Acoustic Parameters of Amino Acids in Aqueous Methanol Solutions at 298.15K

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ABSTRACT: -The acoustical parameters of amino acids have been measured in aqueous methanol solutions, at 298.15K. The molar sound velocity (R), molar compressibility (W), free length (L_f), free volume (V_f), internal pressure (p_i), relaxation time (t), ultrasonic attenuation (a/f^2), and van der Waals constant (b) values have been calculated from the experimental data. These parameters are used to discuss the molecular interactions in the solutions.

KEYWORDS: Acoustical parameters, methanol ,amino acids, Ultrasonic Velocity, Compressibility

I. INTRODUCTION

The measurement of ultrasonic velocity provides qualitative information about the nature and strength of molecular interaction in solutions. The study of solution properties of the solutions consisting of polar and non-polar compounds finds applications in industrial and technical processes. In continuation of our work on determination of acoustic and thermodynamic parameters of the solutions of amino acids in aqueous solutions of hydrotropic agents,[1,2] in the present investigation, we have evaluated the acoustic parameters such as molar sound velocity (R), molar compressibility (W), free length (L_f), free volume (V_f), internal pressure (π_i), relaxation time (τ), ultrasonic attenuation (α/f^2) and van der Waals constant (b) at 298.15K for the solutions of amino acids in water + methanol mixtures, where the wt% percentage of methanol, was varied from 5to15% with 5%increments. The results are discussed in the light of molecular interactions.

II. MATERIALS AND METHODS:

All chemicals used were of AnalaR grades. Conductivity water (Sp and $\sim 10^{-6}$ Scm^{-1}) was used to prepare solutions of methanol in different wt% and the solutions were used on the same day. The solution of amino acids were prepared on the molal basis and conversion of molality to molarity was done by using the standard expression[3] using the density values of the solutions determined at 298.15K. Solutions were kept for 2 hours in a water thermostat maintained at the required temperature accurate to within ± 0.1K before use for density measurements. Density measurements were done by using a specific gravity bottle (25ml capacity) as described elsewhere[4]. At least five observations were taken and differences in any two readings did not exceed ± 0.02%. An ultrasonic interferometer (model No.F-81, Mittal enterprises, New Delhi) operating at a frequency of 2MHz and overall accuracy of ± 0.5 m/s was used for the velocity measurement at 298.15K only. Viscosity measurements were made by using an Ostwald's Viscometer (25 ml capacity) in a water thermostat whose temperature was controlled to ± 0.05K. The values of viscosity so obtained were accurate to within ± 0.3 x 10^{-3} CP. Amino acids content in the solutions varied over a range of 0.006 to 0.08 mol dm^{-3} in all wt% of methanol solutions.

Theoretical Aspects:

From the ultrasonic velocity (U), density (d), and viscosity (η) data, the following parameters have been calculated.

[1] Molar sound velocity[5] (R): $R = \bar{M}d^{-1} U^{1/3}$ where, $\bar{M}$ is the effective molecular weight ($\bar{M} = \sum m_i x_i$), in which m_i and x_i are the molecular weight and the mole fraction of individual constituents, respectively.

[2] Molar compresibility[6] (W) : According to Wada, $W=\bar{M}d^{-1} K_S^{-1/7}$, where, W is a constant called Wada[1]s constant or molecular compressibility which is independent of temperature and pressure.

[3] Intermolecular free length[7](L_f): It is the distance between the surfaces of the molecules. It can be calculated using insentropic compressibility by Jacobson's empirical relation $L_f = K^I K_s^{1/2}$, where K^I is the Jacobson's constant which is

temperature dependent and is obtained from the literature[7].

[4] Free Volume (V_f): Suryanarayan et. al[8] obtained a formula for free volume in terms of the ultrasonic velocity (U) and the viscosity of the liquid (η) as $V_f = (\bar{M}U/K\eta)^{3/2}$ where $\bar{M}$ is the effective molecular weight ($\bar{M}=\sum m_i x_i$), in which m_i and x_i are molecular weight and the mole fraction of the individual constituents, respectively, K is temperature independent constant which is equal to 4.28 x 10^9 for all liquids.

