Ultrasonic Study of the Binary Liquid Mixture Containing Benzene and Ammonia

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ABSTRACT:

Density (ρ), viscosity (η) and Ultrasonic velocity (U) of the binary mixture of Benzene and Ammonia were measured over entire composition range. These measurements were done at constant temperature 301 K and at a frequency 1MHZ. These were used to evaluate various acoustic parameters such as Vanderwaal's constant (b), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), internal pressure (π_i), Rao constant (R), relative association (R_A) and Wada's constant (W). These parameters have been interpreted in terms of intermolecular interactions at frequency 1MHZ and at constant temperature 301K.

KEY WORDS: Benzene, Rao constant, 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 Benzene and ammonia. Benzene is an organic compound. Its molecular formula is C_6H_6. Benzene is classified as a hydrocarbon. It is natural constituent of petroleum. It is one of the important petrochemicals. It has cyclic continuous Pi bonds between the carbon atoms. Benzene is also classified as an aromatic hydrocarbon. It is colorless or slightly yellow colored liquid. It is highly flammable liquid. It has sweet smell. It is responsible for aroma of gasoline. It is primarily used as precursor for manufacturing of complex chemicals. It finds very limited applications in consumer items. It is toxic in nature. Benzene is non-polar. Benzene is symmetric and planar having ring-like structure. Therefore, it has equal number of opposite dipoles which cancel out each other. Its polarity index is 2.2825. Its dielectric constant is 2.28.

Liquid ammonia possesses strong ionizing powers reflecting its high electric permittivity of 22. Liquid ammonia has a very high standard enthalpy change of vaporization and therefore can be used in laboratories in uninsulted vessels without additional refrigeration. Ammonia readily dissolves in water. In an aqueous solution, it can be expelled by boiling. The aqueous solution of ammonia is basic. The maximum concentration of ammonia in water has density about880kg/m^3 and is often known as 880ammonia. It is compound of nitrogen and hydrogen with formula NH3. It is a stable binary hydride and the simplest pnictogen hydride. It is colorless with distinct pungent smell. It is also used for synthesis of many pharmaceutical products and also used in many commercial cleaning products. The global industrial production of ammonia in 2018 was 175 million tones.

In the present work, density, viscosity and ultrasonic velocity of Benzene and ammonia binary mixture have been measured and used to compute the acoustic parameters such as Vanderwaal's constant (b), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), internal pressure (π_i), Rao constant (R), relative association (R_A) and Wada's constant (W). 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; Benzene is obtained from Avantor Performance Materials limited Thane, Maharashtra. It is 99.5% pure chemical. Ammonia 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) [3]. 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 [4]. 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 [5] 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 Vanderwaal's constant (b), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), internal pressure (π_i), Rao constant (R), relative association (R_A) and Wada's constant (W) were computed. The computation was done using the following equations.

THEORATICAL BACKGROUND:

For the measurement of ultrasonic absorption by interferometer skill, the experimental liquid or liquid mixture is kept in the cell of the ultrasonic interferometer. Then the distance between the bottom of the liquid cell 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 corresponding to antinodes and nodes respectively. The distance between consecutive alternate maxima and minima corresponds to half wavelength of the ultrasonic wave in the liquid mixture. The ultrasonic velocity is found using the average values of minima and maxima. The standard equations employed 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.

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

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 or ternary liquid mixture.

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

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

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

3. 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.

$$W = \frac{M}{\rho}\frac{1}{\beta^{1/7}} \quad \text{J/mol} \qquad (3)$$

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.

$$\pi i = bRT\left(\frac{K\eta}{U}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad \text{Pa} \qquad (4)$$

Where b=2, R= 8.314 J/mol°K, K is a constant equal to 4.28×10^{9}

5. 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.

$$\beta_{ad} = \frac{1}{u^2\rho} \ m^2/N \qquad (5)$$

u ultrasonic velocity and ρ is density of liquid in SI

6. VANDERWAAL'S CONSTANT: It is required in the study of acoustical properties of pure liquids & liquid mixtures. The Vanderwaal's constant is equal to four times the actual volume of the molecules per mole of the liquid. Vanderwaal's constant also called co-volume in the Vanderwaal's equation is given by the relation

$$b = V_m[(1-(R_gT/M_{eff}\ U^2))(1+(M_{eff}\ U^2/\ R_gT)^{1/2})] \qquad m^2/mole \qquad (6)$$

