Ultrasonic Study of the Binary Liquid Mixture Containing 1, 4-Dioxane and Ethyl Formate

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ABSTRACT:

Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of 1, 4-Dioxane and Ethyl formate 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 acoustic parameters such as intermolecular free length (L_f), intermolecular free volume (V_f), internal pressure (π_i), Wada's constant (W) and specific acoustic impedance (Z).In addition to these thermo-acoustic parameters excess parameters were computed. These are excess intermolecular free length (L_f^E), excess free volume (V_f^E), excess internal pressure (π_i^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 303K.

KEY WORDS: Ethyl formate, ultrasonic velocity, Wada's constant, free length, internal pressure

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 1, 4-Dioxane and Ethyl formate. 1, 4-Dioxane is a heterocyclic organic compound and classified as ether. It is colorless liquid with faint sweet odor. It is used for variety of practical applications as well as in the laboratory. It is also used as a stabilizer for transport of chlorinated hydrocarbons in aluminum containers [3]. It is non-polar versatile aprotic solvent for such as inks, adhesives and cellulose esters [4]. Dielectric constant of 1, 4-Dioxane is 2.25 and polarity index 4.8. Chemical formula of 1, 4-Dioxane is $C_4H_8O_2$. 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 [5]. It occurs naturally in the body of ants and in the stingers of bees [6]. 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.

In the present work, density, viscosity and ultrasonic velocity of 1, 4-Dioxane and Ethyl formate binary mixture have been measured and used to compute the acoustic parameters such as free length (L_f), intermolecular free volume (V_f), internal pressure (πi), Wada's constant (W) and specific acoustic impedance (Z). In addition to these thermo-acoustic parameters excess parameters were computed. These are excess intermolecular free length (L_f^E), excess free volume (V_f^E), excess internal pressure (π_i^E) and excess specific acoustic impedance (Z^E). 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 obtained from; 1, 4-Dioxane (Analytical reagent) is obtained from Avantor Performance Materials limited Thane, Maharashtra. It is 99.5% pure chemical. Ethyl formate was 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) [7]. 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 [8]. 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 [9] 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 (U), the acoustic parameters free length (L_f), intermolecular free volume (V_f), internal pressure (πi), Wada's constant (W) and specific acoustic impedance (Z). In addition to these thermo-acoustic parameters excess parameters were computed. These are excess intermolecular free length (L_f^E), excess free volume (V_f^E), excess internal pressure (π_i^E) and excess specific acoustic impedance (Z^E) were computed using the following equations.

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.
   $U = n\lambda$ m/s (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 or ternary liquid mixture.
   $L_f = k\,\beta_{ad}^{1/2}$ m (2)
   K is a constant known as Jacobson's constant given by
   K= (93.875+ 0.375 T in degree Kelvin)$\times 10^{-8}$
3. FREE VOLUME: It is defined as the average volume in which the center of molecule can move inside the hypothetical cell due to the repulsion of surrounding molecules. It is very important parameter in explaining the variation in the physico-chemical properties of pure liquids and liquid mixtures. It always show exact reverse trend with internal pressure. Its increasing value shows increasing compactness due to association at higher concentration.
   $V_f = \left(\frac{M_{eFF} U}{k\eta}\right)^{3/2}$ m^3/mole (3)
   k is a constant equal to 4.28×10^9 , η is viscosity of solution
4. WADA'S CONSTANT: It is required in the study of acoustical properties of pure liquids & liquid mixtures. It is also known as molar compressibility. Its value depends on the structure of pure liquid or liquid mixtures. Variations in Wada's constant with mole fraction of the solute provide evidence of molecular interaction between the components of binary or ternary system.
   $W = \frac{M}{p}\frac{1}{\beta^{1/7}}$ J/mol (4)
5. 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.
   $\pi i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eFF}^{7/6}}\right)$ Pa (5)
   Where b=2, R= 8.314 J/mol°K, K is a constant equal to 4.28×10^9
6. 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.
   $Z = U\rho$ Kg/m^2. S (6)

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

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

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), ultrasonic velocity (U) and Viscosity (5) & computed values Intermolecular free length (L_f) with respect to concentrations of 1, 4-Dioxane in Ethyl formate are presented in the table I. Evaluation of all these parameters is done at constant temperature 303K 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 of 1, 4-Dioxane in Ethyl formate. The discussion of the results obtained from these parameters is made below.

