Ultrasonic Investigation of α-Amino Acids with Aqueous Solution of Urea at Different Temperatures: A Physicochemical Study

Nazia Malik[a], Azhar U. Khan[b], Saeeda Naqvi[a] and Tanvir Arfin[c,*]

[a]*Department of Chemistry, Aligarh Muslim University, Aligarh-202002, India*

[b]*Department of Chemistry, Jaipur National University, Jaipur-302017, India*

[c]*Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nehru Marg, Nagpur-440020, India*

Abstract: The present paper reflects the ultrasonic investigations for exploring the inter-ionic interactions of various concentrations of α-amino acids such as L-Arginine, L-lysine monohydrochloride, and L -histidine in aqueous solutions of urea over a wide ranges of temperatures (298.15 to 323.15) K under atmospheric pressure. It also represent the detail showing that molecular interactions between the α-amino acids and urea has much dissociation of proteins in the solvent mixture. The study of ultrasonic speed (U) and sound velocity (Δu) were successfully preformed on the liquid ternary mixtures. With the help of the above mentioned parameter, the values of isentropic compressibility (K_s), change in isentropic compressibility (ΔK_s), relative change in isentropic compressibility (ΔK_r), relative association (RA), specific acoustic impedance (Z), and apparent molal isentropic compressibility (ϕ_{ks}) were calculated. These parameters have been examined in term of the molecular associations such as ion-ion, ion-solvent, solute-solvent, solute-solute etc., and briefly described in terms of the structure-making ability corresponding to α-amino acids in the urea. Efforts have been taken to explore the dependency of the outcomes related to temperature and concentration.

Keywords*:* Amino acids, urea, Zwitterions-ions interactions, ion-solvent, solute-solvent.

INTRODUCTION

A variety of biochemical process takes place in the aqueous medium. The physicochemical properties of biomolecules such as amino acids, sugars and drugs give valuable information aiding to understand the mechanism of molecular interaction between them. To gather the understanding of solute –solvent and solute –solute interactions in solutions, the study of thermodynamic parameters is a necessary factor [1,2]. Heat and chemical denaturants such as urea, sodium dodecyl sulphate (SDS) and guanidium hydrochloride (Gdn HCl) were used to break the bond for stability of the protein structure in the form of secondary, tertiary and quaternary one.

Protein molecules are of the nature of complex structure and their action in solution behaves as a significant role by a combination of many particular interactions. The α-amino acids are considerable to another chemical group since they are obtained by natural process of proteins, and their role is significant in all the chemical and biological process in living cells [3]. Some of the structures of α- amino acids are shown in Figure **1**. It displays both type of properties such as acidic and basic in nature but in the form of neutral condition it behaves as zwitter ions. It exhibits high dielectric constant and large dipole moments suggesting both types of charge such as positive and negative in the same molecule as shown in Scheme **1**. Malik *et al*. [4] have reported that the presence of a urea significantly affects the behavior of α-amino acids in aqueous solution.

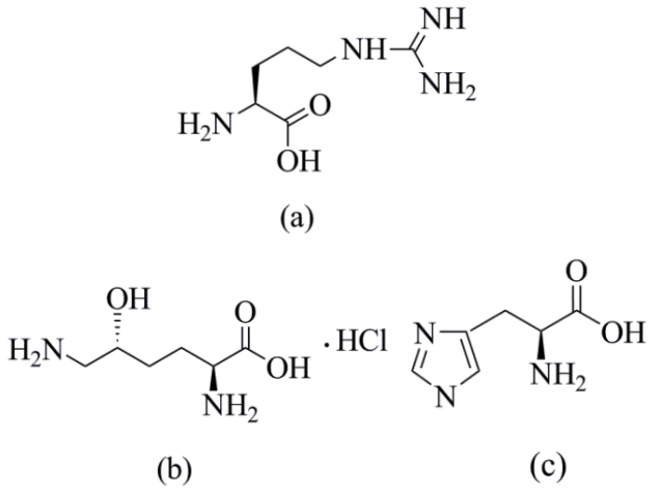
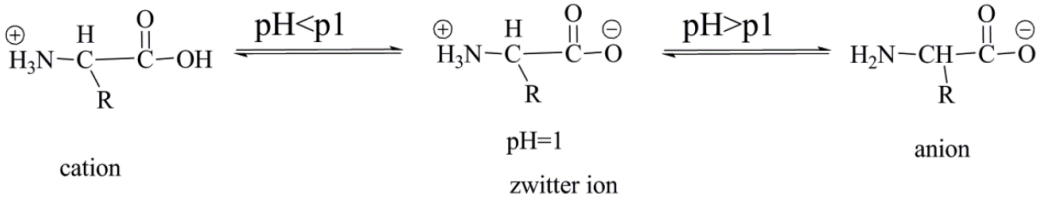


Figure 1: (**a**) L-arginine (**b**) L-lysine monohydrochloride (**c**) L-histidine.

