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Research Article

THERMODYNAMIC AND INTERACTION STUDIES OF L-ARGININE IN AQUEOUS FRUCTOSE SOLUTIONS AT 303K, 308K AND 313K

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A B S T R A C T

The Ultrasonic velocity (U), Density (ρ), and viscosity (η) have been measured for the mixtures of L-arginine in aqueous fructose (10% of fructose) at different concentration and at 303K, 308K and 313K. Thermodynamic parameters such as adiabatic compressibility (β), free length (L_f), acoustic impedance (Z) and relaxation time (τ) have been obtained from the experimental data for the solution. These results are interpreted in terms of molecular interactions between the components of the mixtures.

INTRODUCTION

It is well known that various substances cause changes in the conformation of proteins when present in aqueous-protein solutions. The complex conformational and configurational factors affecting the structure of proteins in solution make the direct study of protein interactions difficult. Therefore, one useful approach is to investigate interactions of the model compounds of proteins, i.e., amino acids in aqueous and mixed-aqueous solution Molecular interactions (i.e. solute-solvent, solute-solute, and solvent-solvent-solvent) have great importance in biological chemistry, physical chemistry, surface chemistry, environmental chemistry, and geo chemistry [3]. Knowledge of the interactions responsible for stabilizing the native state of a solution is essential to understand its structure and function [4]. Water is chosen for preparing mixed solvent because its presence gives rise to hydrophobic forces [5], which are of prime importance in stabilizing the native globular structure of proteins. The interactions of water with the various functional groups of proteins are important factors in determining the conformational stability of proteins[2-4]. The stabilization of native conformations of biological macromolecules (proteins) is related to several non-covalent interactions including hydrogen-bonding, electrostatic and hydrophobic interactions [6,7]

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The sound ultrasonic velocity measurements are helpful to study the ion- solvent interactions in aqueous and non-aqueous solution in recent years Palani etal [8], kesavasamy etal.[9]. Amino acids are the building blocks of all living organisms. It incorporate structural features of proteins, their physicochemical and thermodynamic properties in aqueous solutions and are found to provide valuable information on solute–solute and solute-solvent interactions that are important in understanding the stability of proteins[10]. Direct study of solute/solvent interactions is difficult due to complex conformation of biological macromolecules[11]. Therefore, the convenient approach is to study simpler model compounds i.e. amino acids and peptides, which are the basic components of proteins[11,12]. When dissolved in water amino acids convert into zwitterionic forms due to the ionization of their carboxyl (–COOH) and amino groups (NH_2). In physiological media, this dipolar character of amino acids has an important bearing on biological functions. Amino acids differ from each other in size, charge, hydrogen-bonding capacity, hydrophobicity and chemical reactivity.There have been extensive study on volumetric and thermo-chemical property studies of amino acids in aqueous solutions and very few in aqueous saccharides solutions.

Ultrasonic Studies of amino acids in aqueous Fructose solutions are lacking. L-Arginine stimulates the production of growth hormone. It is very popular for its muscle building and fat burning effect among athletes [13]. However, to the best of our knowledge, no report is available in the literature on the physico-chemical solutions of arginine in aqueous-fructose at

different temperatures. In the present work, the measured values of density, viscosity and ultrasonic velocity behavior of arginine with 10% fructose in water at different temperature were Studied and discussed.

MATERIALS AND METHODS

Analytical reagent grade Arginine, were purchased from Sd fine chemicals and was used as such without further purification. Water used in the experiments was deionized and distilled prior to making solutions. Solutions of amino acid in aqueous fructose were prepared by mass on the molality scale with an accuracy of 0 to .1 g. The density was determined using a 10ml specific gravity bottle by relative measurement method with an accuracy of ±0.01kgm^{-3}. An Ostwald's viscometer of 10ml capacity was used for the viscosity measurement. The ultrasonic velocity was measured by a single crystal interferometer with an accuracy operating at a frequency of 2MHz at 303, 308 and 313K. An electronically operated constant temperature water bath is used to circulate water through the double walled measuring cell made up of steel containing the experimental solution at the desired temperature. The density, viscosity and ultrasonic velocity of the varying concentration of amino acid at different composition were measured at 303, 308 and 313K.