7. RAO CONSTANT OR MOLAR VELOCITY: It is required in the study of acoustical properties of pure liquids & liquid mixtures. Variation in the values of Rao's constant with molar composition is an evidence of significant interaction between the components of binary or ternary system.

$$R = V_m \quad U^{1/3} \qquad m^3/mole \qquad (7)$$

8. 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.

$$R_A = \frac{ds}{do}\left[\frac{Uo}{Us}\right]^{1/3} \qquad (8)$$

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

9. REFRACTIVE INDEX: In optics, the refractive index (or refraction index) of an optical medium is a dimensionless number that gives the indication of the light bending ability of that medium. The refractive index can be seen as the factor by which the speed and the wavelength of the radiation are reduced with respect to their vacuum values: the speed of light in a medium is $V = C / n$

Where C is the velocity of light in vacuum and n is the refractive index of the transparent medium under consideration. Thus the refractive index is given by the formula

$$n = \frac{C}{v} \qquad (9)$$

RESULTS AND DISCUSSION:

The experimentally measured values of density (ρ), Viscosity (η) and ultrasonic velocity are used to compute values of various thermo-acoustic parameters of the binary mixture with respect to concentrations of benzene in ammonia. Evaluation of all these parameters is done at constant temperature 301°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 of benzene in ammonia. The discussion of the results obtained from these parameters is made below.

Table I: The acoustic parameters density, viscosity, refractive index and intermolecular free length are shown in table I. The variation of the above mentioned parameters with rise in mole fraction of benzene in ammonia is illustrated in figures 1 to 4 respectively.

Mole fraction of Benzene in Ammonia	ρ (Kg/m^3)	η (poise)	Refractive index	L_f (m)
T=301°K and Frequency = 1MHZ				
0	769	1.00781E-05	1.3327	4.30959E-11
0.026944	780	1.12517E-05	1.337073	4.38038E-11
0.05865	791	1.28089E-05	1.342219	4.45526E-11
0.0965	802	1.49525E-05	1.348362	4.53453E-11
0.142472	813	1.80442E-05	1.355823	4.58927E-11
0.199497	824	2.27816E-05	1.365078	4.63182E-11
0.272104	835	3.06547E-05	1.376862	4.67639E-11
0.367689	846	4.53116E-05	1.392376	4.73565E-11
0.499214	857	7.75765E-05	1.413722	4.85058E-11
0.691637	868	0.000170364	1.444953	4.93152E-11
1	879	0.000601	1.495	5.36423E-11

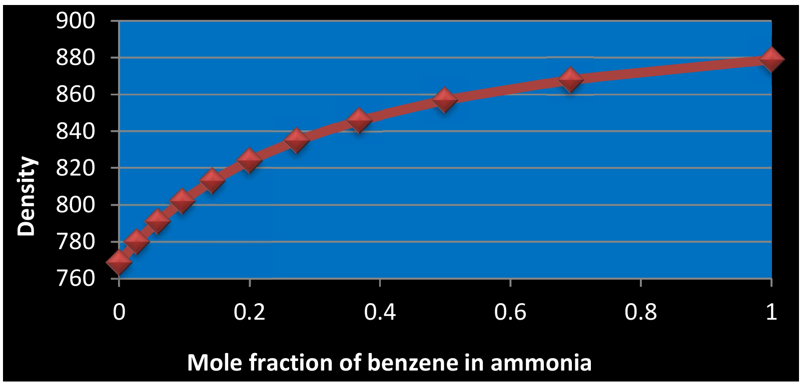

Fig 1 Graph between mole fraction of Benzene in Ammonia and the density of the binary mixture at constant temperature and fixed ultrasonic frequency

