

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, acoustical parameters such as Rao's constant, Wada's constant and van der Waal's 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 (ρ) 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 (π_i), Free Volume (V_f), Rao's constant and Wada's constant:

$$\text{Internal pressure } \pi_i = bRT \left(\frac{k\eta}{u} \right) \frac{1}{2} \times \left(\rho^{\frac{2}{3}} / M_{\text{eff}}^{\frac{7}{6}} \right) \text{atms.}$$

$$\text{Free volume } V_f = \left[M_{\text{eff}} \times u / k\eta \right]^{\frac{3}{2}} \text{cc}$$

$$\text{Rao's constant } R = \frac{M_{\text{eff}} (U)^{\frac{1}{3}}}{\rho}$$

$$\text{Wada's constant } W = \frac{M_{\text{eff}}}{(\rho)\beta^{-\frac{1}{7}}}$$

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 10⁹

η - Viscosity of the solution in poise

R - Gas constant (8.314 x 10⁷)

T - Temperature

B - Cubic constant (2)

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ρ - 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 Figures 3.(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).

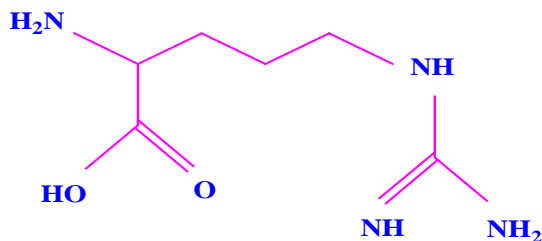


Figure 6.1: Non - Zwitterion - Neutral (Charge Solvated - CS)

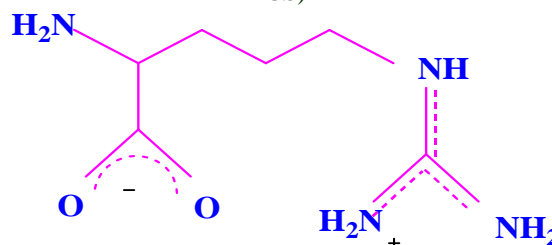


Figure 6.2: Zwitterion (Salt Bridge - SB)

These FT-IR spectral results of L-Arginine with formamide indicate the formation of H-bonds 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].

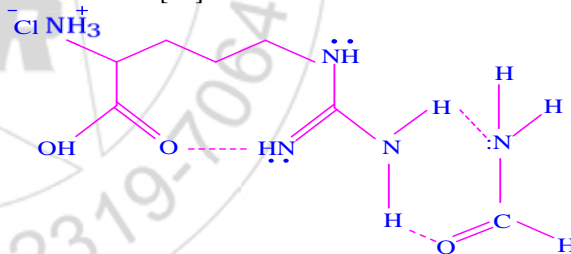


Figure 6.3: Neutral form of L-Arginine mono hydrochloride

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].

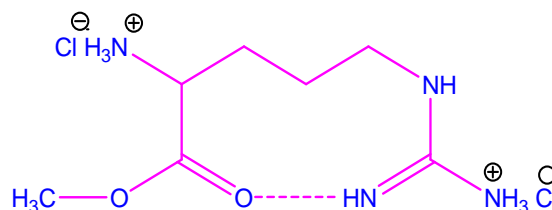


Figure 6.4: Neutral form of L-Arginine methyl ester di hydrochloride

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

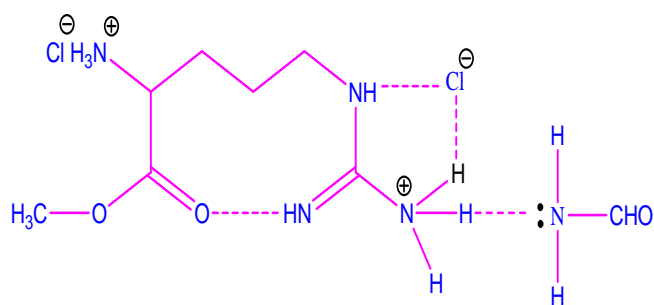


Figure 6.5: Charge solvated form of L-Arginine methyl ester dihydrochloride

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_2 stretching vibration of the solvent indicates binding of the amino acid ester to the NH_2 group of formamide [16]. It exists as mirror image form at chiral center (CH COO CH_3) [17] depicted in (Figs.6.6a and 6.6b) as inferred from the FT-IR spectrum Figure 5.1- 5.7..