Theoretical aspects

From the speed of sound, density and viscosity various acoustical parameters have been calculated from the experimental data to investigate about the nature of molecular interaction between the components of the solution. The derived parameters are adiabatic compressibility, free length, acoustic impedance and relaxation Time of arginine in aqueous 10% fructose solution is

$$\beta = 1/U^2 \rho \quad N^{-1}m^2 \qquad (1)$$

$$L_f = K \beta^{1/2} \quad m \qquad (2)$$

$$Z = \rho U \ Nm^{-2} \text{ where } \rho \text{ is the density} \qquad (3)$$

$$\tau = 4/3 \ \beta \eta \quad s \qquad (4)$$

RESULTS AND DISCUSSION

The values of density (ρ), viscosity (η) and speed of sound (U) of with aqueous fructose (10% wt. of fructose) at 303, 308 and 313K. are shown in Table 1. The related parameters such as adiabatic compressibility (b), and free length from Table 2 and computed values of acoustic impedance and relaxation time shown in Table 3. Ultrasonic velocity (U) which is also found (from Table-1) to be increased with increase in same concentration of amino acids as well as with increase in temperature.. Such an observed increase in the ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration; which may also be due to the overall increase of cohesion brought about by solute-solute and solute-solvent interaction in solution [14] which suggests that solute-solvent interaction also increases. The existence of molecular interactions between solute and solvent molecules is responsible for the observed increase in the ultrasonic velocity of these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by ionic hydration [15].

The gradual increase in density; viscosity and velocity with solute concentration at all temperatures are due to association between solute and solvent molecules. A rise in temperature leads to less ordered structure and more spacing between the molecules. The same decrease with temperature indicates, decrease in intermolecular forces due to increase in thermal energy of the system [5, 16].

Table 1 Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of Arginine in aqueous 10% fructose solution

Molality (mol/Kg)	ρ Kgm^{-3}			η x 10^3 Nsm^{-2}			U ms^{-1}		
	Temperature (K)								
	303K	308K	313K	303K	308K	313K	303K	308K	313K
0	1042	1038	1035	0.9905	.8724	.7717	1511.9	1554.2	1564.6
0.21	1043	1041	1036	.9957	.8773	.8119	1514.5	1558.6	1584.2
0.42	1044	1043	1039	1.0199	.8880	.8205	1520.5	1564.8	1606.3
0.63	1047	1046	1042	1.0355	.8983	8498	1525.4	1580.0	1610.8
0.84	1048	1047	1045	1.0376	.8991	.8546	1531.8	1582.5	1613.0
1.05	1056	1048	1047	1.0471	.9136	.8669	1533.8	1585.0	1626.0

Table 2 Values Adiabatic compressibility, free length of Arginine in aqueous 10% fructose solution

Molality (mol/Kg)	Adiabatic compressibility x10^{-10} N^{-1}m^2			Free length x10^{-11} m		
	303K	308K	313K	303K	308K	313K
0	4.19842	3.98831	3.94687	4.08838	3.98476	3.96401
0.21	4.18001	3.95439	3.8461	4.0794	3.96779	3.91308
0.42	4.14311	3.9156	3.73019	4.06136	3.94827	3.85366
0.63	4.10474	3.82961	3.6987	4.04251	3.90468	3.83736
0.84	4.06663	3.81387	3.67803	4.0237	3.89665	3.82662
1.05	4.0253	3.79822	3.61254	4.0032	3.88864	3.7924

Table 3 Values, Acoustic impedance and Relaxation Time of Arginine in aqueous 10% fructose solution

Molality (mol/Kg)	Acoustic impedance Nm^{-2}			Relaxation Time x10^{-10} s		
	303K	308K	313K	303K	308K	313K
0	1575400	1613260	1619361	5.54333	4.63804	4.06005
0.21	1579624	1622503	1641231	5.54799	4.62443	4.16249
0.42	1587402	1632086	1668946	5.63267	4.63491	4.07981
0.63	1597094	1652680	1678454	5.66586	4.5857	4.18983
0.84	1605326	1656878	1685585	5.62464	4.5709	4.18994
1.05	1619693	1661080	1702422	5.61846	4.62558	4.17457

