5

Acoustical and Themodynamical Study of Binary mixture of NN-Dymethylacetamide and Benzonitrile at Different Temperatures

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ABSTRACT

The measured values of ultrasonic velocity (υ), density (ρ) and viscosity (η) have been used to determinethe other ultrasonic parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), acoustic impedance (Z), free volume (V_f), internal pressure (π_i), relative association (R_A), Rao constant (R), Wada constant (W) and Gibb's free energy (ΔG) over the entire range of composition at 298K and 303K.The plots of ultrasonic velocity (υ), compressibility (β), molecular free length (L_f), and acoustic impedance (Z), free volume (V_f) internal pressure (π_i), at temperature 298K and 303K are non-linear in nature. This non linearity behavior indicates that there exists an intermolecular association between the components of the mixture.This association is among the functional groups of the polar molecules in the mixture.

Key Words : Ultrasonic velocity, density, molecular interaction, adiabatic compressibility,internal pressure, free volume, Wada constant, Raoconstant and Gibbs free energy

Introduction:

The molecular interactions of different materials are studiedby experimental techniques. Some of the methods are Infrared study, Raman Effect, Nuclear magnetic resonance, Dielectric constant, ultraviolet and ultrasonic methods. But in all of these different methods ultrasonic studies have played an important role in liquid mixtures. This study finds application in several industrial and technological processes. As ultrasonic investigations of liquid mixtures consisting of polar or non polar components are of importance in many applied fields in understanding the physical nature and strength of molecular interaction in the liquid mixtures [1-3]. Mainly the ultrasonic velocity of liquid is related to the bonding forces between the atoms and molecules and it helps to understand the nature of molecular interactions in pure and binary mixtures of the liquids [4, 5]. A literature survey reveals that polar liquids & their mixtures are of great interest to organic chemists to have the knowledge of the type bonds and interactions with each molecule in the liquid mixture such as N,N-dimethyleacetamide and Benzonitrile [6, 7]. The excess values of different parameters are very importantin order to understand the nature of molecular interactions between the components of the liquid mixtures.

The present study deals with measurements of the ultrasonic velocity, density and viscosity for the pure NNDMA and Benzonitrile and their binary mixtures for various concentrations at temperatures 298 K and 303K. The other ultrasonic parameters such adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i), Gibb's free energy (ΔG) are also evaluated. The variations of these parameters with concentration at the particular temperature of binary liquid mixtures are studied to understand molecular interaction between the different molecules of the binary mixtures.

Materials and Methods:

The chemicals Benzonitrile of GR grade (99%) purity and NNDMA of excel grade (99.5%) purity are used for the study without further purification. The binary mixtures for different range of composition were prepared at room temperature and kept in a special airtight glass bottles to avoid air contact. These mixtures prepared were used within 24 hours of its preparation. The measurements of ultrasonic velocities were carried out on single crystal multi frequency ultrasonic interferometer operating at 1MHz (M-81). The ultrasonic interferometer (Mittal enterprises, New Delhi, India) is a single and direct device to determine ultrasonic velocity in liquids with a high degree of accuracy [5]. The constant temperature of the liquid inside the interferometer cell was maintained by circulating water through the outer jacket through electronically controlled thermostat. Accuracy of measurement of ultrasonic velocity was within ± 0.01m/s and the temperature of the test liquids during measurement were maintained within an accuracy of ± 0.10C.

The densities of the binary mixtures & pure liquids were measured using 25ml specific gravity bottle and a sensitive mono pan balance (K-Roy, K-12 classic) within ± 0.1mg accuracy. The viscosity of the liquids and their mixtures were measured using the suspended level viscometer.

The experimentally measured ultrasonic velocity (υ) in ms^{-1}, density (ρ) in kgm^{-3} and viscosity (η) in Nsm^{-2} are used to evaluate various thermo dynamical parameters like adiabatic compressibility (β_s), free length (L_f), free volume (V_f), internal pressure(π_i) by using standard relations as below

Adiabatic compressibility $\beta_s = 1/\upsilon^2\rho$ ——1

Free length $L_f = K/\upsilon\rho^{1/2}$ —— 2

Where, K is Jacobson's constant (K=93.875 + 0.375 T) x10^{-8} and T being the absolute temperature

