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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 ($2MH_Z$) 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:

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

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

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

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

Where,

M_{eff} - Effective molecular weight of the solution in gm.u .

u - Ultrasonic velocity in cm/sec.

K - Constant equal to 4.285×10^9

η - Viscosity of the solution in poise

R - Gas constant (8.314×10^7)

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 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).

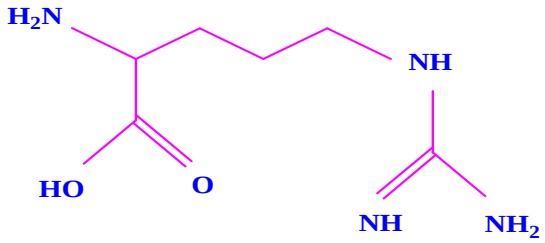

Figure 6.1: Non – Zwitterion –Neutral (Charge Solvated - CS)

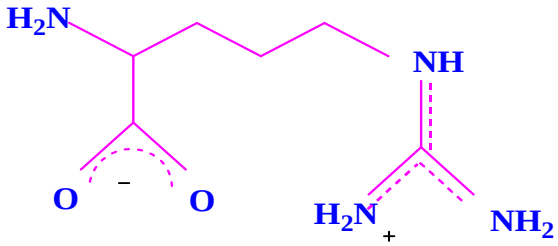

Figure 6.2: Zwitterion (Salt Bridge - SB)

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

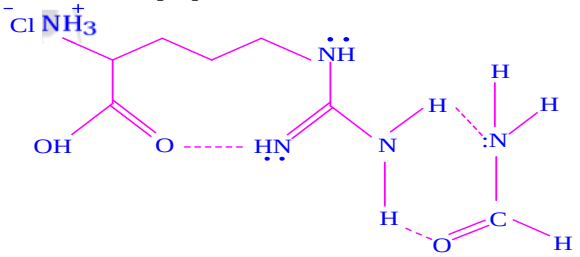

Figure 6.3: Neutral form of L-Arginine mono hydrochloride

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].

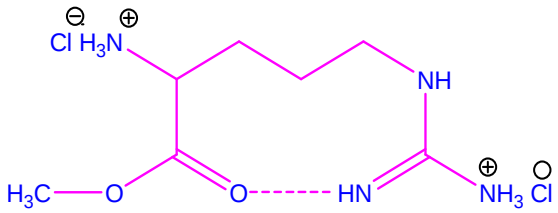

Figure 6.4: Neutral form of L-Arginine methyl ester di hydrochloride

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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

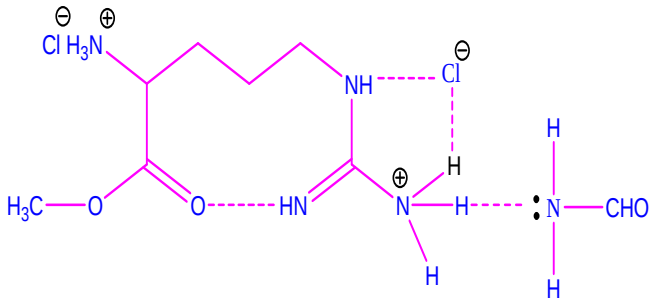

Figure 6.5: Charge solvated form of L-Arginine methyl ester di hydrochloride

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..

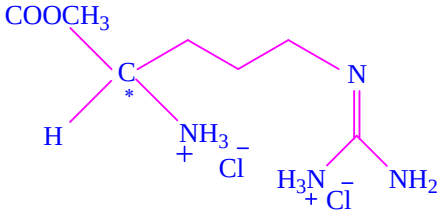

Figure 6.6a

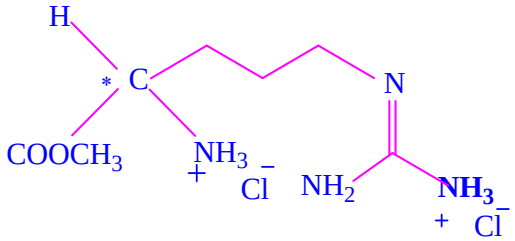

Figure 6.6b: Mirror images of L-Arginine methyl ester di hydrochloride

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.

