ACOUSTICAL AND EXCESS PARAMETER STUDY OF BINARY MIXTURE OF NN-DYMETHYLACETAMIDE AND ACETONITRILE BY ULTRASONIC MESURMENTS

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ABSTRACT

Ultrasonic studies have played an important role for understanding the nature of molecular interaction in liquid mixtures. This study finds several applications in industrial and technological processes. The measurements of ultrasonic velocity (υ) with density (ρ) and viscosity (η) are carried out over the entire range of composition at 308.15K and 313.15K. The other ultrasonic parameters such as adiabatic compressibility (β_a), free length (L_f), free volume (V_f), internal pressure (π_i) with the excess values of all these parameters like, excess adiabatic compressibility (β_a^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E) are also evaluated to throw light on the nature and degree of molecular interaction occurring in the binary mixture. 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 308.15K and 313.15K are non-linear in nature. This non linearity behaviour indicates that there exists an intermolecular association between the components of the mixture. The nature of excess values of (β_a^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E) conforms about the existence of the molecular 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, excess values, compressibility, internal pressure, free volume*

Introduction

To understand the nature of intermolecular interaction between the different molecules of the liquid and its mixtures is very important in many fields of studies. Therefore there are various physical methods developed for investigating the intermolecular interactions in liquid systems. 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 the ultrasonic technique has played an important role in studying the interaction in pure liquid and their binary liquid mixtures. Mainly the ultrasonic velocity is very sensitive to molecular structures. (Eyring H. et.al, 1938; K.S. Pitzer et.al, NY1995; A.N. Kannapan et.al, 2009; V.A. Tabhane et.al, 1999) and the investigations of liquid mixtures. The investigations are of highly importance in understanding the physical nature and strength of molecular interaction in the liquid mixtures consisting of polar and non polar components (R. J. Fort et.al, 1966; V. Srinivasulu et.al, 1995; K. Swain et.al, 2010; Jacobson et.al, 1952). The ultrasonic velocity of liquid is basically related to the bonding forces between the atoms and molecules. In order to understand the nature of molecular interactions between the components of the liquid mixtures, it is of more interest to discuss the same in terms of excess parameters rather than actual values. A literature survey reveals that very less attempt has been made to study the ultrasonic and thermodynamic properties for the binary mixture with the polar liquids.

The liquid NN-Dimethyleacetamide (NNDMA) is used for many organic reactions and industrial applications. It can be applied as a solvent for the manufacturing of films, acrylic fibers, X-ray contrast media, polyimide resins, polysulfones and cellophane. The liquid Acetonitrile is also very important in many pharmaceutical and industrial applications. Therefore the mixtures of these liquid are of interest to organic chemists to know about the types and number of bonds of each molecule in the NNDMA complex (P K Gupta et.al 1977; G Arul et.al, 2005)

The present study deals with measurements of the ultrasonic velocity, density and viscosity for the

pure NNDMA and Acetonitrile and their binary mixtures for various concentrations at temperatures 308.15K and 313.15K. The other ultrasonic parameters such as adiabatic compressibility (β_α), free length (L_f), free volume (V_f), internal pressure (π_i) with the excess values of all these parameters like, excess adiabatic compressibility (β_α^E), excess free length (L_f^E), excess free volume (V_f^E) and excess internal pressure (π_i^E) 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 NNDMA of excel grade (99.5%) purity and acetonitrile of GR grade (99%) 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. Here 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 (V.Srinivasulu et.al 1995).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 $\pm 0.1^0$C. 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 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_α), free length (L_f), free volume (V_f), internal pressure(π_i) and their excess values, as excess adiabatic compressibility (β^E), excess free length (L_f^E), excess free volume(V_f^E) and excess internal pressure (π_i^E) by using standard relations as below.

Adiabatic Compressibility (β_α) by the relation,

$$\beta_\alpha = \frac{1}{\rho v^2} \qquad \text{----------1,}$$

Molecular free length (L_f) by the relation

$$L_f = K\beta_\alpha^{1/2} \qquad \text{----------2,}$$

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

Free volume (V_f) by the relation

$$V_f = \left[\frac{M_{eff} v}{\eta\kappa}\right]^{3/2} \qquad \text{---------- 3,}$$

Where, M_{eff} is the effective molecular weight ($M_{eff}=\Sigma m_i X_i$) in which m_i and X_i are the molecular weight and mole fraction of the individual constituents respectively), k is temperature independent constant which is equal to 4.28×10^9 for all liquids.

