FTIR Spectral Analysis & Physico-Chemical Studies on Some L. Arginine Salts in Non-Aqueous Solution at Various Temperatures

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Abstract: The ultrasonic velocity measurement of liquid plays an important role in the study of molecular systems. The present work deals with the molecular interaction studies on some amino acids in non-aqueous solutions at various temperatures. From the measured parameters such as velocity, density, viscosity and some derived parameters like internal pressure, free volume, Rao’s constant and Wada’s constant are calculated. The structural changes occurring in the solution are envisaged through the FTIR study of L-Arginine derivatives in polar solvent. From the study the existence of interactions are confirmed and the diagnostic bonds observed at certain frequencies are assigned to the carbonyl stretch present is identified.

Keywords: Internal pressure, Free volume, Molecular interactions, FTIR Spectral analysis

1. Introduction

Ultrasonic velocity and its related properties have been extensively used to study physico-chemical behavior and molecular interaction occurring in the solutions. The internal pressure of a solution is a single factor which appears to vary due to all the internal interactions like solvation, ion-solvent interactions, quantum mechanical forces of dispersion and dielectric constant effect [1]. The present study involves the analysis of amino acid derivatives in non-aqueous medium, formamide. Acoustic, thermodynamic parameters have been studied from very low temperature to high temperature at different molalities. The ultrasonic velocity data combined with density and viscosity provide the standard means for determining the internal pressure, free volume, acoustic parameters such as Rao’s constant, Wada’s constant and van der Waals constant. Arginine is found in a wide variety of food sources such as whole-wheat, nuts, seeds, peanuts, brown rice, popcorn, soya, raisins, chocolate, almonds, and oatmeal [2]. L-Arginine mono hydrochloride is commonly used in cell culture media and drug development [3]. L-Arginine methyl ester di hydrochloride increases nitric oxide (NO) production and it also acts as a vasodilator, allowing more blood to flow in muscle tissues, thereby increasing the pump from oxygen and nutrients and delivered where they are needed [4].

2. Experimental Details

Experimental Technique

Solutions of the sample of different concentrations are prepared with AR grade salt. It is used without further purification. The solution is studied at different concentrations (0.001, 0.01, 0.05, 0.1, 0.2) mol. d.m$^{-3}$ with an accuracy of 0.0001gm is maintained. The density of the solutions is determined using 25ml specific gravity bottle, using the thermostatic bath with a compressor unit. A Cannon Fenske viscometer (10ml) was used for the viscosity measurements. Variable bath interferometer having a frequency of 2MHz (Mittal Enterprises, New Delhi) with overall accuracy of 0.1% was used for velocity measurements. With the high purity (99%) the samples are purchased from siscom research laboratories, Mumbai. The samples are measured using an electronic balance precise to 0.0001gm. Ultrasonic velocity ($u$) is measured with a variable path interferometer (2MHZ) with an accuracy of ±2m/s. The density ($\rho$) measurement is made with an accuracy of ±0.001gm. FTIR spectrum of these solution were recorded in the region of 4000 – 400 cm$^{-1}$ using (PERKIN ELMER) model SPECTRUM RXI FTIR spectrometer.

The following formulae are used for the computation of Internal Pressure ($\pi$), Free Volume ($V_f$), Rao’s constant and Wada’s constant:

- Internal pressure $\pi_i = bRT \left(\frac{k\eta}{u}\right) \left(\frac{1}{2}\right) \left(\rho \frac{v}{M_{eff}}\right)^2$ atmos.
- Free volume $V_f = \left[M_{eff} \times u / k \eta^2\right] \text{cc}$
- Rao’s constant $R = \left(\frac{M_{eff} (U)^\frac{1}{3}}{\rho}\right)$
- Wada’s constant $W = \left(\frac{M_{eff}}{(\rho) \beta^\frac{1}{2}}\right)$

Where,
- $M_{eff}$ - Effective molecular weight of the solution in gm.u.
- $u$ - Ultrasonic velocity in cm/sec.
- $K$ - Constant equal to 4.285 x 10$^{9}$
- $\eta$ - Viscosity of the solution in poise
- $R$ - Gas constant (8.314 x 10$^{7}$)
- $T$ - Temperature
- B - Cubic constant (2)

Paper ID: NOV161952

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Volume 5 Issue 3, March 2016
\[ \rho \text{- Density of the solution is gm/cc.} \]

