Ultrasonic Study of the Binary Liquid Mixture Consisting of Methanol and Acetone 312.15 °K

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ABSTRACT:

Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of Methanol and Acetone 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 specific acoustic impedance (Z), intermolecular free length (Lf), relative association (RA), and adiabatic compressibility (β_{ad}). In addition to these thermo-acoustic parameters excess parameters were computed. These are excess available volume (V_a^E), excess acoustic impedance (β_{ad}^E), excess ultrasonic velocity (U^E), excess intermolecular free length (L_f^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 312.15K.

KEY WORDS: Ethanol, ultrasonic velocity, Wada's constant, free length, acoustic impedance

INTRODUCTION:

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 Methanol and Acetone. Acetone is an organic compound with chemical formula (CH3)2CO.This is clear, mobile easy to burn liquid. It is the simplest example of ketones. It can be mixed with water. It is an important solvent. It is commonly used to clean things in laboratory. It is commonly used at homes as active ingredient in nail polish remover and as paint thinner. It is common building block in organic chemistry. It has Pungent, irritating, floral, cucumber like odor. It is miscible in water. It is also miscible in benzene, diethyl ether, ethanol, methanol and chloroform. It has dipole moment 2.91. It is polar molecule due to presence of very electronegative oxygen (3.44) in the center of the molecule. Oxygen pulls electrons from the central carbon and other R-groups with lower negativity (2.55) and creates a partial negative charge.

Methanol is also known as methyl alcohol, amongst other names, is a chemical and the simplest alcohol, with the formula CH3OH. It is a light, volatile, colorless, flammable liquid with a distinctive alcoholic odour similar to that of ethanol (potable alcohol) [3]. It is a polar solvent. Methanol acquired the name wood alcohol because it was once produced chiefly by the destructive distillation of wood. Today, methanol is mainly produced industrially by hydrogenation of carbon monoxide [4]. Methanol consists of a methyl group linked to a polar hydroxyl group. With more than 20 million tons produced annually. It is used as a precursor to other commodity chemicals, including formaldehyde, acetic acid, methyl tert-butyl ether, methyl benzoate, anisole, peroxyacids, as well as a host of more specialized chemicals[5]. Dielectric constant of Methanol at 308K is 30.48. Relative polarity of Methanol is 6.6.

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 specific acoustic impedance (Z), intermolecular free length (Lf), relative association (RA), and adiabatic compressibility (β_{ad}). In addition to these thermo-acoustic parameters excess parameters were computed. These are excess available volume (V_a^E), excess acoustic impedance (β_{ad}^E), excess ultrasonic velocity (U^E), excess intermolecular free length (L_f^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 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 Methanol and Acetone. Methanol obtained from Thermo Fisher Scientific India Private limited Mumbai. Acetone obtained from Thermo Fisher Scientific India Private limited 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) [6]. 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 [7]. 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 [8] 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 specific acoustic impedance (Z), intermolecular free length (Lf), relative association (RA), and adiabatic compressibility (β_{ad}) were evaluated. In addition to these thermo-acoustic parameters excess parameters were computed. These are excess available volume (V_a^E), excess acoustic impedance (β_{ad}^E), excess ultrasonic velocity (U^E), excess intermolecular free length (L_f^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 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. 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 or ternary liquid mixture.

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

2. 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.

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

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

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

3. ADIABATIC COMPRESSIBILITY: It determines the orientation of the solvent molecules around the liquid molecules. The structural change in molecules in a liquid mixture takes place due to the existence of electrostatics field between the interacting molecules. The structural arrangement of the molecules affects the value of adiabatic compressibility. It is defined as fractional degrees of volume per unit increase of pressure when no heat flows in or out. It is therefore a measure of intermolecular association or dissociation or repulsion.

$$\beta_{ad} = \frac{1}{u^2\rho} \quad m^2/N \qquad (3)$$

u ultrasonic velocity and ρ is density of liquid in SI

4. SPECIFIC ACOUSTIC IMPEDANCE: When an acoustic wave travels in a medium there is variation of pressure from particle to particle. The ratio of instantaneous pressure excess at any particle of the medium to the instantaneous velocity of that particle is known as specific acoustic impedance of that medium.

$$Z = U\rho \quad Kg/m^2.S \qquad (4)$$

5. 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.

$$R_A = \frac{ds}{do}\left[\frac{Uo}{Us}\right]^{1/3} \qquad (5)$$

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

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

$$A^E = A_{expt} - A_{id} \qquad (6)$$

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) and viscosity used to evaluate other acoustic parameters. 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 Methanol and Acetone. The discussion of the results obtained from these parameters is made below.