Acoustical impedance $Z = \upsilon\rho$ ——3

Free volume $V_f = \left[\frac{M_{eff}\,\upsilon}{k\eta}\right]^{3/2}$ —4

Where, Meff is the effective molecular weight (Meff=Σ mi Xi) in which mi and Xi are the molecular weight and mole fraction of the individual constituents respectively), k is temperature independent constant which is equal to 4.28 x 10^9 for all liquids

Internal pressure $\pi_i = bRT\left(\frac{k\eta}{\upsilon}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$—5

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Internal pressure $\pi_i = bRT\left(\frac{k\eta}{\upsilon}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right)$—5

Where k is a constant, T is the absolute temperature, b is a constant equal to 2 for the liquid

Rao constant $R = \upsilon^{1/3}.V_m$ —6

Wada constant $W = V_m.\beta_s^{-1/7}$—7

Gibb's free energy $\Delta G = -K_BT\ln(\eta/\tau K_BT)$—8

Where, K_B is Boltzmann constant (1.3806 x 10^{-23} JK^{-1}), T is the temperature, h is Plank constant(6.626x 10^{-34} Js) and τ is the relaxation time

Results and discussion:

The binary mixtures are prepared with the addition of NNDMA in the Benzonitrile by varying concentration .The ultrasonic velocity (υ) density (ρ) and viscosity (η) measurements have been used to calculate the different parameters such as adiabatic compressibility (β_a), intermolecular free length (L_f), acoustic impedance (Z), free volume (V_f), internal pressure (π_i), , Rao constant (R),relaxation time (τ), Wada constant (W), Gibb's free energy (ΔG)at two different temperatures 298, 303 K

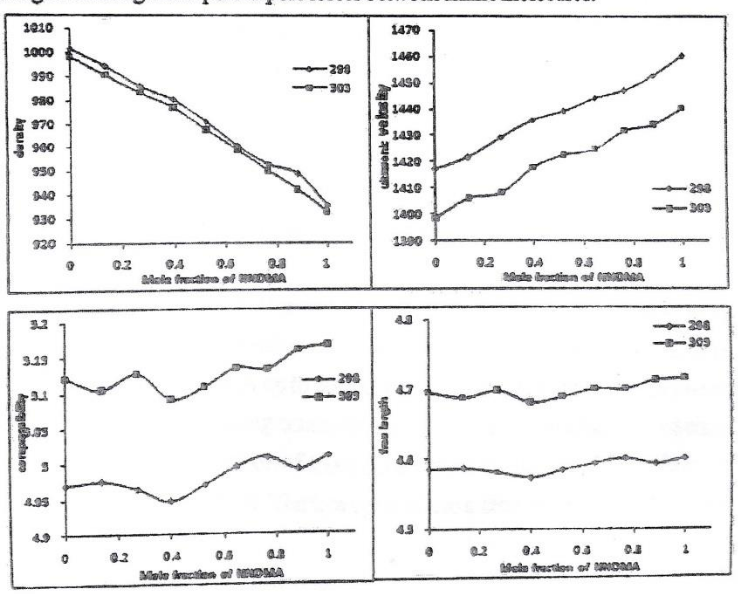
A plot of ultrasonic velocity against mole fraction of N, N-dimethyleacetamide with Benzonitrile for all temperatures as seen in Figure-1 is presenting the variations in the different parameters of the binary mixture of NNDMA and Benzonitrile, the density decreases. The density values decreases for the increase in temperature of the mixture this is the basic nature of liquids. The ultrasonic velocity is showing increasing nature with the increasing concentration of NNDMA in Benzonitrile and the values are decreasing as there is increase in temperature. The viscosity values are decreasing with the increasing concentration of NNDMA in the mixture and decreases as there is increase in the temperature of the binary mixture. The decrease in values of density, viscosity with increase in mole fraction of NNDMA suggests the decrease in magnitude of intermolecular interaction [8-10]. The increase in the velocity is due to slightly increasing value of the intermolecular free length.

