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Thermodynamic Characterization of Dimethyl Formamide and Ethylamine by Using Ultrasonic Techniques at Different Temperatures

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ABSTRACT

Ultrasonic technique provides the interaction of high frequency sound wave with matter resulting to generation of information about physico-chemical properties. Many researchers have been studies the application of ultrasonic waves in different areas like medicines, oceanography, aerospace, navy and material science. Nowadays Ultrasonic became a multidimensional area of study due to its different industrial and medical field. In present research paper, the Ultrasonic velocity (U), density (ρ) and viscosity (η) of binary liquid mixtures of Dimethylformamide (DMF) and Ethylamine (EA) have been measured using Ultrasonic Interferometer at frequency 7MHz and at different temperature (298K-308K). From the measured data of ultrasonic velocity, density and viscosity at different temperatures the acoustical parameters such as adiabatic compressibility(β_a), Free Length(L_f), Acoustical Impedance(Z), Internal Pressure(π_i), Relaxation time(τ), Free Volume(V_f), Molar Volume(Vm), Rao's Constant(R), Wada's Constant (W), Vander Waal's Constant(b), Gibb's Free Energy(ΔG), Classical Absorption(α/f^2), Isothermal Compressibility(β_i), Enthalpy(H) and Internal Latent heat of Vaporization (ΔH_i) of binary liquid mixture dimethylformamide in ethylamine at temperature range 298K-308K and frequency at 7MHz are with mole fraction and some probable reasons on the increase or decrease of acoustic and thermodynamic parameters with temperature change are also have been studied.

Keywords : Ultrasonic Velocity, Physico- Chemical, Thermodynamic, Hydrogen Bonding

I. INTRODUCTION

Recent development in science and technology for non–destructive technique are spectacular and holds significant possibilities for better new applications in molecular structure, molecular interactions, medicines and underwater acoustics. Development of sensors, electronic instrumentation and computer software added sophistication to the experimental and theoretical agreement of different ultrasonic parameters[1-3]. In many technological processes (e.g., in the chemical, petrochemical, food, and plastics industries) liquids are subjected to high pressures and temperatures. Therefore, knowledge of their thermodynamic properties is essential for understanding, design, and control of the process technology. Direct evaluation of the thermodynamic parameters of liquids under high pressure, using conventional methods, is very difficult. Therefore, the application of these methods in industrial conditions, particularly in on-line control of the technological parameters of liquids, is practically impossible[4-8].

The measurement of ultrasonic speed enables us to the accurate measurement of some useful acoustic and thermodynamic parameters and their excess values[9-14]. The study of molecular association in binary liquid mixture having DMF as one of component is of particular interest since DMF is used in the production of acrylic fibers and plastics and also used as a solvent in peptide coupling for pharmaceuticals, in the development and production of pesticides, and in the manufacture of adhesives, synthetic leathers, fibers, films, and surface coatings. The pharmaceutical industry uses DMF as a reaction and crystallization solvent because of its exceptional solvency parameters. Ethylamine is a two-carbon primary aliphatic amine. It has a role as a human metabolite. In order to have clear understanding of intermolecular interaction between component molecules of an attempt has been made to study the ultrasonic behaviors of DMF in EA at different temperature. Thermo-acoustic parameters are the essential sources of information for better understanding of non-ideal behavior of complex binary liquid system[15-18].

