

Viscometric and Ultrasonic studies of Glycine (α - Aminoacid) in the aqueous solution of Methanol and Ethanol

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Abstract

Viscometric and ultrasonic studies of Glycine has been carried out in Methanol + water and Ethanol + water co-solvents at different temperatures 30, 35 and 40°C respectively. From these experimental data, derived thermodynamic parameters such as the isentropic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (z), molar compressibility (w), molar sound velocity (R) and apparent molar compressibility (ϕ_k) have been computed using the standard relations. The results have been analyzed on the basis of variations in thermodynamic parameters. The variations in Ultrasonic velocity and adiabatic compressibility with concentrations in both systems show a similar trend of increasing ultrasonic velocity and decreasing in adiabatic compressibility of the constituent electrolytes at different temperatures. This is due to complex formation and coordinate covalent bond formation between the molecules of the liquid mixtures. The results are discussed in terms of structure – making or structure – breaking effects of amino acids in the mixture.

Key words : Ultrasonic velocities, Amino acids, viscosity, methanol, ethanol, density, adiabatic compressibility, inter molecular free length, acoustic impedance, molar compressibility, molar sound velocity, apparent molar compressibility.

1. Introduction

Amino acids are the organic compounds containing both amino and carboxylic group in their molecular solutions. Amino acids in aqueous solution are ionized and can act as

acids or bases due to formation of zwitter ions. The knowledge of the acid base properties of amino acids is extremely important in understanding many properties of proteins¹ besides, the biological system consists of 75% water and hence the study of interaction of

these amino acids has become significant. These amino acids are very important because they are the building blocks of proteins which are very essential for our body.

There are many approaches used to determine the structure and function relationship of biomolecules. Among these approaches, ultrasonic velocity measurements provide an important tool to study the liquid state. Ultrasonic and thermodynamic parameters derived from these measurements are widely used to study the molecular interactions^{2,3} in pure liquid, aqueous solutions and liquid mixtures. Ultrasonic study on the amino acids with aqueous solution of electrolytes and non-electrolytes provide useful information in understanding the behaviour of liquid systems, intramolecular and intermolecular associations, complex formation and related structural changes. For the past two decades, a considerable study has been carried out to investigate the hydration of proteins through volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration⁴. Due to the complex molecular structure of proteins, direct study is somewhat difficult. Therefore, the useful approach is to study simpler model compounds, such as amino acids. Most of the studies on amino acids have been carried out in pure and mixed aqueous solutions⁵⁻⁷. The physical properties of dilute aqueous solutions of non electrolytes depend on the solute is a water structure maker or structure breaker. The influence of small quantity of amino acids on the hydrogen bonded structure of water in the solution of water, methanol-water system and ethanol water system is quite different from that in the absence of amino acids in order to study the nature of molecular interactions in the above solutions.

Ultrasonic velocity, density and viscosity studies were carried out in aqueous solution of methanol and ethanol containing glycine.

2. Experimental Details

All the chemicals used in present work were analytical reagent (AR) grade and spectroscopic grade of minimum assay of 99.9% obtained from E.Merk and Sdfines. Amino acid (Glycine) was crystallized twice from aqueous solutions and dried under vacuum at 373K for 12 hrs. Then it was stored over P₂O₅ in a desiccators before use. Doubly distilled, degassed water was used for preparation of the solutions. Aqueous methanol and ethanol (10% v/v) binary mixtures were used as solvents to prepare solutions of (0.02, 0.04, 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20 M) amino acid. All the solutions were prepared on molarity basis and were kept in air tight bottles. The weighing was done on an electronic digital balance, SHIMADZU AX200 (Swiss make) accurate up to 1.0×10^{-4} g.

The densities of mixed solvents and solutions of glycine in these solvents were measured using a specific gravity bottle by relative measurement method with an accuracy of $\pm 0.01 \text{ Kg.m}^{-3}$. An Oswald's viscometer (10ml capacity) was used for viscosity measurement and efflux time was determined using a digital chronometer to within ± 0.01 s. Ultrasonic velocity was determined using a single crystal variable path ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at 2 MHz, which was calibrated with water, methanol and benzene at 303.15K. During the measurements, the temperature of the test solution was maintained to an accuracy of ± 0.01 K in an electronically controlled thermostatic water bath (RAAGA INDUSTRIES, INDIA).

The ultrasonic parameters such as molar sound velocity, apparent molar compressibility, isentropic compressibility etc. were computed in these solutions at all the concentrations using the described standard formulae⁸.

3. Results and Discussion

The variation of ultrasonic velocity with the concentration of glycine in the solution

of methanol + water and ethanol + water is tabulated in Table 1.

From Table 1, it is seen that, the ultrasonic velocity of solutions increases with increase in the concentration of electrolyte in the solution of glycine + methanol + water as well as in the solution of glycine + ethanol + water at different temperatures. The values of ultrasonic velocity for same sample decreases on increasing temperature. These values are

Table 1. Ultrasonic velocity of Glycine in Methanol + water and Ethanol + water at 30, 35 & 40°C.