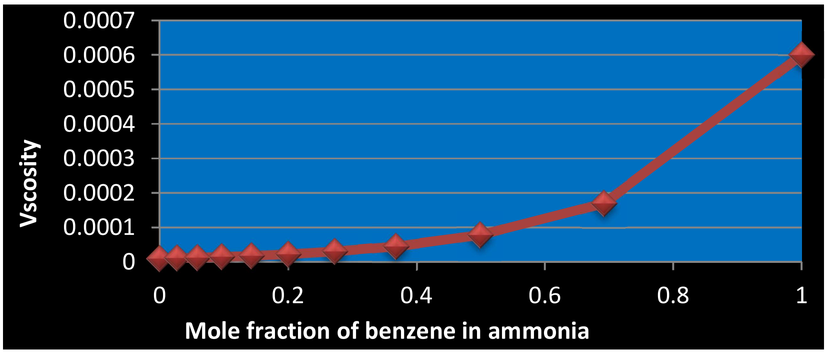

Fig 2 Graph between mole fraction of Benzene in Ammonia and the viscosity of the binary mixture at constant temperature and fixed ultrasonic frequency

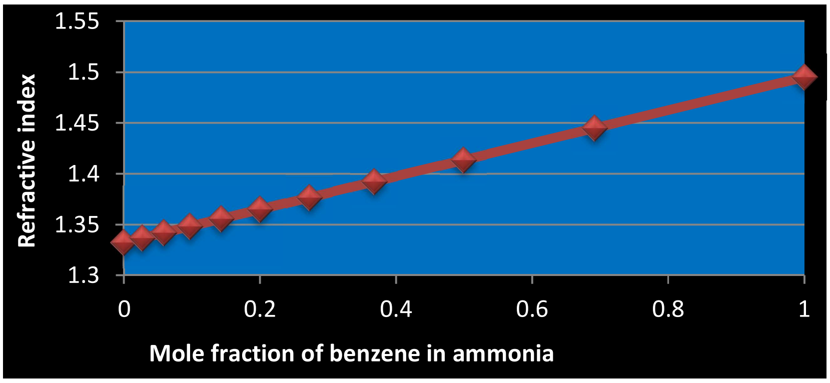

Fig 3 Graph between mole fraction of Benzene in Ammonia and refractive index of the binary mixture at constant temperature and fixed ultrasonic frequency

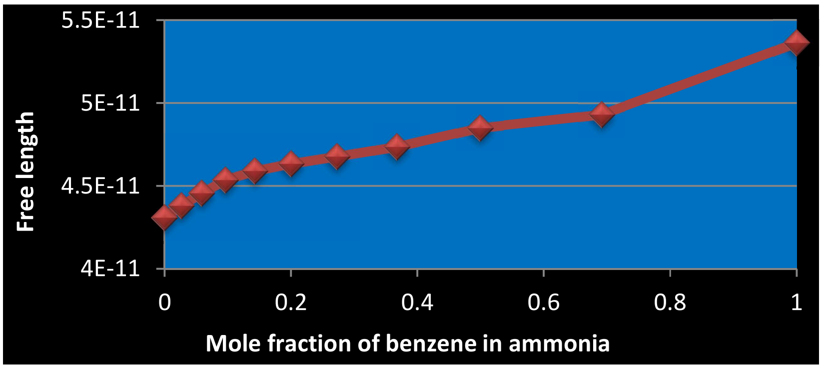

Fig 4 Graph between mole fraction of Benzene in Ammonia and the intermolecular free length of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation of density of the binary mixture with rise in mole fraction of benzene in ammonia is depicted in figure 1. Perusal of figure 1 illustrates that the density is increasing with increase in concentration of benzene in ammonia. 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 benzene in ammonia. It indicates strong molecular interaction between the unlike molecules of the system [6].

The variation of viscosity of the binary mixture with rise in mole fraction of benzene in ammonia is depicted in figure 2. Perusal of figure 2 illustrates that the viscosity is increasing with increase in concentration of benzene in ammonia. The increase in viscosity with increase in concentration of benzene in ammonia indicates the presence of strong molecular interaction between the constituents of the binary mixture [7].

The variation in refractive index with rise of mole fraction of benzene in ammonia is depicted in figure 3. Observation of figure 3 illustrates that the refractive index is increasing linearly with increase concentration of benzene in ammonia. 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 benzene in ammonia, it means that the thickness of binary mixture is increasing due to contraction in the volume of the mixture [8]. 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.