II. METHODS AND MATERIAL

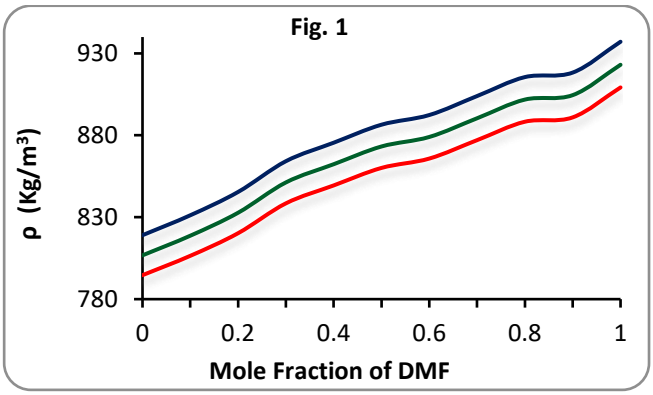
The liquid DMF and Ethylamine were of Analar grade samples and purified before use. The binary mixture of different mole fraction of the two components in the Systems DMF with ethylamine was prepared immediately before use. The velocity of ultrasonic wave (U) of frequency 7 MHz and density (ρ) in these mixtures were measured by using a Multifrequency(1-10MHz) ultrasonic pulse interferometer (Model No. F-83, Mittal Enterprises, New Delhi). It consists of a high Multirange frequency generator (1 to 10MHz) and a measuring cell. The measurements of ultrasonic velocities were made at a fixed frequency of 7 MHz and temperature was controlled by circulating water around the liquid cell from thermostatically controlled constant temperature water bath. . The densities of pure liquids and liquid mixtures were measured by using a specific gravity bottle with an accuracy of ± 0.5%. An Ostwald's viscometer was used for the viscosity (η) measurement of pure liquids and liquid mixtures with an accuracy of 0.0001Nm-2s. The viscometer was calibrated before used. All the precautions were taken to minimize the possible experimental error.

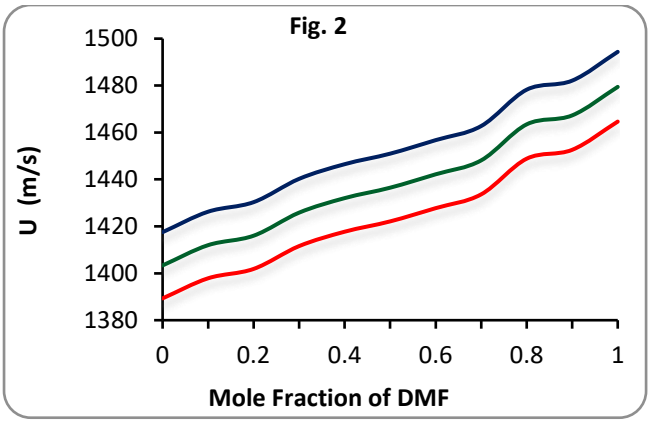
III. RESULTS AND DISCUSSION

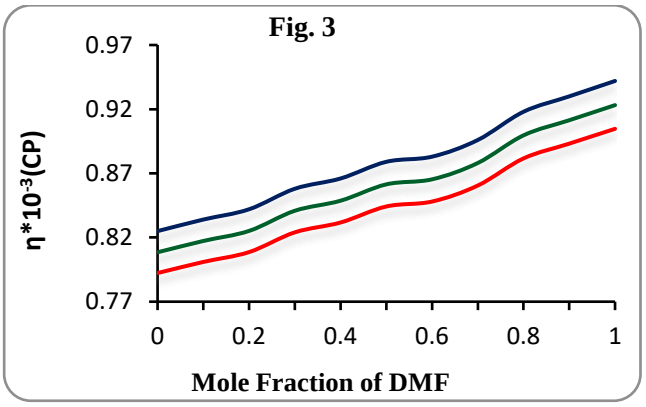
Density(ρ), ultrasonic velocity(U), Viscosity(η) and thermodynamic parameters like adiabatic compressibility(βa), Free Length(Lf),Acoustical Impedance(Z), Internal Pressure(πi), Relaxation time (τ), Free Volume(Vf), Molar Volume(Vm), Rao's Constant(R), Wada's Constant (W), Vander Waal's Constant (b), Gibb's Free Energy(ΔG), Classical Absorption (α/f2), Isothermal Compressibility (βi), Enthalpy (H) and Internal Latent heat of Vaporization (ΔHi) of binary liquid mixture dimethylformamide in ethylamine at temperature range 298K-308K and frequency at 7MHz are shown in fig. 1 to 18 respectively.