[5] Internal Pressure (π_i): According to Suryanarayan[8], internal pressure is given by, $\pi_i = b^I RT (K\eta/U)^{1/2} (d^{2/3}/\bar{M}^{1/6})$, where b^I is the packing factor, which is equal to 1.78 for close packed hexagonal structure and 2 for cubic packing. For many liquids b^I is equal to 2. K^I is a dimensionless constant having a value of 4.28 x 10^9, independent of temperature and nature of liquid.

[6] Relaxation time[8] (τ) : $\tau = 4\eta/3dU^2$ where the symbols have their usual meanings.

[7] Ultrasonic Attenuation[9] (α/f^2): $\alpha/f^2=4\pi^2\tau/2U$.

[8] van der Waals constant[10] : van der Waals constant (b) also called co-volume in van der Waals equation is given by the formula $b=\bar{M}/d[1-(RT/\bar{M}U^2)\{1+\bar{M}U^2/3RT)\}^{1/2}-1]$ where R is the gas constant and $\bar{M}$ is the effective molecular weight.

RESULTS AND DICCUSSION:

From the measured values of the ultrasonic velocity and density of the solutions of amino acids in aqueous methanol solutions, the values of the molar sound velocity (R) evaluated by means of eqn.(1) are given in Table 1.

TABLE – 1 (Values of parameters U(ms^{-1}), R($m^{-8/3}$ $S^{-1/3}$), W (N^{-1} m^{-1}), L_r (m), V_r (m^3/mol), π_i (Nm^{-2}), τ(s), α/f^2 and b for glycine in aqueous solutions of methanol a t 298.15 K.

C mol dm^{-3}	U ms^{-1}	R $m^{-8/3}$ $s^{-1/3}$	W $m^{-1}N^{-1}$	L_f(m) x 10^{-10}	$V_f x10^{-8}$ m^3/mol	π_i Nm^{-2}	τ(s) x 10^{-13}	α/f^2 x 10^{-15}	B m^3mol^{-1}
Glycine + 5wt%									
0.006	1560.8	0.2116	0.4018	5.138	56168	853284.4	6.72	8.433	0.19408
0.008	1563.2	0.2118	0.4022	5.132	56126	853964.6	6.70	8.232	0.19416
0.02	1566.0	0.2125	0.4028	5.130	56108	854862.4	6.68	8.206	0.19426
0.04	1570.2	0.2182	0.4039	5.126	55389	855143.4	6.64	8.198	0.19498
0.06	1572.0	0.2234	0.4046	5.122	55363	856532.2	6.82	8.108	0.19502
0.08	1576.8	0.2242	0.4062	5.118	55341	861236.4	6.61	8.098	0.19512
Glycine + 10wt%									
0.006	1532.8	0.2006	0.3764	4.852	49164	832246.4	5.26	7.224	0.017424
0.008	1536.0	0.2022	0.3766	4.846	49122	833126.2	5.24	7.122	0.017426
0.02	1540.0	0.2026	0.3768	4.832	49098	834262.4	5.22	7.106	0.017431
0.04	1544.8	0.2029	0.3772	4.828	49062	835016.2	5.20	7.087	0.017436
0.06	1550.0	0.2032	0.3781	4.822	49032	835112.4	5.18	7.064	0.017349
0.08	1552.8	0.2038	0.3793	4.816	49.021	835422.4	5.16	7.022	0.017442
Glycine + 15wt%									
0.006	1620.8	0.2364	0.4612	7.124	59624	893462.2	8.86	10.126	0.22382
0.008	1623.2	0.2372	0.4614	7.122	59612	893844.6	8.84	10.120	0.22384
0.02	1626.0	0.2376	0.4618	7.118	59596	893896.4	8.82	10.073	0.22396
0.04	1628.8	0.2382	0.4628	7.112	59587	893912.4	8.79	10.062	0.22398
0.06	1632.0	0.2394	0.4634	7.106	59573	893946.4	8.73	10.048	0.22406
0.08	1636.0	0.2398	0.4642	7.102	59564	893984.2	8.70	10.019	0.22421
α-alanine+ 5wt%									
0.006	1572.8	0.2248	0.4067	5.124	55142	871064.2	7.08	8.639	0.20426
0.008	1575.2	0.2296	0.4069	5.122	55126	871362.4	7.06	8.331	0.20463
0.02	1578.0	0.2332	0.4072	5.118	55104	881112.4	7.02	8.224	0.20468
0.04	1580.0	0.2346	0.4086	5.116	54996	882321.2	6.98	8.168	0.20472
0.06	1584.0	0.2348	0.4163	5.108	54963	883216.4	6.96	8.122	0.20476
0.08	1586.0	0.2353	0.4132	5.106	54952	891012.2	6.89	8.073	0.20482
α-alanine+ 10wt%									
0.006	1541.6	0.2046	0.3792	4.648	48898	853246.2	6.22	7.329	0.017896
0.008	1544.0	0.2048	0.3796	4.642	48872	854134.4	6.20	7.312	0.017898

