

Acoustical studies of some bio-active molecules in aqueous 1,4-dioxane solutions at 298.15K

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ABSTRACT

The Density and Ultrasonic velocity measurement were carried out in aqueous solution of glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine in 10% 1,4-dioxane at 298.15 K. Also from the density and ultrasonic velocity measurement, adiabatic compressibility (β_{ad}), intermolecular free length (L_f), specific acoustic impedance (z), Relative association (R_A) and Hydration number (n_H) are calculated at the temperatures, 298.15 K. All these parameters are related to type and extent of intermolecular interactions in binary liquid mixtures. All the results were interpreted in the light of ion-ion and ion-solvent interactions and of structural effect of solutes in solutions.

Key Words: Ultrasonic velocity, specific acoustic impedance, clusters.

INTRODUCTION

Amino acids are the fundamental substances for building proteins. Ultrasonic studies of some amino acids in 10% 1,4-dioxane are of great importance to obtain about various types of interactions in solutions and have been used to understand the factors responsible for the thermodynamic stability of proteins and their unfolding behavior. Knowledge of various solute-solvent and solute-solute interactions this interaction is very important to understand various fundamental phenomena like stability of proteins, folding/unfolding processes, denaturation of proteins aggregation, several biochemical processes such as protein dehydration in aqueous solutions¹⁻⁴. The interaction of amino acids with electrolyte in the aqueous solutions and their temperature dependence of these interactions also play an important role in understanding the nature of action of bioactive molecule, the thermodynamic behavior of biochemical process in the body and the stability of the organism found in submarine hot springs⁵⁻⁷.

Mixed aqueous solvents are used extensively in chemistry and other fields to control factors like stability, reactivity and solubility of system. 1,4-dioxane is a widely used solvent because it is a non-bonded cyclic ether, miscible with water in proportion with boiling point close to that of water. Moreover, its dipole moment is close to zero and the dielectric constants can be varied over a wide range (2.2-78) in its mixture with water.

MATERIAL

Five amino acids namely glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine of highest purity were obtained from Sigma chemicals Co. Amino acids were dried in vacuum oven for 24 hrs and kept over P_2O_5 in vacuum desiccators. 1,4-dioxane was refluxed and then distilled over sodium metal using a fractionating glass column. The middle fraction distilling at 373 K was collected for use. All the solutions were prepared on the molarity basis. The samples were weighed on a mettler balance having accuracy of 0.01 mg.

Water used to prepare solutions was obtained by distilling deionised water over alkaline KMnO_4 and it was thoroughly degassed prior to its use. The specific conductance of the water used was less than $0.055 \times 10^{-6} \text{ s cm}^{-1}$

METHODS

The densities of the solutions were measured using a single capillary pycnometer made up of borosil glass with a bulb of total volume of 8 cm^3 and capillary with internal diameter of 0.1 cm was chosen⁹⁻¹⁵ for the present work. The details pertaining to calibration experimental set up and operational procedure have been previously described⁹⁻¹⁵. An average of triplicate measurement was taken in to account. The reproducibility of density measurement was $\pm 3 \times 10^{-5} \text{ g cm}^{-3}$. Ultrasonic velocities for the solution were measured using M-81 model, 2 MHz. Ultrasonic interferometer (Mittal Enterprises, New Delhi) with a reproducibility of $\pm 0.4 \text{ ms}^{-1}$ at 298.15 K . The temperature was constantly maintained by controlled temperature water bath (Gemini scientific instruments, Madras) having accuracy of $\pm 0.01^\circ \text{C}$.

RESULTS AND DISCUSSION

Ultrasonic Velocity (U)

It is observed from table 1 that the ultrasonic velocity increases with the increase in concentration of amino acids in aqueous 1,4-dioxane. The increase in ultrasonic velocity in any solution indicates the maximum association among the molecules present in solution. In the present study was observed with steady increase in ultrasonic velocity as concentration, this is due to maximum possible association in aqueous 1,4-dioxane solution. Same behavior is observed in the acoustical properties of fructose and maltose in water, aqueous NH_4Cl solution¹⁶, and some amino acids in binary aqueous $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ ¹⁷.

The ultrasonic velocity of amino acids in aqueous 1,4-dioxane is found to increase with increase in concentrations of amino acids. This behavior is similar to that of pure water, where ultrasonic velocity increases with temperature. As the temperature increase, the hydrogen bonds among the water molecules break and more

monomeric water molecules are formed. These broken water, molecules enter the vacant space present in the cage like water structures and thus get "trapped". As a result the number of close-packed water structure increase with the increase in temperature. This increase in close packed water structure forms the material medium for the propagation of ultrasonic waves. Thus the ultrasonic velocity increases with the increase in temperature for pure water as well as aqueous 1,4-dioxane. This effect favors a decrease in compressibility. With increase in temperature, however, the mean distance between the molecules tends to increase with a corresponding increase in compressibility. These two opposing tendencies results in a net decrease in compressibility and hence increase in ultrasonic velocity.

