

# ULTRASONIC VELOCITY, DENSITY AND VISCOSITY MEASUREMENT OF METHIONINE IN AQUEOUS ELECTROLYTIC SOLUTIONS AT 303K

T. Sumathi\* and M. Varalakshmi

Department of Physics (DDE), Annamalai University, Annamalai Nagar – 608002, Tamilnadu

\*E-mail: tsumathi92@yahoo.com

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## ABSTRACT

The ultrasonic velocity (U), density ( $\rho$ ) and viscosity ( $\eta$ ) measurements have been carried out for L-Methionine in aqueous sodium chloride, potassium chloride and lithium chloride as a function of composition at 303K. Experimental data have been used to estimate the adiabatic compressibility ( $\beta$ ), change ( $\Delta\beta$ ) and relative change in adiabatic compressibility ( $\Delta\beta/\beta^\circ$ ), acoustic impedance (z), limiting apparent metal compressibility ( $\phi k^\circ$ ) limiting apparent molal volume ( $\phi^\circ v$ ) and the constants ( $S_k$ ,  $S_v$ ) and viscosity B co-efficient. The results are discussed in terms of structure-making (or) structure -breaking effects of amino acids in the mixtures.

**Keywords:** Ultrasonic velocities, Amino acids, Adiabatic compressibility, Apparent molal compressibility, Apparent molal volume.

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## INTRODUCTION

Ultrasonic is a versatile non-destructive technique and highly useful for the investigation of various physical properties such as residual stress, hardness, grain size micro structure, elastic constant etc. Recent developments have found use of ultrasonic energy in medicine, engineering and agriculture. Ultrasonic study on the amino acids with aqueous solution of electrolytes and non-electrolytes provides useful information in understanding the behavior of liquid systems<sup>1</sup>. Electrolytes are known to influence the stability of biologically important molecules such as proteins. Since proteins are complex molecules and their behavior in solutions is governed by a combination of many more specific interactions, direct study of electrolyte protein is difficult. Therefore in order to obtain more insight into hydration of proteins and non-covalent forces stabilizing their negative structure it is necessary to determine the effects of salts<sup>2-4</sup>. Amino acids belong to an important family of bio-molecule, which serve primarily as building block of proteins. The most remarkable thing is the amino acids serve not only as precursors of hormones, alkaloids, purphysis prunes, nerves, transition of all growth and many other biomoles<sup>5-7</sup>. Amino acids in aqueous solution are ionized and can act as acids (or) bases. Knowledge of acid-base properties of amino acids is extremely important in understanding many properties of proteins<sup>8</sup>. The addition of salts/solvents to protein solution is known to affect their structure and configuration. Therefore, continuous efforts are being made to study the model compounds in aqueous and mixed aqueous solutions to understand various interactions and their role in confirmation stability of the proteins<sup>9</sup>.

Hence their derived parameters such as adiabatic compressibility ( $\beta$ ), However, the ultrasonic velocity data as such do not provide significant information about the nature and relative strength of various types of intermolecular or inter ionic interactions between the components. Relative ( $\Delta\beta/\beta^\circ$ ) and change in adiabatic compressibility ( $\Delta\beta$ ), apparent molal volume ( $\phi v$ ), apparent molal compressibility ( $\phi k$ ), limiting apparent molal volume ( $\phi^\circ v$ ) and limiting apparent molal compressibility ( $\phi^\circ k$ ) and their constant ( $S_k$ ,  $S_v$ ) and viscosity B co-efficient have been obtained to shed more interactions.

### EXPERIMENTAL

All the chemicals used were of Analytical Reagent (AR) and Spectroscopic Reagent (SR) grades with minimum assay of 99.9%. The speed of sound waves were obtained by using ultrasonic interferometer (Mittal Enterprises, New Delhi) at a fixed frequency of 3 MHz with an accuracy of  $\pm 2\text{ms}^{-1}$ . An electronically digital operated constant temperature bath (RAAGA industries, Madras 61) has been used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The density of pure liquids and liquid mixtures were determined using a pycnometer by relative measurement method with an accuracy of  $\pm 0.1\text{K}$  (Model: SHIMADZU AX-200). The pycnometer was calibrated at 303.15K with double distilled water and gave an estimated reproducibility of  $\pm 0.0001\text{gcm}^{-3}$ . An Ostwald's Viscometer which is 10mL capacity was used for the viscosity measurement of pure liquids and liquid mixtures. The Viscometer was calibrated with fresh conductivity water immersed in the water bath which was kept at the experimental temperature. The time of flow ( $t_w$ ) of water and the time flow ( $t_s$ ) of solution was measured with digital stop clock having an accuracy  $\pm 3 \times 10^{-6} \text{Nm}^{-2}\text{s}$ . The temperature around the viscometer was maintained within  $\pm 0.1\text{K}$  in an electronically controlled thermostatic water bath. In all the mixtures, the mole fraction of the second component, methionine ( $x_2 = 0.05\text{M}$ ) was kept fixed, while the mole fractions of the remaining two were varied from 0.00 to 0.10 so as to have the mixtures of different composition