Table I: The acoustic parameters density, viscosity, ultrasonic velocity and intermolecular free length are shown in table I.

Mole fraction of 1, 4-Dioxane in Ethyl formate	ρ (Kg/m^3)	(poise)	U (m/s)	L_f (m)
T=303°K and Frequency = 1MHZ				
0	917	0.00373	1076.3	6.36649E-11
0.095216	928.59	0.0041349	1132.1	6.0148E-11
0.19145	940.18	0.0045889	1132.6	5.97497E-11
0.288718	951.77	0.0050983	1145.3	5.87263E-11
0.387036	963.36	0.0056708	1159	5.7682E-11
0.486423	974.95	0.0063149	1162.7	5.71557E-11
0.586895	986.54	0.0070404	1183.1	5.58392E-11
0.68847	998.13	0.0078586	1218.1	5.3919E-11
0.791167	1009.72	0.0087825	1300.6	5.02081E-11
0.895004	1021.31	0.0098272	1325.4	4.89883E-11
1	1032.9	0.01101	1350	4.7825E-11

The variation of the above mentioned parameters with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is illustrated in figures 1 to 4 as shown below.

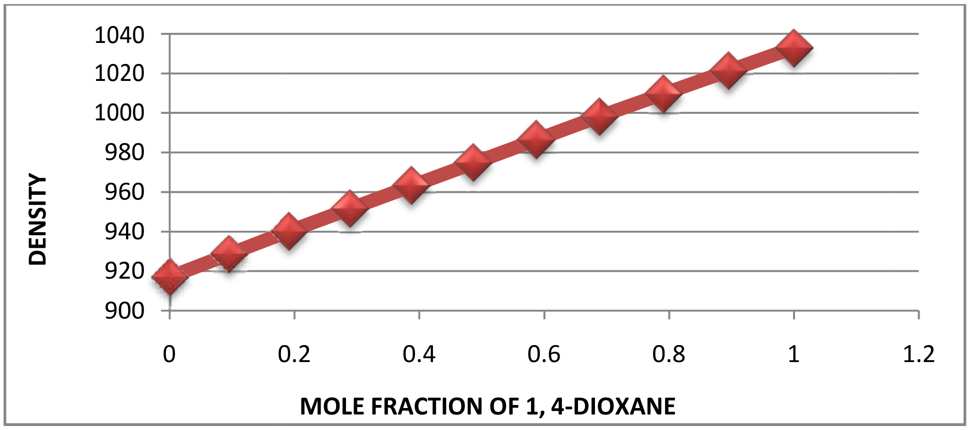

Fig 1 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the density of the binary mixture at constant temperature and fixed ultrasonic frequency

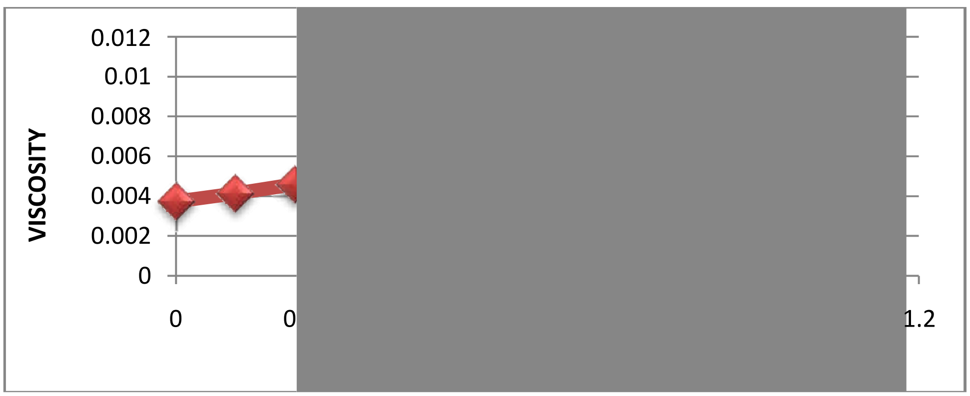

Fig 2 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the viscosity of the binary mixture at constant temperature and fixed ultrasonic frequency