Urea is an essential compound found in every creature on the earth. Urea is a denatured protein and its structure is shown in Figure **2**. It is responsible for

*Correspondence Address to this author at the Environmental Materials Division, CSIR-National Environmental Engineering Research Institute (CSIR-NEERI), Nehru Marg, Nagpur-440020, India; Tel: +91-712-2249885; Fax: +91-712-2247828; E-mail: t_arfin@neeri.res.in, tanvirarfin@ymail.com

E-ISSN: 1929-5030/16



Scheme 1:

constructing protein-water interface forming hydrogen bond between water and amide groups. Urea molecules are rather difficult to react with a group or molecules like hydrophobic or hydrophilic. The denaturation processes occur by the contribution of urea due to change in the solubility of amide back bond [5]. Urea and its derivatives are described to perform as a statistical structural breaker. Brien *et al*. [6] observed that the guanidine hydrochloride and urea molecules react together to form a structural breaker for liquid water.

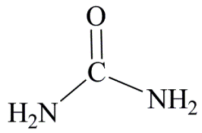


Figure 2: Structure of urea.

According to literature survey on the topic of thermodynamic properties of amino acids in aqueous solution various studies were suggested long-ago [7,8] but yet only little information is provided for aqueous urea solution [5,9]. As per the literature survey, it has been found that study on ultrasonic velocity parameters are still in few amount [10,11]. The study of ultrasonic velocity is an important tool useful in various numbers of physicochemical parameters such as isentropic compressibility (K_s), change in isentropic compressibility (ΔK_s), relative change in isentropic compressibility (ΔK_r), relative association (RA), specific acoustic impedance (Z), and apparent molal isentropic compressibility (ϕ_{ks}). Scientific researchers were interested for the study of solubility and stability of complex molecules like proteins but due to its nature and low molecular weight compound were chosen. As there is a demand of ultrasonic waves increasing day by day for medical applications, the requirement for investigation of ultrasonic character leading to biological media is put into continuous practice.

The value of ultrasonic velocity provides a better concept about the nature and relative strength of different types of intermolecular / interionic interactions, but the thermodynamic parameters provide an essential understanding about the scope of intermolecular interactions like, weak or strong or no interaction at all and it also focuses on the mechanism of intermolecular processes.

In the current paper, we have discussed about the ultrasonic studies of α-amino acids such as L-lysine monohydrochloride, L-Alginine and L-Histidine in aqueous solution of urea at different concentration and temperature.

MATERIAL AND METHODS

L-lysine monohydrochloride, L-Alginine and L-Histidine (≥ 99%) of high purity were taken from Sisco Research Laboratories, India. Urea (≥ 99%) was obtained from Qualigans fine chemicals (a division of Glaxo Smith Kline Pharmaceuticals Limited, Mumbai). All the solvents and chemicals were generally of analytical grade and the chemicals were used without any further purification. The specific conductivity of triply distilled water used for making the stock solutions of L-lysine monohydrochloride, L-Alginine and L-Histidine were less than 1.29×10^{-6} Ω^{-1} cm^{-1}. The weighting of samples were done on an electronic balance (model: GR-202R, AND Japan) with a precision of ± 0.01 mg. All the solutions were stored in particular airtight bottles for avoiding the exposure of solutions to air and desertion.

Densities of the mixed solvent and L-lysine monohydrochloride, L-Alginine and L-Histidine solutions were measured using a single-capillary pycnometer which was made of Borosilicate glass with a bulb capacity of approximately 9 cm^3. The capillary with graduated marks calibrated by using triply distilled water at various temperatures had a bore entangled through glass cap.