### 3. Results and Discussions

In the present work, the internal pressure and free volume shows an increasing trend with respect to molalities. This increasing trend in internal pressure indicates the orientation of the solvent molecules around the L-Arginine ions, which may be due to the influence of electrostatic field of ions. This behavior suggests that the presence of strong ion-solvent interaction occurs in the solution [5]. The binding of the NH\(_3^+\) group of solute into the solvent molecules introduces the greater cohesion by the electrostatic forces in the solution. Thus, the electrostriction effect brings about the shrinkage in the volume of the solvent caused by the Zwitterionic portion of the L-Arginine solution [6]. There is a dip observed at 0.05 m at all temperature in L-Arginine mono hydrochloride solution. Hence there is a reduction in internal pressure with increase in temperature L-Arginine mono hydro chloride exists in ionic form and it is solvated both at NH\(_3^+\) site of guanidino group and COO\(^-\)sites of solute in which the existence of Zwitterionic form to a greater extent. These results support that there is a weak ion-solvent interaction within the solution [7]. However in L-Arginine methyl ester di hydrochloride internal pressure is to be increasing with respect to increasing molality. But at 278.15k and at 0.05 molality it is observed as minimum. This decrease in internal pressure shows that there is a weak solute - solvent interaction prevails in the solution which is shown in Tables 1.1-1.3 and Figure 1.(i)-1.(iii). It is also confirmed by increasing values of free volume given in tables 2.1-2.3 and figures 2.(i)-2.(iii) at low molalities and at low temperature [8].

**Rao’s and Wada’s Constant** In L-Arginine the solvent shows that there may be association taking place between the molecules in the solution [9]. This behavior is exhibited by Rao’s and Wada’s constant (Tables 3.1-3.3 and Figures3.(i)-3.(iii) for the same system. The irregular behavior of Rao’s and Wada’s constants of L-Arginine mono hydrochloride system also supports that there is a molecular dissociation existing in the solution. In L-Arginine Methyl Ester di hydrochloride, Rao’s and Wada’s constants are increasing with increasing concentration and also with temperature. At 308.15k there is a dip observed at 0.01 molality. Though there is a curvilinear variation of these constant at 308.15k the noticeable deviation indicates the weakening the structure of the solvent [10]. This indicates that the structure breaking nature of the solute in the solvent [11]. These values are tabulated in the shown in tables 4.1-4.3 and Figure 4.(i)-4.(iii). Thus, the acoustical parameters, explains the nature and strength of the molecular interaction in the solution[12].

In the FT-IR spectra of formamide and for the samples, the presence of various vibrational frequencies have been identified and analyzed based on shifts in frequencies. L-Arginine, can exist in two forms i.e., charge solvated (CS) and salt bridge (SB) as in (Figure 6.1 and 6.2). These FT-IR spectral results of L-Arginine with formamide indicate the formation of H-bands between NH\(_2\) group of formamide and guanidino group of L-Arginine. The Zwitterionic form of L-Arginine is solvated by both enolic form (monomer) and dimeric forms of formamide. The amino acid exists in both neutral and Zwitterionic forms [13].

In L-Arginine mono HCL system the shifts are small compared to L-Arginine. Hence solvation is of weak type [13]. This indicates the existence of enolic (neutral) form and amide form. Thus solvation is through weak H-bonding results in neutral form (Fig. 6.3). This may be due to dipole-dipole interaction [14].

In the L-Arginine methyl ester di hydrochloride sample there is no acidic COOH proton but it has an O-CH\(_3\) group in the place of O-H. Therefore it has a free C=O group and not having COO\(^-\) group compared to L-Arginine and exist in neutral form (figure 6.4) [15].
A new peak arrived at 2405 cm\(^{-1}\) indicates solvation at this site by formamide, resulting in the structure (Figure 6.5) for the charge solvated

![Figure 6.5: Charge solvated form of L-Arginine methyl ester di hydrochloride](image)

The dilution studies thus indicate the appearance of new peaks at 2405 cm\(^{-1}\) and disappearance of 1442 cm\(^{-1}\) peak (C-N Stretch & NH bending). These changes can be accounted by considering solvation only at guanidino group. The broadening of NH\textsubscript{2} stretching vibration of the solvent indicates binding of the amino acid ester to the NH\textsubscript{2} group of formamide [16]. It exists as mirror image form at chiral center (CH COO CH\textsubscript{3}) [17] depicted in (Figs.6.6a and 6.6b) as inferred from the FT-IR spectrum Figure 5.1- 5.7.

![Figure 6.6a](image)

![Figure 6.6b: Mirror images of L-Arginine methyl ester di hydrochloride](image)

4. Conclusion

The thermodynamic and acoustic studies confirm the hydrophilic interactions occurring between the Zwitterionic center of L-Arginine and Carboxyl group of formamide. These results support that there is a weak ion-solvent interaction within the solution. The behavior in internal pressure suggests that the intermolecular hydrogen bonding exists in the amino acid moiety [18]. These result shows weak-solute-solvent interactions prevail in the solution. The Zwitterionic form of L-Arginine is solvated by both enolic form (monomer) and dimeric forms of formamide.

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