STUDY OF ACOUSTICAL & EXCESS PARAMETERS OF NN- DIMETHYLACETAMYDE AND ACETONITRILE AT 303.15 & 308.15 K

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ABSTRACT

*The Measurment of ultrasonic velocity (**υ**) and Density (**ρ**) measurements of pure liquids and the binary mixtures of acetonitrile and N-N dimethyl acetamide have been carried out at temperatures 303.15 and 308.15^{0}K over the entire range of composition. The measured ultrasonic parameters have been used to evaluate other thermo dynamical parameters such as adiabatic compressibility (β_α), free length (L_f), free volume (V_f), internal pressure (π_i) and their excess values (β_α^E, L_f^E, V_f^E and π_i^E).The results thus obtained are discussed for molecular interaction with varying composition of binary system. The non linearity found in all the plots of these ultrasonic parameters and their excess values with the composition range indicates presence of the intermolecular interaction between the components of the unlike molecules of the mixture. The nature of excess values of the β_α, L_f, V_f and $\pi_i$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

There are many physical methods which play an important role in determining molecular structure of pure liquid and their mixtures. In recent years the advances in the ultrasonic technique has become a powerful tool in evaluating information about the physical and chemical behavior of molecules of the liquids (Ali A. et. al, 1999; Pitzer K.S. et. al,1995; Kannapan A.et. al, 2009; Tabhane V.A., et. al,1999). The ultrasonic studies of the liquids are most preferred in many fields such as pharmaceutical industry, biomedical research, automobile industry, chemical industry, water research& scattering spectroscopy, etc. (Srinivasulu V. et. al, 1995). The information of density (ρ), ultrasonic velocity (υ) and viscosity (η) of the pure liquids and their mixtures plays very important role in different applications that include surface facilities, pipeline systems & mass transfer operations. Here in the present study the ultrasonic velocity, density and viscosity measurements have been carried out for determination of ultrasonic parameters such as compressibility (β_α), molecular free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess values (υ^E, β_α^E, L_f^E, V_f^E and π_i^E) for the different composition range of NN-Dimethylacetamide in acetonitrile at the temperature 303.15 and 308.15^{0}K. The variations of these parameters with concentration of binary liquid mixtures are studied to understand molecular

interaction between unlike molecules of the mixtures.

Material and Methods

The liquids Acetonitrile and N-N dymethylacetamide obtained comercially are of AR grade with purity of 99.5% and used without further purification. All mixtures for different concentration of liquids were prepared at room temperature. To avoid evaporation special air tight glass bottles were used to keep liquid mixtures. The density of pure liquids and their binary mixtures were measured using specific gravity bottle of 25ml capacity calibrated with de-ionized double distilled water and a sensitive mono-pan balance within ±0.1mg accuracy. Ultrasonic velocities (υ) of the above liquid mixtures were measured using single crystal Ultrasonic Interferometer operating at 2 MHz (Mittle enterprises- model M-81). The cell was filled with a desired solution and a constant temperature was maintained by circulating hot water through the outer jacket from constant temperature bath. Accuracy in the measurement of ultrasonic velocity was within ± 0.01m/s.

Theory: The experimentally measured density (ρ) in kgm^{-3} ultrasonic velocity (υ) measured in ms^{-1}, and viscosity (η) in Nsm^{-2} are used to evaluate various thermo dynamical parameters like

1. Adiabaticcompressibility (β_α) by the relation, $\beta_\alpha = 1/\upsilon^2\rho$ ----------1

2. Intermolecular free length (L_f)
$L_f = K\beta_\alpha^{1/2}$ ----------2

Where, K–is temperature dependant constant 207.5 X 10^{-8}at 303.15K &211.25×10^{-8} at 313.15Kand T – absolute temperature[7],

3. The free volume $V_f = \left[\frac{M_{eff}}{k\eta}\nu\right]^{3/2}$ -----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 X 10^9 for all liquids.

4. The internal pressure

$$\pi_i = bRT\left(\frac{k\eta}{\nu}\right)^{1/2}\left(\frac{\rho^{2/3}}{M_{eff}^{7/6}}\right) \quad \text{------4}$$

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

5. The excess values are determined by using the relation

$A^E = A_{exp} - A_{id}$ ---------5

A^E - excess parameters of all 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.

