



Study of vibrational spectra and solvation number of non-Aqueous solutions of L. Arginine through ultrasonic technique

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ABSTRACT

The study of liquid properties using spectroscopy and acoustic methods In the present investigation, non-aqueous solutions of constitutes mining field for scientists. L. Arginine are studied. FTIR spectra have been taken for the sample solutions. The observed vibrational spectra are analysed. Ultrasonic velocity and density are measured for different temperatures(278.15K to 328.15K) and at various molalities. Using the above measurements, adiabatic compressibility solvation number, apparent molal compressibility, apparent molal volume and equivalent conductivity are computed. From the computed results structural influence of the salt in the solvent is studied. The results obtained from spectroscopic study are corroborated with the acoustic behavior of the solutions.

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Introduction

Ultrasonic velocity is a unique technique for the characterization of structure and properties of liquids and solution [1]. The measurement of speed and of sound in liquids plays a significant role in explaining their physico-chemical behavior and structure of liquids[2,3]. The investigation of volumetric and thermodynamic properties of amino acids and peptides in solvents has been the area of interest of number of researchers.

Amino acids differ only in the nature of the R-groups. Amino acids with non-polar substituent are said to be hydrophobic (water hating). Amino acids with polar R-groups that form hydrogen bonds with water are classified as hydrophilic (water loving)[4]. The remaining amino acid has substituent that carries either negative or positive charges in solutions are neutral pH and are therefore strongly hydrophilic [5, 6].

Most of the research works on amino acids has been carried out in dilute electrolytic solutions and various studies have been studied the interaction between some amino acids and simple salts [7,8] but no report has been found in the presence of non-aqueous solution hence an attempt is made to understand the physicochemical properties of L-Arginine and its derivatives in non-aqueous solution at different temperatures, through ultrasonic velocity measurements.

Due to physiological conditions the two terminals of amino acids are changed both positive charge (amino group NH_3^+) and negative charge of carboxyl group, (COO^-), therefore the molecules has the property of 'Zwitterion' [9,10].

Zwitterionic forms of amino acids can be preferentially stabilized by increased proton affinity. Thus Arginine has a relatively high proton affinity due to its guamidino side chain[11].

L-Arginine is an essential amino acid that has been nearly researched for the past thirty years. This powerful amino acid helps to synthesize nitric oxide, which plays a critical role in blood circulations throughout the body[12,13].

Experimental Technique

L-Arginine solutions of different concentration is prepared with AR grade salt. It is used without further purification. The sample 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) is used for the viscosity measurements. Variable bath interferometer having a frequency of 2MHz (Mittal Enterprises, New Delhi) with overall accuracy of 0.1% is used for velocity measurements.

The fundamental parameters such as density, viscosity and ultrasonic velocity are measured for different molalities in the temperature range of 278.15K to 328.15K.

The FTIR spectrum of this solution is recorded in the region of 4000-400 cm^{-1} using (PERKIN ELMER) model SPECTRUM RXI FTIR spectrometer.

Theories and Calculation

Adiabatic compressibility (β) is given by

$$\beta = \left[\frac{1}{u^2 \rho} \right] C m^2 / \text{dyne}.$$

Where u is ultrasonic velocity in cm/sec.,

ρ - density of the solution in gm/cc.

Solvation Number

$$\eta_h = \left(\frac{n_s}{n_i} \right) \left[1 - \frac{\beta}{\beta_0} \right]$$

η_h - Primary Solvation Number

n_i - Moles of Ions

n_s - Moles of Solvent

β - Adiabatic compressibility of solution

β_0 - Adiabatic compressibility of solvent

Apparent Molal Volume

$$\varphi_v = \frac{1000}{c_1 \rho_0} (\rho_0 - \rho) + \frac{M_1}{\rho_0} \frac{ml}{m_o l}$$

C_1 - molal concentration

M_1 - molecular weight of the solute

ρ - density of the solution

ρ_0 - density of the solvent

Apparent molal compressibility (ψ_k) is calculated by

$$\psi_k = \frac{1000}{m\rho_0}(\rho_0\beta - \rho\beta_0) + \left[\frac{\beta_0 M}{\rho_0} \right]$$

Where ρ_0 is the density of the solvent, β_0 is the molal concentration and ' M_1 ' is the molecular weight of the solute.