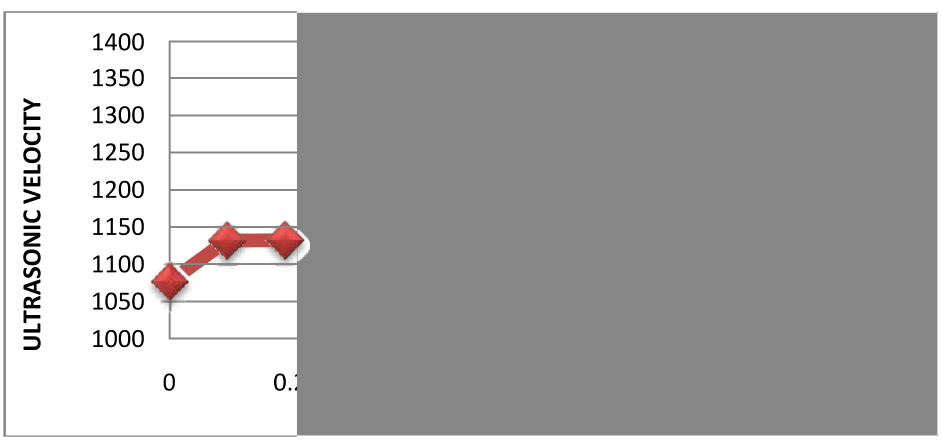

Fig 3 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the ultrasonic velocity of the binary mixture at constant temperature and fixed ultrasonic frequency

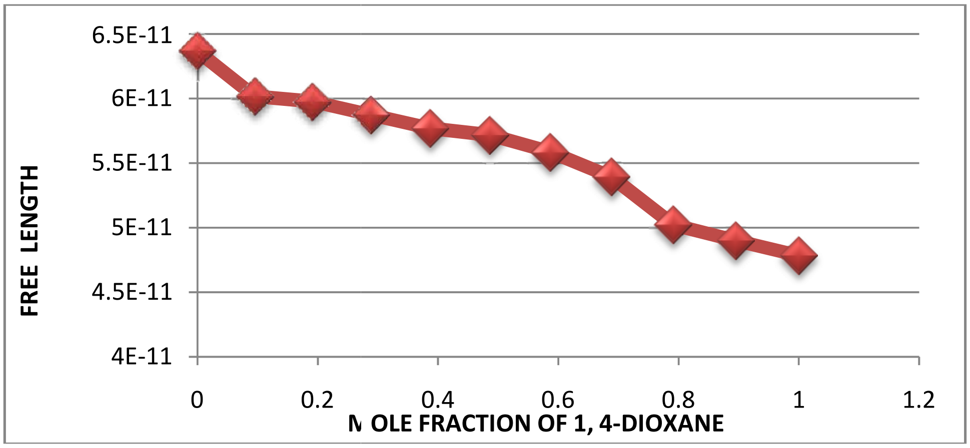

Fig 4 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of density of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is depicted in figure 1. Perusal of figure 1 illustrates that the density is increasing with increase in concentration of 1, 4-Dioxane in Ethyl formate. The density rise is due to shrinkage in volume and increase in cohesive forces in the binary system. It means that there is contraction in volume of the binary system with increase in concentration of 1, 4-Dioxane in Ethyl formate. It indicates strong molecular interaction between the unlike molecules of the system [10].

The variation of viscosity of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is depicted in figure 2. Perusal of figure 2 illustrates that the viscosity is increasing with increase in concentration of 1, 4-Dioxane in Ethyl formate. The increase in viscosity with increase in concentration of 1, 4-Dioxane in Ethyl formate indicates the presence of strong molecular interaction between the constituents of the binary mixture [11].

