

Ultrasonic studies of some amino acids in aqueous 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ solutions at 298.15 K

A.R. MAHAJAN, S.R. MIRGANE*, V.K. PAGARE, S.B. DESHMUKH and S.B. BIKKAD

Post Graduate Department of Chemistry, J.E.S. College, Jalna - 431203 (India)

(Received: August 18, 2007; Accepted: October 12, 2007)

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 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ 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

Ionic species play significant role in governing the physical, chemical and biological behavior of biological macromolecules like proteins, nucleic acids, etc. To explain the behavior of these biological molecules one must understand the ionic solutions in terms of ion-water and ion-ion interactions along with the biomolecules-water interactions and how these interactions are altered in the presence of proteins and other bio-molecules. These two aspects remain mystery for the physical and biological chemists and can be well understood by investigating the physico-chemical behavior of ionic species in biological systems. Accurate knowledge of thermodynamic mixing properties of binary mixtures has great relevance in theoretical and applied area of research. These data are needed for design processes in chemical, petrochemical and pharmaceutical industries. Amino acids are fundamental structural units of proteins. Due to the complex nature of proteins direct study is somewhat difficult therefore it is necessary to study the low molecular weight model such as amino acids. Knowledge of various solute-solvent and solute-solute interaction this interactions

is very important to understand various fundamental phenomenon like stability of proteins, folding/unfolding processes, denaturation of proteins aggregation, several biochemical process such as protein dehydration in aqueous solutions¹⁻⁴. The interaction of amino acids with electrolyte in the aqueous solutions and there temperature dependence of these interactions also play a important role in understanding 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.

Lithium (Beryllium and aluminum) are not essential element but they can interfere with biochemical process in vivo by interacting with phosphate containing molecule. One interesting possibility is the involvement of lithium with phosphate compounds, this can occur at two levels.

1. Lithium could interact with the phosphate compounds of Na^+/K^+ or $\text{Mg}^{2+}/\text{Ca}^{2+}$ pumps.
2. It could interact with the inositol phosphate.

Lithium is of course a major psychotherapeutic drug and its action may in part

to be based on these possibilities⁸. Definitive evidence as to mode of action of lithium is currently unavailable⁹. Therefore thermodynamic study of amino acids in presence of Lithium salt is undertaken. The results obtained may be useful in order to understand mode of acting of Lithium.

MATERIALS

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 on kept over P_2O_5 in vacuum desiccators. Lithium perchlorate (LOBA Chemie) were used without any purification. All the solutions were prepared on the molarity basis. The samples were weighted on a mettler balance having accuracy of 0.01mg. 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 0.1cm 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 maintain 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 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$.

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 LiClO_4 solutions. Same behavior is observed in the acoustical properties of fructose and maltose in water, aqueous NH_4Cl solution¹⁶, ultrasonic studies of some amino acids in binary aqueous $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ ¹⁷ and in aqueous 1,4 dioxane¹⁸ solutions. In addition, in aqueous $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ solution, the polar perchlorate molecules form more compact structure with the solvent water molecules. 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.

Adiabatic compressibility (β_{ad})

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 gets 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 decreases 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 molecules are more compactly packed. This hydration effect in turn, results in reducing the compressibility with increasing ionic solute concentrations.

Adiabatic compressibility $\beta_{ad} (\text{N}^{-1}\text{m}^2)$ were 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), ρ = density of the solution at the same temperature (Kg/m^3).

Tables 1: Densities(ρ), Ultrasonic velocities(U), adiabatic compressibility (β_{ad}), intermolecular free length (L_f), specific acoustic impedance (z), Relative association (R_A) and Hydration number (H_n) of some amino acid in 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ solutions at 298.15K.