When an ion is added to a solvent, it attracts certain solvent molecules towards itself by wrenching the molecules from bulk of the solvent due to the force of electrostriction. Because of this, the available solvent molecule for the next incoming ion get decreased, this process is called as compression. Every solvent has a limit for the compression called the limiting compressibility value. The compressibility of a solvent is higher than that of a solution and it decrease with increase in concentration of the solution. With increase in ionic solute concentration, their electrostrictive forces cause the water structure to break and the solute surrounded water molecule are more compactly packed. This hydration effect in turn, results in reducing the compressibility with increasing ionic solute concentrations.

Adiabatic compressibility(β_{ad})

Adiabatic compressibility β_{ad} (N^{-1}m^2) was calculated from both density and sound velocity values using the following equation.

$$\beta_{ad} = 100/u^2\rho \quad \dots(1)$$

where u =Sound velocity of solution (m/sec) and ρ = Density of the solution at the same temperature (Kg/m^3).

In the present study adiabatic compressibility decrease with the increase in

temperature and the concentration of amino acids in aqueous 1,4-dioxane. This confirms the presence of solute solvent interaction through dipole-dipole interaction of the 1,4-dioxane with the surrounding water molecule¹⁸.

Intermolecular free length (L_f)

The variation of ultrasonic velocity in a solution depends on the increase or decrease in the molecular free length (L_f) after mixing the components.

On the basis of a model for sound propagation proposed by Eyring and Kincaid¹⁹, ultrasonic velocity should increase if the intermolecular free length (L_f) decrease as a result of mixing and vice-versa. It is reported²⁰ that intermolecular free length is the predominant factor in determine the ultrasonic velocity in a solution. The nature of L_f variation with composition of binary mix depends on the size of the molecules of components²⁰. If the molecular size of both the components are equal then curve is linear, if the size of molecule of second component is increased then the deviation is found it be positive. If it is decreased deviation is found to be negative.

Intermolecular free length (L_f) is calculated using following expression.

$$L_f = K_T (\beta_{ad})^{1/2} \quad \dots(2)$$

where K_T = temperature dependence constant = $(193.875 + 0.0375T) \times 10^{-8}$ T is absolute temperature²³¹

L_f shows a similar behavior as reflected by compressibility value. The decreased compressibility brings the molecules to closer packing in a decrease of intermolecular free length as observed in table 1.

In the present investigation it has been observed that the L_f values decrease on increasing the concentration of amino acids aqueous 1,4-dioxane This behavior indicates significant interaction between the solute and solvent molecule suggesting a structure-making tendency of 1,4-dioxane, which support the conclusion drawn from B-coefficient.

Acoustic impedance (Z)

Acoustic impedance (Z) calculated from the following relation

$$Z = U\rho \quad \dots(3)$$

It is observed from tables 4.8-4.11, that the values of acoustic impedance varies linearly with the increase in concentration of amino acids in aqueous 1,4-dioxane. The linear variation of Z with concentration confirms the presence of molecular association between solute and solvent molecules

Relative association (RA)

Relative association (RA) is influenced by two factors 1) the breaking up of the solvent molecule on addition of solute to it and 2) solvation of solute that are simultaneously present i.e. specific interactions leading to complex formation between molecules of system. The former factor results in decrease and later in increase in relative association.

The increase in RA with concentration suggests that solvation of solute predominant over breaking up of the solvent aggregates. As the temperature of solution rises the aggregates of solvent molecules breaks down, resulting in increased solvation of solute by free solvent molecule and there by increase in RA with increase in temperature. The decrease in RA with concentration and rise in temperature, suggest that breaking up of the solvent molecule is predominant over solvation added solute.

Relative association RA are calculated using following expression

$$RA = (\rho_s / \rho_o)(U_o / U_s)^{1/\beta} \quad \dots(4)$$

where, ρ_o , ρ_s are the densities of solvent and solution

U_o , U_s are the ultrasonic velocities of solvent and solution

In the present study, RA values decrease linearly with concentration of solute which, shows that the breaking up of the solvent molecule is predominant over solvation of added solute.