The variation of intermolecular free length of the binary mixture with rise in mole fraction of benzene in ammonia is depicted in figure 4. Perusal of figure 4 illustrates that the intermolecular free length is increasing non-linearly with increase in concentration of benzene in ammonia. 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 is not true here with the concentration of benzene in ammonia. So there may significant intermolecular interaction due to non-linear behavior of free length with increase in concentration of the solute [9]. This may support weak interaction between the constituents of the system.

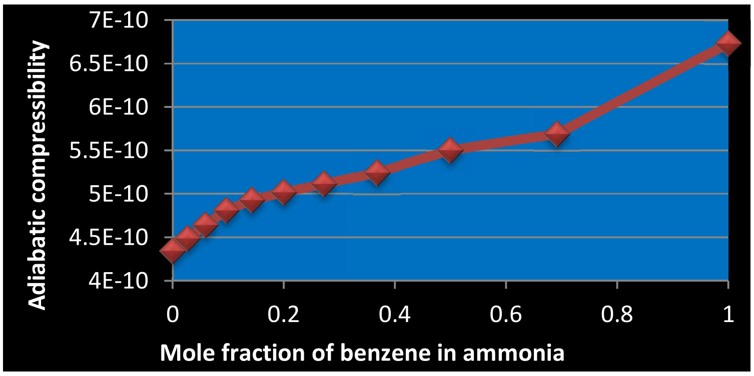

Fig 5 Graph between mole fraction of Benzene in Ammonia and adiabatic compressibility of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in adiabatic compressibility with rise of mole fraction of Benzene in Ammonia is shown in figure 5. Examination of figure 5 indicates that the adiabatic compressibility is increasing non-linearly with increase in concentration of Benzene in Ammonia. The nature of adiabatic compressibility is exactly identical to that of intermolecular free length. The structural change of molecules in a liquid mixture takes place due to the existence of electrostatic field between the interacting molecules. The structural arrangement of the molecules affects the value of adiabatic compressibility. It is measure of intermolecular association or dissociation or repulsion. If adiabatic compressibility of a binary mixture increases with increase of concentration of the solute, the structural order of the solvent may result in more dissociation between the unlike constituents of the binary mixture [10]. This is true in this case.

Table II: The evaluated thermo-acoustic parameters adiabatic compressibility, internal pressure and Vanderwaal's constant are illustrated in table II. The variation in these parameters with rise in mole fraction of benzene in ammonia is represented in figures 5 to 7 respectively.

Mole fraction of Benzene in Ammonia	βad Pa^{-1}	πi (Pa)	Vanderwaal's constant b
T=301°K and Frequency = 1MHZ			
0	4.34492E-10	242827970	7.5932E-05
0.026944	4.48882E-10	231810695	8.519E-05
0.05865	4.64361E-10	221958364	9.635E-05
0.0965	4.81032E-10	213456824	0.00011005
0.142472	4.92714E-10	205971229	0.0001279
0.199497	5.01894E-10	200393315	0.00015136
0.272104	5.116E-10	198024481	0.00018271
0.367689	5.24648E-10	201036392	0.00022588
0.499214	5.50423E-10	214565602	0.00028666
0.691637	5.68945E-10	247888516	0.00038524
1	6.73169E-10	352222615	0.00052882

. The variation of internal pressure of the binary mixture with rise in mole fraction of benzene in ammonia is depicted in figure 6. Perusal of figure 6 illustrates that the internal pressure is increasing non-linearly with increase in concentration of benzene in ammonia. 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 benzene in ammonia that is between the unlike constituents of the binary mixture [11].

The variation in Vanderwaal's constant with rise of mole fraction of benzene in ammonia is shown in figure 7. Examination of figure 7 reveals that the Vanderwaal's constant is increasing linearly with increase concentration of benzene in ammonia. This is linear increase of Vanderwaal's constant b with rise of mole fraction of benzene in ammonia. b is

Vanderwaal's constant and is equal to four times the actual volume of the molecules per mol of the liquid. Vander Waals' constant (b), called the co-volume in the Vander Waals' equation. Increase in concentration of solute in the binary mixture increases the Vanderwaal's constant. This indicates that molecular interaction exist [12] between the unlike molecules of the binary mixture.

