STUDIES ON ACOUSTIC PARAMETERS OF 3-(4-CHLORO 1-HYDROXYNAPTHALENE-2-YL)-5-(FURAN-2-YL),4-5 DIHYDRO PYRAZOLE -1-CARBOTHIOAMIDE IN 70% DIOXANE-WATER MIXTURE AT 301^0K AND FREQUENCY 1 MHz

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Abstract: Ultrasonic velocity and density measurements have been carried out for solution of 3-(4-chloro-1-hydroxynapthalene-2-yl)-5-(furan-2-yl),4-5 dihydro pyrazole-1-carbothioamide (L1) in 70% dioxane-water at 301^0K and frequency 1 MHz. By using this data, various acoustic/thermodynamic parameters viz. adiabatic compressibility, apparent molar compressibility, apparent molar volume, intermolecular free length, relative association and specific acoustic impedance have been determined. Further these properties have been used to interpret weak molecular solute-solvent, solute-solute interactions in the system.

Key words- Pyrazoles, Ultrasonic velocity, 70% Dioxane-Water mixture.

INTRODUCTION

Study of ion association and complex formation have become more significant and easy due to the ultrasonic velocity and adsorption studies in case of electrolyte solution[1,2]. Sondawale and Narwade[3] have provided useful information about the ultrasonic velocity of peptide in binary mixture. Rohankar[4] has studied the ultrasonic velocity of mono-chloro acetic acid and tri-chloro acetic acid in tetrahydrofuron (THF) and dioxane-water mixture. Agrawal[5-6] investigated ultrasonic velocity of substituted acrylophenones and its complexes in acetone and substituted thiadiazoles and carboxylate at different liquid mixture. Ikhe and Narwade[7] have investigated ultrasonic velocities and densities of isoxazole and pyrazole at 303^0 K.

Salvation number of ions can be determined by using data of adiabatic compressibilities. For this the wavelength of ultrasonic velocities in solvents and solutions had been evaluated. Salvation numbers are calculated from these velocities, densities of solutions and adiabatic compressibilities. Pasynski[8] concluded from adiabatic compressibility studies of aqueous electrolytic solution that, introduction of ions makes the structure of water more highly coordinated and compacted. Adiabatic compressibility of gelatin solution[9] and aqueous solution of sugar[10] and dicarboxylic and hydroxy carboxylic acids were determined. Asal[11] have reported ultrasonic velocities of hydration and dehydration of polyelectrolyte solutions.

Apparent molar volume and adiabatic molar compressibilities of some amino acids in aqueous medium have been determined by Milerio[12] and coworkers. Hydration numbers were evaluated using partial molar volume and adiabatic compressibility data. In this filed significant research have been carried out because of its vast applicability, which can be judged from recent publications[13-18]. Compressibility and apparent molar volumes of many electrolytes in mixed organic solvents were found out earlier[19-22]. But, the compressibility and apparent molar volumes and other acoustic properties of 0.1 M concentration of 3-(4-chloro-1-hydroxynapthalene-2-yl)-5-(furan-2-yl),4-5 dihydro pyrazole-1-carbothioamide (L1) in water-dioxane solvent mixture are not studied so far. Therefore, the present work was planned to make systematic study of compressibilites and apparent molar volumes of 3-(4-chloro-1-hydroxynapthalene-2-yl)-5-(furan-2-yl),4-5 dihydro pyrazole-1-carbothioamide (L1) at different percentage and also at different concentrations of the same in 70% dioxane-water mixture.

Experimental:

Materials and Methods:

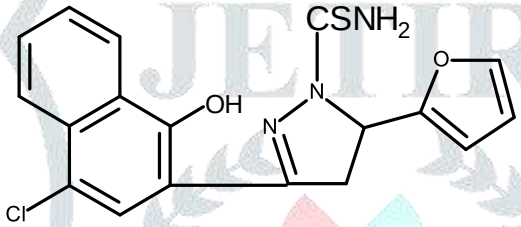
All weighing were carried out on SHIMADZU AUY-220 of accuracy ± 0.1 mg balance.

Ultrasonic interferometer from Mittal Enterprises, Model MX-3 with accuracy of ± 0.03% and frequency 1 MHz was used for the measurement of ultrasonic velocities of different solutions.

