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Study of interactions in L-Lysine monohydrochloride with solvent as Urea (aq)

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ABSTRACT

The measurements of density, viscosity and sound speed have been determined by experimental procedures using bicapillary pyknometer, Ostwald's viscometer and Ultrasonic interferometer respectively. The experimental data related to density, viscosity, sound speed for the system as Urea (aq) and L-Lysine monohydrochloride are further utilized to derive parameters viz. isentropic compressibility (β), apparent molal volume (Φ_v), apparent molal compressibility (Φ_k), intermolecular free length(L_f), Relative association(R_A) and Specific acoustic impedance(Z). From these derived parameters we calculate limiting apparent molal volume (ϕ_v°), limiting apparent molal compressibility (ϕ_k°) and experimental slope (S_v^* and S_k^*) by using Masson's equation. The viscosity data are analysed using Jones-Dole equation. The concentration range selected for L-Lysine monohydrochloride is 0.10m to 1.0m. The measurements are conducted at three temperatures viz. 298, 308, 318K. The constancy of temperature is maintained by the use of refrigerated bath with water as circulating medium. The results are interpreted on the basis of solute-solvent and solute-solute interactions where the addition of solute and its concentration produces a major variation on the interactions. This shows the dependency of interactions on the concentration and L-Lysine monohydrochloride behaves as a structure maker in aqueous urea.

Keywords: apparent molal volume, apparent molal compressibility, relative association, intermolecular free length, solute-solvent interactions.

INTRODUCTION

Urea is known to denature proteins regardless of composition of amino acid. Previous studies have shown that urea builds up protein-water interface and is capable of hydrogen bonding with both water and amide groups in small molecules. Therefore changes in the solubility of amide back bone upon the introduction of urea to solution are considered to be primary contributor to the denaturation process [1-3].Most of the studies on amino acids have been carried out in pure and mixture of two or more aqueous solutions of solvents. During the last two decades, the ultrasonic study has been carried out to explore hydration of proteins through volumetric and ultrasonic measurements, since these properties are perceptive to the degree and temperament of hydration. Previous work has been reported on aqueous urea but at higher concentrations i.e. above 0.1M or 0.1m solutions [4, 5].

Since urea at a higher concentration works as a better denaturing agent hence this work is based on the study using urea in relatively inferior concentration. The work is reported with the increasing concentration of amino acid as we uptake protein from various peripheral sources. The density, viscosity and sound speed have been measured for the system of L-Lysine monohydrochloride in 0.01M aqueous urea solution as solvent. The concentration array selected for study is 0.10m to 1.0m. The interactions in the amino acids can be interpreted by simple thermodynamic parameters. Hence the derived parameters such as isentropic compressibility (β), apparent molal volume (Φ_v), apparent molal compressibility (Φ_k), limiting apparent molal volume(ϕ_v°), limiting apparent molal compressibility(ϕ_k°), experimental slope (S_v^* and S_k^*), Specific acoustic impedance(Z), Relative association(R_A), Intermolecular free length(L_f) have been investigated so as to ascertain the type of interactions.

MATERIALS and METHODS

Analytical range (AR) grade L-Lysine monohydrochloride, with minimum assay of 99% obtained from Himedia was used as such without further purification. Distilled water was used to make the solutions. Aqueous solution of Urea (minimum assay 99%, Qualigens) was prepared w/v and used as such on the day they were prepared. The concentration range selected for amino acid is 0.1m to 1.0 m and 0.01M solution of Urea were prepared to be used as solvent with a precision of $\pm 1\text{x}10^{-4}$g on electronic digital balance. Density was determined using precalibrated bicapillary pyknometer having two limbs with 50 equal divisions with an error value up to ±0.06% [6], viscosity by the use of precalibrated Ostwald's viscometer, error up to ±0.07% [7]. Sound speed was measured using Ultrasonic interferometer (Mittal Enterprises, New Delhi, Model F-81) working at a fixed frequency of 2 MHz up to an accuracy of ±0.04% [8]. All the experiments have been carried out at constant temperature in a refrigerated water bath maintaining temperature up to ±0.1°C. The solutions were stored in airtight bottles so as to minimize absorption of atmospheric moisture. The experimentation is carried out at three different temperatures viz. 298, 308, 318K [9] so as to study the interactions more precisely.