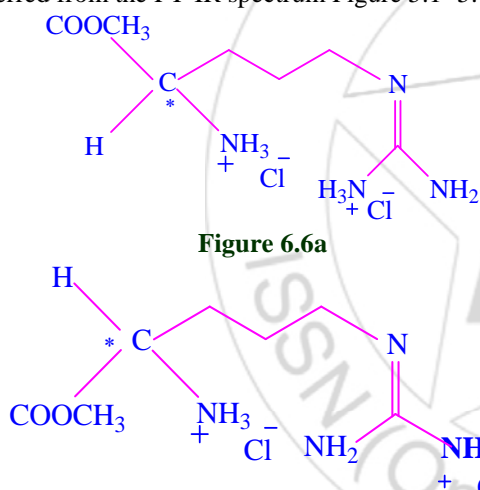


Figure 6.6a

Figure 6.6b: Mirror images of L-Arginine methyl ester dihydrochloride

4. Conclusion

The thermodynamic and acoustic studies confirm the hydrophilic interactions occurring between the Zwitterionic center of L-Arginine and Carbonyl 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.

References

- [1] Gnanamba S, RamachandraRao B, Ind J Pure &ApplPhy, 11 (1973) 99.
- [2] Gokce N, Myer B, Journal of Nutrition, 134 (2004) 2807-2811.
- [3] Takeshi Naito, Hiroshi Irie, Abcouwer S F, Kazuko Tsujimoto, Keikokkeda, International J Mol Medicine, 23 (2009) 495-499.
- [4] Karapetyan H A, Antipin M Yu, Sukiasyan R P, Petrosyan AM, J MolStruc, 831 (2007) 90-96.
- [5] Andrew P J, Myer B, Cardiovascular Research 43 (1999) 521-531.
- [6] Devlin T M, Textbook of Biochemistry with Clinical Correlations, 5th ed Wiley-Liss (New York) 97 (2002) 791- 871.
- [7] Jasmine Vasantha Rani E, Kannagi K, Padmavathi R, Proceedings of NSA, Bhandelkand University, Jhansi (UP), 17th-19th November, Appl Ultrasonic, (2012) 102 – 110.
- [8,9] Jasmine Vasantha Rani E, Kannagi K, Padmavathi R, Radha N, Proceedings of NSA, Bhandelkand University, Jhansi (UP), 17th-19th November, Acoustic waves,1 (2012) 410 – 417.
- [10] Jasmine Vasantha Rani E, Kannagi K, Padmavathi R, Radha N, Proceedings of National symposium on Acoustics, National physical Laboratory -New Delhi, 46 (2013) 410-414.
- [11] Santhakumari S, Padmavathi R, Jasmine Vasantha Rani E, International Soc Socio Techno Welfare - J ApplPhys, 4 (2013) 53-60.
- [12] Sujatha S, Padmavathi R, Jasmine Vasantha Rani E, International J Phys Appli, 5 (2013) 109-114.
- [13] Solachi V, Ambika R, J AcousSoc India, 34 (2005) 207-209.
- [14] Palani R, Jayachitra K, Ind J Pure &ApplPhys, 46 (2008) 251.
- [15, 17] Jasmine Vasantha Rani E, Kannagi K, Padmavathi R, Radha N, Proceedings of National Conference on EXFOVIS, Nagarcoil 1st&2nd September 34 (2011) 402 – 408.
- [18] Kannagi K, Jasmine Vasantha Rani E, Padmavathi R, Radha N, International J Current Res & Rev, 4 (2012) 156 – 166.
- [19] Jasmine Vasantha Rani E, Kannagi K, Padmavathi R, Radha N, J Basic & ApplPhys, 3 (2012) 96 – 101.