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INTERNAL PRESSURE (atms)

Figure 1. (i) L-ARGININE

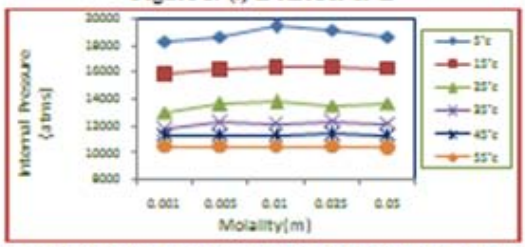


Figure 1.(ii)L-ARGININE MONOHYDROCHLORIDE

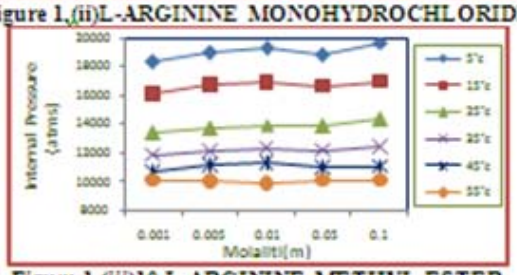
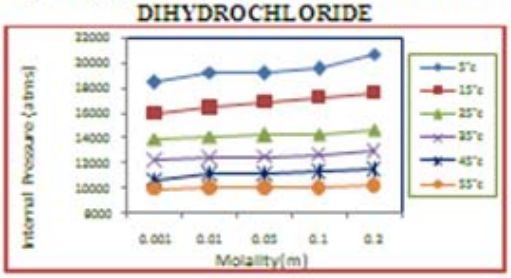


Figure 1.(iii)10 L-ARGININE METHYL ESTER DIHYDROCHLORIDE



FREE VOLUME (CC)

Figure 2. (i) 15 L-ARGININE

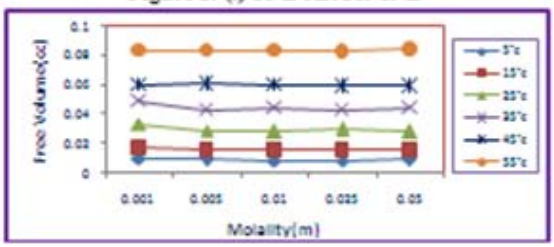


Figure 2. (ii) 16 L-ARGININE MONOHYDROCHLORIDE

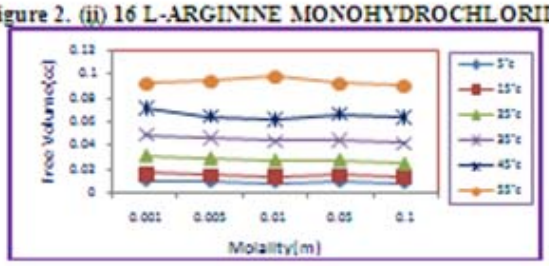
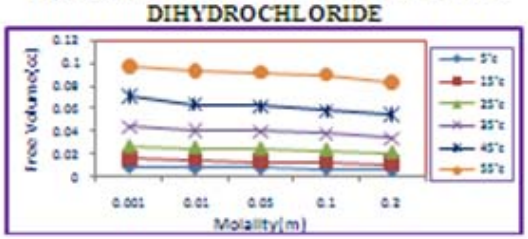


Figure 2. (iii) L-ARGININE METHYL ESTER DIHYDROCHLORIDE



RAO'S CONSTANT

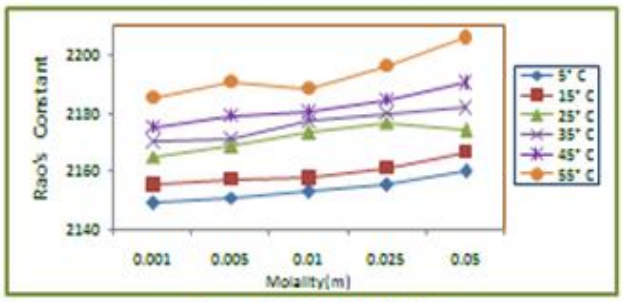


Figure 3. (i) L-ARGININE

Figure 3. (ii)L-ARGININE MONOHYDROCHLORIDE

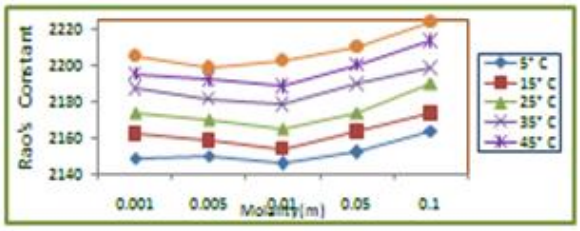
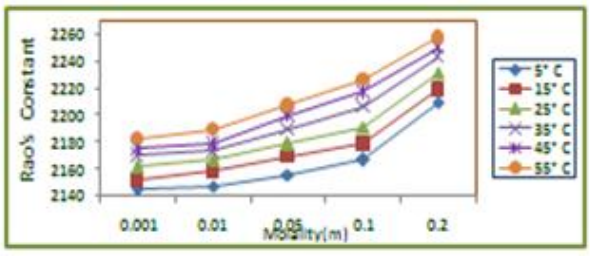