The internal pressure (π_i) by the relation

$$\pi_i = bRT\left[\frac{\eta\kappa}{v}\right]^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \qquad \text{---------- 4,}$$

Where k is a constant, T is the absolute temperature, b is a constant equal to 2 for the liquid and the excess values of these parameters are determined by using the relation

$$A^E = A_{exp} - A_{id} \qquad \text{---------- 5,}$$

A^E - excess value of any acoustic parameters,

$$A_{id} = \sum_{i=1}^{n} A_i X_i \ ,$$

A_i is any acoustical parameter and X_i – the mole fraction of liquid component.

Result and Discussion

The binary mixtures are prepared with the addition of NNDMA in the acetonitrile by varying concentration. The values of ultrasonic velocity (υ) measured with interferometer and density (ρ) measured with specific gravity bottle are seen to be increasing with the concentration of NNDMA in Acetonitrile binary mixture at 308.15K and 313.15K. The values of viscosity (η) measured with suspended level viscometer show increase with the increase in concentration of NNDMA in the binary mixture at that temperature.

It is observed from figure 1**,** the plots of different parameters that the ultrasonic velocity increases with the increase in NNDMA in the binary mixture, the increase in the density shows increase in the ultrasonic velocity which is the basic properties of the liquid (Eyring H. et.al, 1938). The viscosity values showing increasing trend is the indication of increasing frictional resistive force may be due to a change in effective molecular area of the components by the cohesive or adhesive forces or relative random velocity between the components of the mixture, adiabatic compressibility (β_α) decreases with the increase in concentration of NNDMA. As the intermolecular free length depends upon intermolecular attractive and repulsive forces (A Ali, et.al; 1999) it is observed that free length (L_f) also seen to be having similar relation with the concentration as that of compressibility. The values of adiabatic compressibility (β_α) and free length (L_f) decreases with increase in the mole fraction of NNDMA in the mixture. The decrease in the values of free length with increasing concentration can be concluded as there is significant interaction between the molecules of the two liquids (K. Rajgopal et.al; 2010). The decreasing free length with the increase in concentration of NNDMA in the binary mixture suggests the close packing of the molecules, which may be concluded as the increasing magnitude of the interaction (G Nath et.al, 2009; P S Naidu et.al, 2002; G Arul et.al; 2001).The values of free volume (V_f) shows decreasing trend with increasing concentration of NNDMA in the mixture and increase with increasing the temperature. The internal pressure (π_i) is seen to be decreasing with increasing concentration of NNDMA in the mixture and decrease with increasing the temperature. From figure 01, it is observed that most of the plots are non linear and the variations can be seen at 0.5 of molar concentration of NNDMA in the mixture. The non linear variation in the above parameters is an indication of existence of interaction between the components of the mixture (A.N. Kannappan et.al, 1996; Sadasiva Rao et.al, 2000). It is observed from figure 2. It is essential to study the excess parameters in order to determine the extent and presence of molecular interaction between the molecules, the extent of deviation & sign of these parameters depends on the strength of interaction between unlike molecules (Redlich et.al, 1948; A Ali et.al, 1999).

The excess compressibility and free length are negative for all concentrations. This is the indication of the presence of strong attractive or repulsive forces acting between the different components of the mixture. The close perusal of the excess values as shown in the figure conform the existence of interaction between the different components of the mixture for all the concentration range. Mostly interaction occurs from 0.5 of the mole fraction of NNDMA in the mixture. The sign of excess free length plays a vital role in assessing compactness due to molecular interaction through dipole-dipole interaction (Anwar Ali and Anil Kumar Nain, Study of molecular interactions in non aqueous binary mixtures through ultrasonic measurements (Anwar Ali *et.al,* 2000; Nisha Sharma *et.al,* 2010). Plots of excess adiabatic compressibility (β_α^E) and excess free length (L_f^E) are negative which also indicates the strong molecular interaction between the components of the mixture. Excess free volume(V_f^E) and excess internal pressure (π_i^E) are also negative which convey that chances of induced dipole-dipole interaction are overruled and strong dipole-dipole interaction alone are confirmed (R A Patil et.al, 2012; P B Dabrase et.al 2012).