The free length is the separation between the molecules of the liquid any change in this value can be assumed as to be the molecules come closure or going away from each other. The free length in this system shows slightly increasing nature with the increasing concentration of NNDMA in the binary mixture, whereas the free length shows increasing trend with the increasing value of temperature of the system. The nonlinear but slightly increase of free length results in the slight increase of compressibility for the increasing concentration of NNDMA. This shows that there is increasing the separation between the molecules of the mixture which can be attributed as there is some interaction between the components of molecules of the mixture [11]. The interactions become weaker with increase of temperature. The nonlinearity in adiabatic compressibility in this system indicates that there is a definite relaxation on mixing of NNDMA. It is observed that the acoustic wave when travels in the medium there is variation of pressure occurs from molecules to

119

molecules. The acoustical impedance is the property of the liquid depends upon the density of the liquid. Therefore there is the variation of the mole fraction of the solute the impedance varies correspondingly[12]. The value of acoustical impedance decreases with the increase in concentration of the NNDMA in the binary mixture of NNDMA and benzonitrile. The trend is similar for increase in the temperature; it means the impedance decreases with the increase in the temperature of the binary mixture. The corresponding plots of acoustical impedance vs mole fraction of the NNDMA in mixtures is given in Figure-1 at temperatures 298, 303K.

According to the study done by Anwar Ali et al[13] the densities and viscosities of pure N, N-dimethyleacetamide (DMA) and benzyl alcohol (BA), and nine of their binary mixtures covering the entire composition range were correlated with composition and temperature by using some empirical relations. The variations of these parameters with composition and temperature indicate the presence of specific interactions, namely hydrogen bonding and dipole-dipole forces between unlike molecules.



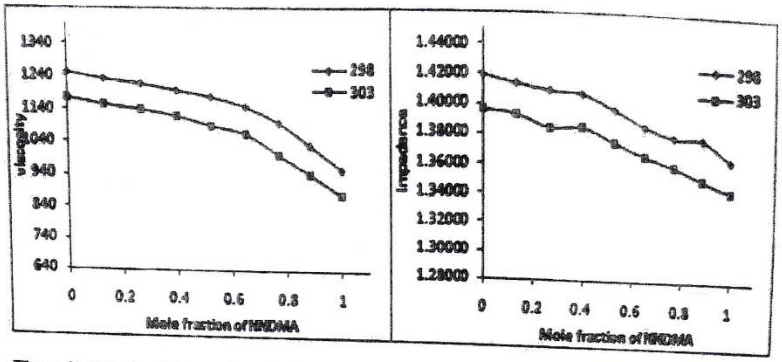


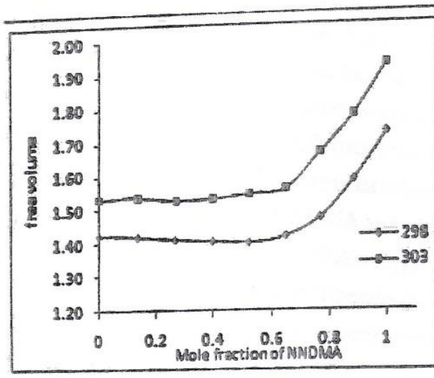
Figure 01: Graph of ultrasonic velocity (υ), density (ρ), compressibility (β_{ad}), free length (L_f), impedance (Z) and viscosity (η) with respect to concentration of NNDMA in Benzonitrile mixture at 298, 303, K

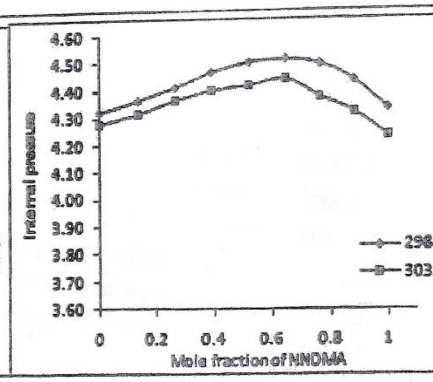
Suryanarayana [14] reported that an increase of temperature would result in a decrease of internal pressure in liquids and liquid mixtures. Figure-2 indicates that internal pressure of the liquid mixtures in the present study decreases with rise in temperature. There is a rise in the internal pressure in the initial state for the increase in molar concentration of NNDMA up to 0.6 of the mole concentration of the NNDMA in the mixture. After that as the concentration of the NNDMA increases beyond the 0.6 mole fraction the internal pressure shows decreasing nature. This non linear variation in the internal pressure can be attributed as there is definite interaction presents between the unlike components of the mixture.