The variation of intermolecular free length of the binary mixture with rise in mole fraction of Methanol and Acetone is depicted in figure 1. Perusal of figure 1 illustrates that the intermolecular free length is increasing and decreasing non-linearly with increase in concentration of Methanol and Acetone. 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. Behavior of intermolecular free length is identical to adiabatic compressibility. Behavior of intermolecular free length is opposite to ultrasonic velocity and specific acoustic impedance; it is clear from the following figures. 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 Methanol and Acetone. So this irregular behavior of intermolecular free length may be due to significant molecular interaction between the unlike molecules of the binary mixture. Thus intermolecular free length with increase in concentration of the solute supports molecular interaction between the constituents of the binary mixture [13].

The variation of specific acoustic impedance of the binary mixture with rise in mole fraction of Methanol and Acetone is shown in figure 2. Perusal of figure 2 indicates that the specific acoustic impedance is increasing and decreasing non-linearly with increase in concentration of Methanol and Acetone. Behavior of acoustic impedance is identical to ultrasonic velocity and opposite to intermolecular free length and adiabatic compressibility. The acoustic impedance increases and decreases irregularly with increase in concentration of Methanol and Acetone. It represents that there is significant interaction between the Methanol and Acetone system. This type of interaction is of associative type producing contraction in the volume of the mixture [10].

Table I: The intermolecular free length, ultrasonic velocity, specific acoustic impedance and adiabatic compressibility are shown in table I. The variation of the above mentioned parameters with rise in mole fraction of Methanol in Acetone is illustrated in figures 1 to 4 as shown below.

Mole fraction of Methanol in Acetone	Lf	Z (Kg /m^{2}s)	U (m/s)	β_{ad}
T=312.15°K and Frequency = 1MHZ				
0	6.7241E-11	892946.9	878624.3	1.01622E-09
0.16898	6.6942E-11	894558.2	882966.5	1.00721E-09
0.313901	7.3603E-11	940185.8	803449.2	1.2176E-09
0.43956	6.7681E-11	962760.7	874157.9	1.02957E-09
0.549558	7.0176E-11	995066.1	843491.3	1.10685E-09
0.646651	7.1704E-11	1043122	825904.7	1.15559E-09
0.732984	6.9176E-11	1071831	856499	1.07553E-09
0.810252	6.8651E-11	1118663	863449.5	1.05929E-09
0.879811	7.1983E-11	1131358	823874.9	1.16461E-09
0.942761	6.4504E-11	1162224	919836	9.35175E-10
1	6.9343E-11	1204852	856057	1.08074E-09

