Interferometric Evaluation of thermo-acoustic parameters in the Binary Liquid Mixture Consisting of Ethyl Formate and Distilled water at constant temperature 303 °K

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ABSTRACT:

Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of Ethyl Formate and distilled water were measured over entire composition range. These measurements were done at constant temperature 303 K and at frequency 1MHZ. These were used to evaluate various thermo-acoustic parameters. These parameters are relative association (R_A), internal pressure (πi) and Repulsive exponent (n). In addition to these thermo-acoustic parameters, excess parameters were computed and studied. These are excess adiabatic compressibility (β_{ad}^{E}), excess intermolecular free length (L_f^E), excess ultrasonic velocity (U^E) and excess specific acoustic impedance (Z^E). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 303 °K.

KEY WORDS: Repulsive exponent, ultrasonic velocity, internal pressure, free length, acoustic impedance

INTRODUCTION:

A large number of studies have been made on the molecular interaction in liquid mixture by various methods like Ultraviolet, Dielectric constant, Infrared, Raman Effect, Nuclear magnetic resonance and Ultrasonic method. Recently, ultrasonic method has become a powerful tool to provide information regarding the physical and chemical properties of liquid system. The ultrasonic study of liquid and liquid mixtures is useful in understanding the nature of molecular interactions in pure liquids and in liquid mixtures. 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 Ethyl Formate and Distilled water.

Ethyl Formate is an ester formed when ethanol reacts with formic acid. Its chemical formula is $C_3H_6O_2$. Ethyl formate has the characteristic smell of rum and is also partially responsible for the flavor of raspberries [3]. It occurs naturally in the body of ants and in the stingers of bees [4]. Ethyl formate is an ethyl ester of formic acid. Its microwave spectrum indicates the presence of two isomeric forms having the ethyl group collective investment scheme (cis) to the carbonyl oxygen atom but having different arrangement of the methyl group about the $-CH_2-O$ bond. Kinetics of its pyrolytic decomposition to the corresponding acid and alkene has been reported. Ethyl formate has been used in the preparation of *N*-(2-triethoxysilylpropyl) formamide. It has been used in the synthesis of *N*-methyl-3-phenylbicyclo heptan-2-amine hydrochloride. It may be used in the synthesis of isoflavone. In industry, it is used as a solvent for cellulose nitrate, cellulose acetate, oils, and greases. It can be used as a substitute for acetone.

Water is an inorganic compound. Its chemical formula is H2O. It is transparent, tasteless, odorless & nearly colorless. It uses covalent and H-bonds for its formation from oxygen & hydrogen. It is very important for all living organisms. Water can exist in all the three states on earth. It is found in solid, liquid and gaseous form on the earth. It is used everywhere for various purposes. Its density is 1000 Kg/m^3. It's melting and boiling point temperatures are 273 and 373 °K respectively. It is a good polar solvent. Dielectric constant of water is 80. Relative polarity of water is 1.0.

In the present work, density, viscosity and ultrasonic velocity of Ethyl Formate and Distilled water binary mixture have been measured and used to compute various acoustic parameters such as relative association (R_A), internal pressure (πi) and Repulsive exponent (n). In addition to these thermo-acoustic parameters, excess parameters were computed and studied. These are excess adiabatic compressibility (β^{E}_{ad}), excess intermolecular free length (L^{E}_{f}), excess ultrasonic velocity (U^{E}) and excess specific acoustic impedance (Z^{E}). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 303 °K. 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 Ethyl Formate and Distilled water. Ethyl Formate is obtained from SDFCL, Mumbai. It is AR type chemical. Density of the pure components and their mixtures were measured by using 10 ml specific gravity bottle up to the accuracy (0.001 g) [5]. 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 [6]. 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 [7] 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 were evaluated. These are relative association (R_A), internal pressure (πi) and Repulsive exponent (n). In addition to these thermo-acoustic parameters, excess parameters were computed and studied. These are excess adiabatic compressibility (β_{ad}^E), excess intermolecular free length (L_f^E), excess ultrasonic velocity (U^E) and excess specific acoustic impedance (Z^E). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 303 °K.