Figures: 1

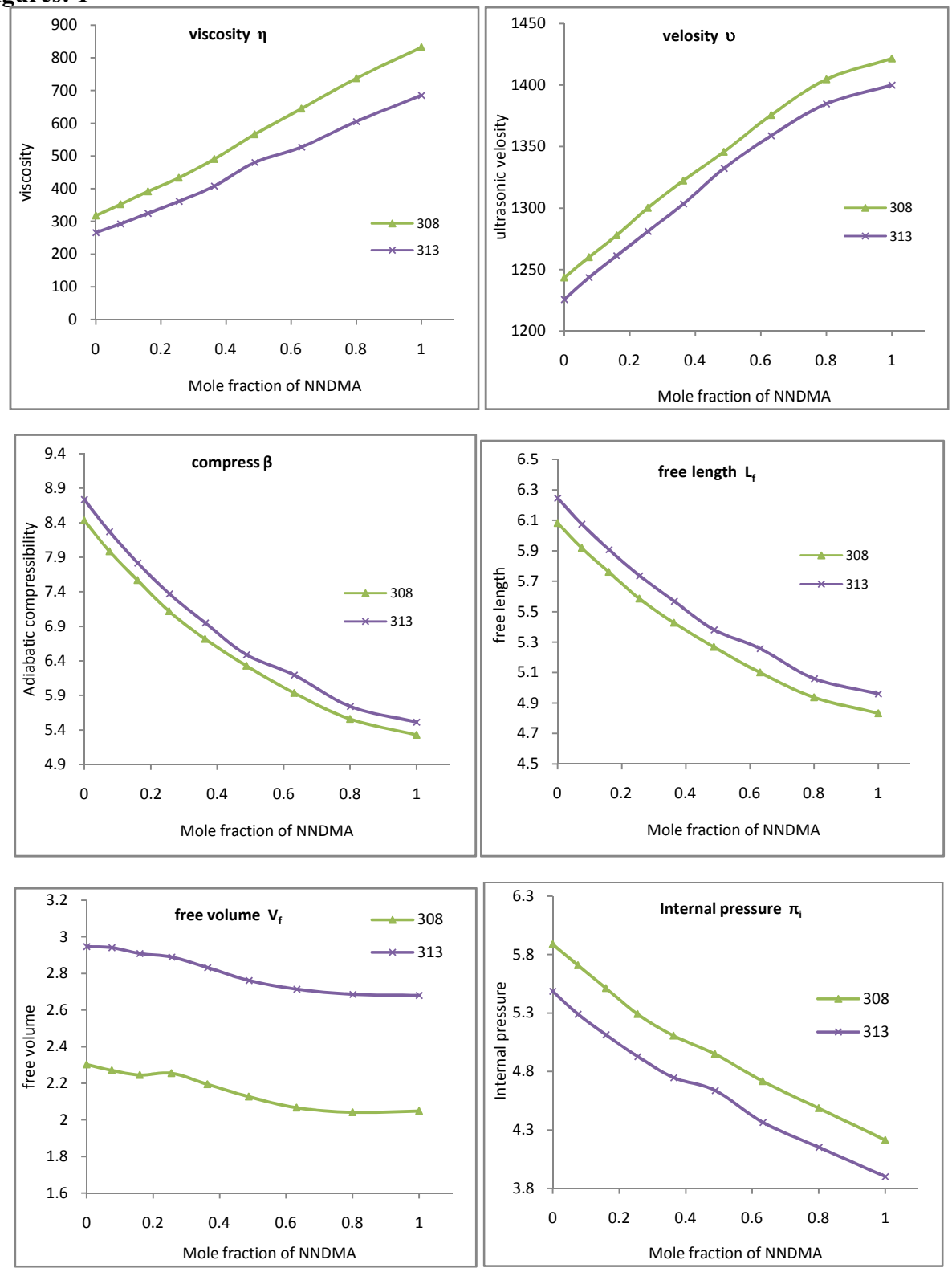
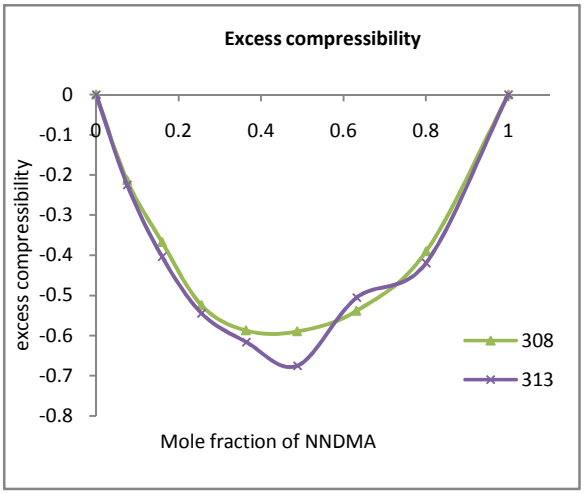
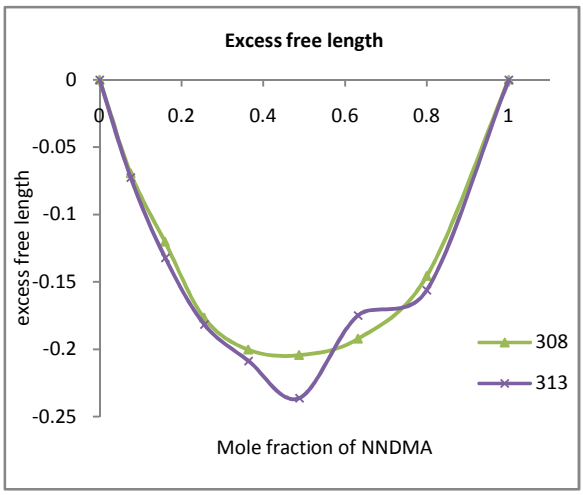