INTERNAL PRESSURE (atms)

Figure 1. (i) L-ARGININE

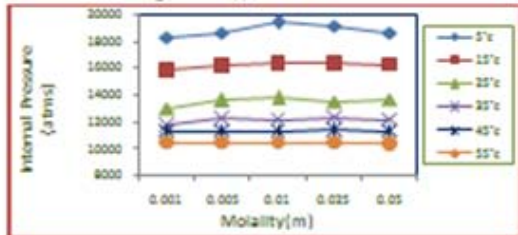


Figure 1.(ii)L-ARGININE MONOHYDROCHLORIDE

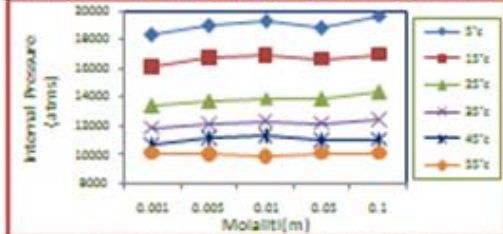
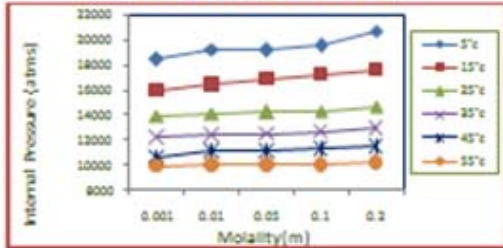


Figure 1.(iii)10 L-ARGININE METHYL ESTER DIHYDROCHLORIDE



FREE VOLUME (CC)

Figure 2. (i) 15 L-ARGININE

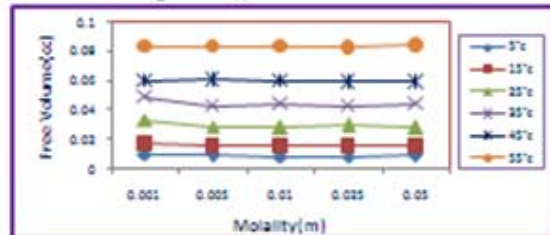


Figure 2. (ii) 16 L-ARGININE MONOHYDROCHLORIDE

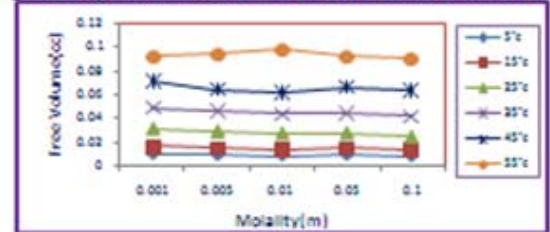
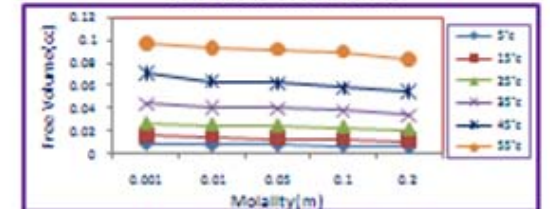


Figure 2. (iii) L-ARGININE METHYL ESTER DIHYDROCHLORIDE



RAO'S CONSTANT

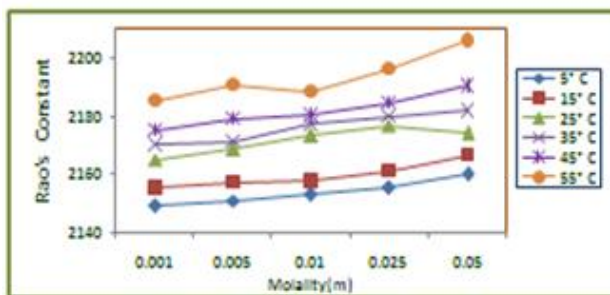


Figure 3. (i) L-ARGININE

Figure 3. (ii)L-ARGININE MONOHYDROCHLORIDE

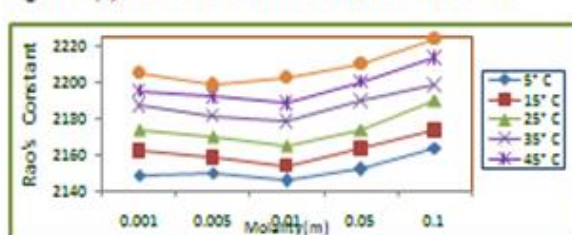
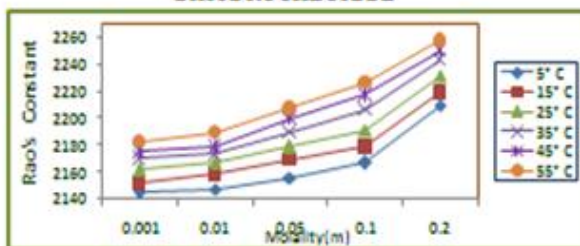