ρ_0 , - Density of the Solvent

β_0 - Compressibility of the Solvent

ρ - Density of the Solution

β - Compressibility of the Solution

M - Molecular Mass of the Solute

m - Molecular concentration of the Solute

Equivalent Conductance:

$$\Lambda_c = \frac{K \times 1000}{N} \text{ mho.cm}^2$$

K - Specific Conductance in mho observed from conductivity molar)

N - Normality of the solution

Results and Discussion

Adiabatic Compressibility

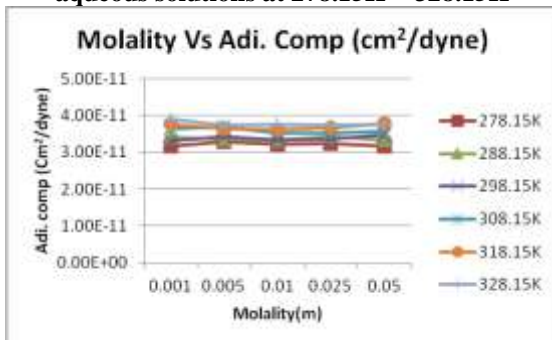
The adiabatic compressibility is the fractional decrease of volume per unit increase of pressure, when no heat flows in or out. The decrease of compressibility implies that there are enhanced molecular association in these system which increases in the solute context, as the new exhibits which is due to molecular association become compact and less compressible[14].

The orientation of solvent molecules around the solute is determined by adiabatic compressibility[15]. Elastic deformation is propagated by acoustic waves. The longitudinal waves are generated by isotropic pressure, causing a uniform compression and thus a deformation in the direction of propagation[16].

The primary effect of dissolving a solute is to lower the compressibility of the solvent[17]. The lowering is attributed to the influence of the electrostatic field of the ions on the surrounding solvent molecules.

In the L-Arginine solution, the variation of β shows Table 1 and Fig.1 that there may be association taking place between the molecules in the solution.

Figure 1: Variations of adiabatic compressibility (cm²/dyne) with molality of L-Arginine mono hydrochloride in non-aqueous solutions at 278.15K - 328.15K



This variations represents the existence of strong ionic bonding between the solvent and solute molecules due to the Zwitterions as a result of electrostatic forces[18].

Apparent molal volume:

The concentration dependence of the apparent molal volumes of electrolytes can be used to study ion-ion interaction. Faure and

Valson [19] assumed that the change in volume on adding a salt to solvent was the resultant of two opposing effects.

1. Contraction in volume due to the absorption of solvent on the dissolved salt.
2. The ability of the solute to cause electrostriction.

Electrostriction is a volume reducing process, which involves polarisation and attraction of solvent molecules around the ionic species.

Figure 2: Variations of Apparent molal volume(ml/mol) with molality of L-Arginine mono hydrochloride in non-aqueous solutions at 278.15K - 328.15K.

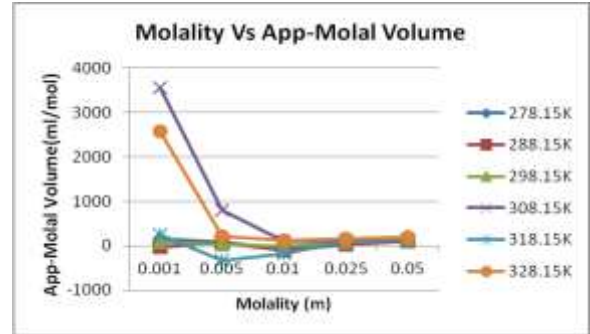
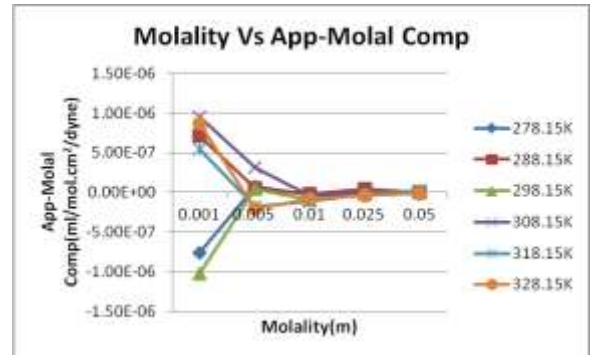