C (Mol Kg ⁻¹)	$\rho^* 10^{-3}$ (Kg m ⁻³)	U(m s ⁻¹)	$\beta_{ad} \cdot 10^{-10}$ (N ⁻¹ m ²)	L_f (Å)	$Z \cdot 10^3$ (Kg m ⁻² s ⁻¹)	RA	H_n
Glycine							
0.00	1.01334	1504	4.3626	0.04128	1524.06	-	3.09
0.025	1.01409	1515	4.2963	0.04097	1536.35	0.99831	
0.075	1.01561	1536	4.1734	0.04038	1559.98	0.99524	
0.125	1.01713	1558	4.0503	0.03978	1584.64	0.99202	
0.175	1.01867	1580	3.9324	0.03919	1609.5	0.98889	
0.225	1.02022	1600	3.8288	0.03867	1632.35	0.98626	
L-Alanine							
0.00	1.01334	1504	4.3626	0.04128	1524.06	-	4.54
0.025	1.01403	1514	4.3023	0.04099	1535.06	0.99848	
0.075	1.01543	1532	4.1960	0.04049	1555.64	0.99593	
0.125	1.01684	1550	4.0934	0.03999	1576.10	0.99344	
0.175	1.01827	1566	4.0045	0.03955	1594.61	0.99144	
0.225	1.01970	1574	3.9584	0.03932	1605.01	0.99115	
L-valine							
0.00	1.01334	1504	4.3626	0.04128	1524.06	-	5.16
0.025	1.01400	1517	4.2854	0.04091	1538.063	0.99778	
0.075	1.01532	1544	4.1314	0.04017	1567.65	0.99323	
0.125	1.01665	1566	4.0109	0.03958	1592.07	0.98986	
0.175	1.01799	1589	3.8905	0.03898	1617.58	0.98636	
0.225	1.01935	1612	3.7753	0.03840	1643.19	0.98267	
L-leucine							
0.00	1.01334	1504	4.3626	0.04128	1524.06	-	6.55
0.025	1.01392	1517	4.2857	0.04092	1538.12	0.99771	
0.075	1.01508	1542	4.1432	0.04023	1565.25	0.99343	
0.125	1.01626	1566	4.0125	0.03959	1591.46	0.98948	
0.175	1.01745	1592	3.8779	0.03892	1619.78	0.98522	
0.225	1.01865	1604	3.8156	0.03861	1633.91	0.98392	
L-phenyl alanine							
0.00	1.01334	1504	4.3626	0.04128	1524.06	-	7.29
0.025	1.01444	1518	4.2779	0.04088	1539.92	0.99800	
0.075	1.01665	1542	4.1368	0.04020	1567.67	0.99496	
0.125	1.01888	1568	3.9919	0.03949	1597.60	0.999161	
0.175	1.02111	1586	3.8933	0.03900	1619.48	0.99001	
0.225	1.02336	1616	3.7419	0.03823	1653.75	0.98620	

In the present study adiabatic compressibility decrease with the increase in the concentration of amino acids in 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$.

This confirms the presence of solute solvent interaction through dipole-dipole interaction of the ClO_4^- ion of LiClO_4 with the surrounding water molecule²⁰¹. The variation of adiabatic

compressibility of amino acids with respect to concentration of amino acids are shown in Fig. 1.

Inter molecular free length (L_f)

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

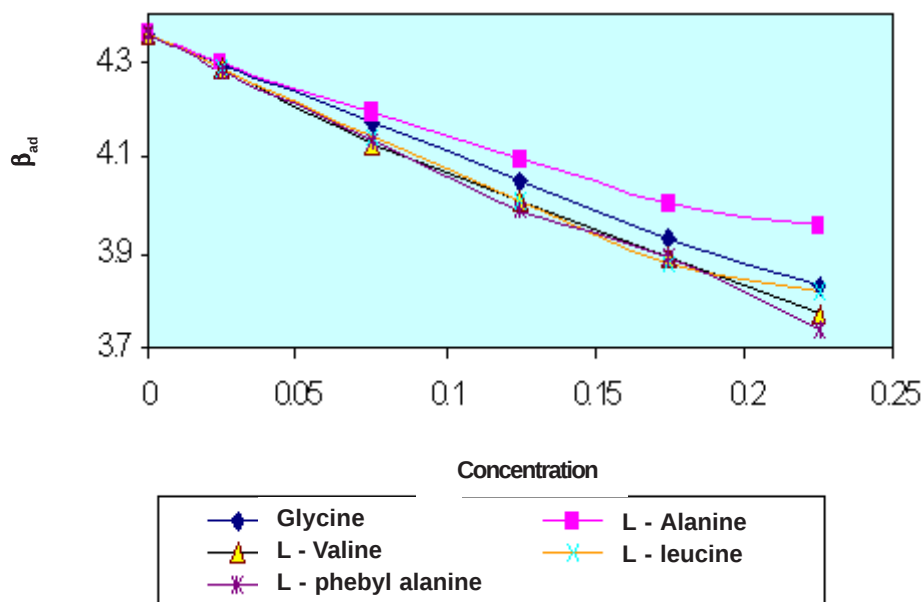


Fig. 1: A graph of β_{ad} verses C of some amino acids in 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ solutions at 298.15 K

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 reported¹⁹ that intermolecular free length is the predominant factor in determining 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) are 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 temperature

L_f shows a similar behavior as reflected by compressibility value. The decreased compressibility brings the molecules to a 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 in 0.02 M $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. This behavior indicates significant interaction between the solute and solvent molecule suggesting a structure making tendency of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. The plot of L_f vs. C is linear in all cases.