Figure 3. (iii)L-ARGININE METHYL ESTER DIHYDROCHLORIDE



WADA'S constant

Figure 4.(i) L-ARGININE

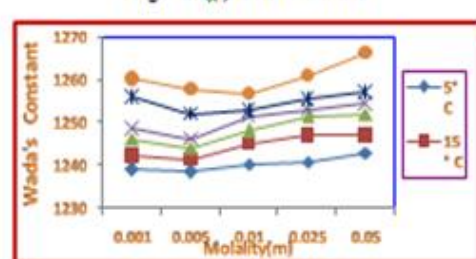


Figure 4. (ii) L-ARGININE MONOHYDROCHLORIDE

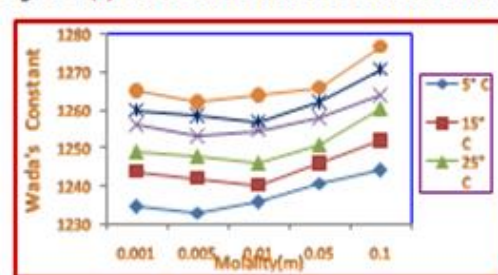
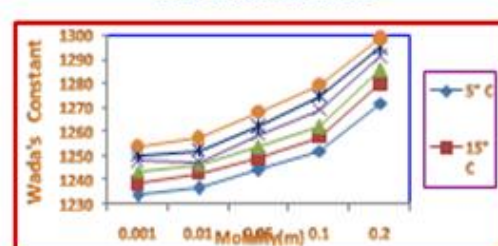


Figure 4.(iii) L-ARGININE METHYL ESTER DIHYDROCHLORIDE



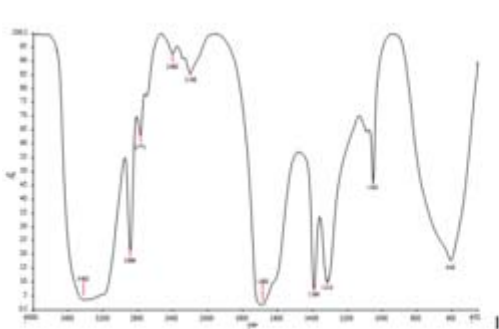


Figure 5.1: FT IR Spectrum of formamide

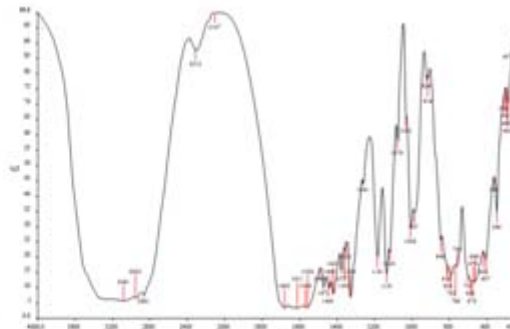


Figure 5.2: FT IR Spectrum of L-Arginine Salt

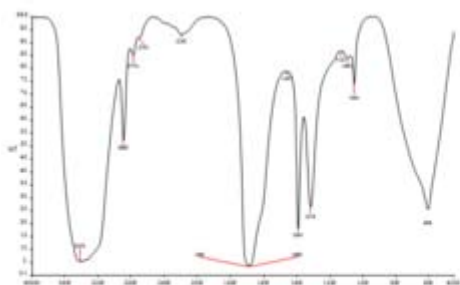


Figure 5.3: FT IR Spectrum of L-Arginine

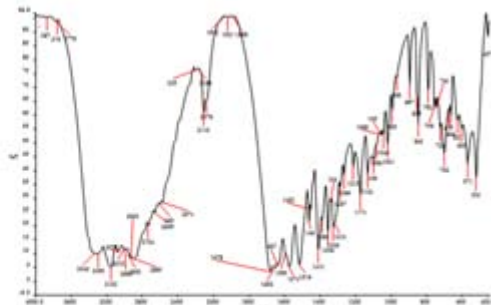


Figure 5.4: FT IR Spectrum of L-Arginine (Saturation molality)

