

DENSITY & VELOCITY STUDY OF ACETONITRILE AND N-N DIMETHYL ACETAMIDE

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ABSTRACT

The Ultrasonic velocity (v) and Density (ρ) measurements of pure liquids and the binary mixtures of acetonitrile and N-N dimethyl acetamide have been carried out at 298⁰K temperature using 2 MHz ultrasonic interferometer. The measured ultrasonic parameters have been discussed and graphically plotted with varying composition of the binary system. All the plots of ultrasonic velocity (v), compressibility (β), molecular free length (L_f) and acoustic impedance (Z) with the composition are non-linear in nature. This non linearity behavior indicates that there is intermolecular association between the components of mixture. This association is among the functional groups of the polar molecules in the mixture.

Key Words: *Ultrasonic velocity, density, molecular interaction, free length, compressibility, binary mixtures.*

Introduction

There are many physical methods used in determining molecular structure and molecular properties of the liquids. There have been many number of studies done on the molecular interactions in pure liquid systems and their mixtures (Eyring, H. et. al, 1938; Kannappan, A.N. et. al, 1992). But the intermolecular interaction studies always play an important role in the molecular sciences. In recent years, ultrasonic technique has become a powerful tool in providing information regarding the molecular behavior of liquids owing to its ability of characterizing the physiochemical behavior of liquids.

Non-linear variation of adiabatic compressibility, free length and impedance of the mixture as function of concentration

was qualitatively described by hydrogen bonding. The results confirm that the sign and magnitude of such deviation depends on the strength of interaction between unlike molecules.

The present investigations deals with the study of molecular interaction in binary liquid mixtures (Acetonitrile + N-N dimethyl acetamide) at 298⁰K. Departure from linearity of velocity versus concentration in liquid mixtures is taken as an indication of the existence of interaction between the molecules of the components. The physical and chemical properties of different liquid mixtures have been studied by numbers of workers (Hyderkhan, V. et.al, 1971; Temperley, H.N.V., et.al, 1968) and they emphasized that the non-linear variation of ultrasonic

velocity, compressibility and other related parameters can be attributed with structural changes occurring in liquid mixture. Though spectroscopic methods play a major role in the determination of molecular behavior, the non-spectral studies such as calorimetric, magnetic, ultrasonic velocity and viscosity measurements have also been widely used to explore the formation of complexes (Shanmuga Priya C., et.al, 2010). In the present work we have determined the ultrasonic parameters, namely the adiabatic Compressibility (β_α), free Length (L_f) and acoustic Impedance (Z) of the binary mixture (Acetonitrile + N-N dimethyl acetamide) at 298⁰K. The results obtained here are discussed in terms of molecular associations. Intermolecular association between the binary components is conferred by determining excess values of ultrasonic parameters (v^E , β_α^E , L_f^E and Z^E), however excess values are not reported in this paper.

Experimental

The liquids N-N dymethyl acetamide and Acetonitrile obtained commercially 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 25ml specific gravity bottle and a sensitive mono-pan balance within ± 0.1 mg

accuracy. Ultrasonic velocities (v) 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 ± 0.01 m/s. The experimentally measured density (ρ) and Ultrasonic velocity (v) are used to evaluate various thermodynamic parameters like compressibility (β_α), molecular free length (L_f), and acoustic impedance (Z) by using following standard relations:

$$\begin{aligned} \beta_\alpha &= 1/v^2 \rho & \text{----- 1} \\ L_f &= K/v \rho^{1/2} & \text{----- 2} \\ Z &= v \rho & \text{----- 3} \end{aligned}$$

Where, K [12] –is Jacobson’s constant $(93.875 + 0.375 T) \times 10^{-8}$ and
T – absolute temperature

Results and Discussion

The measurements were recorded in the Table no. 01 which shows ultrasonic velocity (v) and density (ρ) of the binary mixture along with thermodynamic values such as adiabatic compressibility (β_α), free length (L_f) and impedance (Z) at 298K. It is observed that Ultrasonic velocity (v), density (ρ) and impedance (Z) increases with increase in the mole fraction of NNDMA (NN- Dimethyl Acetamide), in binary mixture.

Table 01. Ultrasonic Velocity and other thermodynamic parameters for Acetonitrile + N-N dimethyl acetamide mixtures at 298⁰ K.

Temp ⁰ K	Mole fraction	Density ρ kgm ⁻³	Velocity V ms ⁻¹	Compre- -ssibility β 10 ⁻¹⁰ m ² N ⁻¹	Free length L _f X 10 ⁻¹¹ m	Impedance Z X 10 ⁶ Kg m ⁻² s ⁻¹
298	0.0000	777.0927	1277.7778	7.8816	5.7728	0.9930
	0.0750	798.9739	1295.5556	7.4568	5.6150	1.0351
	0.1590	815.5309	1315.5556	7.0850	5.4733	1.0728
	0.2540	838.6443	1335.5556	6.6850	5.3165	1.1201
	0.3620	860.5452	1355.6757	6.3229	5.1705	1.1666
	0.4860	878.6307	1375.5556	6.0150	5.0431	1.2086
	0.6300	901.3729	1409.1429	5.5871	4.8604	1.2702
	0.7989	922.1639	1440.9524	5.2227	4.6992	1.3288
	1.0000	935.735	1460.303	5.0114	4.6032	1.3665

Ultrasonic velocity (v) in the mixtures depends on free length (L_f). Decrease of free length (L_f) and increase of impedance (Z) with mole fraction of NNDMA in the mixture indicate existence of molecular interaction between the unlike functional groups. It is also observed that adiabatic compressibility (β_α) decreases in the mixture with increase of NNDMA concentration. And free length (L_f) decreases with the concentration of NNDMA. It has been observed as there is decrease in the free length leads to increase in the ultrasonic velocity and decrease in the compressibility. This indicates that the molecules in the medium are closer with each other.

