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ULTRASONIC STUDY OF INTERMOLECULAR ASSOCIATION THROUGH HYDROGEN BONDING IN BINARY LIQUID MIXTURE AT 308K .

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ABSTRACT

Density(ρ) and ultrasonic in the mixture of aqueous solution of Urea have been measured over the entire range of composition at temperature 308.15K. The ultrasonic velocity measurements of binary mixture were carried out at frequency 2MHz. From these experimental values, acoustical parameters such as adiabatic compressibility (β) and specific acoustic impedance (Z) have been calculated and reported. The variations of these properties with composition of solution are discussed in terms of molecular interactions present in the binary mixtures.

KEYWORDS: Density, Ultrasonic velocity, adiabatic compressibility, acoustic impedance, Urea, molecular interaction.

1. INTRODUCTION

Knowledge of thermodynamic and acoustical properties is of great significance in studying the physic-chemical behaviour and molecular interactions in a variety of liquid mixtures [1-3]. Considerable scientific and practical interest has been stimulated by the investigation of organic liquids using ultrasonic measurements [4-5]. Such a type of study has been found to yield information regarding the intermolecular process and the structure of the liquid state [6]. The compositional dependence of thermodynamic properties has proved to be a very useful tool in understanding the nature and extent of pattern of molecular aggregation resulting from intermolecular interaction between components.

Liquids and liquid mixtures are widely used in processing and product formulation in many industrial applications. Thermodynamic properties such as ultrasonic velocity and their variation with temperature and composition of the binary mixture are useful to design engineering processes and in chemical and biological industries. Acoustic parameters also have been used to understand different kinds of association, the molecular packing, molecular motion and various types of intermolecular interactions and their strengths, influenced by the size in pure components and in the mixtures [7].

Literature survey reveals that data on Urea in aqueous solution is scanty. Hence it was found interesting to study the thermodynamic behaviour of urea in aqueous medium. In the present work, the study on aqueous urea interaction has been carried out using thermodynamic parameters. Ultrasonic velocity and density measurement of aqueous solution of urea at various concentrations at 308.15K temperature can be used to compute various thermodynamic parameters. The result obtained from these thermodynamic parameters was interpreted on the basis of molecular interactions.

2. EXPERIMENTAL DETAILS

The urea used was purified AR grade sample in solid state. All chemicals were used without further purification. To prepare binary liquid mixture of urea+water system, the glass distilled water was used.

To prepare urea+water mixture, urea from BDH were used. A standard solution of 10% urea was prepared. To enhance the dissolution, the mixture was kept in warm water bath during preparation. From above standard solution, solutions of concentration 1,2,3,4,5,6,7,8,9 and 10% were prepared by using a matter balance(Switzerland) with a precision of 0.01 mg..

These solutions were kept in special airtight bottles and used within 12 hours after preparation.

The ultrasonic velocity was measured by a single crystal interferometer (F-81, Mittal Enterprise, New Delhi.) operating at frequency of 2 MHz The interferometer was calibrated against the ultrasonic velocity of water used at T=298.15K. The present experimental value is 1497.08 ms-1 which is in good agreement with literature value [8] 1496.69 and accuracy in velocity measurement is +- 10ms-1.

The density measurements were carried out by using specific gravity bottle of 25 ml with an accuracy in measurements is +- 1x10-4 g/cm3. An average of triple measurements was taken into account. During experiment desire temperature was maintained constant by circulating water with the help of thermostatic water bath with accuracy in temperature
+-0.1K.

3. Results and Discussion:

The ultrasonic velocities and densities of binary liquid mixture of urea+water at temperature 308.15K are experimentally evaluated. Thermodynamic parameters such as adiabatic compressibility (β), intermolecular free length (Lf) and acoustic impedance (z) were calculated from empirical Jacobson's relations [9-11] as given below.

$$\beta = 1/u^2\rho \qquad ....(1)$$

$$L_f = K/u\rho^{1/2} \qquad ....(2)$$

$$z = u\rho \qquad ....(3)$$

Where, K is temperature constant, u the ultrasonic velocity, ρ the density of solution. Calculated thermodynamic derived parameters are reported.

Ultrasonic velocity of urea+water has been measured with the help of ultrasonic interferometer at 2 MHz. Study of the variation of ultrasonic velocity of urea at various concentrations at 308.15K temperature in solvent of water shows the variations to be non-linear. This indicates that there is strong interaction in the urea+water systems. Adiabatic compressibility (β) is influenced by the ultrasonic velocity and the density (ρ). The variation of ultrasonic velocity of a system with concentration of urea in water can be expressed in terms of density and adiabatic compressibility by equation (4).

$$du/dc = u/2 \times 1/d \times d\rho/dc + 1/\beta \times d\beta/dc \quad ......(4)$$

The sign and magnitude of quantity dρ/dc and dβ/dc indicate that H-bonded structure of H_2O is disrupted by increasing concentration of urea in water. Consequently, ultrasonic velocity of a system increases depending on the structural properties of solutes [12]. The solute that increase the ultrasonic velocity is of structure maker [13, 14] types.