THEORATICAL BACKGROUND:

For the measurement of ultrasonic absorption by interferometer technique, the experimental liquid is filled 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. ULTRASONIC VELOCITY: It is the velocity of the sound waves propagating through the binary liquid mixture. λ is the wavelength of the sound waves inside the binary liquid mixture.

$$U = n\lambda \quad \text{m/s} \qquad (1)$$

Where λ is the wavelength of the ultrasonic waves in m

2. 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.

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

$b = 2$, 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

3. 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.

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

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

4. REPULSIVE EXPONENT: Repulsive exponent is associated with fractional free volume. It is used to interpret the type of interaction existing between the constituents of a liquid mixture. The formula to compute repulsive exponent is

$$n = 3[(2/f)-5] \qquad (4)$$

Where f is the fractional free volume of a liquid mixture

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

$$A^E = A_{expt} - A_{id} \qquad (5)$$

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, ultrasonic velocity (U) and viscosity were used to compute various acoustic parameters with respect to concentrations of Ethyl Formate and Distilled water. Evaluation of all these parameters is done at constant temperature 303 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 Ethyl Formate and Distilled water. The discussion of the results obtained from these parameters is made below.

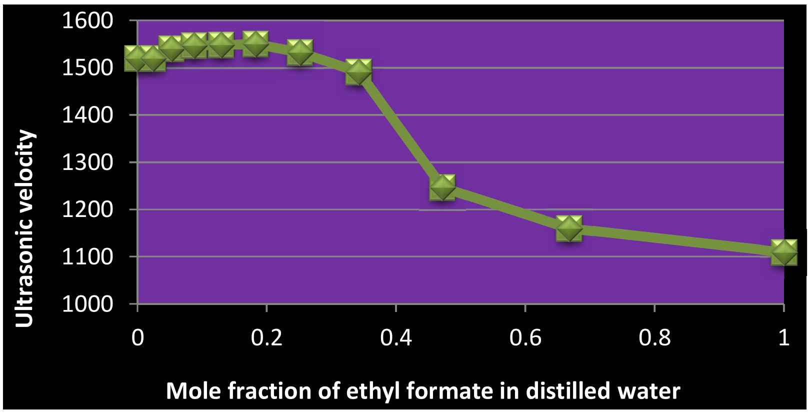

Fig 1 Graph between mole fraction of Ethyl formate in distilled water and the ultrasonic velocity of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of ultrasonic velocity of this mixture with concentration of solute Ethyl formate in distilled water is depicted in figure 1. Perusal of figure 1 represents the variation of ultrasonic velocity with concentration of ultrasonic velocity. The decrease or increase in ultrasonic velocity depends on the behavior of intermolecular free length and adiabatic compressibility. It is always reverse to that of behavior of intermolecular free length and adiabatic compressibility. The increase in ultrasonic velocity with the concentration of solute supports strong interaction between the unlike molecules of the mixture. The decrease in ultrasonic velocity with the concentration of solute supports weak interaction between the unlike molecules of the mixture. The non-linear behavior of ultrasonic velocity suggests that there may weak and significant molecular interaction between the unlike molecules of this mixture [8].

Table I: The acoustic parameters ultrasonic velocity, viscosity and internal pressure are shown in table I. The variation of the above mentioned parameters with rise in mole fraction of Ethyl formate in distilled water is illustrated in figures 1 to 3 respectively.

Mole fraction of Ethyl Formate in Distilled water	Ultrasonic velocity U	Internal pressure π_i	Viscosity η
T=303°K and Frequency = 1MHZ			
0	1520	8.65E+09	0.0089
0.024179	1520	7.83E+09	0.008731
0.052807	1540	6.97E+09	0.008534
0.087236	1546.6	6.16E+09	0.008304
0.129428	1548	5.36E+09	0.00803
0.182342	1550	4.59E+09	0.007699
0.25066	1532	3.85E+09	0.007292
0.342255	1491	3.14E+09	0.00678
0.471465	1246.6	2.64E+09	0.006119
0.667448	1160	1.94E+09	0.005236
1	1108.8	1.23E+09	0.00402