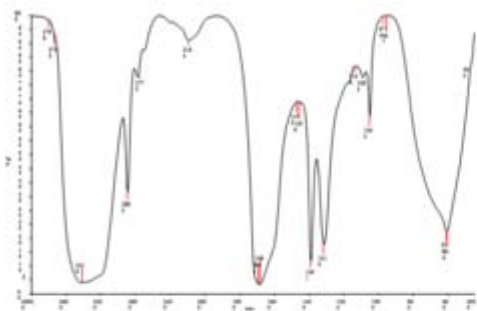


Figure 5.5: FT IR Spectrum of L-Arginine mono hydrochloride (Saturation molality)

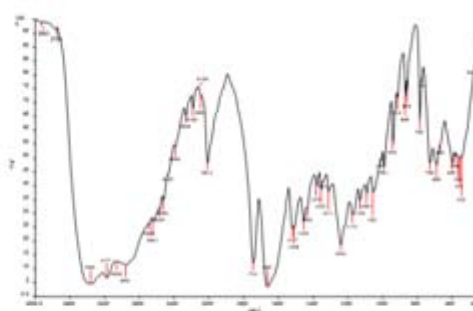


Figure 5.6: FT IR Spectrum of L-Arginine methyl ester dihydrochloride salt

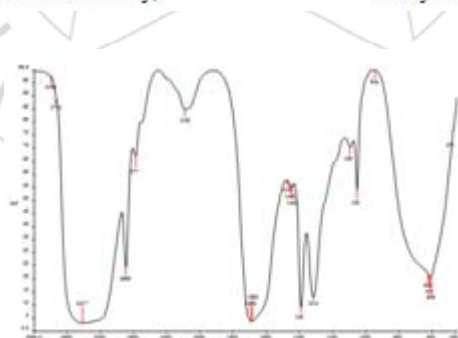


Figure 5.7: FT IR Spectrum of L-Arginine methyl ester dihydrochloride (Saturation molality)

INTERNAL PRESSURE (mm)

Table 1.1 L-ARGININE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	18306	18784	12984	11791	11278	10398
0.005	18641	18817	13591	12249	11288	10398
0.01	19251	18275	13757	12185	11315	10399
0.025	19102	18293	13905	12299	11332	10403
0.05	18654	18287	13899	12098	11316	10304

FREE VOLUME (CC)

Table 2.1 L-ARGININE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	0.0100	0.0172	0.0338	0.0484	0.0806	0.0835
0.005	0.0095	0.0181	0.0293	0.0433	0.0808	0.0838
0.01	0.0085	0.0157	0.0283	0.0445	0.0802	0.0837
0.025	0.0088	0.0158	0.0298	0.0429	0.0795	0.0832
0.05	0.0094	0.0155	0.0284	0.0448	0.0804	0.0847

RAO'S CONSTANT

Table 3.1 L-ARGININE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	2149	2158	2168	2170	2178	2182
0.005	2151	2157	2169	2171	2179	2191
0.01	2183	2158	2173	2177	2180	2188
0.025	2155	2161	2178	2180	2182	2194
0.05	2180	2187	2174	2181	2190	2208

Table 1.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	18271	18105	13321	11841	10669	10091
0.005	18912	18877	14026	12082	11082	10023
0.01	19279	18905	13920	12334	11263	9876
0.05	18772	18594	13844	12190	10937	10066
0.1	18672	18929	14348	12363	11054	10086

Table 2.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	0.0100	0.0162	0.0312	0.0483	0.0714	0.0914
0.005	0.0091	0.0148	0.0291	0.0454	0.0699	0.0932
0.01	0.0088	0.0140	0.0273	0.0426	0.0808	0.0973
0.05	0.0091	0.0148	0.0275	0.0441	0.0857	0.0911
0.1	0.0079	0.0136	0.0244	0.0413	0.0829	0.0895

Table 3.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	2149	2162	2174	2187	2195	2205
0.005	2190	2158	2170	2181	2192	2198
0.01	2146	2154	2168	2178	2188	2202
0.05	2152	2163	2174	2189	2200	2210
0.1	2164	2173	2190	2198	2213	2223

Table 1.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	18427	15984	13939	12203	10702	9904
0.01	19236	18424	14136	12493	11101	10039
0.05	19187	18872	14215	12602	11130	10037
0.1	19208	17249	14303	12646	11322	10037
0.2	20723	17602	14679	12908	11448	10217