0.02	1548.0	0.2056	0.3810	4.638	48822	855264.2	6.18	7.264	0.017932
0.04	1552.8	0.2069	0.3812	4.632	48724	856012.4	6.16	7.124	0.017936
0.06	1558.0	0.2076	0.3826	4.628	48638	856214.6	6.14	7.097	0.017936
0.08	1560.0	0.2088	0.3828	4.624	48631	856312.2	6.72	7.093	0.017948
				α-alanine+ 15wt%					
0.006	1629.6	0.2492	0.4654	6.998	58824	915464.4	8.96	10.228	0.23228
0.008	1632.0	0.2494	0.4656	6.996	58818	915612.2	8.92	10.222	0.23229
0.02	1634.4	0.2412	0.4663	6.986	58812	915.616.6	8.90	10.218	0.23232
0.04	1636.8	0.2436	0.4674	6.982	58806	915713.2	8.88	10.212	0.23236
0.06	1640.0	0.2444	0.4682	6.980	58796	915814.6	8.86	10.208	0.23238
0.08	1644.8	0.2452	0.4694	6.976	58716	915818.2	8.82	10.202	0.23243
				β-alanine+ 5wt%					
0.006	1580.8	0.23126	0.4208	5.098	54716	897362.1	7.78	9.098	0.21128
0.008	1584.0	0.23169	0.4214	5.096	54711	898460.2	7.76	8.986	0.21144
0.02	1588.8	0.23182	0.4216	5.092	54682	907463.4	7.74	8.972	0.21146
0.04	1592.0	0.23312	0.4220	5.091	54612	917164.2	7.72	8.964	0.21152
0.06	1594.0	0.23420	0.4296	5.088	54606	918264.2	7.70	8.872	0.21156
0.08	1596.0	0.23624	0.4312	5.082	53828	919964.4	7.68	8.864	0.21162
				β-alanine+ 10wt%					
0.006	1548.8	0.2116	0.3886	4.224	48264	872463.1	6.92	7.826	0.018402
0.008	1552.0	0.2119	0.3894	4.220	48262	873216.2	6.90	7.822	0.018412
0.02	1556.8	0.2132	0.3898	4.196	48258	874012.4	6.88	7.816	0.018432
0.04	1560.8	0.2134	0.3904	4.194	48246	875126.2	6.86	7.801	0.018448
0.06	1564.0	0.2136	0.3906	4.188	48242	875232.2	6.82	7.796	0.018462
0.08	1567.2	0.2138	0.3912	4.182	48238	8761.24.4	6.80	7.792	0.018472
				β-alanine+ 15wt%					
0.006	1638.4	0.2532	0.4698	6.824	57928	931234.6	9.64	10.624	0.24342
0.008	1641.6	0.2534	0.4699	6.826	57929	932236.4	9.62	10.622	0.24344
0.02	1644.8	0.2542	0.4712	6.798	57924	932296.4	9.60	10.618	0.24348
0.04	1650.0	0.2556	0.4717	6.786	57922	933216.2	9.56	10.612	0.24352
0.06	1652.8	0.2562	0.4726	6.782	57898	933418.2	9.52	10.608	0.24364
0.08	1656.0	0.2576	0.4728	6.684	57892	934216.4	9.48	10.601	0.24368