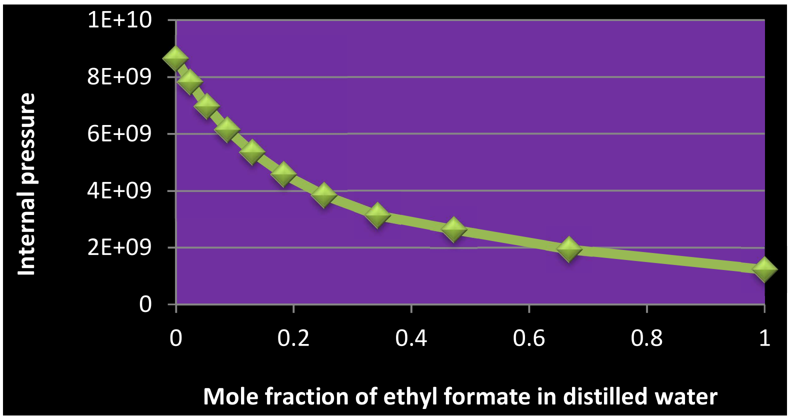

Fig 2 Graph between mole fraction of Ethyl formate in distilled water and internal pressure of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of internal pressure of the binary mixture with rise in mole fraction of ultrasonic velocity is depicted in figure 2. Perusal of figure 2 illustrates that the internal pressure is decreasing non-linearly with increase in concentration of ultrasonic velocity. 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 ultrasonic velocity between the unlike constituents of the binary mixture [9].

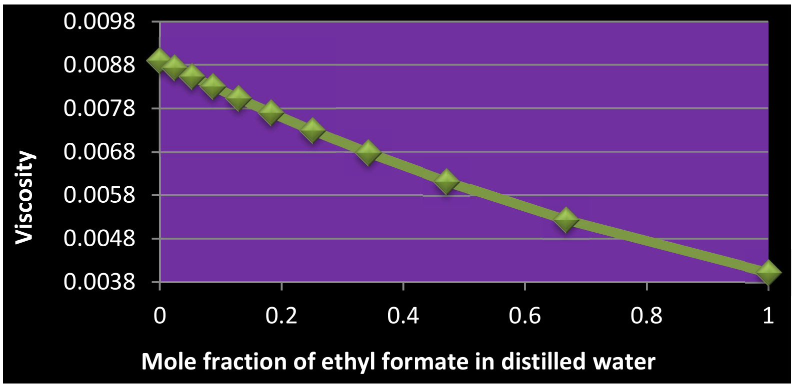

Fig 3 Graph between mole fraction of Ethyl formate in distilled water viscosity of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of viscosity with the mole fraction of Ethyl formate in distilled water is depicted in figure 3. Examination of figure 3 reveals that the viscosity decreases approximately linearly with the mole fraction of Ethyl formate in distilled water. The decrease in viscosity with increase in concentration of Ethyl formate in distilled water indicates the presence of weak molecular interaction between the constituents of the binary mixture [10].

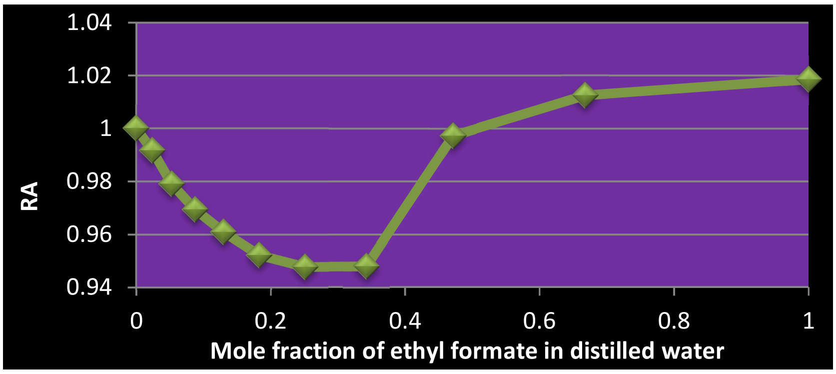

Fig 4 Graph between mole fraction of Ethyl formate in distilled water and relative association of the binary mixture at constant temperature and fixed ultrasonic frequency

The nature of variations in relative association with increase in concentration of Ethyl formate in distilled water is illustrated in figure 4. Observation of figure 4 reveals that the relative association in the binary mixture is decreasing non-linearly with increase in concentration of Ethyl formate in distilled water up to mole fraction 0.25. After this mole fraction of Ethyl formate in distilled water, it increases non-linearly with increase in concentration of Ethyl formate in distilled water. The decreasing nature of relative association [11] 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 4.