The variation of ultrasonic velocity of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is depicted in figure 3. Perusal of figure 3 illustrates that the ultrasonic velocity is increasing non-linearly with increase in concentration of 1, 4-Dioxane in Ethyl formate. This non-linear increase in ultrasonic velocity with increase in concentration of 1, 4-Dioxane in Ethyl formate 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 strong 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 [12].

The variation of intermolecular free length of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is depicted in figure 4. Perusal of figure 4 illustrates that the intermolecular free length is decreasing non-linearly with increase in concentration of 1, 4-Dioxane in Ethyl formate. 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 1, 4-Dioxane in Ethyl formate. So this decrease in intermolecular free length with increase in concentration of the solute supports molecular interaction between the constituents of the mixture [13].

Table II:

Mole fraction of 1, 4-Dioxane in Ethyl formate	Vf (m^3/mol)	i (Pa)	Z (Kg /m^2s)	W (J/mol)
T=303°K and Frequency = 1MHZ				
0	1.11613E-08	1206407925	986967.1	0.001573
0.095216	1.05961E-08	1223145672	1051257	0.001607
0.19145	9.31404E-09	1272333269	1064848	0.001619
0.288718	8.30418E-09	1317224619	1090062	0.001636
0.387036	7.39807E-09	1364026353	1116534	0.001653
0.486423	6.49295E-09	1419526303	1133574	0.001667
0.586895	5.81008E-09	1467744122	1167175	0.001687
0.68847	5.28122E-09	1509655014	1215822	0.001713
0.791167	5.05972E-09	1525749240	1313242	0.001758
0.895004	4.51089E-09	1579423874	1353644	0.00178
1	4.01044E-09	1636467558	1394415	0.001803

The evaluated thermo-acoustic parameters free volume, internal pressure, specific acoustic impedance and Wada's constant are illustrated in table II. The variation in these parameters with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is represented in figures 5 to 8 respectively.

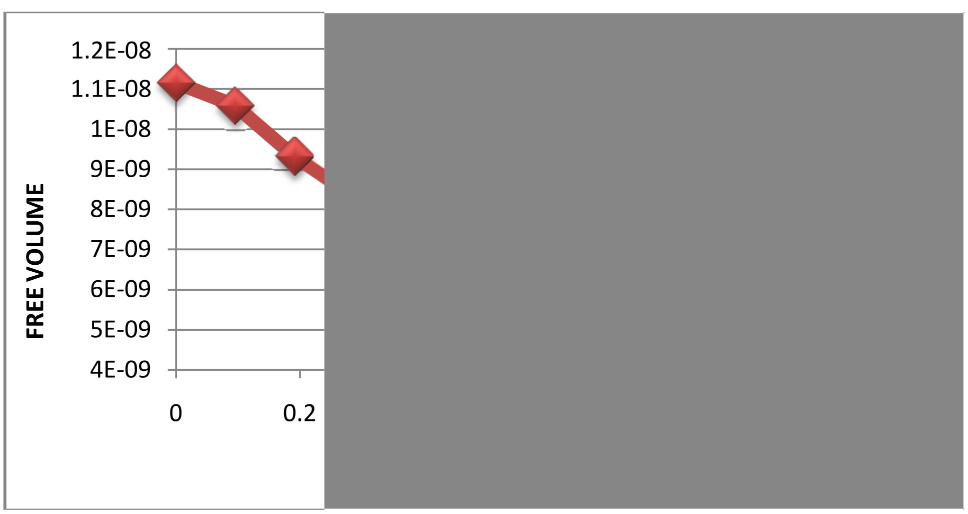

Fig 5 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the free volume of the binary mixture at constant temperature and fixed ultrasonic frequency