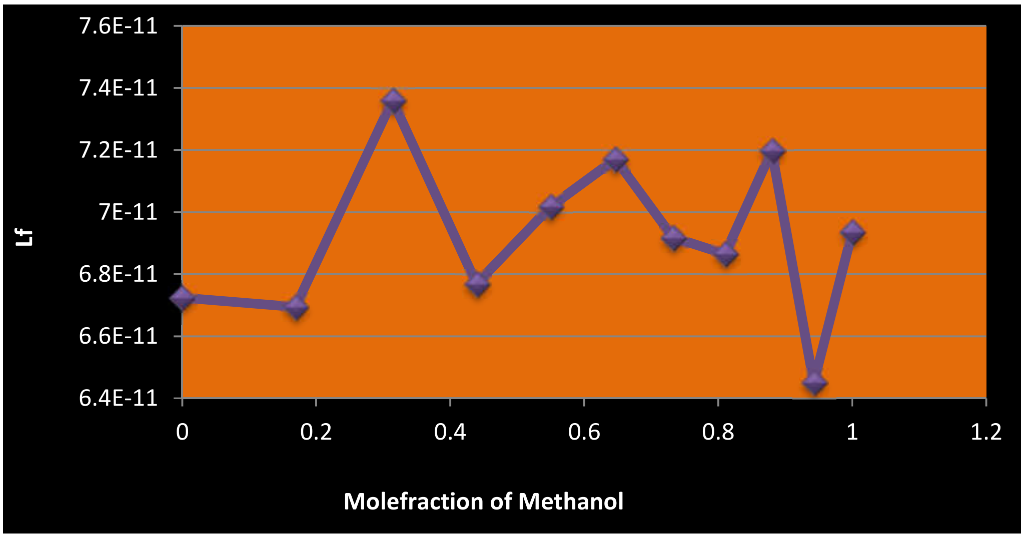

Fig 1 Graph between mole fraction of Methanol in Acetone and intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

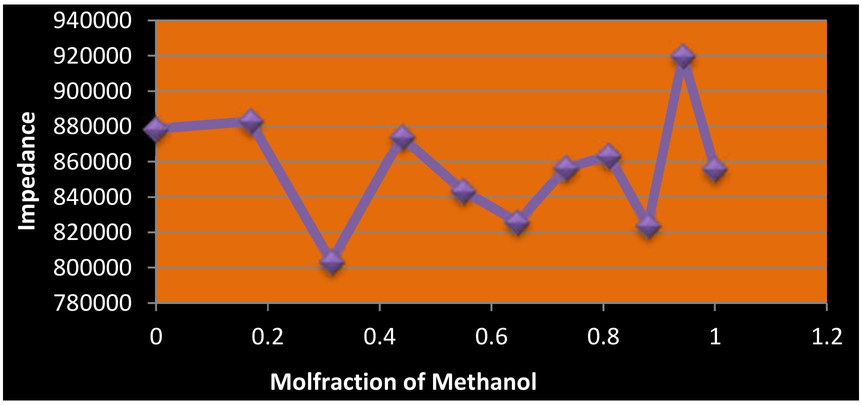

Fig 2 Graph between mole fraction of Methanol in Acetone and specific acoustic impedance of the binary mixture at constant temperature and fixed ultrasonic frequency

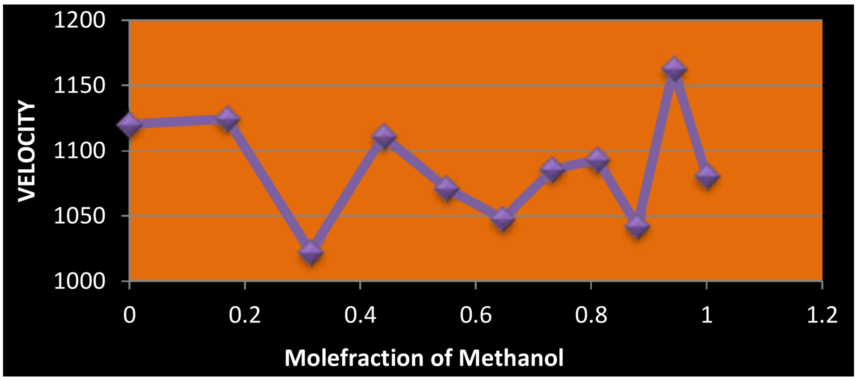

Fig 3 Graph between mole fraction of Methanol in Acetone and the ultrasonic velocity of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of ultrasonic velocity of the binary mixture with rise in mole fraction of Methanol in Acetone is depicted in figure 3. Perusal of figure 3 illustrates that the ultrasonic velocity is increasing and decreasing non-linearly with increase in concentration of Methanol in Acetone. This non-linear increase and decrease in ultrasonic velocity with increase in concentration of Methanol in Acetone may be due to complex formation because of formation H-bond. The increase in ultrasonic velocity depends on the behavior of intermolecular free length. It is always reverse to that of behavior of intermolecular free length. The increase in ultrasonic velocity with the concentration of solute supports significant interaction between the unlike molecules of the mixture. This suggests that dipole-induced dipole attraction is stronger than induced dipole-induced dipole attraction where linear plots are normally obtained [11].