The thermostated paraffin bath (JULABO, model-MD Germany) were used for measuring densities maintained at a required temperature (± 0.02K) for 30 min to record the readings. The average of different reading of density was taken out at each temperature. The uncertainty rate for ultrasonic velocity was limited to be as 0.03%.

RESULT AND DISCUSSION

Table **1** shows the list of the ultrasonic velocities of aqueous urea solution with different amino acids at different temperatures for each of the composition where the value of ultrasonic velocity increases with rise in temperature and molal concentration of amino acids due to the overall rise of cohesive force carried by the interactions like solute-solute, solute-solvent and solvent-solvent in solutions. Various other authors have also reported about the similar patterns of variation about ultrasonic velocity [12,13].

Deviation in sound velocity can be obtained by the following expression

$$\Delta u = u - u_0 \quad (1)$$

where u is the sound velocity of α- amino acid +aqueous urea and u_0 the sound velocity of aqueous urea (solvent)

Table **2** shows an increase in deviation in sound velocity (Δu) values with decrease in temperature and increase in concentration due to formation of hydrogen bond between urea and water. A part of ultrasonic wave passing through the medium is used for deteriorating or infringement of O—H---O bonds. Hence, a condition may arise at the compression cycle of the particular wave that hydrogen atom tends to come closer leading to the partially irretrievable weakening or breaking of hydrogen bonds which is caused by integration of energy. The increase in the absorption of the solution shows association of intermolecular interaction within itself [14].

Isentropic compressibility of solution is the dynamic process possessing the physical parameter showing the intermolecular interactions. The isentropic compressibility K_s is calculated using the value of sound velocity, u, and the density 'ρ' by applying Laplace equation as given below:

$$K_s = 1/u^2 \rho \quad (2)$$

Table **3** shows that isentropic compressibility (K_S) value decreases with an increase in temperature as

Table 1: Ultrasonic Velocities (u /ms^{-1}) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L-Histidine in 0.5 M aqueous Urea solution						
0.000	1510.10	1521.28	1531.13	1539.19	1546.04	1551.59
0.048	1514.78	1525.88	1535.57	1543.55	1550.36	1555.76
0.099	1518.07	1529.13	1538.54	1546.51	1553.09	1558.34
0.149	1522.63	1533.00	1541.25	1550.07	1556.48	1561.68
0.203	1526.36	1536.92	1546.11	1553.71	1560.03	1565.16
0.255	1530.76	1541.90	1550.73	1558.18	1564.29	1569.12
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.000	1510.10	1521.28	1531.13	1539.19	1546.04	1551.59
0.049	1515.76	1526.84	1536.58	1544.53	1551.28	1556.67
0.100	1519.55	1530.71	1540.04	1547.94	1554.47	1559.70
0.151	1524.90	1535.74	1544.79	1552.48	1558.83	1563.93
0.204	1528.78	1539.72	1549.36	1556.89	1563.06	1567.94
0.256	1533.72	1544.50	1553.97	1561.25	1567.26	1572.04
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.000	1510.10	1521.28	1531.13	1539.19	1546.04	1551.59
0.049	1515.99	1527.07	1536.82	1544.76	1551.54	1557.02
0.100	1520.00	1531.04	1540.75	1548.70	1555.03	1560.36
0.151	1525.35	1536.51	1545.67	1552.99	1559.16	1564.31
0.204	1529.23	1540.29	1549.98	1557.64	1563.88	1568.02
0.256	1534.00	1544.38	1554.07	1561.95	1567.97	1572.94

Table 2: Deviation in Sound Velocity (Δu /ms^{-1}) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.048	4.68	4.60	4.44	4.36	4.32	4.17
0.099	7.95	7.85	7.51	7.32	7.05	6.75
0.149	12.53	11.72	10.92	10.88	10.44	10.09
0.203	16.26	15.64	15.08	14.52	13.99	13.51
0.255	20.66	20.62	19.70	18.99	18.25	17.53
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.049	5.66	5.56	5.45	5.34	5.24	5.08
0.100	9.45	9.43	8.91	8.75	8.43	8.11
0.151	14.80	14.46	13.66	13.29	12.79	12.34
0.204	18.68	18.44	18.23	17.70	17.02	16.35
0.256	23.62	23.22	22.84	22.06	21.22	20.45
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.049	5.89	5.79	5.69	5.57	5.50	5.43
0.100	9.90	9.76	9.62	9.51	8.99	8.77
0.151	15.25	15.23	14.54	13.80	13.12	12.72
0.204	19.13	19.01	18.85	18.45	17.84	16.43
0.256	23.90	23.10	22.94	22.76	21.93	21.35