Using the measured data, some acoustical parameters have been calculated using the standard relations,

Adiabatic compressibility ( $\beta$ ) is given by<sup>10</sup>

$$\beta = \frac{1}{U^2 \rho} \quad (1)$$

The change and relative change in adiabatic compressibility is give by

$$\Delta\beta = \beta - \beta_0, \quad \Delta\beta / \beta_0 \quad (2)$$

Acoustic impedance is calculated by

$$Z = UP \quad (3)$$

The entire viscosity data have been analyzed in the light of Jones Dole<sup>11</sup> Semi empirical equation.

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad (4)$$

Where  $\eta$  and  $\eta_0$  are viscosities of the solutions and solvent respectively and  $m$  is the molal concentration.  $A$  and  $B$  are constants which are definite for a solute solvent system.  $A$  is known as the Flakenhagen co-efficient<sup>12</sup> which characterize the ionic interaction and  $B$  is the Jone-Dole (or) viscosity  $B$  co-efficient which depends on the size of the solute and nature of solute – solvent interactions. Apparent molal compressibility ( $\phi_k$ ) is given by

$$\phi_k = \frac{1000}{m\rho_0} (\rho_0\beta - \beta_0\rho) + \frac{\beta_0 M}{\rho_0} \quad (5)$$

Where,  $\beta$ ,  $\rho$  and  $\beta_0$ ,  $\rho_0$  are the adiabatic compressibility and density of solution and solvent respectively,  $m$  is the molal concentration,  $M$  is the molecular mass of the solute.  $\phi_k$  is the function of  $m$  as obtained by Gocker from Debye<sup>13</sup> Hockel theory and is given by

$$\phi_k = \phi_k^\circ + S_k m^{1/2} \quad (6)$$

Apparent molal volume ( $\phi_v$ ) is obtained by

$$\phi_v = \frac{1000}{m\rho_0} (\rho_0 - \rho) + \frac{M}{\rho_0} \quad (7)$$

The apparent molal volume has been found to differ with concentration according to Masson's empirical relation.

$$\phi_v = \phi_v^\circ + S_v m^{1/2} \quad (8)$$

## RESULTS AND DISCUSSION

The experimental values of density ( $\rho$ ), viscosity ( $\eta$ ) and ultrasonic velocity ( $U$ ), adiabatic compressibility, change and relative change, for different molal composition of L-Methionine in aqueous sodium chloride, potassium chloride and lithium chloride at temperature 303K are shown in Table 1. Acoustic impedance, apparent molal compressibility apparent molal volume, limiting apparent molal compressibility limiting apparent molal volume and constant  $S_k$  and  $S_v$  and viscosity  $B$  co-efficient are listed Table 2 & 3. The ultrasonic velocity, density and viscosity increases with increase in concentration of amino acid in all the systems under investigation. Usually the values of density, viscosity and ultrasonic velocity of any other system vary with increase in concentration of solutions. The change in structure of solvent or solutions as a result of hydrogen bond formation or dissociation or hydrophobic or hydrophilic character of solute<sup>14</sup>. The increase in ultrasonic velocity (Table.1) values of Methionine 0.05M aqueous KCl, NaCl & LiCl solutions may attributed to the overall increase of cohesion brought about by the solute – solute, solute – solvent and solvent – solvent interactions in Solutions<sup>10</sup>. It also increases in the order of electrolytes as LiCl < NaCl < KCl.

Amino acids and di-peptide in aqueous solutions essentially behave as zwitterions having  $NH_4^+$  and  $COO^-$  groups at two ends of the molecule. The  $Na^+$ ,  $K^+$ ,  $Li^+$  and  $Cl^-$  ions furnished by electrolytes interact electrostatically with  $NH_4^+$  and  $COO^-$  groups of amino acids and di-peptide zwitterions. In addition, the water dipoles are strongly aligned to the cations / anions as well as to the amino acids di-peptide zwitterions by electrostatic forces<sup>15</sup>. These interactions comprehensively introduce the cohesion into solution under investigation.  $K^+$ ,  $Na^+$  &  $Li^+$  ions furnished (or) affinity for  $COO^-$  end groups of zwitterions of methionine whereas the  $Cl^-$  ions of salts may interact with  $-NH_3^+$  groups of zwitterions of the same amino acids. Acoustic impedance ( $Z$ ) of both the system is found to increase with increase of concentration of amino acid. An increase in  $Z$  is in good agreement with the requirement of product of  $U$  and  $\rho$ .