Table II: The evaluated thermo-acoustic parameters relative association, repulsive exponent and excess intermolecular free length are illustrated in table II. The variation in these parameters with rise in mole fraction of Ethyl formate in distilled water is represented in figures 4 to 6 respectively.

Mole fraction of Ethyl formate in distilled water	Relative association R_A	Repulsive exponent RE	Excess Intermolecular free length L_f^E
T=303°K and Frequency = 1MHZ			
0	1	105	1.17E-14
0.024179	0.9917	105	-2.58E-13
0.052807	0.979124	145	-1.17E-12
0.087236	0.969477	164.7753	-1.82E-12
0.129428	0.960935	169.6154	-2.46E-12
0.182342	0.952276	177	-3.31E-12
0.25066	0.947713	126.1765	-3.89E-12
0.342255	0.947967	73.07339	-4.19E-12
0.471465	0.997393	12.16469	2.54E-12
0.667448	1.012537	6.818182	3.22E-12
1	1.018668	4.543974	1.68E-14

The nature of variations in repulsive exponent with increase in concentration of Ethyl formate in distilled water is illustrated in figure 5. Observation of figure 5 reveals that the repulsive exponent in the binary mixture is increasing non-linearly with increase in concentration of Ethyl formate in distilled water up to mole fraction 0.18 of the solute. After this mole fraction of Ethyl formate in distilled water, it decreases non-linearly with increase in concentration of Ethyl formate in distilled water. The increasing nature of repulsive exponent represents dominance of attractive forces over repulsive forces in the binary liquid mixture [12]. The non-linear decrease of repulsive exponent represents significant interaction. The irregular behavior of repulsive exponent with the concentration of Ethyl formate in distilled water supports significant molecular interaction between the unlike molecules of the binary mixture.

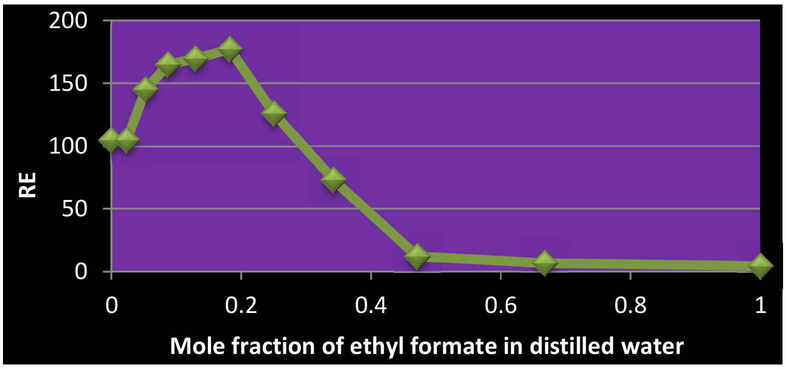

Fig 5 Graph between mole fraction of Ethyl formate in distilled water and repulsive exponent of the binary mixture at constant temperature and fixed ultrasonic frequency

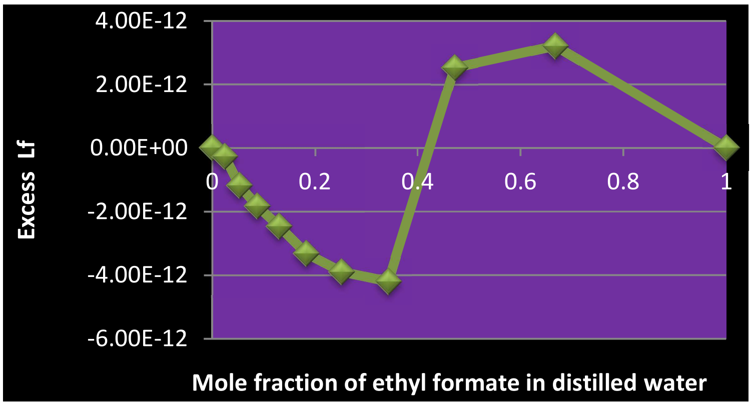

Fig 6 Graph between mole fraction of Ethyl formate in distilled water and the excess intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of excess intermolecular free length of the binary mixture with rise in mole fraction of Ethyl formate in distilled water is shown in figure 6. Perusal of figure 6 indicates that the excess intermolecular free length is deviating non-linearly negative and positive with increase in concentration of Ethyl formate in distilled water. 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 [13].