As observed, the molar sound velocity increases with increase in concentration of the solutions of amino acids in all wt% of methanol solutions studied. This type of behavior is similar to that observed earlier [10,11]. It is of interest to note that the acoustic parameters including the sound velocity decrease in the solutions of amino acids as follows:

β-Alanine>α-alanine>glycine .It follows that the β-alanine has a greater contribution toward the molecular interactions followed by α-alanine and in turn glycine.

It is known that when a solute dissolves in a solvent some of the solvent molecules are attached to the ions (generated from the solute) because of ion-solvent interactions. Since the solvent molecules are oriented in the ionic field (i.e., electrostatic fields of ions) the solvent molecules are more compactly packed in the primary solvation shell as compared to the packing in the absence of the ions. This is the reason, why the solvent is compressed by the introduction of ions. Thus the electrostatic field of the ions causes compression of the medium giving rise to a phenomenon called electrostriction. Since the solvent molecules are compressed, they do not respond to any further application of pressure. So the solution becomes harder to compress; i.e., the compressibility decreases and internal pressure increases. Hence isentropic compressibility as well as internal pressure describes the molecular arrangement in the liquid medium. The increase in internal pressure π_i due to electronic field of ion is given by eqn(5).

Suryanarayan et. al[8] showed that the free energy of activation, ΔG is almost equal to the cohesive energy, $\pi_i V_m$. Positive values of π_i indicate the presence of some specific interactions between unlike molecules in the components.

Free volume, V_f is the effective volume accessible to the centre of a molecule in a liquid. The structure of a liquid is determined by strong repulsive forces in the liquid with the relatively weak attractive forces providing the internal pressure which held the liquid molecules together.[12]

The free volume seems to be conditional by repulsive forces, whereas the internal pressure is more sensitive to attractive forces. These two factors together uniquely determine the entropy of the system. Thus, the internal pressure, free volume and temperature seem to be thermodynamic variables that describe the liquid system of fixed composition[13,14].

It is seen that free volume decreases with increase in concentration of the solutions of surfactants. As observed, the internal pressure changes in a manner opposite to that of free volume. The decrease of V_f (or increase of π_i) indicates the formation of hard and/or tight solvation layer around the ion[15,16].

The fractional free volume (V_f/V) is a measure of disorderliness due to increased mobility of the molecules in a liquid. It is observed that mobility decreases with concentration. This implies that the frictional force exerted by different layers of liquid increases with concentration and the wt% of methanol in water. As the frictional force increases, ultrasonic absorption increases[17]. In the present case, ultrasonic absorption or attenuation increases with concentrations of the amino acids contents.

CONCLUSION

From the ultrasonic velocity and density values of the solutions of amino acids in aqueous solutions of methanol; the acoustic parameters like molar sound velocity, molar compressibility, free volume, free length, internal pressure, and ultrasonic attenuation. The results show that the specific ion-ion, ion-solvent and solvent-solvent interactions play an important role for explaining the acoustic parameters. However, any deviation from the usual behavior is probably due to characteristic structural changes in the systems concerned.

ACKNOWLEDGEMENTS

One of the authors (SP) is very much thankful to the President of the Governing Body, and the Principal, U.N. (Auto) College, Adashpur, Odisha for sanction of the leave for doing research work in , I.T.E.R., S 'O' A University, Bhubaneswar

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