From the Table.1, the values of adiabatic compressibility ( $\beta$ ) decreases with increases of concentration. The decrease in  $\beta$  is due to the increase in electrostriction compression of solvent around the molecules at which results in a large decrease in the compressibility of solution<sup>16</sup>. The adiabatic compressibility is in the order LiCl < KCl < NaCl. As the concentration of amino acids increases, interactions between  $NH_3^+$  and  $Cl^-$  between  $COO^-$  and of L-methionine.

The negative values of  $\Delta\beta$  and  $\Delta\beta / \beta^\circ$  is due to the solute – solvent interaction<sup>17-18</sup>. Such an increase in  $\Delta\beta$  and  $\Delta\beta / \beta^\circ$  values with increase in amino acids / zwitterions concentration may be attributed to an overall increase in the cohesive forces in the solutions<sup>19</sup>. These cohesive forces may be results of zwitterions – ions and zwitterions – water dipoles interaction in solution. In addition, the successive increase of amino acids concentration in the salt solution enhances the incompressible part of the solution. This behavior lends to support weak solute – solute and solute – solvent inter molecular inter ionic interactions in these systems.

From the Table. 2 the following observation have been made on  $\phi_k$  of the amino acids in electrolyte + water mixture.

1. The values of  $\phi_k$  all are negative over the entire range of molality.
2. A non-linear relation between  $\phi_k$  and solute has been observed throughout the concentration range.
3. In both systems, the maximum  $\phi_k$  is recorded and order of LiCl < NaCl < KCl.

The above observation clearly indicates the electrostriction and hydrophilic interaction occurring in the systems, thereby indicating solute – solvent interaction. The limiting apparent molal compressibility  $\phi_k^0$  and related constant  $S_k$  of all the amino acids have been computed using least square method. It provides the information regarding solute-solvent and related constant  $S_k$  that of solute interaction respectively.<sup>20</sup>

From Table. 2 the following observation have been made for  $\phi_v$  values of two amino acids in aqueous electrolytes.

1. The  $\phi_v$  values are negative for all the concentration.
2. There is a non-linear observation observed with increase in molality of amino acids.

The above observation clearly suggest that the negative values of  $\phi_v$  indicate the presence of solute – solvent interaction and electrostritive solvation of ions.<sup>21-22</sup> The  $\phi_v^0$  and related constant  $S_v$  for all the concentration is negative. The negative value of  $S_v$  suggests the weak solute – solute interaction. The positive values indicate the strong solute- solute interaction.<sup>23</sup> In order to get more information about this amino acid the role of viscosity B co-efficient is also obtained. The values of the B-coefficient represent the solute–solvent interaction and are a measure of the order or disorder introduced by the solute into the solvent structure<sup>24</sup>. From the Table.3 it is observed that all the A & B values are negative. Since, A is measure of ionic interactions it is evident that the negative values of A is indication of weak ion-ion interaction. Whereas, the negative values of B is indicative of weak solute-solvent interaction. The magnitude of A & B clearly conforms that the amino acids is acting as an effective structure – breaker in aqueous NaCl, KCl and LiCl systems<sup>25</sup>.

### CONCLUSION

The observed trends and variations of thermodynamical parameters with molar concentrations of amino acid provide useful information about the nature of intermolecular forces existing in the mixture. The existence of ion-solvent (or) solvent – solvent interaction resulting in attractive forces promote the structure – making tendency, while ion-ion are solute – solute interaction resulting dipole-dipole dipole-induced dipole and electrostrictive forces enhance the structure – breaking properties of amino acid. An appreciable existence of solute – solvent and solute – solute interactions present in the system with varying degrees and the order of the electrolytes as LiCl < NaCl < KCl. Hence it is evident that the ultrasonic velocity measurement in the given medium serves as a parerful probe in characterizing the physico-chemical properties of the medium.