Figure 3. (iii)L-ARGININE METHYL ESTER DIHYDROCHLORIDE



WADA'S constant

Figure 4.(i) L-ARGININE

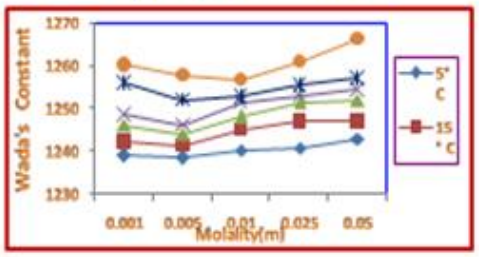


Figure 4. (ii) L-ARGININE MONOHYDROCHLORIDE

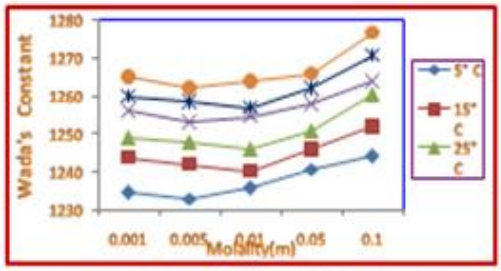
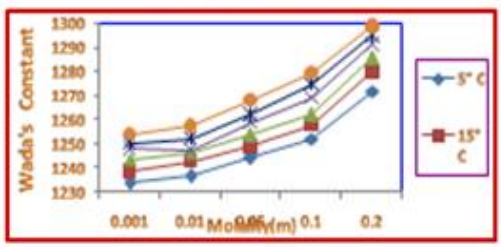


Figure 4.(iii) L-ARGININE METHYL ESTER DIHYDROCHLORIDE



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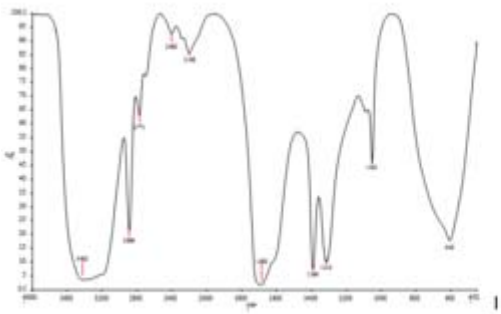

Figure 5.1: FT IR Spectrum of formamide

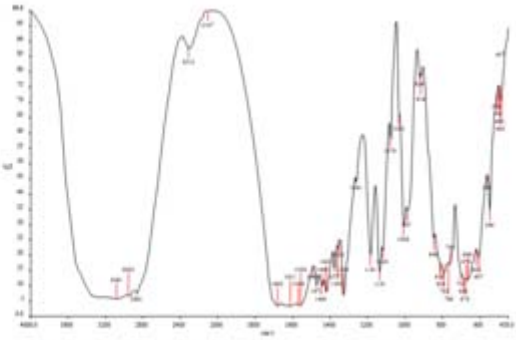

Figure 5.2: FT IR Spectrum of L-Arginine Salt

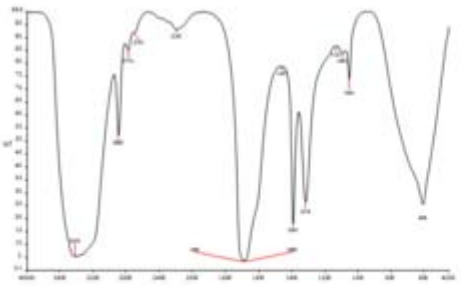

Figure 5.3: FT IR Spectrum of L-Arginine

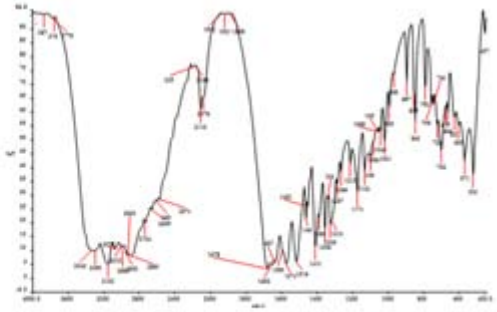

Figure 5.4: FT IR Spectrum of L-Arginine (Saturation molality)