Formulae:

Apparent Molal Volume

$$\phi_v = \frac{1000(\rho_o - \rho)}{m\rho_o\rho} + \frac{M}{\rho} \tag{1}$$

Apparent Molal Compressibility

$$\phi_k = \frac{1000(\rho_o\beta - \rho\beta_o)}{m\rho\rho_o} + \frac{\beta M}{\rho} \tag{2}$$

Specific Acoustic Impedance

$$Z = u\rho \tag{3}$$

Relative Association

$$R_A = (\rho / \rho_o)(u_o / u)^{1/3} \tag{4}$$

Intermolecular free length

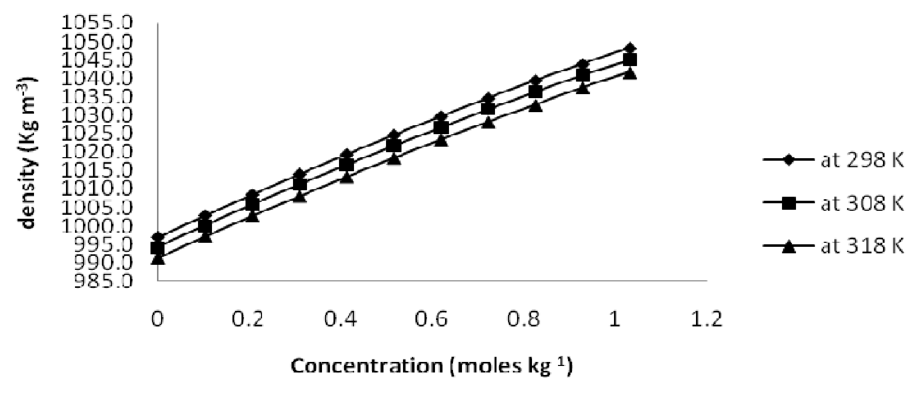
$$L_f = K\beta^{1/2} \tag{5}$$

where m is the concentration in moles kg^{-1}, ρ_0 is the density of solvent, ρ is the density of solution, M is the Molecular weight of solute, β is adiabatic compressibility of solution and β_0 that of solvent.

RESULTS AND DISCUSSION

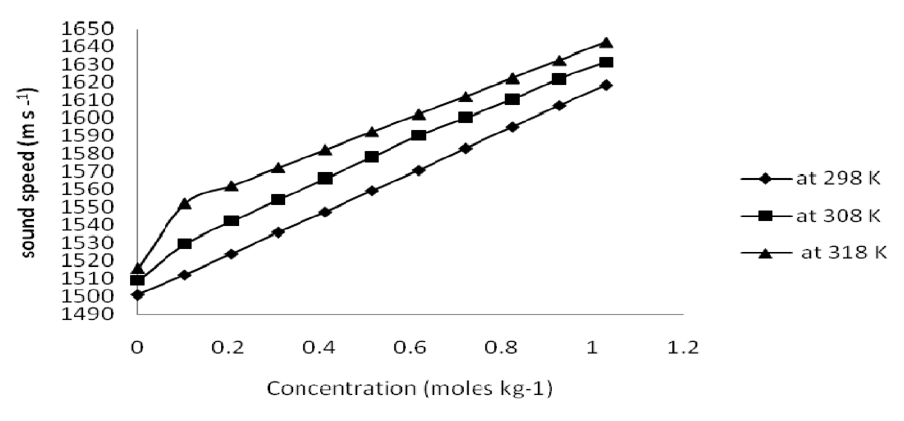
The experimentally measured values of density and sound speed of the solutions of L-Lysine monohydrochloride in aq Urea at 298,308 and 318 K are expressed as a comparison of temperature in Figure 1, 2.

Figure 1
Variation of density with concentration for L-Lysine monohydrochloride + urea(aq) system at 298, 308, 318K



Density (ρ) is a measure of solvent-solvent (aq Urea) and ion–solvent interactions as they in a way portray the mass per unit volume.