Results and Discussion

The experimentally determined values of density (ρ), viscosity (η) and ultrasonic velocity (υ) of all the pure liquids and their mixture were used to obtain the adiabatic compressibility (β_α), free length (L_f), free volume (V_f) and internal pressure (π_i) at different concentration and temperature (not reported in table 1) and the excess values of adiabatic compressibility (β_α^E), free length (L_f^E) free volume (V_f^E)and internal

pressure (π_i^E) at 303.15 and 308.15K are furnished in Table1. It is observed that Ultrasonic velocity (υ), density (ρ) and viscosity (η) increases with increase in the mole fraction of NNDMA (NN-Dimethylacetamide), in binary mixture. The increase in ultrasonic velocity with the increase in concentration of DMAC may be due to the structural changes occurring in the binary mixture resulting in the increase in intermolecular forces between the components of liquid (Dabrase P.B.et.al, 2012**)**. There is increase in the density of mixture as the mole fraction of NNDMA increases. In general it can be seen that,the increase in density is due to increase of concentration. The increase in the density shows increase in the ultrasonic velocity which is the basic property of liquid (Erying H. et.al, 1938). The decrease in adiabatic compressibility and intermolecular free length of DMAC reveal the presence of specific interactions between the components in the binary liquid mixture (Bhatnagar Deepa et.al, 2011). In order to highlight the presence of intermolecular interaction between molecules it is essential to study the excess parameters. The deviation of the physical properties of the liquid mixtures from the ideal behavior is a measure of interaction between the molecules which may be due to the either adhesive or cohesive force which indicates the presence of strong or weak interactions. The effect of deviation depends upon the nature of the constituents and composition of the mixtures (Thirumaran S. et. al, 2009).

Inpresent's investigation from fig(1), the excessvalues of 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 negative over the entire range of composition (Shridevi et.al, 2004).

The values of excess free length (L_f^E) are supported by the variation of excess compressibility exhibits interaction in the system. The excess compressibility and excess free length are negative which indicates the strong molecular interaction between the components. Negative excess free length indicates the ultrasonic wave's needs to cover larger distance because of dominant nature of interaction between unlike molecules. According to Fort & Moore (Fort & Moore et.al,1995**)** a negative volume is an indication of strong hetero-molecular interaction in the liquid mixtures and is attributed to charge-transfer, dipole-dipole, dipole–induced dipole interactions & hydrogen bonding between the unlike compounds, while a positive sign indicates a weak interaction & is attributed to dispersive force, which are likely to be operative. Here the excess free volume is negative, the excess free volume (V_f^E) and excess internal pressure (π_i^E) are also negative which convey that the chances of induced dipole-dipole interactions are overruled & strong dipolar interactions alone are conformed. (Dabrase P.B. et.al, 2012; Patil R.A**.** et.al, 2013; Rajgopal K. et al, 2010).

Thus it is clear from the above evaluated parameters that there is a strong association between the NN-dimethylacetamide and acetonitrile molecules. This association is stronger at ratio 1:1of mole fractions of the mixture.

Table 01. Excess values of Ultrasonic Velocity and other thermodynamic parameters β_α^E,L_f^E,V_f^E & π_i^E for NN-Dimethylacetamide + Acetonitrile mixtures at temperature 303.15 & 308.15K .

Temp K	Mole fraction DMA	Density ρ kgm^{-3}	Velocity υ ms^{-1}	Viscocity ημPas	β^E 10^{-10} m^2N^{-1}	L_f^E X 10^{-11} m	π_i^E X 10^8	V_f^E X 10^{-7}
303	0	773.1826	1258.8889	329.575	0	0	0	0
	0.075079	793.5075	1276.6667	366.627	-0.204232	-0.06699	-0.05458	-0.01659
	0.159244	813.0189	1296.6667	405.0463	-0.368875	-0.12267	-0.13504	0.00594
	0.254249	836.0454	1316.7568	452.8904	-0.501417	-0.16992	-0.16179	0.00151
	0.362333	856.2085	1340.5405	514.5682	-0.577262	-0.19916	-0.16240	-0.02943
	0.486397	875.9529	1362.2222	603.6087	-0.553032	-0.19217	-0.07443	-0.14158
	0.630267	895.6459	1385.1429	675.1577	-0.455156	-0.15911	-0.09672	-0.08834
	0.799097	916.3421	1422.3529	770.0006	-0.374963	-0.14102	-0.07084	-0.03909
	1	932.3975	1440.6061	878.3054	0	0	0	0
308	0	766.8868	1243.3333	317.5339	0	0	0	0
	0.075398	788.5823	1260	352.1683	-0.213311	-0.06943	-0.053245	-0.01191
	0.159858	808.9705	1277.7778	391.3629	-0.36727	-0.12031	-0.107844	-0.01667
	0.255119	831.3058	1300	433.0266	-0.524351	-0.17645	-0.170514	0.01727
	0.363392	851.3464	1322.2222	490.6968	-0.587057	-0.20019	-0.173319	-0.01451
	0.487541	872.5285	1345.5556	565.8514	-0.589702	-0.20444	-0.122314	-0.0815
	0.631334	890.5113	1375.5556	644.9857	-0.538216	-0.19211	-0.112544	-0.07477
	0.799831	911.5907	1404.7059	737.4940	-0.389888	-0.14569	-0.061714	-0.05697
	1	929.0522	1421.4483	832.9541	0	0	0	0