A special thermostatic arrangement was made during the study. Elite thermostatic water bath was used and temperature variation was maintained within ± 0.1°C.

Result and Discussion:

Adiabatic compressibility (β), apparent molar volume (ϕv), apparent molar compressibility (ϕk), intermolecular free length (L_f), relative association (R_A), specific acoustic impedance (Z) and partial molar volume properties directly interact and reflects the structural interaction of solvent (water/organic solvent) with solute and give significant and useful information about internal structure, molecular association, complex formation, internal pressure and stability of complexes. Weak molecular interactions can also be studied by this technique. The study of density of solutions at different concentrations is very much significant because it helps to calculate the properties like apparent molar volume ϕv and apparent molal expansibility. The Structure of 3-(4-chloro-1-hydroxynapthalene-2-yl)-5-(furan-2-yl),4-5 dihydro pyrazole-1-carbothioamide (L1), is given below.



3-(4-chloro-1-hydroxynapthalene-2-yl)-5-(furan-2-yl), 4-5 dihydro pyrazole -1-carbothioamide (L_1)

Adiabatic compressibility (β):

Velocity of propagation of mechanical disturbances had to be considered a basic property of liquids in a molecular kinetic theory. A number of theoretical equations relating the ultrasonic velocity and other molecular properties have been established.

By measuring ultrasonic velocity (v) and density (d) experimentally, the adiabatic compressibility (β) can be determined by using Laplace's equation.

$$\beta = 1/v^2.d$$

Apparent molar compressibility (ϕk):

Apparent molar compressibility (ϕk) is one of important acoustic property which can be determined by measuring density and ultrasonic velocity and depends upon the molality of solution and molecular weight of the solute, by the relation,

$$\phi k = [1000(\beta s\ do - \beta o\ ds)/m\ ds\ do] + ([\beta s\ M/ds)$$

Apparent molar volume (ϕv):

Apparent molar volume did not depend upon ultrasonic velocity but depends upon densities of solution and solvent, molecular weight of solute (M) and molality of solution (m). It can be determined by the relation,

$$\phi v = [1000(do - ds)/m\ ds\ do] + (M/ds).$$

Intermolecular free length (L_f):

Intermolecular free length (L_f) created its own identity in acoustic properties for studying the intermolecular interactions. Hildebrands[23] showed that the center of attraction does not coincide with geometrical center of molecule of liquid as the distance between the centers of attraction is a property extremely difficult to define. The distance between the surfaces of molecules, on the other hand has a clear physical significance so it is used in defining free length. Intermolecular free length can be determined from adiabatic compressibility (β) by Jacobson's formula,

$$Lf = K.\beta s^{1/2}$$

Relative association (R_A):

Relative association is a function of ultrasonic velocity and can be obtained by the equation,

$$R_A = ds/do\ (V_O/V_S)^{1/3}$$

Where, V_O and V_S are ultrasonic velocities in solvent and solution.

Specific acoustic impedance (Z):

Specific acoustic impedance can be obtained from the measurement of ultrasonic velocity and density by formula,

$$Z = v_S.d_S$$

The solute-solvent interactions may be interpreted in terms of acoustic impedance.

Conclusion

It is observed that the apparent molar volumes (ϕv) decreases with decrease in concentration of solute; intermolecular free length (L_f) increases on decreasing the concentration of solute hence decrease in ultrasonic velocity with the concentration. This indicates that there is a weak interaction between ion and solvent molecules, which suggests non-promoting behavior of the added solute. The increase of βs with the decrease in concentration may be due to the departure of solvent molecules around the ions due to weak ion- solvent interactions. The increase of RA with concentration suggests that salvation of ions is preferred over the breaking up of the solvent aggregate on addition of solutes. Acoustic impedance (Z) increases with increase in concentration. It is concluded that the molecular interactions are present between the solute and solvent mixture and solute-solvent interactions are more favorable than other interactions shows in Table-I and Fig-I to Fig-IV.