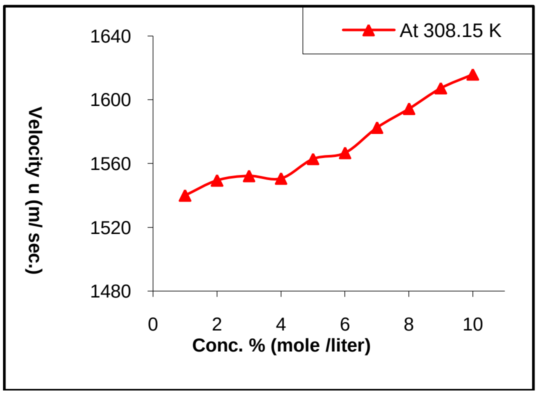

Fig.1 : *Plot of Variation of Ultrasonic Velocity (u) with Conc.at 308K temperaturefor urea + water system*

In urea+water binary system the ultrasonic velocity increases as concentration increases as shown in Fig.1. This is due to maximum possible association in aqueous urea solution because of the presence of OH-groups. The urea occupy the interstitial space of water and tend to break the original ordered state of water due to its self-association [15, 16]

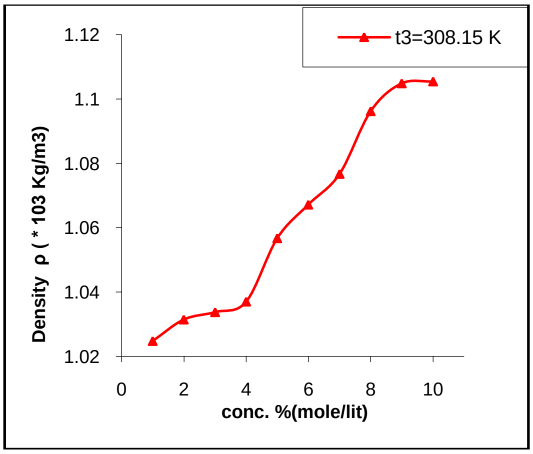

Fig 2: *Plot of Variation of Density (ρ) with Conc. at 308K temperature for urea + water system*

Density of urea+water binary system was determined as a function of concentration at 308.15K temperature as shown in Fig.2. Density is known to be a measure of ion-solvent and solvent-solvent interactions. As expected for given composition density increased with the increase in concentration of urea in binary mixture. With increase in concentration density increases as electrostriction between the ions of particles was increased in binary system. This electrostriction decreases the volume and hence increases the density [17, 18]. This shows that there is dipole-dipole interaction between binary system.

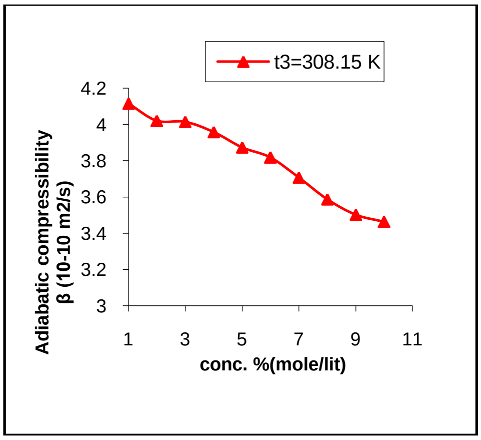

Fig.3 : *Plot of Variation of Adiabatic Comp. (β) with Conc.at 308K temperature for urea + water system.*

In pressent system Adiabatic compressibility (β) decreases with increase in conc. of urea in water, as a result of a large portion of the water molecules in electrostatic and amount of bulk water decreases as shown in above Fig.3. It is well known that solutes causing electrostriction lead to decrease in the compressibility of the solution. Hydrophilic [8,19] solutes show negative compressibility and also, due to ordering that is induced by them in water structure. In the present study dβ/dc is negative which indicates the electrostriction of water molecules.

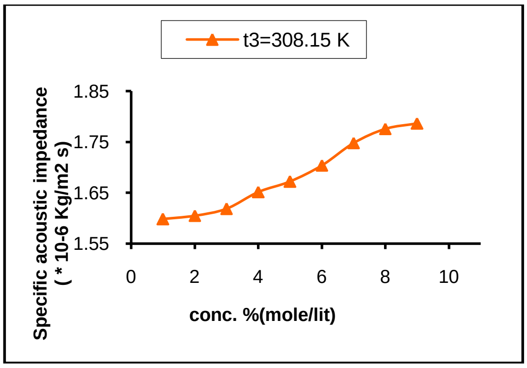

Fig. 4 : *Plot of Variation of Specific acoustic impedance (Z) with Conc.at 308K temperature for urea + water system.*

In binary system it is observed that values of acoustic impedance(z) varies with increase in solute concentration at 308.15K temperature. As shown in Fig.4, the curve exhibits exactly reverse variation compared to adiabatic compressibility (β). Because adiabatic compressibility and acoustic impedance are inversely related to each other[18]. This indicates significant interaction in the system. It also indicates the presence of molecular association between solute-solvent molecules in the binary system.