The variation in specific acoustic impedance with increase in concentration of Methanol in Acetone is illustrated in figure 4. Perusal of fig. 4 indicates that the specific acoustic impedance is varying non-linearly with concentration of Methanol in this binary mixture. The non-linear behavior of the specific acoustic impedance with increase in concentration of Methanol in Acetone strongly suggest interaction between the unlike molecules of the binary mixture. Strictly speaking the interaction is changing with the variation of the concentration of Methanol in Acetone. Therefore, there is existence of molecular interaction between the constituents of the binary system. The nonlinear variation of specific acoustic impedance exposes that there is presence of specific interaction and cluster formation between the mixing constituents [12].

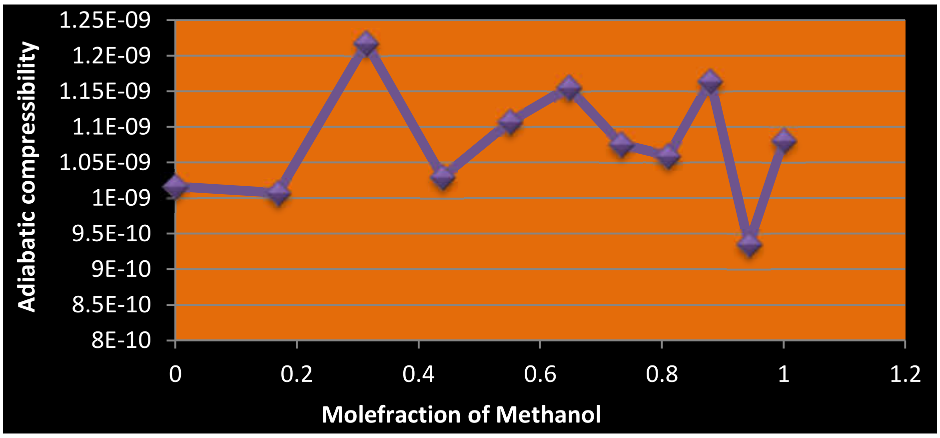

Fig 4 Graph between mole fraction of Methanol in Acetone and the adiabatic compressibility of the binary mixture at constant temperature and fixed ultrasonic frequency

Table II: The evaluated thermo-acoustic parameters relative association, excess ultrasonic velocity and excess intermolecular free length are illustrated in table II. The variation in these parameters with rise in mole fraction of Methanol in Acetone is represented in figures 5 to 7 respectively.

Mole fraction of Methanol in Acetone	RA	Excess U	Excess Lf
T=312.15°K and Frequency = 1MHZ			
0	1	0	0
0.16898	0.999631	11.06712	-6.5E-13
0.313901	1.03289	-85.5065	5.7E-12
0.43956	1.005533	8.306807	-4.8E-13
0.549558	1.018867	-27.3923	1.78E-12
0.646651	1.027351	-46.9259	3.1E-12
0.732984	1.016258	-5.77032	3.94E-13
0.810252	1.014809	5.020856	-2.9E-13
0.879811	1.03211	-43.3594	2.89E-12
0.942761	0.996151	79.39195	-4.7E-12
1	1.02159	0	0

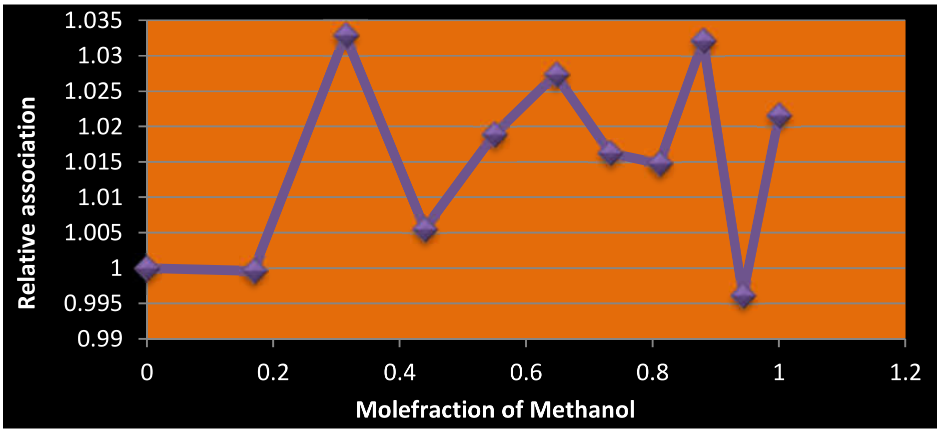

Fig 5 Graph between mole fraction of Methanol in Acetone and the relative association of the binary mixture at constant temperature and fixed ultrasonic frequency