Table-I

Conc. M	√C	Us (m sec^{-1})	ds (Kg m^{-3})	βs x 10^{-10} (Pa-1)	ϕv (m^3mol^{-1})	ϕk x 10^{-10} (m^3mol^{-1} Pa^{-1})	Lf (A^0)	RA	Z x 106 (Kg m^{-2} sec-1)
0.1	0.299	1425.5	1002.2	4.171	0.0463	-2.5524	0.01201	1.0021	1.5210
0.08	0.264	1423.1	1002.1	4.186	0.0315	-3.1252	0.01203	1.0026	1.5184
0.06	0.239	1416.5	1001.5	4.225	0.0153	-3.6276	0.01210	1.0034	1.5109
0.04	0.188	1405.1	1000.1	4.299	0.0029	-3.7178	0.01221	1.0046	1.5073
0.02	0.128	1400.1	1000.0	4.328	-0.0927	-6.3796	0.01225	1.0055	1.5020

Acoustic parameters at different concentration of ligand (L1) in 70% Dioxane-water.

Temp. = 28±0.1°C Ultrasonic Frequency = 1 MHz

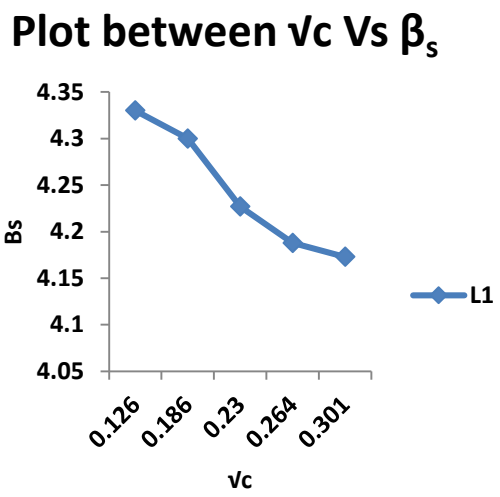


Figure 1

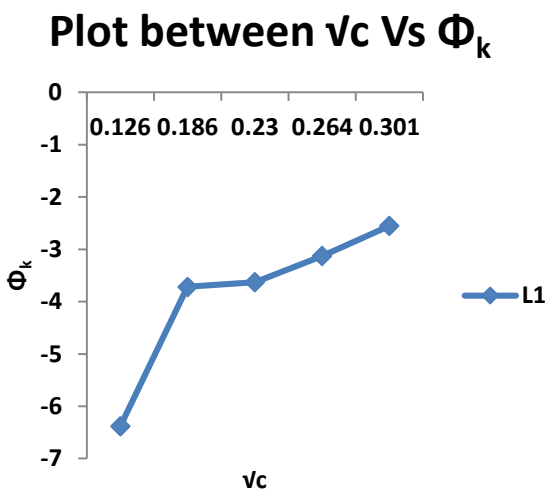


Figure 2

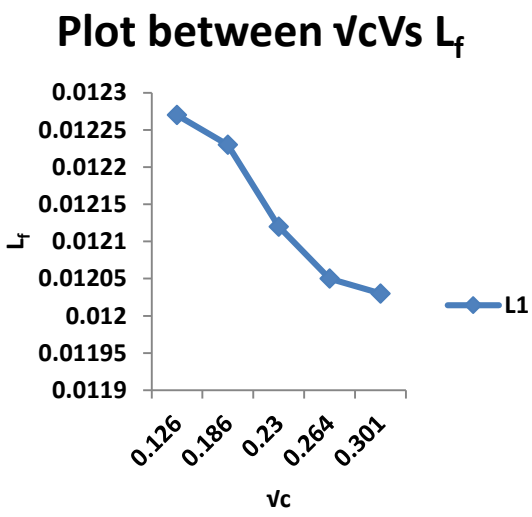


Figure 3

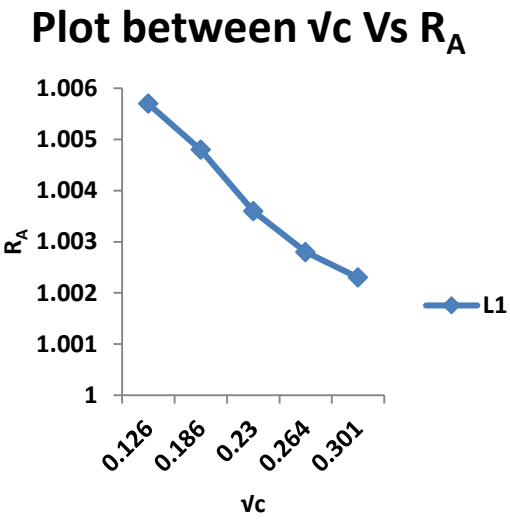


Figure 4

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