Conc. (mol/L)	Glycine + Methanol + water			Glycine + Ethanol + water		
	30°C	35°C	40°C	30°C	35°C	40°C
0.02	1511	1506	1502	1462	1459	1455
0.04	1514	1509	1505	1465	1462.5	1459
0.06	1517.5	1512	1507	1468.5	1466	1462
0.08	1520	1515.5	1511	1471	1469	1466
0.10	1523	1518	1514.5	1474	1471.5	1469
0.12	1526.5	1521	1517	1477.5	1475	1471
0.14	1529	1524	1520.5	1481	1478	1474
0.16	1532	1527.5	1523	1484.5	1482	1479
0.18	1535.5	1530	1526	1487	1484.5	1482
0.20	1538	1533	1529	1490	1487	1483.5

Table 2. Density of Glycine in Methanol + water and Ethanol + water at 30, 35 & 40°C.

Conc. (mol/L)	Glycine + Methanol + water			Glycine + Ethanol + water		
	30°C	35°C	40°C	30°C	35°C	40°C
0.02	0.9228	0.9142	0.9087	0.9130	0.9053	0.8976
0.04	0.9235	0.9149	0.9093	0.9137	0.9059	0.8984
0.06	0.9242	0.9155	0.9099	0.9144	0.9065	0.8991
0.08	0.9249	0.9163	0.9105	0.9149	0.9071	0.8997
0.10	0.9255	0.9169	0.9111	0.9155	0.9076	0.9002
0.12	0.9262	0.9175	0.9117	0.9161	0.9083	0.9008
0.14	0.9269	0.9182	0.9123	0.9167	0.9089	0.9013
0.16	0.9276	0.9189	0.9129	0.9173	0.9097	0.9019
0.18	0.9283	0.9196	0.9135	0.9179	0.9102	0.9023
0.20	0.9290	0.9202	0.9191	0.9185	0.9107	0.9028

Table 3. Viscosity (η) of Glycine in Methanol + water and Ethanol + water at 30, 35 & 40°C.

Conc. (mol/L)	Glycine + Methanol + water			Glycine + Ethanol + water		
	30°C	35°C	40°C	30°C	35°C	40°C
0.02	1.1199	0.9856	0.8594	1.8239	1.5976	1.3448
0.04	1.1227	0.9885	0.8619	1.8299	1.6042	1.3486
0.06	1.1266	0.9915	0.8645	1.8362	1.6097	1.3556
0.08	1.1301	0.9944	0.8691	1.8428	1.6151	1.3595
0.10	1.1327	0.9972	0.8697	1.8492	1.6204	1.3653
0.12	1.1367	1.0003	0.8722	1.8551	1.6259	1.3694
0.14	1.1399	1.0032	0.8748	1.8611	1.6312	1.3738
0.16	1.1433	1.0061	0.8724	1.8668	1.6368	1.3787
0.18	1.1466	1.0091	0.8799	1.8728	1.6421	1.3836
0.20	1.1499	1.0122	0.8826	1.8794	1.6478	1.3885

Table 4. Isentropic compressibility (β_s) of Glycine in Methanol + water and Ethanol + water ($\text{cm}^2/\text{dyne} \times 10^{12}$) at 30, 35 & 40°C.

Conc. (mol/L)	Glycine + Methanol + water			Glycine + Ethanol + water		
	30°C	35°C	40°C	30°C	35°C	40°C
0.02	47.464	48.229	48.780	51.243	51.892	52.625
0.04	47.240	48.001	48.553	50.994	51.609	52.290
0.06	46.987	47.779	48.393	50.713	51.329	52.035
0.08	46.797	47.517	48.105	50.513	51.086	51.717
0.10	46.583	47.330	47.851	50.274	50.884	51.477
0.12	46.334	47.112	47.663	50.004	50.604	51.303
0.14	46.148	46.891	47.412	49.735	50.366	51.066
0.16	45.933	46.641	47.226	49.468	50.050	50.688
0.18	45.689	46.453	47.009	49.270	49.854	50.461
0.20	45.506	46.242	46.540	49.040	49.660	50.331

also agreed with the result of A Srinivas Rao⁹.

The values of density of the solution of glycine in methanol + water and ethanol + water are tabulated in Table 2. The densities of the solutions increase with increase in concentration of glycine and decrease on increase of the temperature. The viscosity of solutions are tabulated in Table 3 and it is seen that the values increase with increase in the concentration of glycine. Isentropic compressi-

bility, intermolecular free length and apparent molar compressibility are recorded in Table 4, 5 and 6 respectively. The variation in the values are also agreed with Aswar and Rohankar¹⁰.