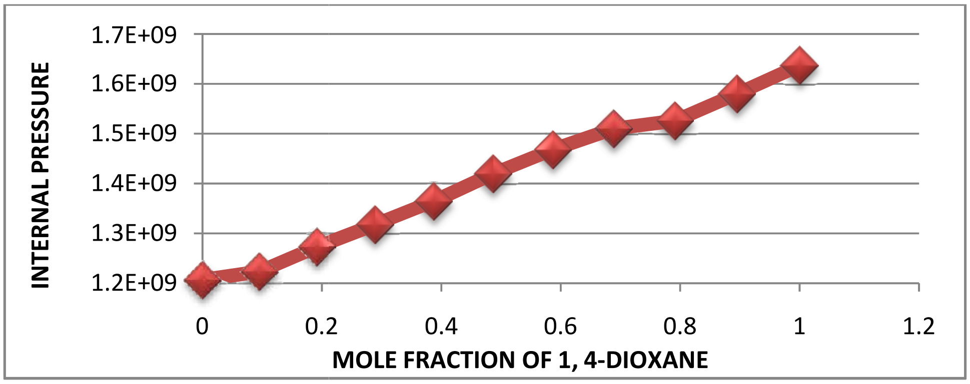

Fig 6 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the internal pressure of the binary mixture at constant temperature and fixed ultrasonic frequency

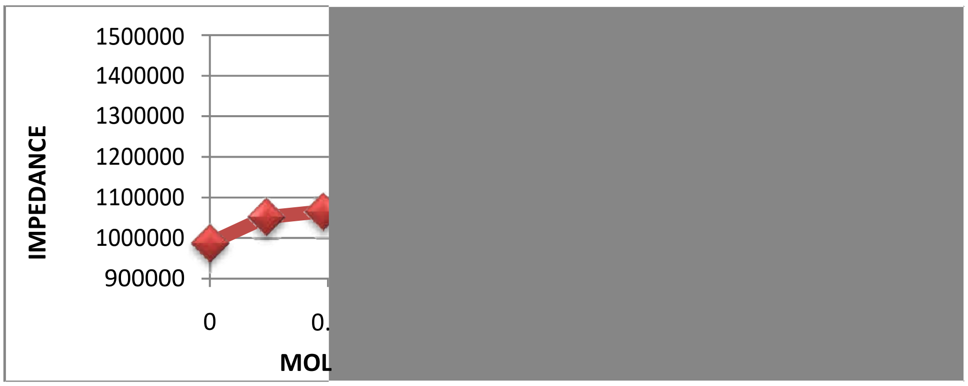

Fig 7 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the specific acoustic impedance of the binary mixture at constant temperature and fixed ultrasonic frequency

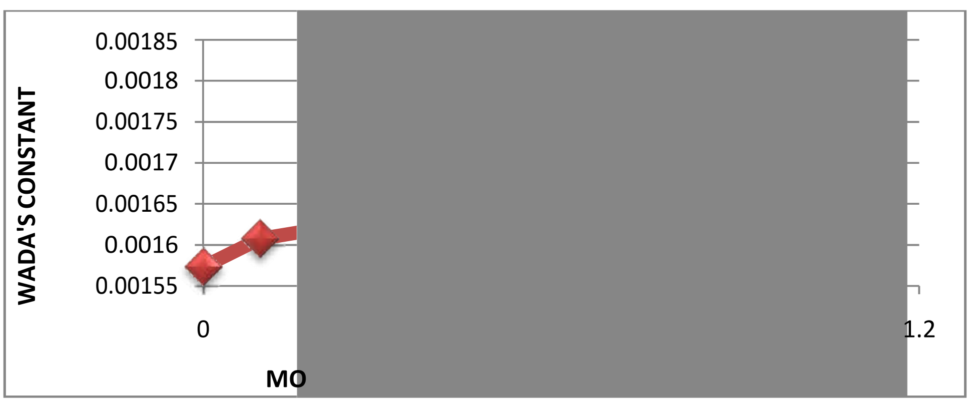

Fig 8 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the Wada's constant of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of intermolecular free volume of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is depicted in figure 5. Perusal of figure 5 illustrates that the intermolecular free volume is decreasing non-linearly with increase in concentration of 1, 4-Dioxane in Ethyl formate. The decrease in free volume with increase in concentration of the solute in the mixture indicates weak interaction between the unlike molecules and the non-linearity suggests significant solute-interaction between the constituents of the binary mixture [14].