As seen in the Figure-2 the free volume of the system is showing non linearity in its behaviour the free volume values are almost remaining uniform for the increase in the concentration of the NNDMA up to 50% in the mixture but beyond that the free volume is increasing with the increasing concentration of NNDMA and which can be concluded that there must be the formation of some complexes beyond 0.5 of the mole fraction of NNDMA in the binary mixture. The free volume also increases with rise in temperature in the binary mixtures. [15].

The Rao's constant Rdecreases linearly with the increase in mole fraction of NNDMA in the binary mixture of NNDMA and Benzonitrile systems, indicating the presence of specific interactions in the binary liquid mixture without complex formation.It was reported [16, 17] that a linear variation in Rao's constant and Wada's constant with change in mole fraction is indicative of the absence of complex formation in binary mixtures. The linear variations of Rao's constant and Wada's constant as seen from Figures-2 suggest the absence of complex formation in the binary mixtures in the present study. Figure-2 shows that Rao's constant is independent of temperature [18, 19]

The relaxation time depends on temperature and impurities. From the Figure-2, it is found that the values of relaxation time decreases with concentration and temperature of the binary liquid system. The variations in specific relaxation time are mainly due to the change in viscosity depending on concentration and temperature. The relaxation time is of the order of 10-12 sec is due to the structural relaxation process and such type of situations are suggested to be because of rearrangement of molecules due to cooperative process [20]. The non linear variation of the relaxation time with the mole fraction is interpreted as possible molecular association between the molecules of NNDMA and Benzonitrile in the mixture [21]. The Gibbs free energy also conform the same results. This suggests the weaker approach of the unlike molecule due to hydrogen bonding.[22]The decrease in Gibbs free energy in the system indicates the need of less time for the rearrangement of the molecules and therefore there is decrease in the energy that leads to the association of the molecules in the mixture.





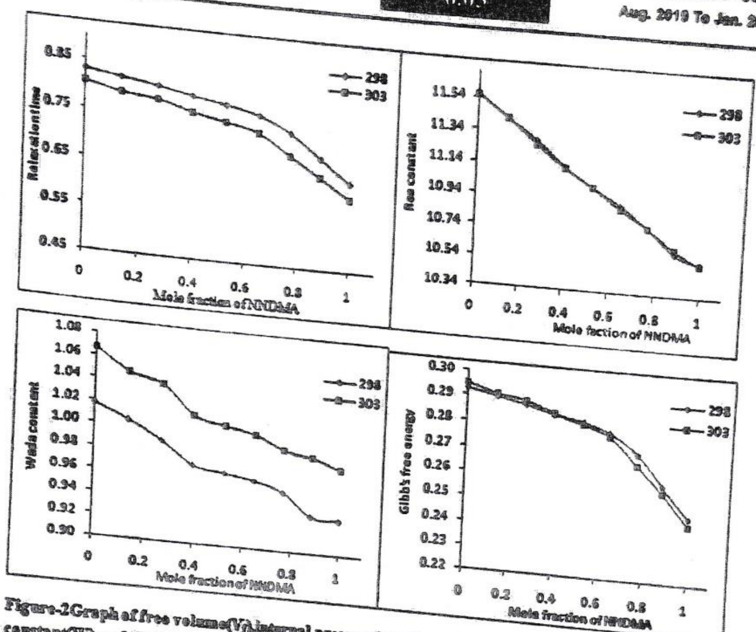


Figure-2Graph of free volume(V_f),internal pressure(π_i),relaxation time (τ), Rao's constant(R),Wada constant(W),and Gibb's free energy(ΔG) of NNDMA + Benzonitrile mixture with respect to concentration of NNDMA in Benzonitrile mixture at 298,303, K

CONCLUSION :-

Ultrasonic velocity (υ), density (ρ) and viscosity (η) have been measured for NNDMA and Benzonitrile mixtures at298 and 303K. The variations of different thermodynamic parameters indicate the presence of specific interactions, namelyhydrogen bonding and dipole-dipole forces between unlike molecules.The internal pressure of the liquid mixtures in the present study decreases with rise in temperature and free volumeof the system is showing non linearity in its behavior the free volume is increasing with the increasingconcentration of NNDMA and which can be attributed as there is definite interaction presents between the unlikecomponents of the mixture.The decrease in Gibbs free energyand non linear variation of the relaxation time with the mole fraction is interpreted as possible molecular association between the molecules of NNDMA and Benzonitrile in the mixture.

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