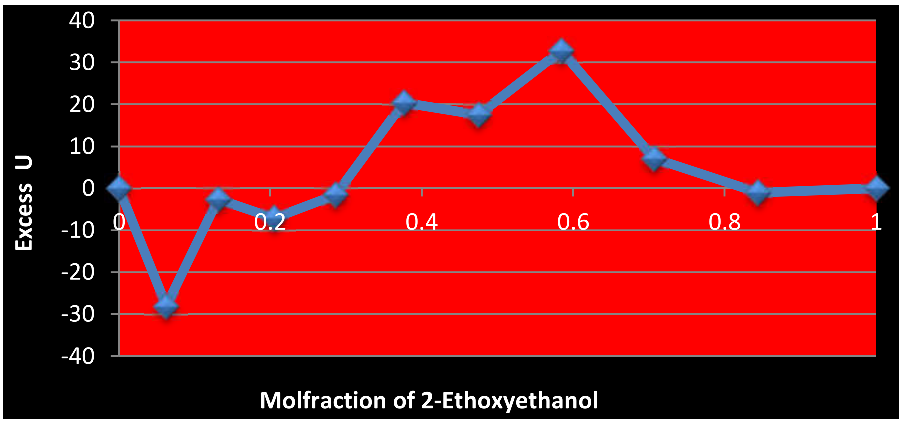

Fig 10 Graph between mole fraction of 2-Ethoxyethanol in Ethanol and the excess ultrasonic velocity of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in excess ultrasonic velocity with increase in concentration of 2-Ethoxyethanol in Ethanol is illustrated in figure 10. Perusal of figure 10 reveals that the excess ultrasonic velocity is varying non-linearly with concentration of 2-Ethoxyethanol in Ethanol in this binary mixture. Nature of graph of excess ultrasonic velocity is exactly reverse to that of excess adiabatic compressibility. It shows negative as well as positive deviations. Negative deviations are for very small portion and positive deviation are for large portion of the graph, as seen from the above figure. It means that there is presence of strong interactions and dispersive forces for significant interactions in the [16] Binary liquid mixture of 2-Ethoxyethanol in Ethanol.

CONCLUSION:

In the present work, we have studied various thermo-acoustic parameters of 2-Ethoxyethanol in Ethanol. Refractive index, Relative association and relaxation time show linear variation with concentration of 2-Ethoxyethanol in Ethanol. Viscosity, intermolecular free length and Gibb's free energy show linear variation with increase in concentration of 2-Ethoxyethanol in Ethanol. Internal pressure and real volume show linear decrease with increase in concentration of 2-Ethoxyethanol in Ethanol. The excess parameters excess intermolecular free length and excess ultrasonic velocity show non-linear positive and negative deviations. Varying positive deviations and negative deviations for different portions of the graphs are explained above. This investigation supports strong molecular interaction and so contraction in the volume of the mixture with increase of 2-Ethoxyethanol in Ethanol. Thus, it can be concluded that there exist strong molecular interaction between the constituents of this binary mixture that is 2-Ethoxyethanol in Ethanol.

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