The variation of internal pressure of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is depicted in figure 6. Perusal of figure 6 illustrates that the internal pressure is increasing non-linearly with increase in concentration of 1, 4-Dioxane in Ethyl formate. This behavior of the internal pressure may be attributed to possibility of strong interaction due to dipole-dipole or H-bonding or complex formation. This suggests strong molecular interaction with increase in concentration of 1, 4-Dioxane in Ethyl formate between the unlike constituents of the binary mixture [15].

The variation of specific acoustic impedance of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is shown in figure 7. Perusal of figure 7 indicates that the specific acoustic impedance is increasing non-linearly with increase in concentration of 1, 4-Dioxane in Ethyl formate. The acoustic impedance increases with increase in concentration of 1, 4-Dioxane in Ethyl formate. It represents that there is strong interaction between the 1, 4-Dioxane and Ethyl formate system. This type of interaction is of associative type producing contraction in the volume of the mixture [16].

The variation of Wada's constant of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is shown in figure 8. Perusal of figure 8 indicates that the Wada's constant is increasing non-linearly with increase in concentration of 1, 4-Dioxane in Ethyl formate. As the Wada's constant is increasing with increase in concentration of 1, 4-Dioxane in Ethyl formate it indicates solute-solvent interaction in the binary mixture. Therefore, there is existence of strong intermolecular interaction between the constituents of the mixture. It is increasing with increase of concentration of 1, 4-Dioxane in Ethyl formate [17].

Table III.

Mole fraction of 1, 4-Dioxane in Ethyl formate	L_f^E m	V_f^E (m³/mol)	π_I^E (Pa)	Z^E (Kg /m²s)
T=303°K and Frequency = 1MHZ				
0	0	0	75733.09169	0
0.095216	-2.00868E-12	1.15702E-10	-24132616.3	25494.03
0.19145	-8.82619E-13	-4.7821E-10	-16328733.84	-125.084
0.288718	-3.65325E-13	-7.9252E-10	-13265768.85	-14542.3
0.387036	1.4771E-13	-9.9557E-10	-8744296.296	-28130
0.486423	1.19564E-12	-1.19E-09	4016153.705	-51584.7
0.586895	1.47065E-12	-1.1544E-09	9027710.079	-58920.6
0.68847	1.15935E-12	-9.5692E-10	7257889.029	-51660.6
0.791167	-9.24809E-13	-4.4405E-10	-20810905.25	3915.539
0.895004	-4.99856E-13	-2.5036E-10	-11789633.83	2009.812
1	0	0	102135.4282	0

The excess thermo-acoustic parameters excess intermolecular free length, excess intermolecular free volume, excess internal pressure and excess specific acoustic impedance are depicted in table III. The variation of these parameters with rise of mole fraction is shown in figures 9 to 12 respectively.

Fig 9 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the excess intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

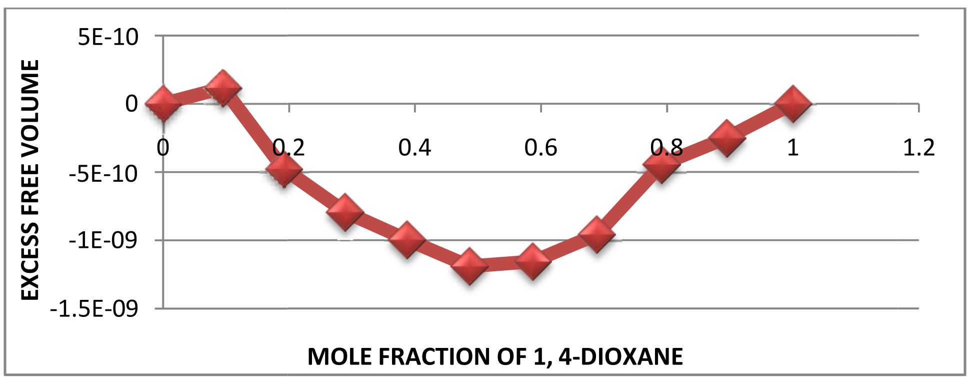

Fig 10 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the excess intermolecular free volume of the binary mixture at constant temperature and fixed ultrasonic frequency