Figure 2
Variation of sound speed with concentration for L-Lysine monohydrochloride + urea(aq) system at 298, 308, 318K



Increase in density with concentration [Table1] indicates the increase of solvent-solvent and solute-solvent interactions, whereas dwindle in density indicates lesser magnitude of solvent-solute and solute-solvent interactions. Boost in density with concentration is due to the shrinkage in the volume, which in turn is due to the presence of solute molecules. In other words, increase in density is due to the structure maker property of the solvent due to the added solute [10].

Table 1: Density, Viscosity, sound speed of system (aq)Urea+ L-Lysine monohydrochloride at 298, 308, 318K

Conc. (mol Kg^{-1})	Density $\rho/(Kg\ m^{-3})$			Viscosity $\eta/(x10^{-3}\ Ns\ m^{-2})$			Sound speed $u/(m\ s^{-1})$		
	298K	308K	318K	298K	308K	318K	298K	308K	318K
0	996.9	994.3	991.3	0.8799	0.7150	0.6019	1501.4	1509.2	1516
0.1030	1002.8	1000.2	997.1	0.9010	0.7571	0.6522	1512.6	1529.6	1552.4
0.2060	1008.4	1005.9	1002.7	0.9455	0.7891	0.6783	1524.2	1542.4	1562.4
0.3090	1014.0	1011.3	1008.0	0.9911	0.8187	0.7006	1536.4	1554.4	1572.4
0.4120	1019.4	1016.6	1013.3	1.0368	0.8534	0.7289	1547.8	1566.2	1582.6
0.5149	1024.6	1021.8	1018.4	1.0879	0.8917	0.7586	1559.6	1578.4	1592.6
0.6179	1029.7	1026.7	1023.4	1.1391	0.9301	0.7883	1571	1590.4	1602.6
0.7209	1034.6	1031.7	1028.2	1.1984	0.9775	0.8271	1583.4	1600.4	1612.4
0.8239	1039.4	1036.4	1032.8	1.2477	1.0250	0.8659	1595.4	1610.8	1622.8
0.9269	1043.9	1041.0	1037.5	1.3176	1.0760	0.9084	1607.2	1622.2	1632.8
1.0298	1048.2	1045.0	1041.7	1.3796	1.1260	0.9499	1618.8	1631.6	1642.8

Table 1 represents the increase in sound speed which is attributed to the formation of hydrogen bonds between Urea and water. When the ultrasonic oomph passes through the medium, part of it is used in the deteriorating or infringement of O—H….O bonds. So it is very likely that during the compression cycle of the ultrasonic wave, hydrogen atoms are pushed closer resulting in a partially irretrievable weakening or breaking of hydrogen bonds due to the assimilation of energy. The absorption increase is a trait feature of the solutions in which association due to molecular interactions is present [10].

Table 2: Specific acoustic impedance(Z), Apparent molal Compressibility(Φ_k), Adiabatic compressibility(β) of system (aq)Urea+ L-Lysine monohydrochloride at 298, 308, 318K

Conc. (mol Kg^{-1})	Z $(x10^6 kg\ m^{-2}\ s^{-1})$			Apparent molal compressibility $-\Phi_k\ (x\ 10^{-10} m^2\ N^{-1})$			Adiabatic compressibility $\beta\ (x10^{-10} m^2\ N^{-1})$		
	298K	308K	318K	298K	308K	318K	298K	308K	318K
0	1.4967	1.5006	1.5028				4.4501	4.4155	4.3894
0.1030	1.5168	1.5299	1.5479	1.1425	1.6321	2.4702	4.3585	4.2733	4.1615
0.2060	1.5370	1.5514	1.5666	1.1219	1.3882	1.7158	4.2685	4.1790	4.0855
0.3090	1.5578	1.5719	1.5849	1.1113	1.2736	1.4469	4.1780	4.0926	4.0126
0.4120	1.5778	1.5922	1.6036	1.0842	1.2034	1.3085	4.0949	4.0101	3.9403
0.5149	1.598	1.6128	1.6219	1.0634	1.1569	1.2060	4.0125	3.9283	3.8714
0.6179	1.6176	1.633	1.6401	1.0391	1.1165	1.1492	3.9350	3.8506	3.8046
0.7209	1.6382	1.6511	1.6579	1.0227	1.0708	1.0948	3.8552	3.7844	3.7409
0.8239	1.6583	1.6694	1.676	1.0039	1.0341	1.0532	3.7798	3.7187	3.6766
0.9269	1.6778	1.6887	1.6939	0.9828	1.0071	1.0169	3.7085	3.6504	3.6155
1.0298	1.6968	1.705	1.7112	0.9615	0.9713	0.9832	3.6406	3.5946	3.5572