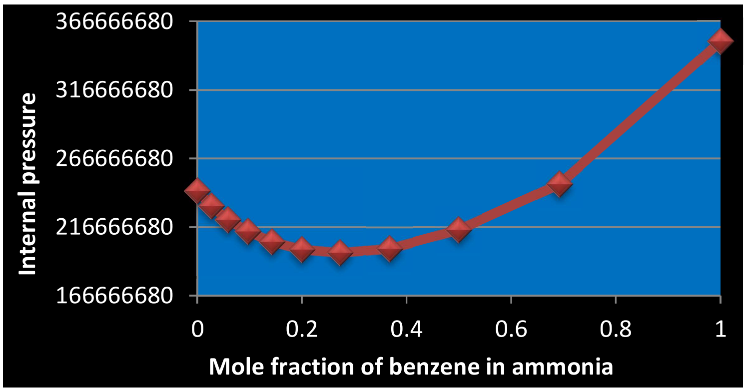

Fig 6 Graph between mole fraction of Benzene in Ammonia and the internal pressure of the binary mixture at constant temperature and fixed ultrasonic frequency

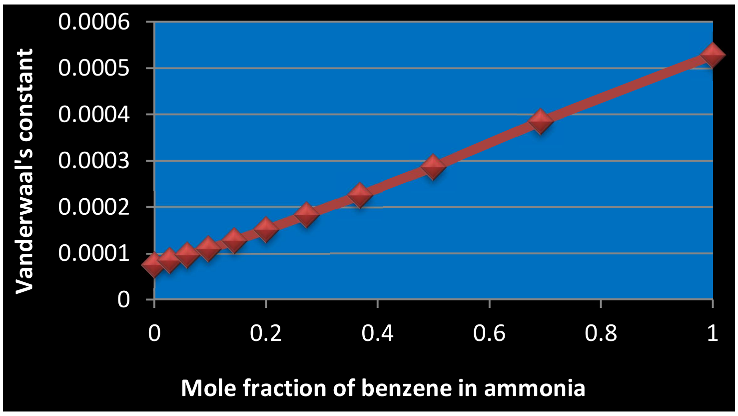

Fig 7 Graph between mole fraction of Benzene in Ammonia and the Vanderwaal's constant of the binary mixture at constant temperature and fixed ultrasonic frequency

The variation in Rao's constant with rise of mole fraction of Benzene in Ammonia is depicted in figure 8. Observation of figure 8 indicates that the Rao's constant is increasing linearly with increase concentration of Benzene in Ammonia. The nature of the graph for Rao's constant is similar to that of Vanderwaal's constant. It is also known as molar velocity. It is important factor in deciding the molecular association in liquid mixture. If R increases with increase in concentration of the solute [13], it indicates solute-solvent interaction occurs in the liquid mixture. Increase/decrease of molar velocity with the concentration of solute is an evidence of significant interaction between the constituents of the binary liquid mixture.

Table III. The thermo-acoustic parameters Rao constant, relative association and Wad's constant 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 Benzene in Ammonia	Rao constant R M^3/mol	Relative association RA	Wada's constant W J/mol
T=301°K and Frequency = 1MHZ			
0	0.000266	1	0.000482
0.026944	0.000289	1.022244	0.000525
0.05865	0.000316	1.044971	0.000576
0.0965	0.000348	1.068205	0.000636
0.142472	0.000387	1.089667	0.00071
0.199497	0.000436	1.110297	0.000802
0.272104	0.000498	1.131214	0.000919
0.367689	0.000579	1.15345	0.001071
0.499214	0.000688	1.180364	0.001276
0.691637	0.000849	1.204685	0.001579
1	0.001082	1.257273	0.002025