The decrease in adiabatic compressibility and free length with increase in mole fraction of NNDMA indicates the significant interaction between N-N

dymethyl acetamide and acetonitrile molecules.

Decrease in free length is due to compression of liquid, which indicates that the molecules are coming closer to each other; hence the intermolecular cohesion is stronger leading to strong molecular associations. The graphs between ultrasonic parameters with composition (fig. no. 01 to 05) show the non linear nature indicating intermolecular association between the binary solutions. There is increase in the density of mixture as the mole fraction of NNDMA increases (Fig. no. 02). 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 (Eyring, H., et.al, 1938).

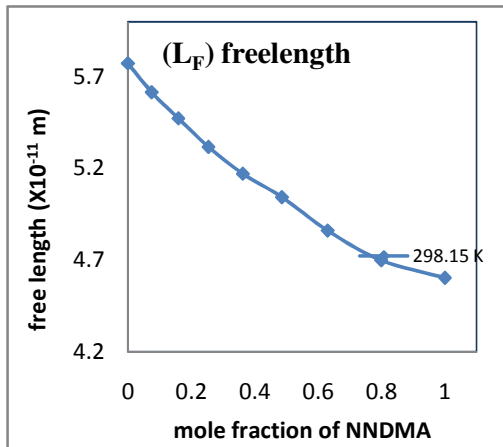


Fig-1- Plot of Free length versus Mole fraction of NNDMA at 298⁰K

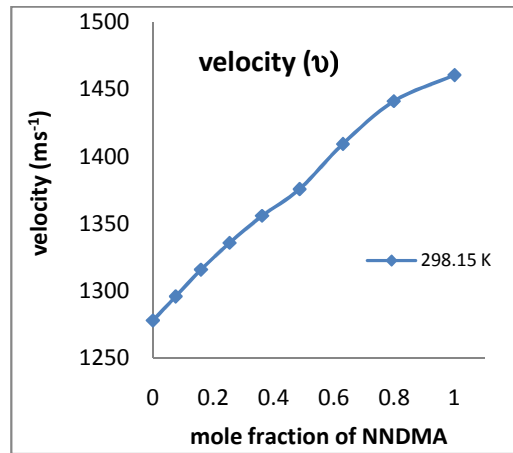


Fig-2- Plot of Ultrasonic Velocity versus Mole fraction of NNDMA at 298⁰K

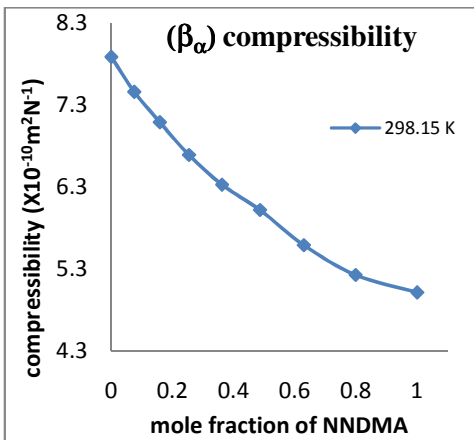


Fig-3- Plot of Adiabatic Compressibility versus Mole fraction of NNDMA at 298⁰K

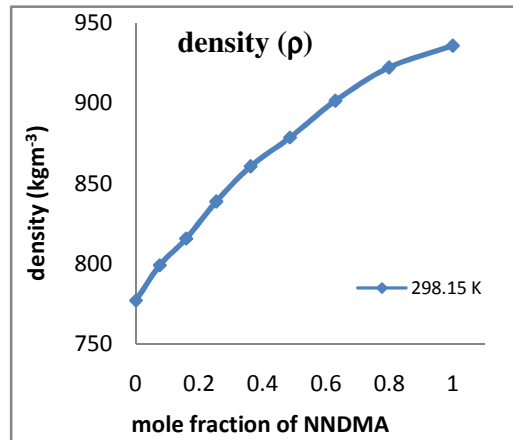


Fig-4- Plot of Density versus Mole fraction of NNDMA at 298⁰K

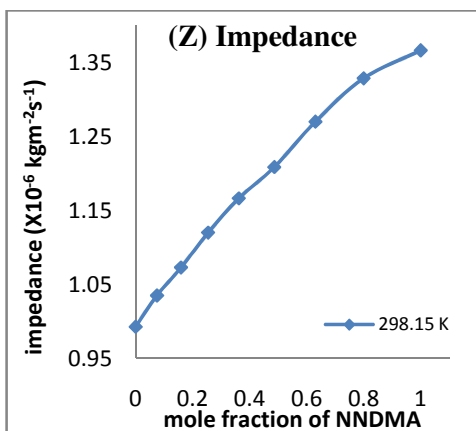


Fig-5- Plot of Impedance versus Mole fraction of NNDMA at 298⁰K

Plot of adiabatic compressibility with concentration of NNDMA shows compressibility decreases as the concentration increases this favors molecular interactions in liquids. The decrease in free length with increase in the concentration (fig. 03) indicates that the

ultrasonic energy propagates through the binary medium slowly and hence free length decreases.

The increase of impedance with increase of concentration (fig. 05) indicates that propagation of ultrasound increases and this is opposite to the free length.

Conclusion

Here Ultrasonic velocity (v) and density (ρ) have been measured for Acetonitrile and N-N dimethyl acetamide mixtures at 298⁰K. All the plots of ultrasonic velocity (v), compressibility (β), molecular free length (L_f) and acoustic impedance (Z) drawn corresponding to the composition are non-linear in nature. This non linear behavior indicates that there is intermolecular association between the components of the mixture. This association is among the functional groups of the polar molecules in the mixture (Glasstone, S., 1947).

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