Ultrasonic velocity in the aqueous solution of Methanol and ethanol increases with the addition of amino acid (Glycine). When glycine is dissolved the water structure is disturbed initially, followed by a structural reorganization leaving the molecules in closely

Table 5. Intermolecular free length (L_f) of Glycine in Methanol + water and Ethanol + water at 30, 35 & 40°C.

Conc. (mol/L)	Glycine + Methanol + water			Glycine + Ethanol + water		
	30°C	35°C	40°C	30°C	35°C	40°C
0.02	4.3494	4.3843	4.4093	4.5192	4.5477	4.5798
0.04	4.3391	4.3739	4.3990	4.5083	4.5354	4.5652
0.06	4.3275	4.3638	4.3917	4.4958	4.5230	4.5540
0.08	4.3187	4.3518	4.3787	4.4869	4.5123	4.5401
0.10	4.3088	4.3432	4.3671	4.4763	4.5034	4.5296
0.12	4.2973	4.3333	4.3585	4.4643	4.4910	4.5219
0.14	4.2887	4.3231	4.3470	4.4522	4.4804	4.5114
0.16	4.2787	4.3115	4.3385	4.4403	4.4663	4.4947
0.18	4.2673	4.3029	4.3285	4.4314	4.4576	4.4846
0.20	4.2588	4.2930	4.3068	4.4210	4.4489	4.4788

Table 6. Apparent Molar compressibility (ϕ_k) of Glycine in Methanol + water and Ethanol + water ($\text{cm}^2/\text{dyne} \times 10^9$) at 30, 35 & 40°C.

Conc. (mol/L)	Glycine + Methanol + water			Glycine + Ethanol + water		
	30°C	35°C	40°C	30°C	35°C	40°C
0.02	-259.43	-252.96	-248.28	-238.62	-233.68	-228.67
0.04	-260.66	-254.17	-249.43	-239.79	-234.80	-229.77
0.06	-261.89	-255.35	-250.59	-240.92	-236.13	-230.86
0.08	-263.12	-256.58	-251.75	-242.04	-237.39	-232.01
0.10	-264.33	-257.76	-252.65	-243.18	-238.16	-233.07
0.12	-265.67	-258.95	-254.11	-244.34	-239.28	-234.17
0.14	-266.81	-260.16	-255.51	-245.48	-240.44	-235.28
0.16	-268.06	-261.39	-256.47	-246.62	-241.57	-236.47
0.18	-269.31	-262.61	-257.61	-247.78	-242.71	-237.51
0.20	-270.60	-263.81	-258.79	-248.94	-243.84	-238.62

fitting helical cavities¹¹. This will increase the close packed structure of water which means increased cohesion in the medium. The increase in the ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration. It is known that aqueous solutions of glycine contains in addition to the unchanged molecules ($\text{NH}_2 \text{CH}_2 \text{COOH}$), an electrically neutral zwitter ion ($^+\text{NH}_3 \text{CH}_2 \text{COO}^-$). When glycine is dissolved in aqueous alcohol, the cations NH_3^+ and anions COO^-

are formed. The water molecules are attacked to the ions strongly by the electrostatic forces which introduce a greater cohesion in the solution. The cohesion generally increases with the increase of concentration of glycine. The increased associations observed in these solutions, may also be due to water structure enhancement brought by the increase electrostriction in the presence of ethanol and methanol. The electrostriction effect which brings about the shrinkage in the volume of solvent, caused by the zwitter ion portion of glycine, is

increased in mixed solvent as compared to that in pure water. This effect is similar to the results of Sandu *et al.*¹² the decrease in adiabatic compressibility, observed in aqueous methanol and ethanol solutions with glycine in the present study generally confirms that conclusion drawn in the viscometric and ultrasonic studies. The importance of the interactions of the water molecule in biological structures can not be overemphasized. The structures and functions of biological molecules are directly linked with its aqueous medium. Water molecules constitute an integral part of the protein structure and interaction of the protein with the water molecules decides the conformation of the residues, which are on the surface of the protein molecule. The interaction has an important role in protein folding. Ordered water molecules also mediate protein-ligand interactions. Water molecules bound to active sites are found to reduce the entropy of activation when replaced by the ligands. Water bridges between carbonyl oxygen atoms and amide protons of different peptides lead to formation of linkages that stabilize the protein-ligand and protein-protein interfaces. Water molecules provide the necessary plasticity to the protein molecules which is essential for its internal dynamics and thus for its biological activity. In the molecular recognition process in enzymes and binding proteins, optimization energy of mutual hydrogen bonded networks between protein, water and ligand plays an important role. Linear results of viscometric studies have also been reported for some ternary electrolytes in Dioxane water mixture¹³. These results of viscosity indicate that there is a significant interactions between the solute and solvent molecules because the presence of amino and carboxylic group of glycine, with

alcohols create the possibility of interactions between the molecules.

Therefore in the light of viscometric and ultrasonic studies and their acoustic properties, it is concluded that there is a significant interactions between solute and solvent molecules.

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