Table 2.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	0.0098	0.0185	0.0273	0.0444	0.0714	0.0977
0.01	0.0068	0.0152	0.0280	0.0415	0.0698	0.0932
0.05	0.0069	0.0138	0.0293	0.0405	0.0823	0.0919
0.1	0.0080	0.0127	0.0244	0.0384	0.0882	0.0902
0.2	0.0064	0.0118	0.0218	0.0348	0.0547	0.0829

Table 3.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	2145	2152	2162	2170	2178	2183
0.01	2148	2158	2167	2174	2179	2189
0.05	2158	2169	2179	2189	2200	2207
0.1	2187	2179	2191	2206	2217	2227
0.2	2210	2219	2232	2243	2260	2268

WADA'S CONSTANT

Table 4.1 L-ARGININE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	1239	1242	1248	1248	1250	1260
0.005	1238	1241	1244	1246	1252	1258
0.01	1240	1245	1248	1251	1255	1257
0.025	1241	1247	1251	1253	1259	1261
0.05	1243	1247	1252	1254	1257	1266

Table 4.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	1235	1244	1249	1256	1280	1285
0.005	1233	1242	1248	1253	1258	1262
0.01	1238	1240	1248	1255	1257	1264
0.05	1241	1248	1251	1258	1262	1266
0.1	1244	1252	1260	1264	1271	1277

Table 4.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	8° C	18° C	28° C	38° C	48° C	58° C
0.001	1234	1239	1244	1248	1250	1254
0.01	1237	1243	1247	1248	1253	1257
0.05	1244	1249	1254	1259	1262	1268
0.1	1262	1258	1262	1269	1278	1279
0.2	1275	1280	1288	1291	1298	1299

Table 5 FT-IR observed spectral vibrational frequencies

Name of the sample	Stretching Vibrations: cm ⁻¹			CONH amide II band cm ⁻¹	ν _{COO} cm ⁻¹	NH out of phase Bending δ _{NH} cm ⁻¹
	ν _{as}	ν _s	Amide I Band ν _{CO}			
L-Arginine Salt	3000	2912	1602	1181	1139	948-790
	2895	1813	1473-1426	1078	701-607	
0.05 m	3416	2891	1701	1687	1391	1052
	2199	1892	1314			
0.025 m	3135	2770	1893	1473	1089	813
	3433	2889	1702	1692	1457	1008
Saturation m	3416	2891	1701	1687	1391	1051
	3203	2199	1878	1313		456

Table 6 FT-IR observed spectral vibrational frequencies

Name of the Sample	Stretching Vibrations: cm ⁻¹			CONH amide II band cm ⁻¹	ν _{COO} cm ⁻¹	NH out of phase Bending δ _{NH} cm ⁻¹
	ν _{as}	ν _s	Amide I Band ν _{CO}			
L-Arginine methyl ester dihydrochloride Salt	3117	2889	1743	1379	1081	881
	3491	2841	1683	1393	1091	781
0.1 m	3382	2858	1678	1317	1311	1025
	3103	2104	1818	1313		484
0.05 m	3391	2770	1703	1473	1458	1092
	3795	2891	1693	1442	1382	1001
0.02 m	3417	2190	1814	1313		453
	3739	2892	1710	1683	1431	1091
Saturation m	3417	2894	1683	1318	1052	471

Table 7 FT-IR observed spectral vibrational frequencies

Name of the Sample	Stretching Vibrations: cm ⁻¹			CONH amide II band cm ⁻¹	ν _{COO} cm ⁻¹	NH out of phase Bending δ _{NH} cm ⁻¹
	ν _{as}	ν _s	Amide I Band ν _{CO}			
L-Arginine methyl ester dihydrochloride Salt	3010	2110	1292	1484	1094	853
	3873	2893	1734	1516	1174	1034
0.05 m	3770	2810	1673	1410	1069	753
	3343	2893	1683	1356	1045	668
0.1 m	3152-3070	2173	1574	1319		457
	3299	2314	1637			481
0.05 m	3730	2778	1688	1472	1089	808
	3723	2895	1682	1391	1052	
0.1 m	3735	2894	1693	1472	1089	807
	3413	2187	1682	1391	1052	
Saturation m	3790	2893	1694	1391	1092	811
	3413	2184	1682	1318	1052	484