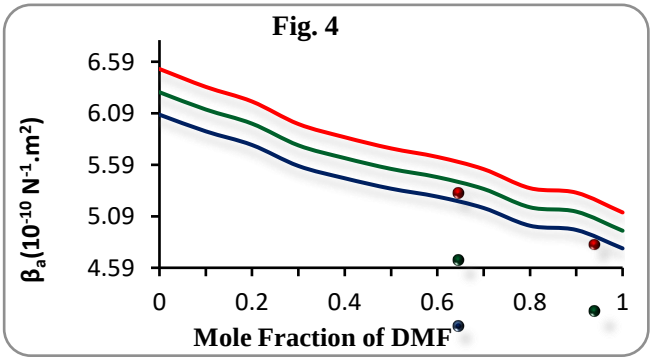
In this system the molecules of dimethylformamide and ethylamine are polar with dipole moment 3.86D and 4.3D respectively. When discussing solvent effect, it is important to distinguish between the macroscopic effects of the solvents and effects that depend upon the details of the structures. Macroscopic properties refer to properties of the bulk solvent. An important example is the dielectric constant, which is a measure of the availability of the bulk material to increase the capacitance of the condenser. In terms of the structures, dielectric constant is a function of both permanent dipole moments of the molecules and its polarizibiity refers to the distortion of molecules electron density. Dielectric constant increase with both dipole moment and polarizibiity. An important property of solvent molecules with regard to reaction is the response of the solvent to change in charge distribution as the reaction occurs. The dielectric constant is a good indicator of the ability of the solvent to accommodate separation of charges.