Table 1: Densities (ρ), Ultrasonic velocity (U), Adiabatic compressibility (β_{ad}), Intermolecular free length (L_f), Acoustic impedance (Z), hydration number (Hn) and Relative association (RA) of some amino acids in 10% aqueous 1,4-dioxane at 298.15 K

Conc.	r	U	β_{ad}	Lf	Z	Hn	RA
Glycine							
0.00	1.01252	1520	4.2747	0.04070	1538.7	3.46	1.00000
0.025	1.01327	1531	4.2649	0.04050	1544.9		1.00037
0.075	1.01478	1552	4.1017	0.04040	1543.3		1.00330
0.125	1.01630	1570	3.9971	0.04030	1553.1		1.00201
0.175	1.01782	1585	3.8863	0.04030	1557.1		1.00080
0.225	1.01938	1600	3.1745	0.04010	1564.5		0.99970
L-alanine							
0.00	1.02152	1520	4.2747	0.04070	1538.7		1.00000
0.025	1.01320	1530	4.2162	0.04060	1535.5		1.000432
0.075	1.01458	1550	4.1025	0.4040	1537.6		1.00100
0.125	1.01597	1570	3.9932	0.04030	1570.0		0.99980
0.175	1.01736	1585	3.9126	0.04020	1543.9		0.99470
0.225	1.01878	1600	3.8342	0.04020	1547.1		0.98800s
L-valine							
0.00	1.01252	1520	4.2747	0.04070	1538.7	5.16	1.00000
0.025	1.01317	1533	4.1998	0.04070	1535.5		1.00190
0.075	1.01448	1568	4.0609	0.04070	1537.6		0.99610
0.125	1.01581	1580	3.9434	0.04060	1570.0		0.99200
0.175	1.01714	1600	3.8404	0.04050	1543.9		0.98200
0.225	1.01840	1618	3.7505	0.04040	1547.1		0.98960
l-leucine							
0.00	1.01252	1520	4.2747	0.04070	1538.7	6.72	1.00000
0.025	1.01308	1532	4.2057	0.04062	1540.0		0.99770
0.075	1.01421	1556	4.0724	0.04060	1542.9		0.99340
0.125	1.01535	1581	3.9402	0.04060	1546.8		0.98980
0.175	1.01699	1598	3.8525	0.04051	1548.7		0.98220
0.225	1.01765	1614	3.7722	0.04052	1550.0		0.98220
L-phenyl alanine							
0.00	1.01252	1520	4.2747	0.04070	1538.7	7.91	1.00000
0.025	1.01339	1533	4.1981	0.04060	1538.8		0.99800
0.075	1.01579	1558	4.0559	0.04050	1540.1		0.99500
0.125	1.01791	1580	3.9353	0.04040	1546.2		0.99160
0.175	1.02008	1600	3.8294	0.04030	1553.3		0.99000
0.225	1.02260	1620	3.7274	0.0402	1553.4		0.98620

Hydration number

The hydration of solute molecule in water is explained on the basis of Frank and Wen²¹ model of solute-solvent interaction, which pictures three different solvent interactions, regions in the neighborhood of the solute. Just outside the molecule, there is layer of immobilized and compressed water as a result of electrostrictive and other attractive forces exerted by the solute. The solute is surrounded by slightly less compressed or "structure broken" region of water molecule distantly affected by these forces. The outermost layer is bulk water, which possesses the typical tetra coordinated hydrogen-bonded structure not affected by any of the above forces. Compressibility measurements indicate the changes in the first two layers of solvent around the solute molecule. In case of carbohydrate molecule, the water structure is slightly disturbed by the hydrogen-bonded network around the solute; this holds the water around the solute firmly, making the hydration layer even less compressible.

The number of water molecule n_H hydrated to the amino acids were calculated using the method discussed elsewhere.

From the computed values of n_H , it is found that in all the concentration, each in aqueous 1,4-dioxane molecule is closely bound and forms a complex in cluster organization with a fixed number of water molecules.

CONCLUSION

The ultrasonic velocity increase with increase in concentration of amino acids indicates the maximum association among the molecules

present in solution; this is due to maximum possible association in aqueous 1,4-dioxane solutions. In the present study adiabatic compressibility decrease with the increase in temperature and the concentration of amino acids in aqueous 1,4-dioxane. This confirms the presence of solute-solvent interaction through dipole-dipole interaction of the 1,4-dioxane with the surrounding water molecule. The variation of ultrasonic velocity with the compressibility of mixture is explained on the basis of a model for sound propagation proposed by Eyring and Kincaid. This model has been found to be suitable in all binary mixtures. The L_f values decrease on increasing the concentration of amino acids in aqueous 1,4-dioxane. This behavior indicates significant interaction between the solute and solvent molecule suggesting a structure-making tendency of 1,4-dioxane. The value of acoustic impedance varies linearly with the increase in concentration of amino acids in aqueous 1,4-dioxane. The linear variation of Z with concentration confirms the presence of molecular association between solute and solvent molecules. In the present study, RA values decrease linearly with concentration of solute, showing that the breaking up of the solvent molecule is predominant over solvation of added solute. From the computed values of n_H , it is found that in all the concentration each in aqueous 1,4-dioxane molecule is closely bound and forms a complex in cluster organization with a fixed number of water molecules.

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