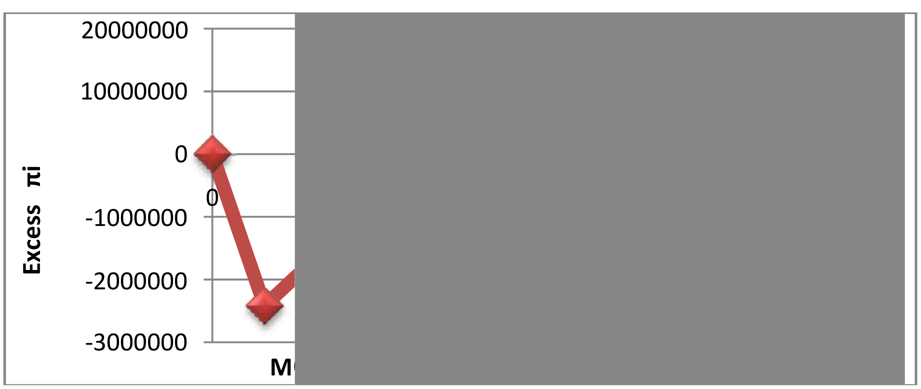

Fig 11 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the excess internal pressure of the binary mixture at constant temperature and fixed ultrasonic frequency

Fig 12 Graph between mole fraction of 1, 4-Dioxane in Ethyl formate and the excess specific acoustic impedance 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 1, 4-Dioxane in Ethyl formate is shown in figure 9. Perusal of figure 9 indicates that the Wada's constant is non-linearly positive and negative deviations with increase in concentration of 1, 4-Dioxane in Ethyl formate. 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 [18].

The variation of excess intermolecular free volume of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is illustrated in figure 10. Perusal of figure 10 indicates that the excess intermolecular free volume is non-linearly positive and negative deviations with increase in concentration of 1, 4-Dioxane in Ethyl formate. For most of the portion excess free volume is negative. Positive deviation corresponds to weak interaction which seen just at beginning. For the entire remaining portion it shows negative deviation which supports strong interaction between the constituents of the binary mixture [19].

The variation of excess internal pressure of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is illustrated in figure 11. Perusal of figure 11 indicates that the excess internal pressure is non-linearly positive and negative deviations with increase in concentration of 1, 4-Dioxane in Ethyl formate. It is negative a small portion for which it indicates weak interaction. For most of the portion it is positive which signifies strong molecular interaction due any of the cohesive forces [20].

The variation of excess specific acoustic impedance of the binary mixture with rise in mole fraction of 1, 4-Dioxane in Ethyl formate is illustrated in figure 12. Perusal of figure 12 indicates that the excess specific acoustic impedance is non-linearly positive and negative deviations with increase in concentration of 1, 4-Dioxane in Ethyl formate. 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 [21].

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CONCLUSION:

In the present investigation, we have studied various thermo-acoustic parameters of 1, 4-Dioxane in Ethyl formate. Density, Viscosity show linear increase with concentration of 1, 4-Dioxane in Ethyl formate. Ultrasonic velocity show non-linear increase and intermolecular free length nonlinear decrease with increase in concentration of 1, 4-Dioxane in Ethyl formate. Free volume shows non-linear decrease with increase in concentration of 1, 4-Dioxane in Ethyl formate. Internal pressure, specific acoustic impedance and Wada's constant show non-linear increase with increase of concentration of 1, 4-Dioxane in Ethyl formate, the binary mixture. The excess parameters excess intermolecular free length, excess free volume , excess internal pressure and excess specific acoustic impedance shoe non-linear positive and negative deviations. Positive deviations are for more portions and negative deviations are for small portions of the graphs as explained above. This investigation supports strong molecular interaction and so contraction in the volume of the mixture with increase of 1, 4-Dioxane in Ethyl formate. Thus, it can be concluded that there exist strong molecular interaction between the constituents of 1, 4-Dioxane in Ethyl formate binary mixture.

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