Table-1: Values of density ( $\rho$ ), viscosity ( $\eta$ ), and velocity (U) Adiabatic compressibility ( $\beta$ ), Change in adiabatic compressibility ( $\Delta\beta$ ) and Relative change in adiabatic compressibility ( $\Delta\beta / \beta^0$ ) of Methionine in aqueous electrolytes (LiCl/NaCl/KCl)

Molality (m) of Methionine	$\rho$ kg m <sup>-3</sup>	$\eta \times 10^3$ Nsm <sup>-2</sup>	Ums <sup>-1</sup>	$\beta \times 10^{10}$ pa <sup>-1</sup>	$-\Delta\beta \times 10^{12}$ pa <sup>-1</sup>	$-\Delta\beta / \beta^0 \times 10^3$
Aqueous LiCl						
0.00	996.14	0.7869	1514.4	4.3773	-	-
0.02	997.37	0.7885	1518.2	4.3499	2.73	6.23
0.04	998.70	0.7996	1520.1	4.3328	4.44	10.14
0.06	1000.17	0.8004	1524.4	4.3025	7.46	17.04
0.08	1001.26	0.8116	1529.8	4.2671	11.00	24.14
0.10	1002.72	0.8132	1532.2	4.2476	12.96	29.60
Aqueous NaCl						
0.00	997.78	0.7885	1520.1	4.3370	-	-
0.02	998.53	0.7955	1524.4	4.3093	2.77	6.39
0.04	999.23	0.8004	1529.7	4.2742	6.28	14.48
0.06	1000.44	0.8108	1532.0	4.2585	7.85	18.104
0.08	1001.64	0.8124	1534.8	4.2382	9.88	22.79
0.10	1002.84	0.8236	1538.6	4.2122	12.48	28.77
Aqueous KCl						
0.00	998.03	0.7988	1523.2	4.3183	-	-
0.02	999.04	0.7996	1527.2	4.3290	1.07	2.48
0.04	1000.12	0.8108	1530.6	4.2680	5.03	11.66
0.06	1000.70	0.8116	1533.8	4.2477	7.06	16.36
0.08	1002.32	0.8228	1536.9	4.2237	9.46	21.92
0.10	1003.09	0.8244	1539.4	4.2065	11.17	25.88

Table-2 : Values of acoustic impedance ( $Z$ ), apparent molal compressibility ( $\Phi_k$ ) and apparent molal volume ( $\Phi_v$ ) of Methionine in aqueous electrolytes (LiCl / NaCl / KCl)

Molality (m) Methionine	$Z \times 10^{-6} \text{ kg m}^{-2} \text{ s}^{-1}$	$-\Phi_k \times 10^8 \text{ m}^2 \text{ N}^{-1}$	$-\Phi_v \times 10^3 \text{ m}^3 \text{ mol}^{-1}$
Aqueous LiCl			
0.00	1.5085	-	-
0.02	1.5142	16.312	61.738
0.04	1.5182	13.903	64.247
0.06	1.5246	15.389	67.426
0.08	1.5318	16.563	64.247
0.10	1.5365	15.851	66.054
Aqueous NaCl			
0.00	1.5167	-	-
0.02	1.5222	15.080	27.555
0.04	1.5294	17.710	46.343
0.06	1.5327	15.593	41.082
0.08	1.5373	14.345	45.842
0.10	1.5429	14.592	48.698
Aqueous KCl			
0.00	1.5202	-	-
0.02	1.5257	13.182	50.599
0.04	1.5307	14.869	52.352
0.06	1.5348	13.701	44.587
0.08	1.5404	14.152	53.807
0.10	1.5442	13.368	50.990

Table-3: Values of limiting apparent molal compressibility ( $\Phi_k^0$ ), limiting apparent molal volume ( $\Phi_v^0$ ) and constants  $S_k$  and  $S_v$ , A and B parameters of Jones – Dole equation of amino acids in aqueous electrolytes (LiCl / NaCl / KCl)

Amino acid	Aqueous alkali halide	$(\Phi_k^0 \times 10^8 \text{ m}^2 \text{ N}^{-1})$	$(S_k^0 \times 10^8 \text{ N}^{-1} \text{ m}^{-1} \text{ mol}^{-1})$	$\Phi_v^0 \text{ m}^3 \text{ mol}^{-1}$	$S_v \text{ m}^3 \text{ kg}^{1/2} \text{ mol}^{3/2}$	A $\text{dm}^{3/2} \text{ mol}^{-1}$	B $\text{dm}^3 \text{ mol}^{-1}$
Methionine	LiCl	-14.880	-3.055	-59.597	-21.722	-0.7856	-23.050
	NaCl	-15.278	-0.782	-17.503	-103.009	-0.4175	-25.050
	KCl	5.976	-84.42	-48.810	-25.272	-0.6134	-29.878

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