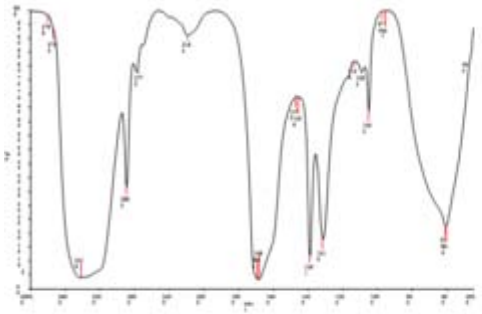

Figure 5.5: FT IR Spectrum of L-Arginine mono hydrochloride (Saturation molality)

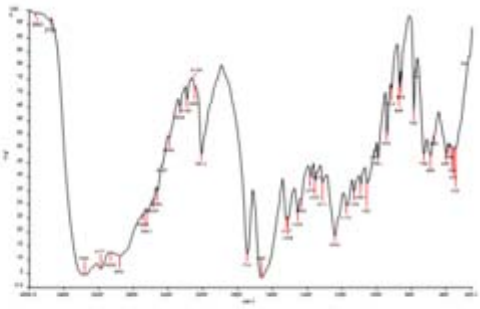

Figure 5.6: FT IR Spectrum of L-Arginine methyl ester dihydrochloride salt

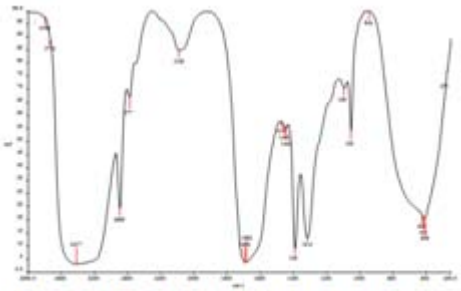

Figure 5.7: FT IR Spectrum of L-Arginine methyl ester dihydrochloride (Saturation molality)

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INTERNAL PRESSURE (atm)

Table 1.1 L-ARGININE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	18306	15764	12964	11731	11278	10398
0.005	18641	16117	13591	12249	11288	10396
0.01	19351	16275	13757	12165	11315	10399
0.025	19102	16293	13505	12299	11332	10403
0.05	18654	16267	13699	12098	11316	10304

Table 1.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	18271	16105	13321	11841	10669	10091
0.005	18912	16677	13626	12082	11082	10023
0.01	19279	16905	13920	12334	11263	9876
0.05	18772	16594	13844	12150	10937	10066
0.1	19672	16929	14345	12363	11054	10086

Table 1.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	18427	15984	13939	12203	10702	9904
0.01	19236	16424	14136	12453	11101	10035
0.05	19187	16872	14215	12602	11130	10037
0.1	19506	17249	14306	12646	11322	10037
0.2	20723	17602	14679	12908	11448	10217

FREE VOLUME (CC)

Table 2.1 L-ARGININE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	0.0100	0.0172	0.0338	0.0494	0.0606	0.0835
0.005	0.0095	0.0161	0.0293	0.0433	0.0606	0.0838
0.01	0.0085	0.0157	0.0283	0.0445	0.0602	0.0837
0.025	0.0088	0.0156	0.0298	0.0429	0.0595	0.0832
0.05	0.0094	0.0155	0.0284	0.0448	0.0594	0.0847

Table 2.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° 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	0.0639	0.0932
0.01	0.0085	0.0140	0.0273	0.0426	0.0608	0.0973
0.05	0.0091	0.0146	0.0275	0.0441	0.0657	0.0911
0.1	0.0079	0.0136	0.0244	0.0413	0.0629	0.0895

Table 2.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	0.0098	0.0165	0.0273	0.0444	0.0714	0.0977
0.01	0.0086	0.0152	0.0260	0.0435	0.0638	0.0932
0.05	0.0085	0.0138	0.0253	0.0405	0.0623	0.0919
0.1	0.0080	0.0127	0.0244	0.0384	0.0582	0.0902
0.2	0.0064	0.0118	0.0218	0.0348	0.0547	0.0829

RAO'S CONSTANT

Table 3.1 L-ARGININE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	2149	2155	2165	2170	2175	2185
0.005	2151	2157	2169	2171	2179	2191
0.01	2153	2158	2173	2177	2180	2188
0.025	2155	2161	2176	2180	2185	2196
0.05	2160	2167	2174	2181	2190	2206

Table 3.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	2149	2162	2174	2187	2195	2205
0.005	2150	2158	2170	2181	2192	2198
0.01	2146	2154	2165	2178	2188	2202
0.05	2152	2163	2174	2189	2200	2210
0.1	2164	2173	2190	2198	2213	2223