The values of β [Table 2] in system show a fading trend. The adiabatic compressibility values represent the mounting electrostrictive compression of solvent around the solute molecules that results in a larger decrease in the compressibility of the solutions [11]. The values of apparent molal compressibility (Φ_k) are negative over the entire range of molality [Table 2] which indicates occurrence of electrostriction and hydrophilic interactions in these systems, foremost to solute-solvent interactions as well as trouncing of structural compressibility of solvent molecules due to the increased population of four bonded water molecules showing that the structural interruption is much more effective in water [12].

Z increases with the increase in concentration of solute as well as with temperature [Table 2]. The behavior can be explained on the basis of lyophobic interaction between solute and solvent molecules, which increases the intermolecular distance and becomes conscientious for the propagation of ultrasonic waves [13].

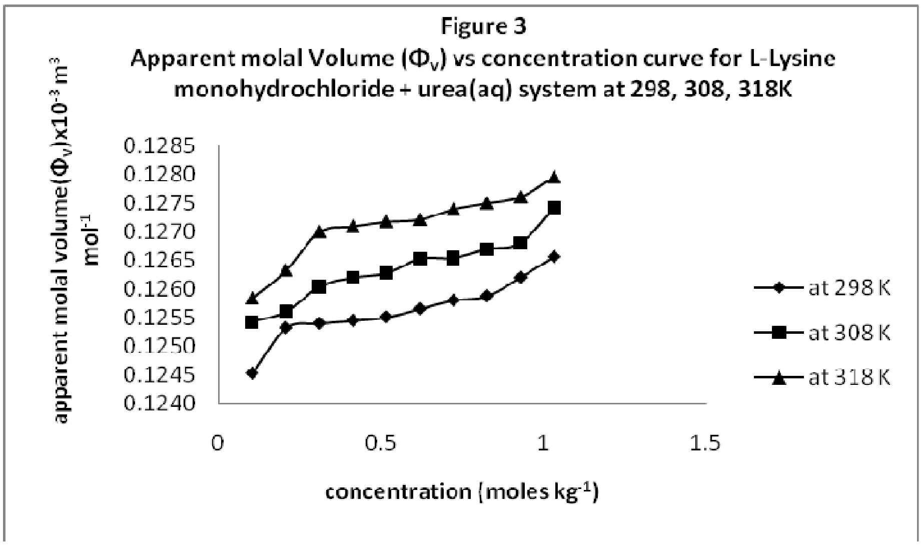


Figure 3

Apparent molal Volume (Φ_v) vs concentration curve for L-Lysine monohydrochloride + urea(aq) system at 298, 308, 318K

The Φ_v [Fig 3] was found to be a linear function of the molality m over the concentration range studied. The standard state (infinite dilution) partial molal volumes Φ_v° were obtained from the relation

$$\phi_v = \phi_v^o + S_v^* \sqrt{m} \qquad (6)$$

where S_v^* [Table 3] is the experimental slope and is a measure of solute-solute interactions, while Φ_v° [Table3] provides information regarding solute-solvent interaction.

The Φ_v° and S_v^* values were obtained from the intercept and slope of Φ_v vs. $m^{1/2}$ plots. The evaluated values of Φ_v° and S_v^* are summarized in table 3.