there is a rise in thermal breakdown of the solvent constituents resulting in more attractive forces within the molecules. Later on with an increase in concentration, the value of isentropic compressibility decreases attributed with a rise in the solute-solvent interactions resulting in the change of ultrasonic velocity. If the attractive force is more between the molecules of liquid, the compressibility is small. In relation to it, the isentropic compressibility values refer to the mounting electrostrictive compression of solvent surrounding the solute molecules resulting in enormous decrease in the value of compressibility of the solutions [15].

The study of change in isentropic compressibility (ΔK_s) helps in influencing the concept of solute-solvent interaction on molecular configuration [16]. The change in isentropic compressibility value can be attained by the equation given below:

$$\Delta K_s = K_s^0 - K_s \tag{3}$$

Table **4** shows the increase in value of ΔK_s with concentration and also displays irregular pattern in case of temperature. The number of incompressible solute molecules rises with an increase in concentration of the solution resulting in a decrease in value of compressibility [17].

Relative change in isentropic compressibility can be estimated by the equation given below:

$$\Delta K_r = \Delta K_s / K_s^0 \tag{4}$$

Table **5** depicts the deviation of relative change in isentropic compressibility (ΔK_r) corresponding to concentration and temperature. It shows that the value of ΔK_r increases with an increase in concentrations as it exhibit a rise in the existence of incompressibility and the solvation of the molecules. But it does not show any such pattern in case of temperature.

The equation below shows that the product of density and ultrasonic velocity gives specific acoustic impedance:

$$Z = u \times \rho \tag{5}$$

The measure Z is an important parameter that depicts the medium and cohesive force between the molecules of the liquids than u and ρ independently, on the grounds that Z is the property of a medium alone. This feature follows by the inertial and elastic properties of the medium. Table **6** shows the increase in value of specific acoustic impedance, Z, corresponding to the concentration and temperature.

Table 3: Isentropic Compressibility, ($K_s \times 10^{-7}/m^2N^{-1}$) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.000	4.36	4.30	4.26	4.22	4.19	4.17
0.048	4.32	4.27	4.22	4.19	4.16	4.14
0.099	4.29	4.24	4.19	4.16	4.13	4.11
0.149	4.26	4.21	4.17	4.13	4.11	4.09
0.203	4.23	4.18	4.14	4.10	4.08	4.06
0.255	4.19	4.14	4.10	4.07	4.05	4.03
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.000	4.36	4.30	4.26	4.22	4.19	4.17
0.049	4.32	4.26	4.22	4.18	4.15	4.13
0.100	4.28	4.23	4.19	4.15	4.13	4.11
0.151	4.25	4.19	4.15	4.10	4.09	4.08
0.204	4.21	4.16	4.11	4.08	4.06	4.05
0.256	4.18	4.13	4.08	4.05	4.03	4.01
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.000	4.36	4.30	4.26	4.22	4.19	4.17
0.049	4.31	4.26	4.21	4.18	4.15	4.13
0.100	4.28	4.23	4.18	4.15	4.12	4.10
0.151	4.24	4.19	4.14	4.11	4.09	4.07
0.204	4.21	4.16	4.11	4.08	4.06	4.04
0.256	4.17	4.12	4.08	4.05	4.02	4.01

Table 4: Change in Isentropic Compressibility, ($\Delta K_s \times 10^{-9}/m^2N^{-1}$) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.048	4.50	3.40	4.70	3.26	3.53	3.79
0.099	7.30	6.60	7.90	6.02	6.38	6.04
0.149	10.60	9.90	9.30	9.50	8.21	8.10
0.203	13.80	12.60	12.01	12.60	11.51	11.62
0.255	17.60	16.10	16.82	15.72	14.32	14.01
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.049	4.01	4.53	4.01	4.50	4.71	4.80
0.100	8.90	7.74	7.60	7.53	6.34	6.74
0.151	11.70	11.21	11.99	12.59	10.16	9.74
0.204	15.71	14.00	15.50	14.70	13.80	12.30
0.256	18.40	17.50	18.50	17.60	16.70	16.30
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.049	5.15	4.10	5.25	4.71	4.09	4.10
0.100	8.03	7.27	8.00	7.94	7.10	7.50
0.151	12.85	11.63	12.41	11.20	10.99	10.40
0.204	15.50	14.70	15.50	14.78	13.84	13.20
0.256	19.70	18.10	18.50	17.40	17.20	16.88