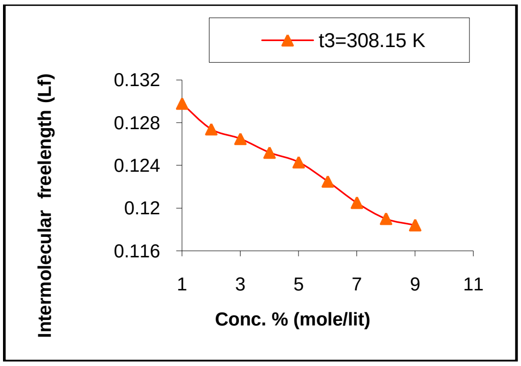

Fig. 5 *: Plot of Variation of Intermolecular free length (Lf) with Conc at 308K temperature. For Urea +Water sytem.*

The variation in ultrasonic velocity depends on the intermolecular free length (L_f) on mixing which is a predominant factor in determining the variation of ultrasonic velocity in the fluids and their solution. It has been observed in the present study that in urea+water binary system intermolecular free length decreases with conc. of solute at 308.15K temperature as shown in Fig.5. This behaviour indicates significant interaction exist between the solute and solvent molecules suggesting structure promoting behavior.

4. CONCLUSIONS

The results of the present study indicate that the thermodynamic parameters are sensitive to the molecular interactions present in the binary mixture. The variation in ultrasonic velocity, density and other related thermodynamic parameters such as adiabatic compressibility, acoustic impedance and intermolecular free length of urea+water binary system at various concentrations and at 308.15K temperature shows the variation to be non-linear. Consequently, values of ultrasonic velocity, compressibility reveal that urea was structure maker and Hydrophilic. The non-linearly confirms presence of solute-solvent, ion-ion, dipole-dipole, ion-solvent interactions. This provides useful information about inter and intera molecular interactions of the mixture as existing in the liquid system.

REFERENCES

[1] Sekar J R & Naidu P R, J. Chem. Eng Data. 41 (1996) 170.
[2] Miyanaga S, Tamura K & Murakami S, J. Chem. Thermodyn.24 (1992) 1077.
[3] Subbaranugaiah R, Murthy N. M. & Subramanyam S. V, Acoustica. 58 (1985) 105.
[4] Kannappan V & Jaya Santhi R, Indian J. Pure & Appl Phys. 44 (2006) 815.
[5] Shukla R. K, Atul Kumar, Kirti Srivastava & Shilpi Yadav, Indian J. Pure & Appl Phys. 45 (2007) 726.
[6] Rendra V., Indian J. Pure & Appl Phys. 34 (1996) 52.
[7] Gokhan Savroglu & Ertunc Aral, Indian Academy of Sciences, 66 (2006) 435.
[8] B.H. Jahagirdar, B.R. Arbad, Smt C. S. Patil & A. G. Shankarwer, Indian J Pure & Appl Phys, 38(2000)645.

[9] A lkhe Shashikant & M. L. Narwade, Indian J Chem, 44A (2005) 1203.
[10] R Palani, S. Sarvanan & A. Geetha, Asian J of Chem, 19 no 7 (2007) 5113
[11] R. Thiyagarajan & L Palaniappan, Indian J Pure & Appl Phys, 46 (2008) 852.
[12] Rita Mehra, Indian J Chem, 44A (2005) 1834.
[13] J.D. Pandey, Sangura Vinay, M.K. Yadav & Aruna Singh, Indian J Chem, 47A (2008) 1020.
[14] Rohini Badarayani & Kumar Anil, J Chem Thermodynamic, 35 (2003) 897.
[15] Singh Gandandeep & T.S. Banipal, Indian J Chemistry, 47 A (2008) 1355.
[16] S. Thirumaran & K. Job Sabu, J Pure & Appl Phys, 47 (2009) 87.
[17] N. somanathan, V. Arumugam*, R. Sanjeevi, N. D. Naresh, V. Sivaramakrishnan and D. Ramaswamy, Indian. Pure & Appl. Phys. 32 (Oct. 1994) 830.
[18] Blokhra & Anupma Nag, Ind. J. Pure & Appl Phys, 29 (1991) 756.
[19] Riyazuddeen & Nurul Islam, J Pure and Appl Ultrason, 19 (1997) 16.