The variations in relative association with increase in concentration Methanol in Acetone are illustrated in figure 5. Observation of figure 5 reveals that the relative association in the binary mixture is increasing and decreasing non-linearly with increase in concentration of Methanol. The decreasing nature of relative association [13] 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 5.

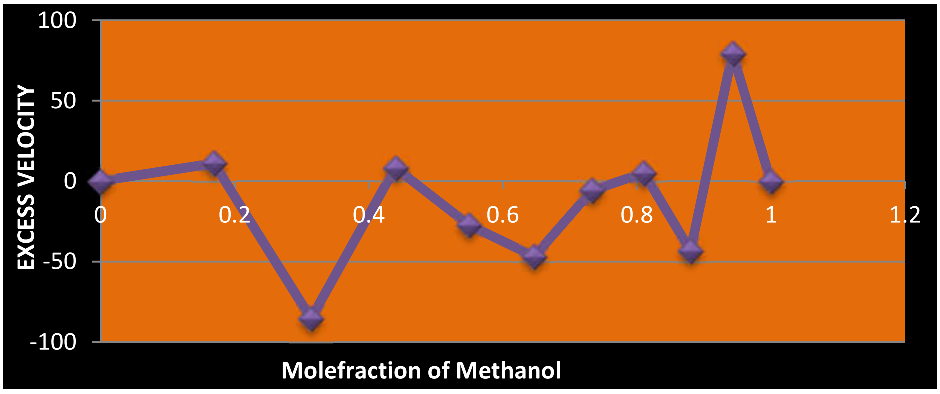

Fig 6 Graph between mole fraction of Methanol in Acetone and excess ultrasonic velocity of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in excess ultrasonic velocity with increase in concentration of Methanol in Acetone is illustrated in figure 6. Perusal of figure 6 reveals that the excess ultrasonic velocity is varying non-linearly with concentration of Methanol in this binary mixture. Nature of graph of excess ultrasonic velocity is exactly reverse to that of excess available volume. It shows negative as well as positive deviations. It means that there is presence of significant interactions in the [14] Binary liquid mixture of Methanol in Acetone. It is opposite to excess adiabatic compressibility and excess intermolecular free length.

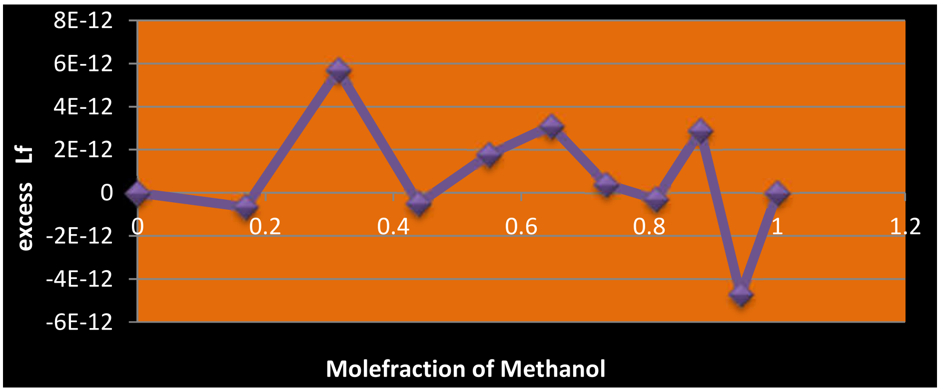

Fig 7 Graph between mole fraction of Methanol in Acetone and excess intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of excess intermolecular free length of the binary mixture with rise in mole fraction Methanol in Acetone is shown in figure 7. Observation of figure 7 indicates that the excess intermolecular free length is non-linearly positive and negative deviating with increase in concentration of Methanol in Acetone. 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 [15].