Table 3: Limiting apparent molal compressibility(Φ_k°), Limiting apparent molal volume(Φ_v°), constants S_k*, S_v*, Falkenhagen coefficient A, Jones-Dole coefficient B for system (aq)Urea+ L-Lysine monohydrochloride at 298, 308, 318K

	298K	308K	318K
Φ_k°(x10^{-10}m^2 N^{-1})	-1.1650	-1.5271	-2.0439
Φ_v°(x10^{-3}m^3 mol^{-1})	0.1247	0.1253	0.1261
S_k^* (x10^{-10}N^{-1}m^{-1}mol^{-1})	0.2030	0.6213	1.2698
S_v^* (x10^{-3}m^3 lt$^{1/2}$ mol$^{-3/2}$)	0.0017	0.0018	0.0019
A(dm$^{3/2}$ mol$^{-1/2}$)	-0.1541	-0.0328	0.0651
B(dm^3 mol^{-1})	0.6870	0.5589	0.4567

Amino acids when dissolved in untainted water exist as zwitterions. The hydration behavior of amino acids can be explained in terms of the following interactions.

1. The terminal ionic groups NH_3^+ and COO^- of zwitterions of amino acids are hydrated in an electrostatic comportment, whereas, hydration of prevailing backbone depends on its nature which may be hydrophobic, hydrophilic or amphiphilic.
2. The overlap of hydration co sphere of terminal NH_3^+ and COO^- groups and of contiguous groups' results in volume change.

The pragmatic values of Φv° are due to the net collective effect of the aforementioned possible interaction processes in the mixtures of amino acids +Urea (aq).

The standard state (infinite dilution) Φ_k° were obtained from the relation

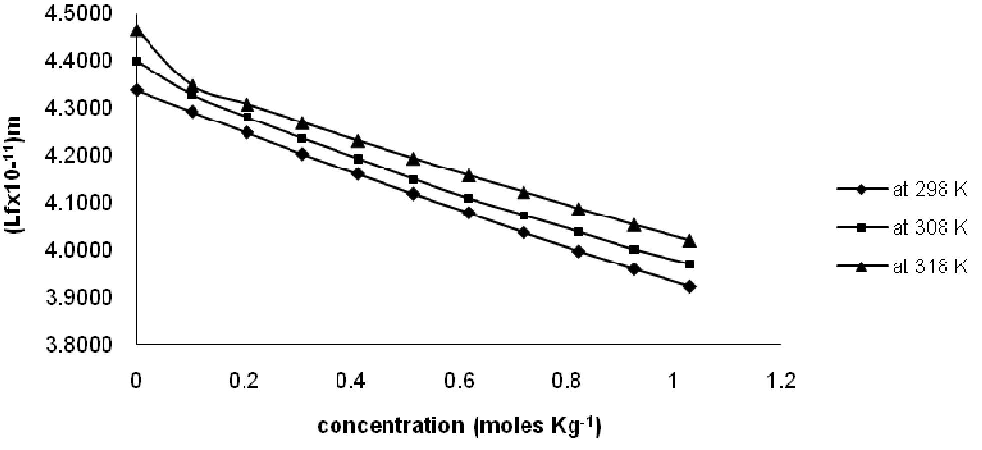
$$\phi_k = \phi_k^o + S_k^* \sqrt{m} \tag{7}$$

where S_k^* is the experimental slope, while Φ_k° provides information regarding solute-solvent interactions. One can scrutinize that Φ_k° values are negative, reinforcing the view that there exist solute-solvent interactions in the present system. It is well known that solutes causing electrostriction lead to decrease in the compressibility of the solution, which is reflected by the negative values of Φ_k°. The values of S_k^* are positive at at all temperatures [Table 3] portentous the existence of solute-solute interactions and the values increase with the rise in temperature indicating the increase of solute-solute interactions with the temperature [14]. The result is similar to that indicated by the increasing values of S_v^* and A [Table 3]. The assenting values of S_v^* for the current system are less than Φ_v° indicating weaker solute-solute interactions are than solute-solvent interactions. The volume behavior of a solute at inestimable dilution is satisfactorily represented by Φ_v° which is sovereign of solute-solute interactions and reflects solute-solvent interactions. The hefty positive values of Φ_v° counsel strong solute- solvent interactions and vice-versa. Thus for this system the sanguine values of Φ_v° indicate strong solute-solvent interactions, the increase in values with rise in temperature in contrast to the S_v^* values, thus indicates the increase of solute-solute and solute-solvent interactions [15].