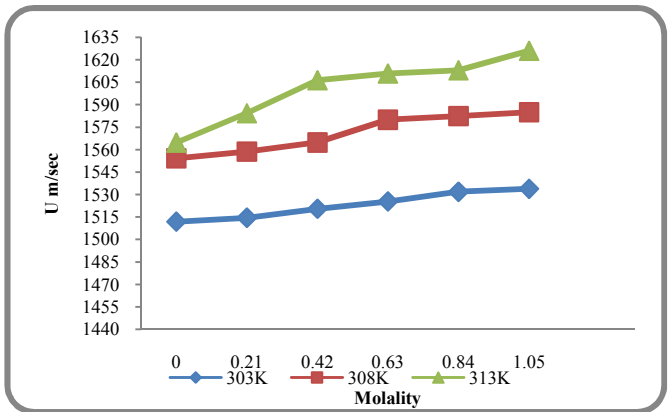

Fig 1 Plot of Ultrasonic Velocity vs. Molality

Fig.1 shows the plot of Ultrasonic Velocity of amino acid in aqueous fructose solution over the entire composition range respectively. The density (ρ) which is a measure of solute-solvent interactions, which can be attributed as increase of density with concentration indicates the increase in solute-solvent interactions, whereas the decrease in density indicates the lesser magnitude of solute-solvent interactions. Increase in density with concentration is due to the shrinkage in the volume which in turn is due to the presence of solute molecules. As observed in Table-1, an increasing trend of

density values may be interpreted to the structure-making behavior of the solvent due to the added solute [17].

Viscosity is another important parameter to understand the structure and interactions occurring in the solutions. Viscosity variations are attributed to structural changes. The structural changes influence the viscosity to a greater extent than they affect density and compressibility. As shown in Table 1, Fig 1, the viscosity increases with increasing solute concentration and decrease with increasing temperature. This increasing trend indicates the existence of molecular interactions in these mixtures [16].

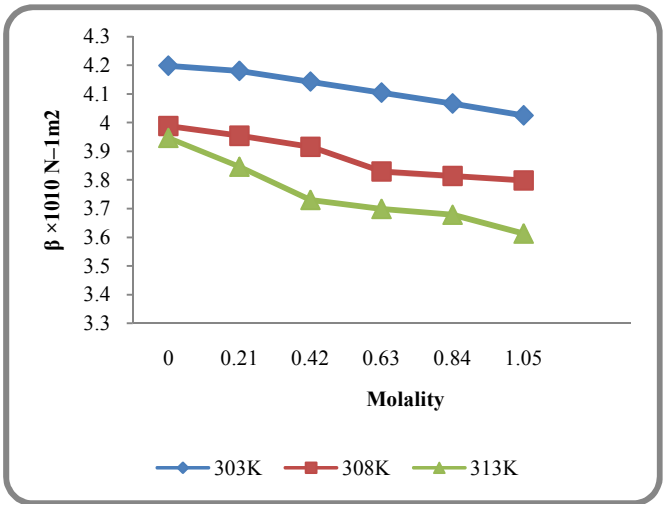

Fig 2 Plot of Adiabatic Compressibility vs. Molality

Fig.2 shows the plot of adiabatic compressibility of amino acid in aqueous fructose solution over the entire composition range respectively.

From the Table-2, and Fig-2, the adiabatic compressibility (β) of the solute can be expressed as the extent to which hydration around the solute molecule can be expressed. The perusal of Table-3 exhibits the values of adiabatic compressibility (β), which are found to be decreased with increase in molar concentration of solute (amino acids) as well as mass percentage of sucrose content. Such a decrease in adiabatic compressibility observed in solvent (aqueous sucrose solution) may be attributed to weakening of hydrogen bond in the solution. It is well known fact that when a solute dissolves in a solvent, some of the solvent molecules are attached to the ions (produced from the solutes), because of ion-solvent interaction. Since, the solvent molecules are oriented in the ionic field; these molecules are more compactly packed in the primary salvation shells as compared to the packing in the absence of the ions. This is the reason, why the solvent is compressed by the introduction of the ions. Thus, the electrostatic field of the ions causes the compression of the medium giving rise to a phenomenon called *'Electrostriction'*. Since the water molecules are compressed, they do not respond to a further application of pressure. So the solutions become harder to compress. Consequently, this will lead to in decrease in compressibility values. It may also be inferred that weakening of hydrogen bond strength formed by the solute and solvent molecules may also be the reason for decrease in compressibility[17]. The adiabatic compressibility shows decreasing trend with increase in the concentrations of amino acid. The decreasing trend of adiabatic compressibility for amino acids in aqueous fructose solution at all temperatures generally confirms the conclusion drawn from the velocity data. The increasing electrostrictive compression of water around the molecules results in a large decrease in the compressibility of solutions. The decrease in the compressibility implies that there are enhanced molecular associations in this system with increases in the solute content, as the new entities (formed due to molecular association) become compact and less compressible [17].

From Table 2 and fig3, Intermolecular Free Length (L_f) decreases with the increase in concentration of solute and increases with the increase of temperature for L-Arginine solutions. The decreasing compressibility brings the molecules to closer approach resulting in decreasing L_f with increasing concentration. Increasing temperature leads to increase in mean free distance between molecules and increase of free length [18].