Table III. The excess thermo-acoustic parameters excess adiabatic compressibility, excess specific acoustic impedance and excess available volume are depicted in table III. The variation of these parameters with rise of mole fraction is shown in figures 8 to 10 respectively.

Mole fraction of Methanol in Acetone	Excess β_{ad}	Excess Z	Excess Va
T=312.15°K and Frequency = 1MHZ			
0	0	0	0
0.16898	-2E-11	8155.631	-3.6E-07
0.313901	1.81E-10	-68091.2	3.57E-06
0.43956	-1.5E-11	5453.326	-1.1E-07
0.549558	5.52E-11	-22731	1.15E-06
0.646651	9.77E-11	-38126.4	1.72E-06
0.732984	1.2E-11	-5583.85	3.39E-07
0.810252	-9.2E-12	3110.402	-2.1E-08
0.879811	9.16E-11	-34894.4	1.29E-06
0.942761	-1.4E-10	62487.34	-2.1E-06
1	0	0	0

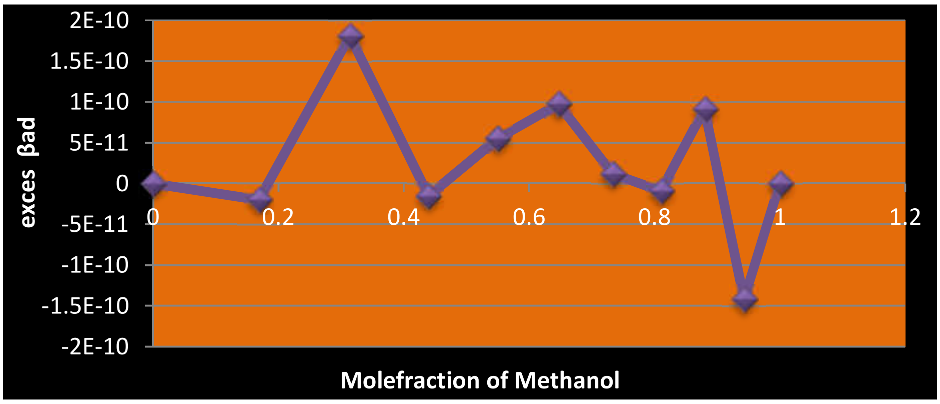

Fig 8 Graph between mole fraction of Methanol in Acetone and excess adiabatic compressibility of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in excess adiabatic compressibility with rise of mole fraction of Methanol in Acetone is shown in figure 8. Examination of figure 8 indicates that the excess adiabatic compressibility shows negative and positive deviations with increase concentration of Methanol in Acetone. 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 some part of the graph in figure 8.The positive deviation seen for the remaining portion of the graph which 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 Methanol in Acetone [16]. This means that positive deviation in excess adiabatic compressibility with mole fraction of the solute indicates weak molecular interaction between the unlike molecules of Methanol in Acetone. The non-linearity may form complexion in the binary mixture. It is due to significant molecular interaction due to non-linear behavior of the excess adiabatic compressibility.