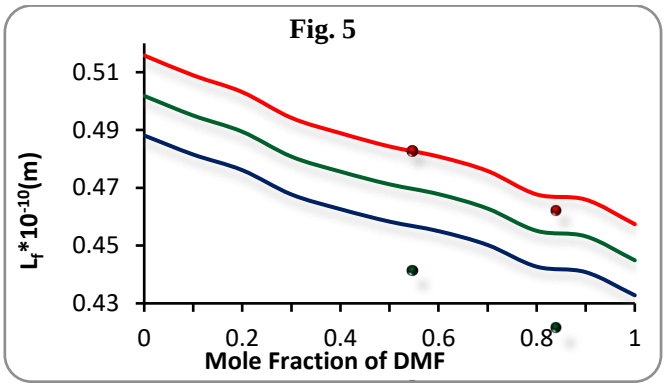
298K 303K 308K

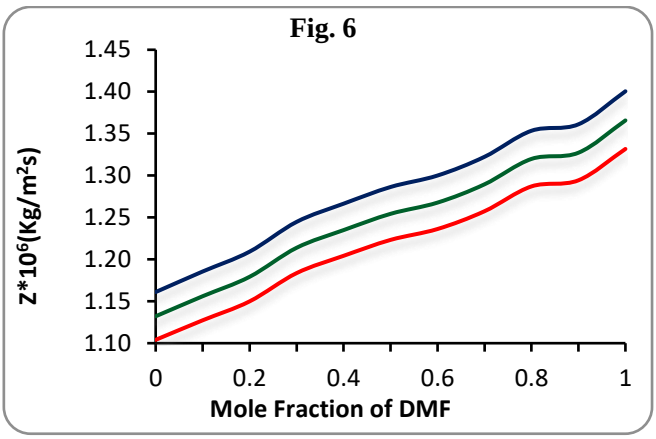


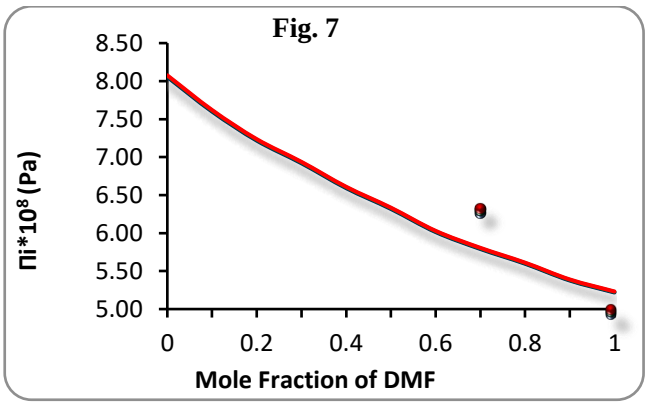












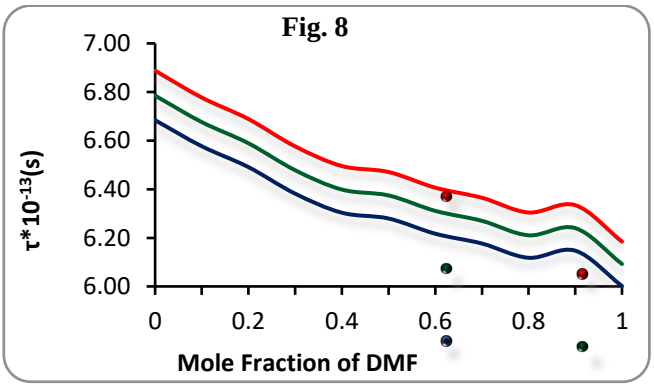
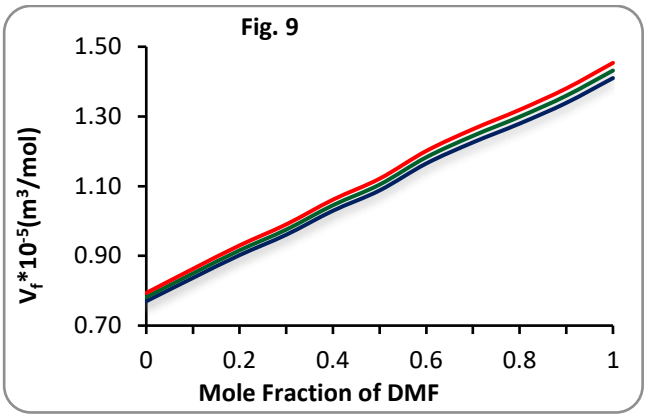


Fig. 9



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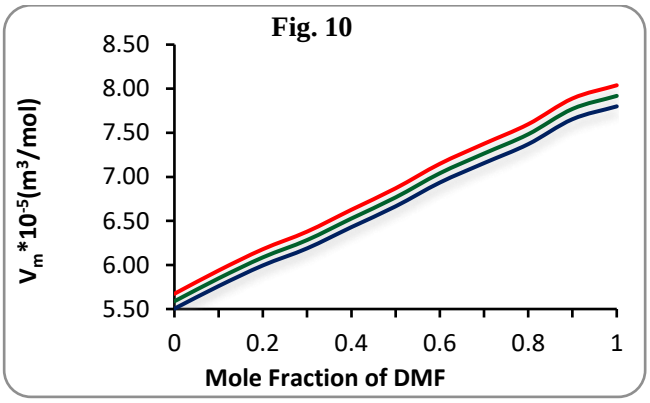

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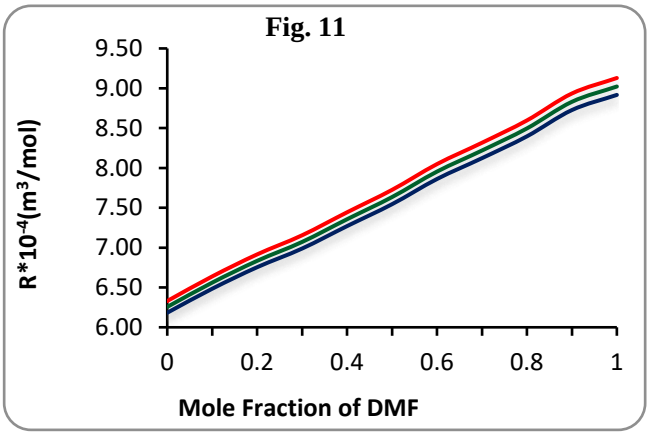

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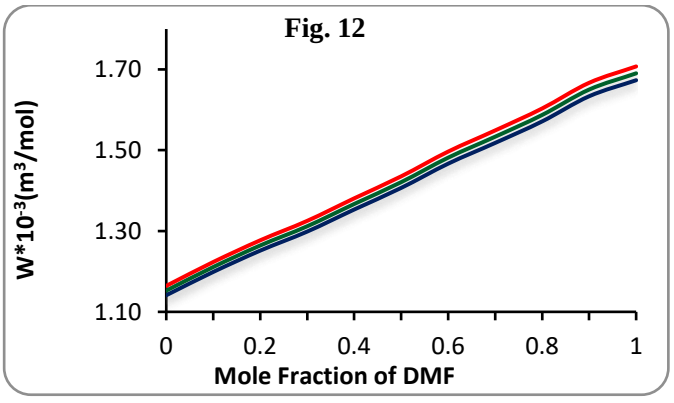