Table 5: Relative Change in Isentropic Compressibility, ($\Delta K_r \times 10^{-3}/m^2N^{-1}$) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.048	8.30	8.60	8.90	8.10	8.40	8.18
0.099	16.00	16.60	16.30	16.30	16.70	16.21
0.149	24.10	24.60	24.30	27.30	22.90	22.12
0.203	32.30	32.20	32.00	35.80	35.00	35.31
0.255	44.90	44.40	44.00	42.50	42.90	42.01
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.049	9.17	9.30	9.38	9.47	9.54	9.59
0.100	18.30	16.27	16.43	16.58	14.32	14.38
0.151	25.22	25.58	25.82	28.43	23.86	21.58
0.204	34.40	34.82	34.90	37.70	37.10	36.90
0.256	45.90	45.40	45.10	48.56	48.50	46.32
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.049	11.46	9.30	11.70	9.47	9.54	9.59
0.100	18.34	16.27	18.77	16.58	16.70	16.78
0.151	27.50	25.50	28.11	26.00	23.80	23.98
0.204	34.40	32.50	35.20	33.00	31.00	31.10
0.256	43.50	41.80	42.20	40.28	40.57	38.36

Table 6: Specific Acoustic Impedance, ($Z \times 10^3$/Kg.m^{-2}s^{-1}) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.000	1517.80	1525.84	1533.12	1537.65	1541.40	1543.83
0.048	1525.96	1533.93	1541.06	1545.52	1549.24	1551.52
0.099	1532.89	1540.82	1547.69	1552.15	1555.65	1557.79
0.149	1540.88	1548.16	1553.87	1559.20	1562.53	1564.63
0.203	1548.33	1555.82	1562.46	1566.57	1569.82	1571.79
0.255	1556.23	1564.32	1570.61	1574.57	1577.61	1579.35
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.000	1517.80	1525.84	1533.12	1537.65	1541.40	1543.83
0.049	1526.67	1534.59	1542.11	1546.53	1550.19	1552.46
0.100	1534.45	1542.49	1549.12	1553.68	1557.11	1559.23
0.151	1543.21	1550.94	1557.45	1561.64	1564.90	1566.90
0.204	1550.65	1558.52	1565.62	1569.65	1572.75	1574.52
0.256	1559.02	1566.74	1573.70	1577.48	1580.42	1582.16
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.000	1517.80	1525.84	1533.12	1537.65	1541.40	1543.83
0.048	1525.96	1533.93	1541.06	1545.52	1549.24	1551.52
0.099	1532.89	1540.82	1547.69	1552.15	1555.65	1557.79
0.149	1540.88	1548.16	1553.87	1559.20	1562.53	1564.63
0.203	1548.33	1555.82	1562.46	1566.57	1569.82	1571.79
0.256	1562.04	1569.96	1576.74	1581.47	1584.56	1586.19

Table 7: Change in Specific Acoustic Impedance, ($\Delta Z \times 10^3$/Kg.m^{-2}s^{-1}) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	**303.15**	**308.15**	**313.15**	**318.15**	**323.15**
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.048	8.16	8.09	7.94	7.89	7.84	7.69
0.099	15.07	14.98	14.57	14.50	14.25	13.96
0.149	23.08	22.32	20.75	21.55	21.13	20.80
0.203	30.53	29.98	29.34	28.92	28.42	27.96
0.255	38.43	38.48	37.49	36.92	36.21	35.52
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.049	8.87	8.75	8.99	8.88	8.79	8.63
0.100	16.65	16.65	16.00	16.03	15.71	15.40
0.151	25.41	25.10	24.33	23.99	23.50	23.07
0.204	32.85	32.68	32.50	32.00	31.35	30.69
0.256	41.22	40.98	40.58	39.83	39.02	38.27
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.049	9.86	9.78	9.69	9.58	9.52	9.54
0.100	17.91	17.81	17.70	17.61	17.11	16.90
0.151	27.24	27.27	26.63	25.91	25.26	24.87
0.204	35.16	35.12	34.99	34.67	34.09	32.70
0.256	43.79	43.08	43.01	42.90	42.09	41.53