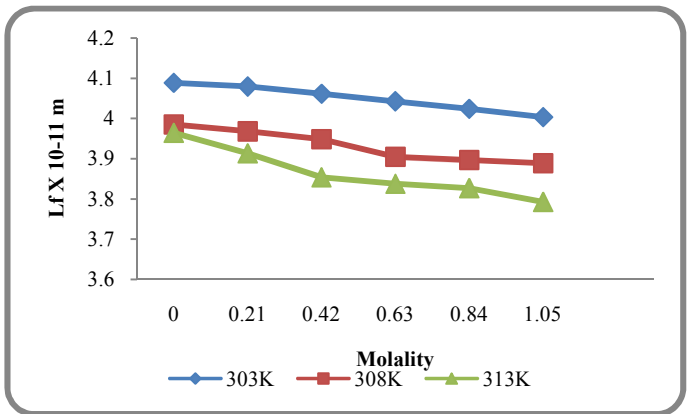

Fig 3 Plot of Free Length vs. Molality

Fig.3 shows the plot of free length of amino acid in aqueous fructose solution over the entire composition range respectively.

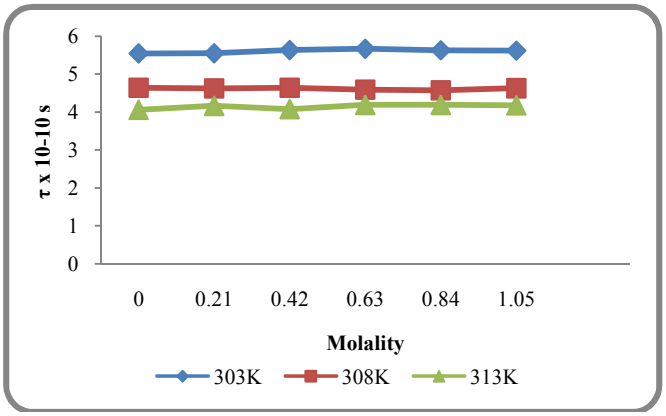

Fig 4 Plot of Relaxtion Time vs. Molality

Fig.4 shows the plot of relaxtion time of amino acid in aqueous fructose solution over the entire composition range respectively.

Table-3 shows specific acoustic impedance (Z) increases with concentration and also with temperature for solutions of L-Arginine with Fructose (aq). This may be due to the variation of pressure from particle to particle [19]. The increase in Z values with solute concentration can be attributed to the effective solute-solvent interactions. Similar type of behavior has been observed for some amino acids studied in various solvent systems [20]. Since the acoustic impedance is a measure of the resistance offered by the liquid medium to the

sound wave and is a function of the elastic property of the medium, gets affected by the structural changes of the solution. The increasingly higher values with increase in the solute concentration shows that the solution medium in each case starts gaining its elastic property [21]. The relaxation time is in the order 10^{-10} sec is due to structural relaxation process[22, 23] showing the presence of molecular interactions and in such a situation it is suggested that the molecules get rearranged due to co-operative process[24]. This suggest that the closed packing of molecules inside the shield.

In general,[25] the types of interactions occurring between arginine and fructose can be classified as follows (a) The hydrophilic–ionic interaction between OH groups of fructose and zwitterions of arginine. (b) Hydrophilic–hydrophobic interaction between the OH groups of fructose molecule and non-polar ($–CH_2$) in side chain of arginine molecule. Arginine in aqueous-sugar solutions can be explained by considering the size of primary and secondary salvation layers around the zwitterions. At higher temperatures the solvent from the secondary salvation layer of arginine zwitter ions is released into the bulk of the solvent, resulting in the expansion of the solution [26], [27]. This further supports the conclusion that the hydrophilic– ionic group interactions between OH groups of fructose with zwitter ions dominate in these systems.

CONCLUSION

The acoustical behaviors of L-arginine in aqueous fructose solutions at different temperatures have been investigated and are summarized as, It is obvious that L-arginine serves as an effective structure-maker in the aqueous fructose solution The addition of solute (amino acids) in the solvent enhances strong molecular interionic interactions such as ion-solvent, solute-solute, and solute-solvent etc., in the present systems of mixtures and however a weak ion-ion interaction are observed. Our viscometry study lends another fine support about the existence of strong solute-solvent interactions in the solution. Hence it is evident that the ultrasonic velocity measurements in a given medium serve as a powerful probe in characterizing the physico-chemical properties of that medium.

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