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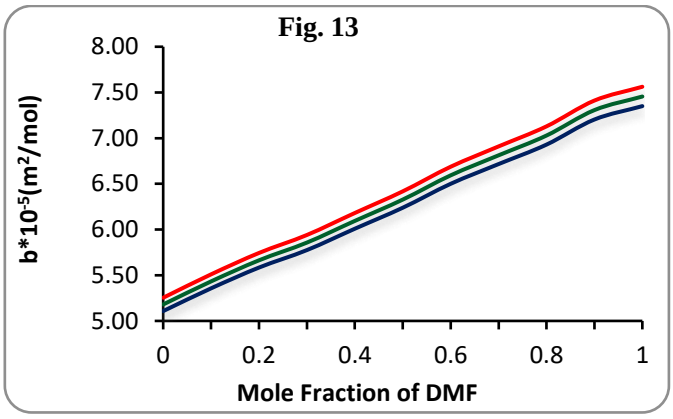

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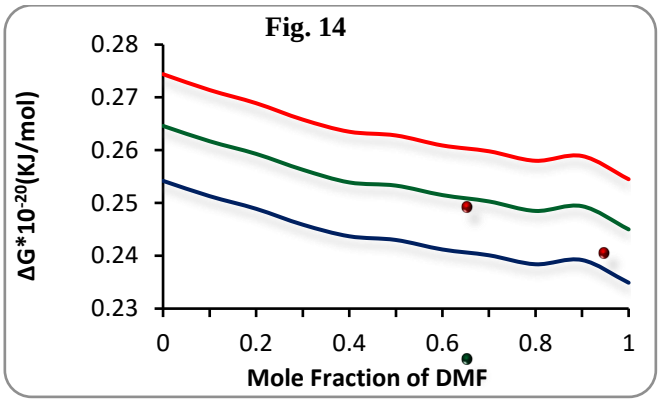

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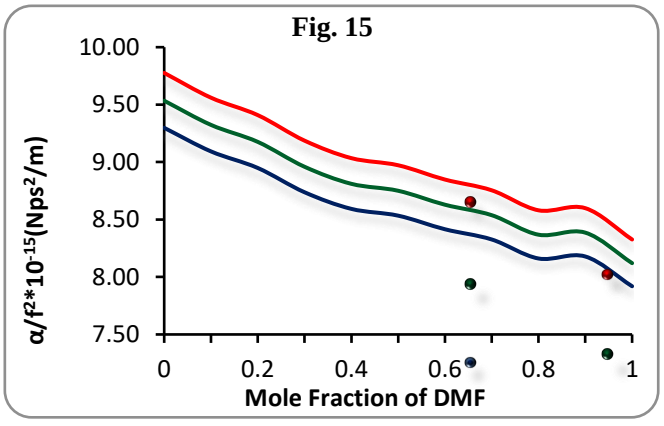

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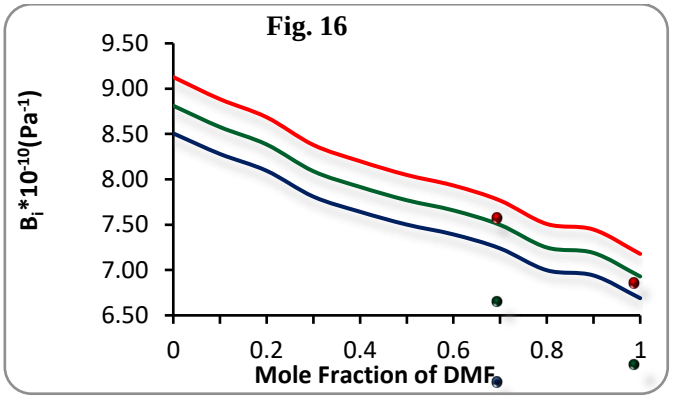