This trend is mainly based on lyophobic interaction between solute and solvent molecules, increasing the intermolecular distance and it acts as reliable source for the propagation of ultrasonic waves [18]. From the above context, it is observed that the structural arrangement is hindered due to the interaction between solute and solvent molecules. The hydrophilic nature is found as there is strong association among water and molecules of amino acid. Specific acoustic impedance shows interaction of solute-solute and solute-solvent type of molecules [19]. It is related to the equation where Z is directly proportional to ultrasonic velocity. It is observed that value of specific acoustic impedance for all amino acids is positive in nature and their trend in solute-solute and solute-solvent-solute interaction is in order of L-Lysine monohydrochloride> L-Arginine > L-Histidine.

The change in specific acoustic impedance can be estimated by the equation given below:

$$\Delta Z = \rho u - \rho_0 u_0 \tag{6}$$

Table **7** shows the value of change in specific acoustic impedance (ΔZ) which follows the similar trend as that of value of Z. It reveals about the considerable interaction between solute and solvent molecules leading to the structural arrangement to be hindered. The above study makes it clear that a strong association between water amino acid molecules is formed indicating the hydrophilic nature.

The values of relative association (RA) parameter can be calculated by using the equation given below:

$$RA = \rho/\rho_0 \left(u_0/u\right)^{1/3} \tag{7}$$

where RA is the property used to understand the interactions.

RA is guided by two factors such as (i) The contravention of solvent structure on adding solute to it; and (ii) the solvation of solutes present simultaneously. The first factor leads to the decrease in the value of RA whereas second factor leads to increase in the value of RA. Table **8** shows increase in the value of RA with concentration suggesting that solvation of solutes dominates on the breakdown of solvent structure [20] but with an increase in temperature of the solvent it forms break up resulting to the decrease in the value of RA.

Table 8: Relative Association (RA) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.048	1.00125	1.00128	1.00130	1.00135	1.00137	1.00141
0.099	1.00281	1.00286	1.00297	1.00301	1.00300	1.00317
0.149	1.00399	1.00430	1.00468	1.00454	1.00466	1.00476
0.203	1.00565	1.00583	1.00601	1.00615	1.00630	1.00643
0.255	1.00687	1.00693	1.00720	1.00738	1.00758	1.00777
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.049	1.00098	1.00102	1.00111	1.00114	1.00117	1.00122
0.100	1.00250	1.00254	1.00265	1.00280	1.00279	1.00297
0.151	1.00358	1.00354	1.00391	1.00402	1.00415	1.00427
0.204	1.00492	1.00500	1.00521	1.00537	1.00555	1.00572
0.256	1.00606	1.00629	1.00640	1.00662	1.00684	1.00700
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.049	1.00128	1.00132	1.00135	1.00133	1.00142	1.00144
0.100	1.00302	1.00308	1.00306	1.00314	1.00327	1.00333
0.151	1.00434	1.00444	1.00462	1.00481	1.00498	1.00510
0.204	1.00613	1.00621	1.00627	1.00640	1.00657	1.00691
0.256	1.00753	1.00777	1.00787	1.00796	1.00819	1.00836

Table 9: Apparent Molal Isentropic Compressibility ($\phi_{ks} \times 10^{-5}$ / bar^{-1} m^3 mol^{-1}) as Functions of Concentration and Temperature

m/ mol.kg^{-1}	Temperature/K					
	298.15	303.15	308.15	313.15	318.15	323.15
(a) L -Histidine in 0.5 M aqueous Urea solution						
0.049	-16.20	-12.81	-16.02	-12.71	-12.62	-12.61
0.099	-14.20	-12.62	-14.11	-12.40	-12.30	-12.31
0.149	-13.73	-12.50	-12.42	-12.32	-11.21	-11.20
0.203	-13.20	-12.30	-12.20	-11.13	-11.33	-11.32
0.255	-13.61	-12.90	-12.81	-12.10	-11.43	-11.42
(b) L -Arginine in 0.5 M aqueous Urea solution						
0.049	-18.70	-18.60	-18.53	-18.41	-18.31	-18.21
0.100	-18.52	-16.51	-16.42	-16.31	-14.40	-14.42
0.151	-17.10	-17.01	-16.90	-18.02	-15.51	-14.21
0.204	-17.01	-16.21	-16.83	-16.01	-15.02	-14.10
0.256	-16.61	-15.81	-16.41	-15.62	-14.83	-14.71
(c) L -Lysine monohydrochloride in 0.5 M aqueous Urea solution						
0.049	-23.21	-19.03	-22.81	-18.91	-18.81	-18.71
0.100	-19.05	-17.01	-18.72	-16.81	-16.73	-16.61
0.151	-18.91	-17.52	-18.60	-17.31	-16.04	-15.92
0.204	-17.81	-16.71	-17.51	-16.51	-15.51	-15.41
0.256	-17.92	-17.02	-16.91	-16.13	-16.03	-15.20