Acoustic impedance (Z)

Acoustic impedance (Z) calculated from the following relation

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

It is observed from Table1, that the value of acoustic impedance varies linearly with the increase in concentration of amino acids in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. 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 suggest 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

$$RA = (\rho_s / \rho_o)(U_o / U_s)^{1/3} \quad \dots(4)$$

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 shows that the breaking up of the solvent molecule is predominant over solvation of added solute

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 interaction, which pictures three different solvents structure 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 the solute. The solute this 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 indicates 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. Hydration numbers are computed from compressibility data, method for computation of hydration number discuss elsewhere⁹⁻¹⁵. From the computed values of H_n , It is found that in all the concentration each in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ molecule is closely bound and forms a complex in cluster organization with a fixed number of water molecule

Conclusion

In this paper a systematic ultrasonic studies of glycine, L-alanine, L-valine, L-Leucine and L-phenyl alanine in 0.02M, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ solutions at 298.15 K has been carried out at different concentration of amino acids. The experimental ultrasonic velocity data and other acoustical parameters give valuable information regarding the solute-solvent interactions in aqueous 0.02M, $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$. The decreased compressibility brings the molecules to a closer packing in a decrease of intermolecular free length. The linear variation of Z with concentration confirms the presence of molecular association between solute

and solvent molecules. From the computed values of H_n , it is found that in all the concentration each in $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ molecule is closely bound and forms a complex in cluster organization with a fixed number of water molecule.

These conclusion give scope for further studies on the thermodynamic properties of the systems.

ACKNOWLEDGEMENTS

Authors are thankful to Prof. B.R.Arbad, Dr.B.A.M. University for their valuable suggestions and discussion. Authors are also thankful to Principal, Dr.R.S.Agarwal, J.E.S. College, Jalna for their help and encouragement.

REFERENCES

1. Kikuchi, M., Sakurai M. and Nitta, K., *J. Chem. Eng. Data* **40**: 935 (1995).
2. Yasuda, Y., Tochida, N., Sakurai M and Nitta K. *J. Chem. Eng. Data* **43**: 205 (1998).
3. Filfil, R. and Chelikain, T.V., *J. Mol. Biol.* **299**: 827 (2000).
4. Lin Q, Hu x, Lin R, Sang w and Li, S. *J. Chem. Eng. Data.*, **46**: 522 (2001).
5. Zhao, H., Wood, A.G., Widdel, F. and Bryant, F.M., *J. Bacterial* **3959**: 172 (1990).
6. Hakin, W., Duke, M.M., Klassen, S.A. and Mickay, R.M. Can., *J. chem.* **72**: 362 (1994).
7. Duke, M. M., Hakin, A.W. and Preuss, K.E., *Can. J. Chem.* **1989**: 72 (1994).
8. Bio-Inorganic chemistry-M. Satake and Y. Mido Page No. 242 Discovery Publishing House , New Delhi.
9. Pal, A. and Kumar, S., *J. Indian Chem. Society.* **79**: 866 (2002).
10. Pal, A. and Kumar, S., *J. of Mole. Liq.* **121**: 23 (2005).
11. Pal, A. and Kumar, S., *J. of Mole. Liq.* **121**: 49 (2005).
12. Pal, A. and Kumar, S., *J. Chem. Sci.*, 267 (2005).
13. Pal, A. and Kumar, S., *J. Indian Chem. Society* **81**: 1023 (2004).
14. Pal, A. and Kumar, S., *Indian Journal of Chem.* 44-A: 469 (2005).
15. Pal, A. and Kumar, S., *J Physics and Chemistry Of liq.* **41**: 4 (2003).
16. Nikam, P.S., Ansari, H.R. and Mehdi Hassan., *J. of Mole. Liq.* **84**:169 (2000).
17. Pal, A. and Kumar, S., *J Mol.Liq.* **121**: 148-155 (2005).
18. Banipal, T.S. and Singh, Gagandeep., *Indian J. of Chem.*, **43A**: 1156-1166 (2004).
19. Eyring, H. and Kincaid, J.F., *J Chem. Phys.* **6**: 620 (1938).
20. Rao, S.B., Raman, J. K. and Rajgopal E. *Indian J. of Pure and Applied physics*, **26**: 717 (1998).
21. Frank, S. and Wen, W.Y., *Disc. Faradays soc.* **29**: 133 (1957).