Figure 3: Variations of Apparent molal compressibility(ml/mol.cm²/dyne) with molality of L-Arginine mono hydrochloride in non-aqueous solutions at 278.15K - 328.15K



In the present study of L-Arginine solutions, it is found that apparent molal volume shows noticeable changes at low concentrations. The positive values are noted for higher temperatures except at 278.15K. The negative values are observed for 278.15K and 278.15K only at lower concentration in table 2 and figure 3.

The decrease in ϕ_v upto 0.01m takes place at all temperatures reveals the strong ion-ion interaction occurring in L-Arginine solution.

Apparent molal compressibility:

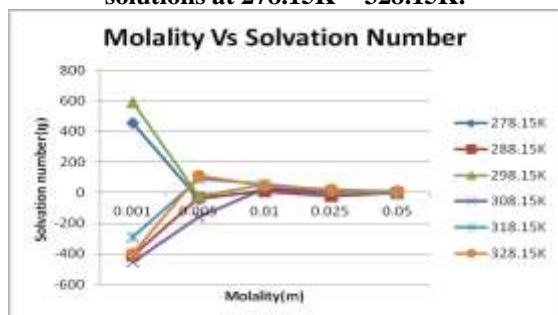
Apparent molal compressibility of an amount of solution containing one mole of the solute minus compressibility of the solvent. The increase in apparent molal compressibility may be attributed to the fact that the charge density of the ions remains practically constant, inspite of the change in ionic size and relative surface area[20]. As the concentration of the solution increases and larger portion of the solvent molecules are electrostricted, the amount of bulk solvent decreases causing the apparent molal compressibility decrease[21].

The apparent molal compressibility values of L-Arginine shows the positive values at 278.15K except 0.01m whereas negative values are observed for other temperatures are shown in table 2 and figure 4. The increasing values of ϕ_k of L-Arginine solutions reveals the strengthening of ion-solvent interaction in the solution.

The apparent molal compressibility values of L-Arginine shows (Table 2 and Fig 4) the positive values at 288.15K except 0.01m, whereas negative values are observed for other temperature[22]. The increasing values of ϕ_k of the solution reveals the strengthening of ion-solvent interaction.

The negative values of ϕ_v and ϕ_k indicate the ionic and hydrophilic interactions occurring in the L-Arginine solution.

Figure 4: Variations of Solvation Number(η) with molality of L-Arginine mono hydrochloride in non-aqueous solutions at 278.15K - 328.15K.



Solvation Number

Solvation is the attraction and association of molecules of the solvent with molecules or ion of the solute. The solvation approach is used to interpret ion-solvent interaction. Negative solvation number with molality is reported by researchers[23]. With the increase in concentration, the solvation number decreases if there is not enough solvent for all ions or if ion-pairing occurs[24]. In low molality solutions there is a basic structural change in the first co-ordinations spheres occurred in a set in relation to their solvation energies[25]. The solvation number of an ion depends on the solvent.

Potential energy of the ion and solvent molecule will be higher than that of kinetic energy of the ion molecules at low temperatures. Positive solvation number of solutions suggests that compressibility of the solution at high temperature and at low molalities will be less than that of the solvent.

The solvation number can be defined as number of solvent molecules per ion, which remains attached to a given ion, long enough to experience its translational movement when solution is formed[26].

Negative values of solvation number emphasize the solutions are more compressible than the solvent. Many authors in literature report the negative solvation number [27].

Zero value of solvation number only indicates that no change occurs in the compressibility of the solvent when the solution is formed[28].

Positive solvation number of solutions suggests that compressibility of the solution at high temperature and at all molalities will be less than that of the solvent.

The compressibility measurements are used for computing the solvation number for the systems studied. It is observed that for L-Arginine solutions exhibits positive solvation number for the temperatures 278.15K, 278.15K and 278.15K almost for all molalities. But, around the room temperature it shows negative solvation number with respect to temperature not for all molalities table 1 and figure 4.