A is the Falkenhagen coefficient, which accounts for the solute-solute interactions and B, the Jones-Dole coefficient is assess of the structural adaptation induced by solute-solvent interactions. The viscosity coefficients, A and B [Table3] were obtained from the intercepts and slopes of the plots $(\eta_r-1)/m^{1/2}$ vs. $m^{1/2}$.The values of B are larger positive as compared to A values, sustaining the behavior of Φ_v° and S_v^*. The superior magnitude of B coefficient suggests the supremacy of solute- solvent interactions over solute- solute interactions [16].

L_f decreases with increase in concentration [Fig 4] but increases with the augment of temperature indicating decrease in intermolecular forces due to increase in the thermal vigor of the system, which causes increase in volume extension.

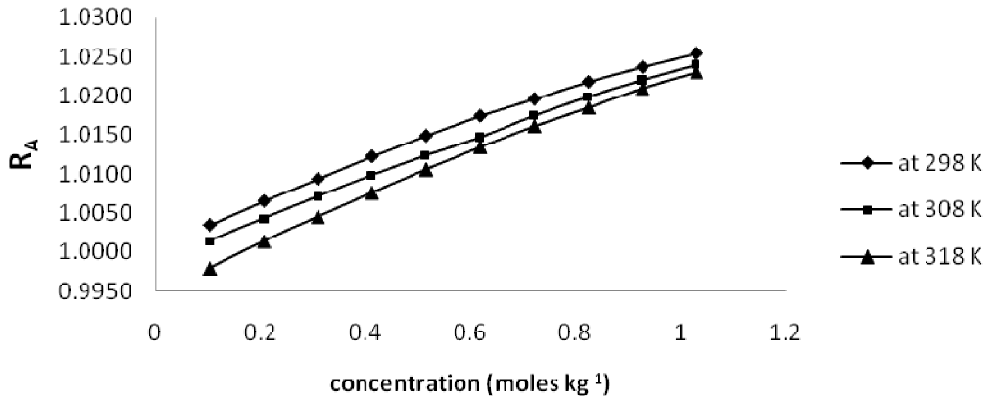
Figure 4
Intermolecular free length(L_f) vs concentration curve for L-Lysine monohydrochloride + urea(aq) system at 298, 308, 318K



The decrease in free length with increase in concentration indicates that there is noteworthy interaction between solute and solvent molecules, suggesting a structure promoting behavior on addition of solute. The increase in temperature makes the free length to increase, as expected due to the thermal expansion of liquids [17].

R_A is prejudiced by two factors (i) The contravention of solvent structure on addition of solute to it; and (ii) the solvation of solutes that are simultaneously present. The former results in decrease whereas latter in increase of R_A. The increase of R_A with concentration [Fig. 5] suggests that solvation of solutes predominates over the breaking up of solvent structure [18] but with the amplification of temperature the solvent structure breaks up which causes R_A to decrease.

Figure 5
Variation of Relative Association (R_A) with concentration for L-Lysine monohydrochloride + urea(aq) system at 298, 308, 318K



CONCLUSION

- As evident from the positive values and higher magnitude of B coefficient, the solute-solute as well as solute-solvent interactions exist in the system, but, solute-solvent interactions govern the solute-solute interactions.
- Thermal confrontation influences the interactions causing an increase in the solute-solute as well as solute-solvent interactions. The values of R_A, Z and L_f suggest that with the increase of temperature the solvent-solvent interactions (molecular organization) takes place.
- Solute-solute interactions increase with the increase of temperature. The compressibility of solution is primarily due to free solvent molecules. The decrease of free solvent molecules due to increase association of solvent-solvent aggregates causes a decrease in the β and increase in the L_f values with temperature.
- Thus a decrease in the free solvent molecules leads to decrease the value of R_A as effect of temperature. It has been implicit that the solvated solvent molecules are fully squashed by the electrical forces of zwitterions.
- Amino acid L-Lysine monohydrochloride behaves as structure maker in the system as already mentioned on the basis of density and also because the dB/dT is negative(B-coefficient decreases with the increase of temperature). The dipolar characters of these biological liquids exemplify the solute-solvent interactions owing to strong hydrogen bonded interactions with solvent.

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