Table 3.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	2145	2152	2162	2170	2175	2183
0.01	2148	2158	2167	2174	2179	2189
0.05	2156	2169	2179	2189	2200	2207
0.1	2167	2179	2191	2206	2217	2227
0.2	2210	2219	2232	2243	2250	2258

WADA'S CONSTANT

Table 4.1 L-ARGININE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	1239	1242	1246	1248	1256	1260
0.005	1238	1241	1244	1246	1252	1258
0.01	1240	1245	1248	1251	1253	1257
0.025	1241	1247	1251	1253	1255	1261
0.05	1243	1247	1252	1254	1257	1266

Table4.2 L-ARGININE MONOHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	1235	1244	1249	1256	1260	1265
0.005	1233	1242	1248	1253	1258	1262
0.01	1236	1240	1246	1255	1257	1264
0.05	1241	1246	1251	1258	1262	1266
0.1	1244	1252	1260	1264	1271	1277

Table 4.3 L-ARGININE METHYL ESTER DIHYDROCHLORIDE

Molality (m)	5° C	15° C	25° C	35° C	45° C	55° C
0.001	1234	1239	1244	1248	1250	1254
0.01	1237	1243	1247	1248	1252	1257
0.05	1244	1249	1254	1259	1262	1268
0.1	1252	1258	1262	1269	1278	1279
0.2	1272	1280	1286	1291	1295	1299

Table 5 FT-IR observed spectral vibrational frequencies

Name of the sample	Stretching Vibrations cm⁻¹				CONH amide II band cm⁻¹	ν_{C-O} cm⁻¹	NH out of plane Bending δ_{NH} cm⁻¹
	ν_{NH}	ν_{CH}	ν_{CN}	Amide I Band $\nu_{C=O}$			
L-Arginine Salt	3080	2953 2865	2312 2313 2107	1682 1613 1568 1556	1473 – 1420 1330	1185 1136 1078 1008 987	848 – 760 701 – 607 509 – 483
0.05 m	3416	2891	2771 2701 2198	1694 1687 1682	[illegible] 1457 1391 1314	1091 1052	610 601
0.025 m	3735 3433 3421 3406 3203	2888	2770 2702 2398 2199	1693 1682 1678	1473 1457 1391 1313	1089 1051	625 606 456
Saturation m	3416-3203 3418	2893	2774 2701 2192	1694 1682	1457 1391 1315	1091 1052	606

Table 7 FT-IR observed spectral vibrational frequencies

Name of the Sample	Stretching Vibrations cm⁻¹				CONH amide II band cm⁻¹	ν_{C-O} cm⁻¹	NH out of plane Bending δ_{NH} cm⁻¹
	ν_{NH}	ν_{CH}	ν_{CN}	Amide I Band $\nu_{C=O}$			
L-Arginine methyl ester dihydrochloride Salt	3177 3941 3342 3055	2958	2689 2641 2526 2014	1743 1665 1517 1508	1379 1355 1311	1007 1081 1005	831 840 858 735 725-668 600 543 484
0.1 m	3931 3735 3417	2891	2772 2405 2198 2190	1703 1694 1682 1614	1475 1456 1442 1392 1315	1092 1052	615 599 933
0.2 m	3738 3417	2892	2773 2695	1693 1682	1458 1391 1315	1091 1052	804 465 453
Saturation m	3788 3417	2894	2776 2183	1694 1682	1391 1316	1098 1052	622 606 471

Table 6 FT-IR observed spectral vibrational frequencies

Name of the Sample	Stretching Vibrations cm⁻¹				CONH amide II band cm⁻¹	ν_{C-O} cm⁻¹	NH out of plane Bending δ_{NH} cm⁻¹
	ν_{NH}	ν_{CH}	ν_{CN}	Amide I Band $\nu_{C=O}$			
L-Arginine monohydrochloride salt	3010 3073 3778 3343 3152-3070 3299	2993 2950 2895	2210 2734 2076 2606 2575 2514	1595 1516 1678 1655 1574 1627	1464 1174 1410 1356 1319	1084l 099 1069 1045	897 855 848 792 758 666 677 627 605 457
0.05 m	3735 3723 3417	2892	2776 2183	1688 1682	1483 1472 1456 1391 1316	1089 1052	606
0.1 m	3735 3418	2894	2775 2187	1693 1682	1456 1472 1391 1316	1089 1052	607
Saturation m	3793 3418	2893	2775 2184	1694 1682	1473 1391 1315 1456	1092 1052	611 608 484

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