The negative values of ϕ_v and ϕ_k prevails the ionic and hydrophilic interaction occurring in the L-Arginine solution.

Equivalent Conductivity: The equivalent conductivity of L-Arginine solution in non-aqueous solution for different molalities and at different temperature are measured. The Λ_c is found to be high at low concentration Table 2 and Fig 5 with

increase in concentration and temperature. The Λ_c decreases almost as an exponential curve. The variation of equivalent conductance is found to be very small, at higher concentrations[29].

Figure 5: Variations of Equivalent Conductivity($\text{cm}^2\cdot\text{mho}$) with molality of L-Arginine mono hydrochloride in non-aqueous solutions at 278.15K - 328.15K.

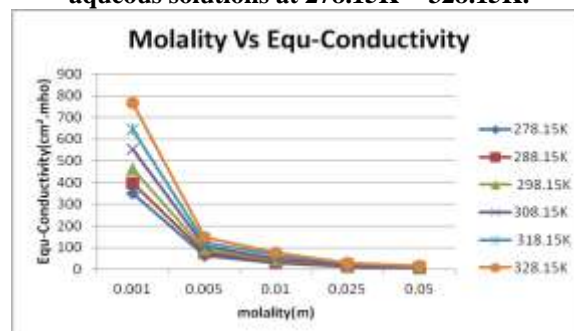


Figure 6: FTIR Spectrum of solvent

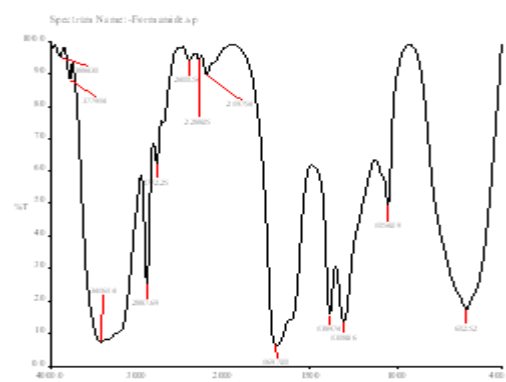


Figure 7: FTIR Spectrum of solute+solvent

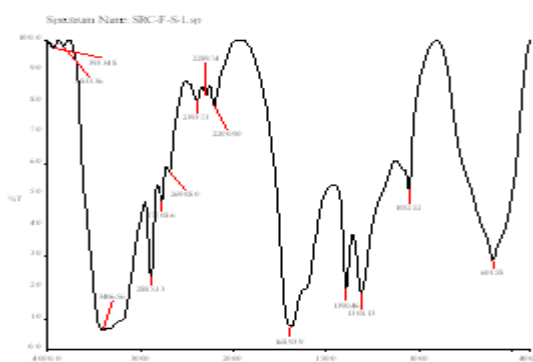


Figure 8: L-Arginine Neutral Enolic form

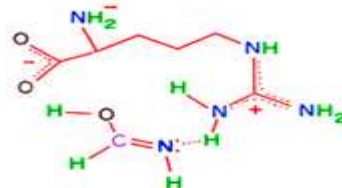


Figure 9: L-Arginine Neutral Amido form



L-Arginine can exist in zwitterionic and non-zwitterionic form depending on the polarity of the solvent. Non-aqueous solution is being a highly polar solvent promotes zwitterionic structure[30]. This is confirmed by the FTIR spectral results, which are shown in Table – 3, Figure – 6 and Figure - 7. The entry of L-Arginine molecule into the solvent molecule results in a shift of the NH₂ stretching vibration. And also there is a shift of 90cm⁻¹ for the enolic form of solvent. The binding vibrations of L-Arginine NH₂ group resulted a shift by 30cm⁻¹. L-Arginine also exists in L-Arginine neutral enolic form Figure – 8 and L-Arginine neutral amido form Figure –10. These significant spectral changes indicate strong solute- solvent binding interactions[31].

Conclusion

The acoustic study of L-Arginine confirms that there is an association takes place between the molecules which is due to Zwitterions.