Figure 01:- Plots of ultrasonic velocity, viscosity, adiabatic compressibility (β, free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess values, for N,N-dimethylacetamide + Acetonitrile mixture at 308.15K and 313.15K temperature.

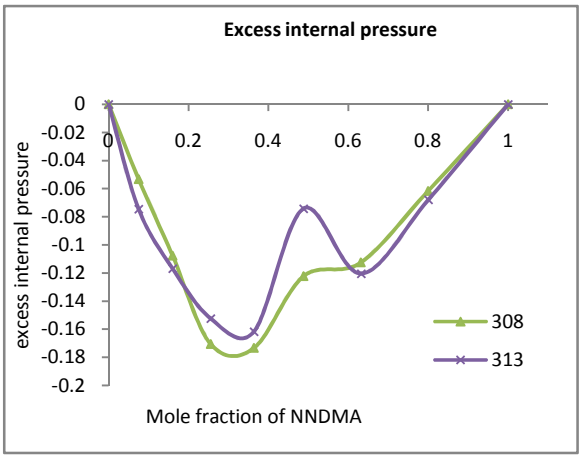
Figure: 2



1: Plot of excess adiabatic Compressibility versus Mole fraction of NNDMA



2: Plot of excess free length versus Mole fraction of NNDMA



3: Plot of excess internal pressure versus mole fraction of NNDMA

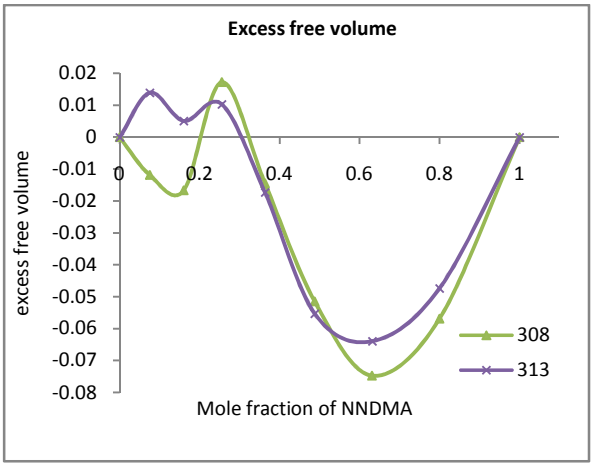


Fig 4: Plot of excess free volume versus mole fraction of NNDMA

Conclusion

All the plots of different parameters obtained from the present study shows the non linear variation for the binary mixture of NNDMA in the Acetonitrile for entire range of concentration at 308.15K and 313.15K, which indicates there is existence of molecular interaction between the different components in the mixture. The non-linearity of the curve is common for all compositions.

The negative values of excess compressibility (β_α^E), excess free length (L_f^E), excess internal pressure (π_i^E) and excess free volume (V_f^E) indicates the existence of the intermolecular interaction between the different molecules of the mixture. The negative excess values seen in these parameters confirm the presence of strong dispersive interaction between the components of molecule in the mixture. The excess values of thermodynamic parameters are sensitive to the molecular association present in the liquid mixture which supports our conclusion.

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