The variation in excess ultrasonic velocity with increase in concentration of Ethyl formate in distilled water is illustrated in figure 7. Perusal of figure 7 reveals that the excess ultrasonic velocity is varying non-linearly with concentration of Ethyl formate in distilled water 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 small portion and positive deviation are for large portion of the graph, as seen from the below figure. It means that there is presence of strong interactions and dispersive forces for significant interactions in the [14] Binary liquid mixture of Ethyl formate in distilled water.

Table III: The evaluated thermo-acoustic parameters excess ultrasonic velocity, excess adiabatic compressibility and excess specific acoustic impedance are illustrated in table III. The variation in these parameters with rise in mole fraction of Ethyl formate in distilled water is represented in figures 7 to 9 respectively.

Mole fraction of Ethyl formate in distilled water	Excess ultrasonic velocity U^E	Excess adiabatic compressibility β^E_{ad}	Excess specific acoustic impedance Z^E
T=303°K and Frequency = 1MHZ			
0	0	0	0
0.024179	9.942507	-7.40E-12	-448.268
0.052807	41.71434	-2.80E-11	21010.22
0.087236	62.47153	-4.40E-11	31989.58
0.129428	81.22084	-6.00E-11	41738.56
0.182342	104.9791	-8.10E-11	57435.08
0.25066	115.0715	-9.80E-11	61846.21
0.342255	111.7352	-1.10E-10	56605.96
0.471465	-79.5337	4.23E-11	-118919
0.667448	-85.5454	6.72E-11	-110772
1	0	0	0

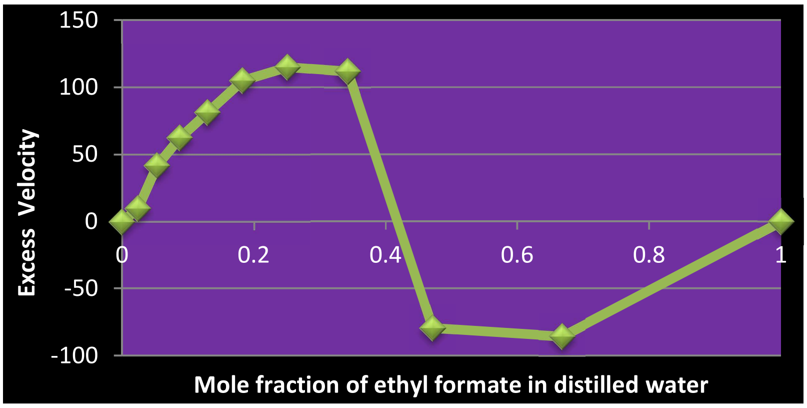

Fig 7 Graph between mole fraction of Ethyl formate in distilled water and the excess ultrasonic velocity of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in excess adiabatic compressibility with rise of mole fraction Ethyl formate in distilled water is shown in figure 8. Examination of figure 8 indicates that the excess adiabatic compressibility shows negative and positive deviations with increase concentration of Ethyl formate in distilled water. Chemical or specific interactions which include charge transfer, H-bond formation and complex forming reactions all resulting in negative deviation in excess adiabatic compressibility. It is true for most part of the graph in figure 8. The positive deviation seen for a small portion of the graph at the middle concentration of the solute may interpret dissociation process. This means that negative deviation in excess adiabatic compressibility with mole fraction of the solute indicates strong molecular interaction between the unlike molecules of Ethyl formate in distilled water [15]. This is true for major part of the graph.