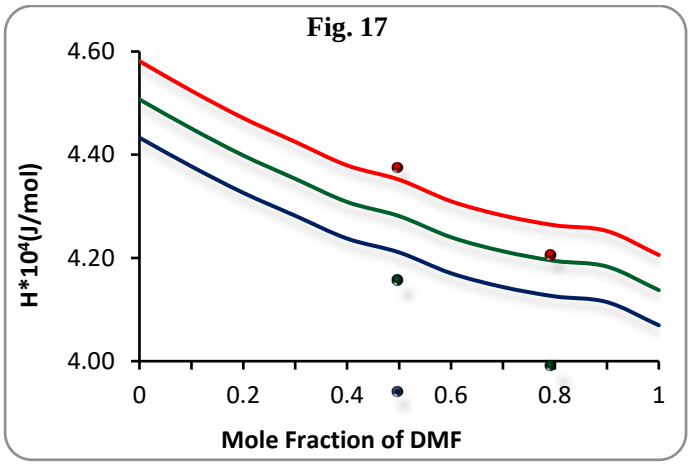

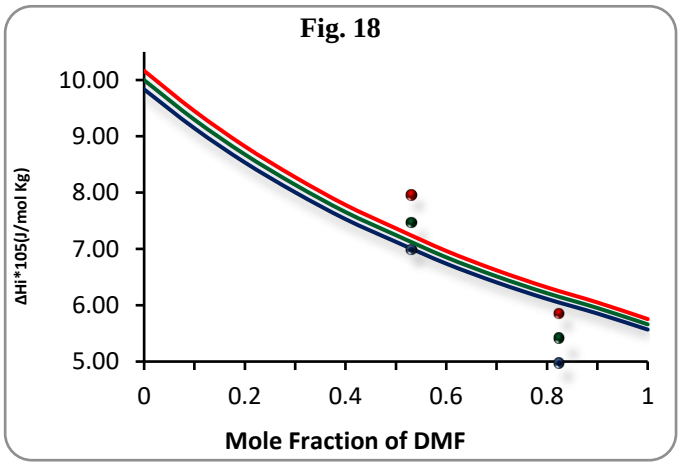

Fig. 1, represent the graph of ultrasonic density versus concentration. As the mole fraction of DMF increases the density increases. Increasing temperature of the mixture decreases its density (ρ). The decrease in density (ρ) with temperature indicates decrease in cohesive force. Thus increase of temperature favors increase of kinetic energy and volume expansion and hence decrease of density. The increasing temperature has two opposite effects namely structure formation and destruction of structure. This increase of temperature favors increase of kinetic energy and volume expansion and hence density decreases.

Fig. 2, shows the graph of ultrasonic velocity versus concentration. It is observed that ultrasonic velocity increase with increase in the concentration of DMF in EA, indicating increase in stiffness of the medium hence association in constituent's molecules[19]. The association may involve due to hydrogen bonding or dipole-dipole interaction between dimethylformamide and ethylamine. The association is due to strong dipole-dipole interaction between the constituent molecules. This is because the size of DMF molecules is more than EA molecules. Hence higher the size more will be the polarizibility. The process may lead strong interaction forces[20,21].

Fig. 3, shows the viscosity (η) versus concentration. It is observed that viscosity increases with increase in the concentration of DMF in EA, indicating strong molecular interaction. The viscosity gives the strength of molecular interaction between interacting molecules. Increase in temperature of the mixture, increasing disorders of the medium and hence entropy increases. As entropy increases, viscosity of binary mixture decreases.

From **Fig. 4,** Adiabatic Compressibility (β_a) decreases with increasing the molar concentration of DMF in EA. This is as per general trend observed for the electrolytic solutions. In more concentrated solution, more cohesion is expected and this lead to a decrease in β_a. The decrease in β_a results in an increase in the value of ultrasonic velocity. The decrease of adiabatic compressibility with increase of concentration of solution may be due to the dispersion of solvent molecules around molecules supporting strong solute-solvent interactions.

The adiabatic compressibility (β_a) and Isothermal compressibility (β_i) exhibit similar trend as shown in the **Fig. 16**. It is observed that adiabatic compressibility (β_a) and isothermal compressibility (β_i) decreases with increase in molar concentration of DMF in EA indicating strong intermolecular interaction in the component molecules in binary mixtures shows associating tendency of the component molecules.

As the ultrasonic velocity increase due to the increases in concentration, the interacting free length has to decrease and vice-versa. Increase on intermolecular free length with rise in temperature result decrease in density and velocity in binary mixtures and this fact supported by the result of experimental observations

given in graph. From **Fig. 5,** freelength (L_f) decreases with increasing the molar concentration of DMF in EA.

In the present investigation, **Fig. 6,** represents the plot of acoustic impedance versus molar concentration. It is observed that these acoustic impedance (Z) values increase with increasing concentration of DMF in EA. Such an increasing values of acoustic impedance (Z), further supports the possibility of molecular interactions between the unlike molecules. It was reported that the linear variation of specific acoustic impedance indicates the absence of specific interaction like compound formation. In fact the specific acoustic impedance depends upon the structure and molecular packing of liquids.