The solvation number, analysis exhibits the effect of solvation is high. The thermo chemical parameters such as apparent molal volume and apparent molal compressibility values suggest the nature of interaction in L-Arginine solution is hydrophilic.

The electrochemical analysis reveals in concentrated solutions of L-Arginine, in the ionic atmosphere appreciably reduces the velocity of the ions and hence the equivalent conductivity.

The FTIR spectra provide clear spectroscopic evidences for the presence of charge solvated condition of L-Arginine. L-Arginine is existing in Zwitterionic form in non-aqueous solution. The significant spectral changes indicate strong solute solvent interaction.

The results obtained from FTIR analysis are found to be in good agreement with the acoustic studies.

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Table 1: Values of Adiabatic compressibility (β cm²/dyne) and solvation number (η)

Molality(m)	278.15K	288.15K	298.15K	308.15K	318.15K	328.15K
0.001	3.18109E-11	3.404E-11	3.32E-11	3.637E-11	3.758E-11	3.89858E-11
0.005	3.27905E-11	3.365E-11	3.43E-11	3.692E-11	3.634E-11	3.73254E-11
0.01	3.22146E-11	3.33E-11	3.33E-11	3.52E-11	3.614E-11	3.74995E-11
0.025	3.24749E-11	3.425E-11	3.37E-11	3.533E-11	3.657E-11	3.73213E-11
0.05	3.16351E-11	3.341E-11	3.47E-11	3.579E-11	3.79E-11	3.75867E-11
Solvation Number (η)						
0.001	455.04	-412.73	591.47	-451.79	-287.92	-397.27
0.005	-41.94	-31.64	-23.36	-159.29	89.83	111.68
0.01	18.11	7.39	51.49	27.18	56.52	45.82
0.025	0.18	-22.18	12.22	7.63	12.27	22.43
0.05	11.49	0.03	-7.35	-1.89	-9.66	8.16

Table 2: Values of L-Arginine Apparent molal volume (ϕ_v), Apparent molal Compressibility (ϕ_k) and Equivalent Conductivity (cm² mho)

	Molality (m)	Temperature in Kelvin					
		278.15K	288.15K	298.15K	308.15K	318.15K	328.15K
ϕ_v (ml/mol)	0.001	159.02	-34.87	89.43	3548.04	249.59	2571.33
	0.005	80.85	63.12	32.48	799.17	-325.31	204.78
	0.01	-67.55	-104.33	-4.51	92.95	-174.59	126.21
	0.025	53.24	34.27	82.87	127.57	102.49	162.03
	0.05	102.35	91.69	132.69	135.48	128.88	203.05
	ϕ_k (ml/mol. cm ² /dyne) X 10 ⁹	0.001	-762.56	710.50	-1030.00	948.50	548.90
0.005		73.40	56.69	42.00	318.50	-180.00	-207.15
0.01		-32.74	-16.20	-90.30	-46.00	-112.00	-83.41
0.025		1.43	39.45	-18.60	-9.35	-19.30	-37.12
0.05		-16.18	3.00	17.50	8.29	23.02	-8.08
cm ² (mho)		0.001	351.0668454	397.25985	461.9301	554.31607	646.70208
	0.005	64.67020608	77.604247	90.53829	107.16777	125.64497	147.8176139
	0.01	27.71580236	33.258963	41.5737	50.812304	67.441786	76.68038653
	0.025	11.08632089	13.673129	17.36857	19.955378	26.60717	29.56352236
	0.05	5.912704462	7.2061086	8.869057	10.162461	13.118813	14.59698914

Table – 3: Signature Peaks of Solvent and L.Arginine Solution

Name of the samples	ν_{NH}	ν_{CH}	$\nu_{\text{C-N}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	$\delta_{\text{C=N}}$	$\nu_{\text{C-O}}$	δ_{CH}
Solvent	3416	2887.69	2772.25	2500 – 2600 (sh) 2401 2289 2198	1697 1550 (sh)	1390 1309	1054	603
Solvent + L.Arginine	3407	2885.13	2770.86	2690 2394 2290 2201	1689 1580 (sh)	1390 1308	1053	602