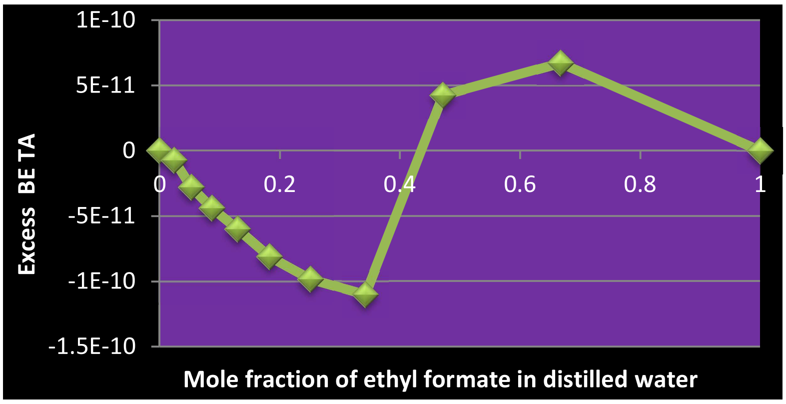

Fig 8 Graph between mole fraction of Ethyl formate in distilled water and the excess adiabatic compressibility of the binary mixture at constant temperature and fixed ultrasonic frequency

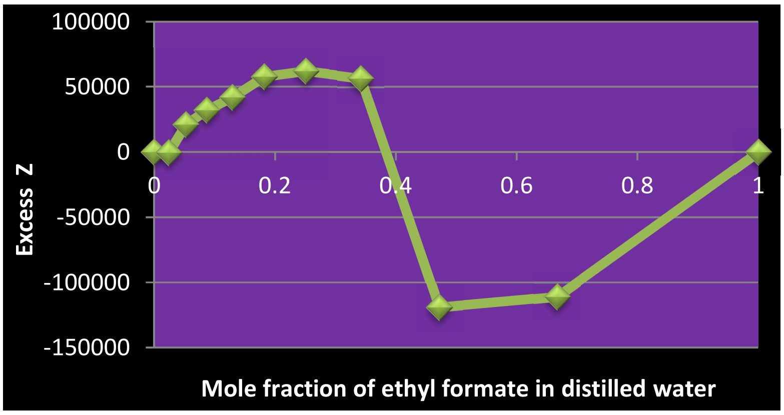

Fig 9 Graph between mole fraction of Ethyl formate in distilled water and the excess specific acoustic impedance of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of excess specific acoustic impedance of the binary mixture with rise in mole fraction of Ethyl formate in distilled water is illustrated in figure 9. Perusal of figure 9 indicates that the excess specific acoustic impedance shows non-linear positive and negative deviations with increase in concentration of Ethyl formate in distilled water. For some portion of the graph excess Z is negative which supports the weak interaction. For most of the portion of the graph the excess Z is positive which supports the forces of cohesion between the unlike constituents of the binary mixture. This causes contraction of the volume of the binary mixture [16]. This is clear from above figure.

CONCLUSION:

In the present investigation, we have studied various thermo-acoustic parameters Ethyl formate in distilled water. Ultrasonic velocity, Viscosity and internal pressure show non-linear decrease with concentration of Ethyl formate in distilled water. Relative association, repulsive exponent and excess intermolecular free length show non-linear increase and decrease with increase in concentration of Ethyl formate in distilled water. The excess acoustic parameters excess ultrasonic velocity, excess adiabatic compressibility and excess specific acoustic impedance show non-linear positive and negative deviations with increase in concentration of Ethyl formate in distilled water. The behavior of excess ultrasonic velocity and excess specific acoustic impedance is identical to each other. This behavior of excess ultrasonic velocity and excess specific acoustic impedance is exactly opposite to that the behavior of excess adiabatic compressibility. Positive deviations are for more portions and negative deviations are for small portions in case of excess ultrasonic velocity and excess acoustic impedance. This investigation supports weak and significant molecular interaction. So contraction in the volume of the mixture for some mole fraction and expansion for remaining mole fractions of Ethyl formate in distilled water. Thus, it can be concluded that there exist significant molecular interaction between the constituents of Ethyl formate in distilled water binary mixture corresponding to cohesion and dissociation.

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