From **Fig. 7,** Internal Pressure (π_i) decreases with increasing the molar concentration of DMF in EA. From graph, it is to be noticed that the variation in the internal pressure values shows exactly reverse trend as that of free volume[22]. In this system, **Fig. 7** and **Fig. 9** shows that, internal pressure decreases and free volume increases. Further the increase in free volume and decrease in internal pressure with rise in concentration clearly shows the increasing magnitude of interaction. Such behavior of internal pressure and free volume generally indicates the association through hydrogen bonding

Fig. 8, relaxation time (τ) decreases with increasing the molar concentration of DMF in EA. The dispersion of the ultrasonic velocity in the system may contain information about the characteristic time (τ) of the relaxation process that causes dispersion. The relaxation time which is in the order of10^{-13} sec., is due to structural relaxation process[23] and in such a situation, it is suggested that, the molecules get rearranged due to co-operative process[24].

Fig. 9 represents, Free Volume (V_f) Increases with increasing the molar concentration of DMF in EA indicating association in the molecules of the component liquids. Free volume is the average volume in which the center of a molecule can move due to the repulsion of the surrounding molecules. This suggests that there is a closed packing of molecules inside the shield.

The molar volume of a liquid mixture depends on the structure arrangement in the liquid as well as on intermolecular interaction. The structural arrangement may be seceded by the molecular forces. **Fig. 10,** it is observed that the molar volume (V_m) increase with increase in concentration of DMF in EA. This is because effective mass is directly proportional to the molar volume. In present system, EA has lower effective mass in binary liquid mixture as compared to the DMF and hence it increases the molar volume of mixture with increase in concentration.

Fig. 11, Fig. 12, Fig. 13, shows the variation of Rao's Constant (R) OR Molar Sound velocity, Wada Constant (W) or Molar Compressibility and Vander Waal's Constant(b) with increasing concentration. Rao's constant is also known as molar sound velocity and it is an additive property. It has been found to be invariant with temperature and pressure for organic and inorganic liquid. It is observed that Rao constant, Wada Constant and Vander Waal's constant increase with increase in the concentration of DMF in EA. Vander Waal's constant (b) is also known as the co-volume in Vander Waal's equation and it varies in similar way to that of the available volume.

Gibb's free energy measures mobility of the medium. Higher the mobility of the medium, higher will be the entropy; lower will be the free energy. **Fig. 14**, represent the variation of Gibb's free energy (ΔG) with concentration. It is observed that Gibb's free energy decreases with increase in the concentration of DMF in EA, indicating increase in mobility of the mixture hence disorder increases due to outstanding salvation. Decrease in ΔG suggests longer time for rearrangement of molecules in the solution. The decrease of Gibb's free energy favors the formation of products after reaction[25].

Fig. 15, contains the plot classical absorption (α/f^2) versus concentration. It is observed that classical

absorption decrease with increase in the concentration of DMF in EA indicates the decrease in the stability of mixture. This process leads to dissociation and hence weak molecular interaction. This may lead solution more structured due to formation of hydrogen bond.

Fig. 17, shows that enthalpy (H) of the system decrease with increase in the concentration of DMF in EA, which indicates association. Lower the values of enthalpy; more is the interaction among the constituent molecules. It suggests less freedom of the molecules and hence strong intermolecular interaction.

Fig. 18, internal latent heat of vaporization (ΔH_i) decrease with increase in the concentration of DMF in EA. Latent heat is energy released or absorbed by a thermodynamic system, during a constant-temperature process. It is known that (ΔHi) decreases with increase in temperature and increases with increase in pressure. Here, since the external pressure is very low, the pressure factor seems to predominate causing an increase in the values of (ΔHi) with increase in temperature.

IV. CONCLUSION

The dependence of ultrasonic velocity and other derived parameters on composition of the mixtures is indication of the presence of molecular interactions. All the experimental determinations of thermodynamic parameters are strongly correlated with each other. In this paper, the all the derived thermodynamic parameter such as for different mole concentration of DMF with ethylamine of the binary mixtures are evaluated and shows the linear trends and hence these parameters suggests the presence of strong molecular interactions. In EA, NH_2 is active subgroup which plays important role in the association. The association in the constituent molecules may involve due to hydrogen bonding or due to dipole-dipole interactions between the constituent molecules. All these process may lead to strong interaction forces.

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