The value of apparent molal isentropic compressibility (ϕ_{ks}), can be calculated by using the following equation given below:

$$\phi_{ks} = \frac{1000\left(Ks\rho^0 - Ks^0\rho\right)}{m\rho^0\rho} + \frac{KsM}{\rho} \quad (8)$$

Table **9** shows the value of apparent molal isentropic compressibility (ϕ_{ks}), at different temperatures and concentrations revealing that value increases by adding amino acids into the aqueous urea solution.

Observed values are negative at different concentration and temperatures respectively, due to the formation of electrostriction and hydrophilic interactions primary to solute-solvent interactions as well as trouncing of structural compressibility of solvent molecules. Quantitative increase of four bonded water molecules has structural disruption effective in water [21]. The assumption states that the functional groups of COO^- of amino acids react with the nearby water molecule through the hydrophilic interactions. The water tends to lose its own compressibility at certain point and degree of organization of water molecules rises in the surrounding area of amino acid. Hence, it becomes less compressible.

CONCLUSION

Ultrasonic and sound velocities of α-amino acids in aqueous urea solutions were measured at temperatures (283.15 to 323.15) K, and the isentropic compressibility (K_s), change in isentropic compressibility (ΔK_s), relative change in isentropic compressibility (ΔK_r), relative association (RA), specific acoustic impedance (Z), and apparent molal isentropic compressibility (ϕ_{ks}) were obtained. The values of ultrasonic velocity increase with an increase in concentration of solute and its temperature. The values of isentropic compressibility reduce with a rise in temperature because of the thermal rupturing of the water clusters. The specific acoustic impedance values increase with an increase in concentrations and temperature. The deviation of relative change in isentropic compressibility values increases with an increase in concentration. Therefore, the above properties are helpful to clarify the concept of structural change and strong solute-solvent interaction.

ACKNOWLEDGEMENTS

We thank an anonymous reviewer for constructive criticism on an earlier manuscript version.

REFERENCES

[1] Nain AK, Lather M, Neetu. Probing solute-solute and solute-solvent interactions in L-arginine + D-xylose/L-arabinose + water solutions at different temperatures by using volumetric and viscometric methods. J Chem Thermodyn 2013; 63: 67-73. http://dx.doi.org/10.1016/j.jct.2013.04.001

[2] Nain AK, Lather M. Solute-solute and solute-solvent interactions of L-histidine and L-arginine in aqueous-streptomycin sulphate solutions at different temperatures: A physicochemical study. J Mol Liq 2015; 211: 178-186. http://dx.doi.org/10.1016/j.molliq.2015.07.018

[3] Fazary AE, Mohamed AF, Lebedeva NS. Protonation equilibria studies of the standard α-amino acids in $NaNO_3$ solutions in water and in mixtures of water and dioxane. J Chem Thermodyn 2006; 38: 1467-1473. http://dx.doi.org/10.1016/j.jct.2006.01.003

[4] Malik N, Khan AZ, Naqvi S, Arfin T. Ultrasonic studies of different saccharides in α-amino acids at various temperatures and concentrations. J Mol Liq 2016; 221: 12-18. http://dx.doi.org/10.1016/j.molliq.2016.05.061

[5] Sagle LB, Zhang Y, Litosh VA, Chen X, Cho Y, Cremer PS. Investigating the hydrogen-bonding model of urea denaturation. J Am Chem Soc 2009; 131: 9304-9310. http://dx.doi.org/10.1021/ja9016057