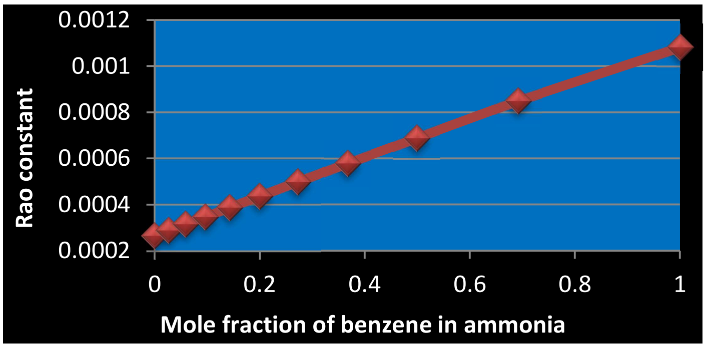

Fig 8 Graph between mole fraction of Benzene in Ammonia and the Rao constant of the binary mixture at constant temperature and fixed ultrasonic frequency

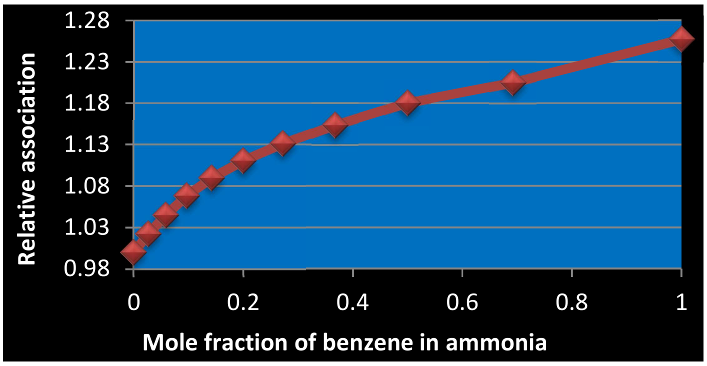

Fig 9 Graph between mole fraction of Benzene in Ammonia and the relative association of the binary mixture at constant temperature and fixed ultrasonic frequency

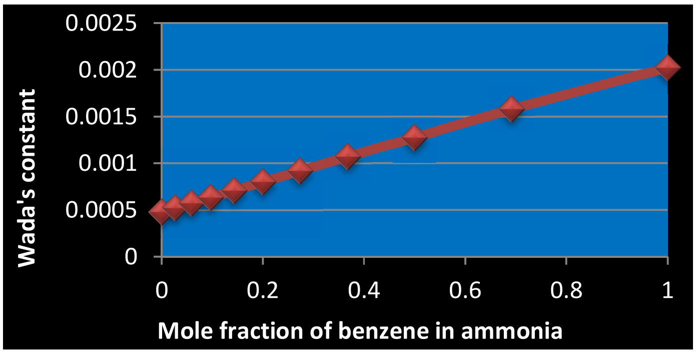

Fig 10 Graph between mole fraction of Benzene in Ammonia and the Wada's constant of the binary mixture at constant temperature and fixed ultrasonic frequency

The nature of variations in relative association with increase in concentration of Benzene in Ammonia is illustrated in figure 9. Observation of figure 9 reveals that the relative association in the binary mixture is increasing non-linearly with increase in concentration of Benzene in Ammonia. The decreasing nature of relative association [14] 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 9.

The variation of Wada's constant of the binary mixture with rise in mole fraction of Benzene in Ammonia is shown in figure 10. Perusal of figure 10 indicates that the Wada's constant is increasing linearly with increase in concentration of Benzene in Ammonia. As the Wada's constant is increasing with increase in concentration of Benzene in Ammonia, 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 Benzene in Ammonia [15].

CONCLUSION:

In the present investigation, we have studied various thermo-acoustic parameters of Benzene in Ammonia. Density, Viscosity show non-linear increase with concentration of Benzene in Ammonia. Refractive index shows linear increase and intermolecular free length shows non-linear rise with increase in concentration of Benzene in Ammonia. Adiabatic compressibility and internal pressure show non-linear increase with increase in concentration Benzene in Ammonia. Vanderwaal's constant and Rao's constant both show linear with increase of concentration of Benzene in Ammonia, the binary mixture. The relative association shows non-linear increase and Wada's constant shows linear increase with increase of concentration of Benzene in Ammonia. This investigation supports significant and strong molecular interaction and so contraction in the volume of the mixture with increase of with increase of concentration of Benzene in Ammonia. Few parameters supports change in structure of the mixture due to weak forces of interaction. Thus, it can be concluded that there exist molecular interaction between the constituents of with increase of concentration of Benzene in Ammonia, in this binary mixture.

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