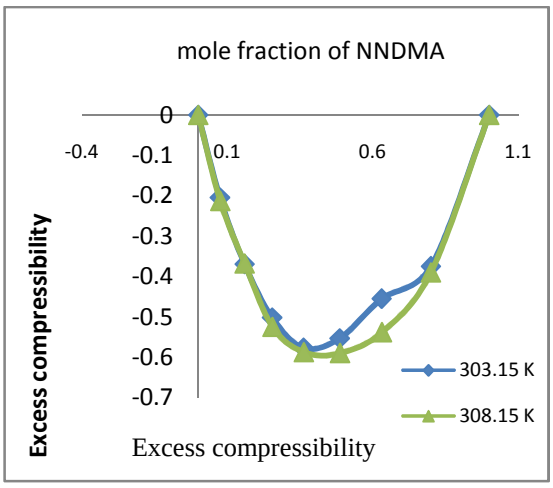

Fig1: Plot of excess adiabatic Compressibility versus mole fraction of NNDMA

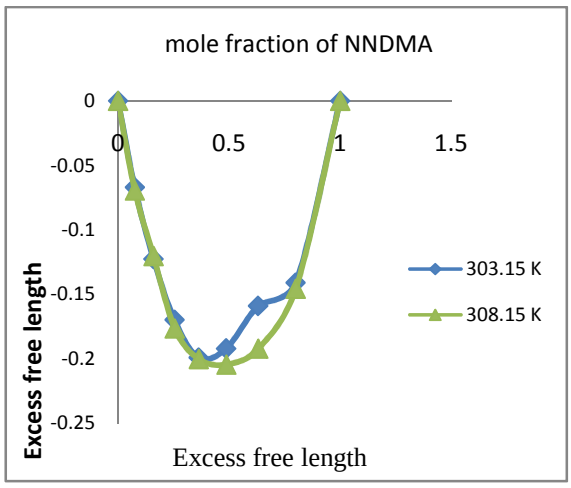

Fig 2: Plot of excess free length versus Mole fraction of NNDMA

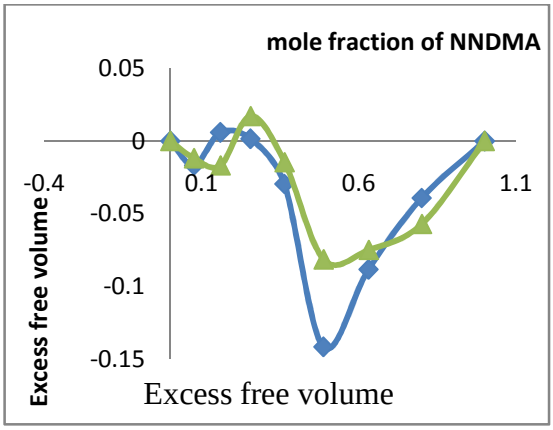

Fig 3: Plot of excess free volume versus mole fraction of NNDMA

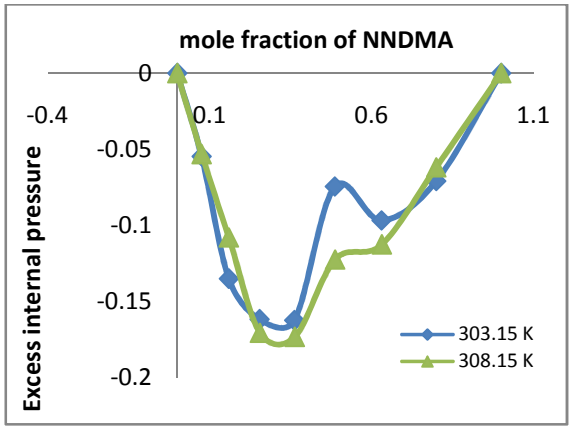

Fig 4: Plot of excess internal pressure versus mole fraction of NNDMA

Conclusion

In the study ultrasonic velocity, density and viscosity measurements have been carried out for determination of ultrasonic parameters such as compressibility (β_α), molecular free length (L_f), free volume (V_f) and internal pressure (π_i) and their excess values (β_α^E, $L_f^E V_f^E$and π_i^E) are evaluatedand these excess parameters are negative. These negative excess values predict the presence of strong intermolecular association between the components of the mixtureThe interaction is strong about 0.5 mole fraction of NN-dimethylacetamide and acetonitrile molecules at both the temperatures 303.15 & 313.15K.This association is among the functional groups of the polar molecules in the mixtures.

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