[6] Brien EPO', Dima RI, Brooks B, Thirumala D. Interactions between hydrophobic and ionic solutes in aqueous guanidinium chloride and urea solutions: lessons for protein denaturation mechanism. J Am Chem Soc 2007; 129: 7346-7353. http://dx.doi.org/10.1021/ja069232+

[7] Hakin AW, Duke MM, Klassen SA, McKay RM, Preuss KE. Apparent molar heat capacities and volumes of some aqueous solutions of aliphatic amino acids at 288.15, 298.15, 313.15, and 328.15 K. Can J Chem 1994; 72: 362-368. http://dx.doi.org/10.1139/v94-056

[8] Kikuchi M, Sakurai M, Nitta K. Partial molar volumes and adiabatic compressibilities of amino acids in dilute aqueous solutions at 5, 15, 25, 35, and 45 °C. J Chem Eng Data 1995; 40: 935-942. http://dx.doi.org/10.1021/je00020a045

[9] Waris BN, Hassan U, Shrivastava N. Viscosities of amino acid-urea-water ternary systems from 298.15 to 318.15 K. Indian J Chem 2001; 40A: 1218-1221.

[10] Islam S, Waris BN. Intermolecular/interionic interactions in leucine-, NaCl, and KCl–aqueous urea systems. Thermochim Acta 2004; 424: 165-174. http://dx.doi.org/10.1016/j.tca.2004.05.016

[11] Ogawa T, Yasuda M, Mizutani K. Volume and Adiabatic Compressibility of Amino Acids in Urea–Water Mixtures. Bull Chem Soc Jpn 1984; 57: 662-666. http://dx.doi.org/10.1246/bcsj.57.662

[12] Pal A, Chauhan N. Volumetric, viscometric, and acoustic behavior of diglycine in aqueous saccharide solutions at different temperatures. J Mol Liq 2009; 149: 29-36. http://dx.doi.org/10.1016/j.molliq.2009.07.014

[13] Nain AK, Pal R, Droliya P. Study of (solute + solute) and (solute + solvent) interactions of homologous series of some α-amino acids in aqueous-streptomycin sulfate solutions at different temperatures by using physicochemical methods. J Chem Thermodyn 2016; 95: 77-98. http://dx.doi.org/10.1016/j.jct.2015.11.015

[14] Ragouramane D, Srinivasa RA. Ultrasonic studies on the influence of some amino acids on molecular interactions in aqueous solutions of ethanol. Indian J Chem 1998; 37A: 659-662.

[15] Palani R, Saravanan S. Volumetric, Compressibility and Transport Studies of Some Amino Acids in Aqueous

Magnesium Acetate at 298.15K. Research J Phys 2008; 2: 13-21. http://dx.doi.org/10.3923/rjp.2008.13.21

[16] Jolicoeur C, Boileau J. Apparent molal volumes and heat capacities of low molecular weight peptides in water at 25 °C. Can J Chem 1978; 56: 2707-2713. http://dx.doi.org/10.1139/v78-446

[17] Uedaira H, Suzuki Y. Ultrasonic Velocity and Compressibility in Aqueous Solutions of Alkali Metal Chlorides. Bull Chem Soc Jpn 1979; 52: 2787-2790. http://dx.doi.org/10.1246/bcsj.52.2787

[18] Kannappan AN, Palani R. Acoustical behaviour of glycerine, dextrose and sucrose in Na_2CO_3 and $NaHCO_3$ buffer solution. Indian J Pure Appl Phys 2007; 45: 573-579.

[19] Kachare AV, Patil DD, Sonar AN. Studies of interactions of aqueous amino acid and glycol ether system at 318.15 K and at various concentrations. Int J Eng Res Technol 2013; 2: 2328-2339.

[20] Siddique M, Idress M, Agrawal, PB, Doshi AG, Raut AW, Narwade ML. Ultrasonic studies of Schiffs base and substituted-2-azetidinones in CCl4-water, ethanol-water and acetone-water mixtures at 298.5±0.1 K. Indian J Chem 2003; 42A: 526-530.

[21] Aswar AS. Molecular interaction studies on binary mixture of lysine and adenosine at different temperatures. Indian J Chem 1997; 36A: 425-428.

Received on 19-04-2016 Accepted on 25-05-2016 Published on 09-12-2016

DOI: http://dx.doi.org/10.6000/1929-5030.2016.05.04.2