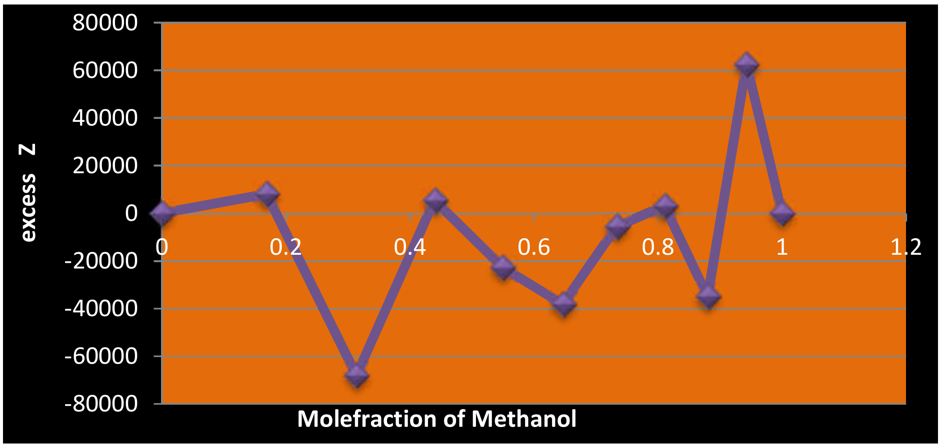

Fig 9 Graph between mole fraction of Methanol in Acetone and the excess specific acoustic impedance of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in excess specific acoustic impedance with increase in concentration of Methanol in Acetone is illustrated in figure 9. Perusal of figure 9 reveals that the excess specific acoustic impedance is varying non-linearly with concentration of Methanol in this binary mixture. Nature of graph of excess specific acoustic impedance is exactly similar to that of excess ultrasonic velocity. It shows negative as well as positive deviations. Positive deviations are more as compared to negative deviations. It means that there is [17] presence of more significant interactions and less dispersive forces in the Binary liquid mixture of Methanol in Acetone. The significant interactions between the unlike molecules are due to non-linearity of excess specific acoustic impedance.

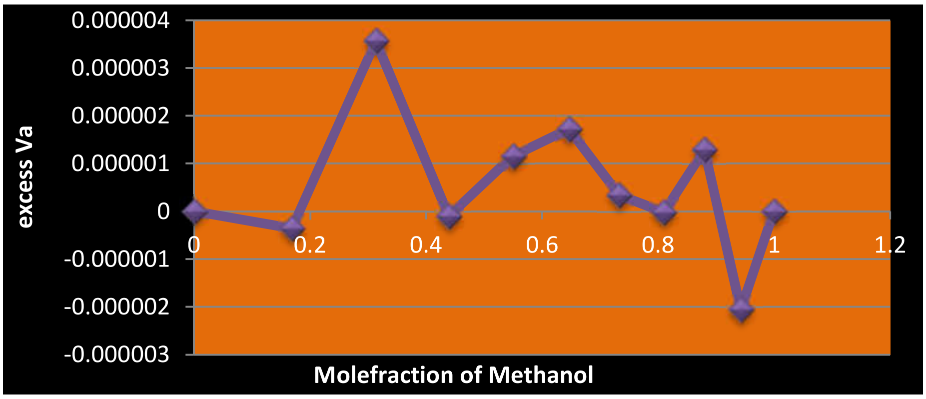

Fig 10 Graph between mole fraction of Methanol in Acetone and the excess available volume of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in excess available volume with increase in concentration of Methanol in Acetone is illustrated in figure 10. Perusal of figure 10 reveals that the excess available volume is varying non-linearly with concentration of Methanol in this binary mixture. The excess available volume shows non-linear positive & negative deviations with increase in concentration of Methanol in Acetone. The strong interactions and dispersive forces [18] are present in the Binary liquid mixture as the values of excess available volume V_a^E show both negative and positive deviations can be seen from figure 10. The non-linear behavior of excess available volume may support significant molecular interaction between the constituents of the binary mixture. .

CONCLUSION:

In the present investigation, we have studied various thermo-acoustic parameters of Methanol in Acetone. Intermolecular free length shows non-linear variation with Methanol in Acetone. Ultrasonic velocity shows non-linear variations with increase in concentration of Methanol in Acetone. Adiabatic compressibility also shows non-linear variations with increase in concentration of Methanol in Acetone. Specific acoustic impedance shows non-linear behavior with increase of concentration of Methanol in Acetone. Relative association also shows non-linear behavior with increase of concentration of Methanol in Acetone. The excess parameters excess intermolecular free length, excess adiabatic compressibility , excess ultrasonic velocity, excess specific acoustic impedance and excess available volume show non-linear positive and negative deviations. These deviations are non-linear and irregular. This investigation supports strong molecular interaction and so contraction in the volume of the mixture with increase of with increase of concentration of Methanol in Acetone. The non-linearity in all the parameters supports significant interactions between the constituents of the binary mixture. Thus, it can be concluded that there exist strong or significant molecular interaction between the constituents of with increase of concentration of Methanol in Acetone, the present binary liquid mixture.

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