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Ultrasonic Studies on Molecular Interaction of Arginine in Aqueous Disaccharides at 298.15K

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Abstract: Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for arginine in three aqueous disaccharide solutions namely galactose, maltose and lactose (0.3m) at 298.15K. Using the experimental values, the adiabatic compressibility (β), apparent molal compressibility (φ_K), apparent molal volume (φ_V) ,limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their constants (S_K, S_V), hydration number (n_H) and A and B coefficients of Jones - Dole equation were calculated for all the ternary systems and these results have been discussed in terms of ion-solvent interactions.

Keywords: Ultrasonic velocity, amino acid, saccharides, compressibility and viscosity B coefficient.

Introduction

Ultrasonic investigation in aqueous solutions of electrolytes and non-electrolytes with amino acids provides useful information in understanding the behaviour of liquid systems, because intramolecular and inter molecular association, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variations in the ultrasonic velocity.

During the last two decades considerable study has been carried out to investigate hydration of proteins through volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration. Due to the complex molecular structure of proteins, direct study is somewhat difficult. Therefore, the useful approach is to study simpler model compounds, such as amino acids which are building blocks of proteins. Most of the studies on amino acids[1] have been carried out in pure and mixed aqueous solutions. The investigation of volumetric and thermodynamic properties of amino acids and peptides in aqueous and mixed aqueous solvents has been the area of interest of a number of researchers[3].

The study of carbohydrates/ disaccharides has become a subject of increasing interest because of the multidimensional, physical, biochemical and industrially useful properties of these compounds. In addition to their importance to the food, pharmaceutical and chemical industries, the simple saccharides have received considerable attention for their ability to protect biological macromolecules. Carbohydrates located at cell surfaces, are important as receptors for the bioactive structures of harmones, enzymes, viruses, antibodies etc. Therefore, the study of carbohydrate-protein interactions is very important for immunology, biosynthesis, pharmacology and medicine. It is widely recognized that sugars help in stabilizing biological macromolecules. This action is performed either due to direct interactions between them and / or through alteration of the water structure. These considerations led us to undertake the study of aminoacids in aqueous disaccharides at 298.15K. Since volumetric, compressibility and viscosity studies of amino acids are lacking in aqueous disaccharides an attempt has been made to understand the behaviour of arginine in aqueous galactose, aqueous maltose and aqueous lactose of 0.3m concentration at 298K through ultrasonic velocity measurements.

However the ultrasound velocity data as such do not provide significant information about the native and relative strength of various types of intermolecular or interionic interactions between the components. Hence their derived parameters such as adiabatic compressibility (β), apparent molal compressibility (φ_K),apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their constants (S_K, S_V), hydration number (n_H) and the value of A and B coefficients of Jones -Dole equation have been obtained to shed more light on such interactions.

Materials and Methods

Analytical reagent (AR) grade and spectroscopic reagent (SR) grade with minimum assay of 99.9% of galactose, maltose, lactose and arginine were obtained from SISCO Research Laboratories and SdFine chemicals, India which is used as such without further purification. Water used in the experiment was deionised, distilled and degassed prior to making solutions. Fresh conductivity water has been used for preparing aqueous disaccharides solutions at a concentration of 0.3m. The required quantity of arginine for given molality was dissolved and similar procedure has been adopted for different molalities of arginine with a precision of 0.1 mg an electronic digital balance (Model: SHIMADZU AX-200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ±0.01 $kg{\cdot}m^{-3}$. An Ostwald's Viscometer (10ml capacity) was used for the viscosity measurement and efflux time was determined using a digital chronometer to within ± 0.01s. An ultrasonic interferometer having the frequency 3MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F-81) with an overall accuracy of 0.1% has been used for velocity measurement. An electronically digital operated constant temperature bath (RAAGA Industries) 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 accuracy in the temperature measurement is ± 0.1 K.

Theory and Calculations

Using the measured data, the following volumetric, compressibility and transport parameters have been calculated using the standard relations.

Adiabatic Compressibility $\beta = \frac{1}{U^2\rho}$ ...(1)

The apparent molal compressibility has been calculated from the relation,

$$\varphi_K = \frac{1000}{m\rho_0}\left(\rho_0\beta - \rho\beta_0\right) + \left(\frac{\beta_0 M}{\rho_0}\right) \qquad ...(2)$$

where β, ρ and β_0, ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molal concentration of the solute, and M the molecular mass of the solute. φ_K is the function of m as obtained by Gucker[4] from Debye Huckel theory[5] and is given by

$$\varphi_K = \varphi_K{}^0 + S_K m^{1/2} \qquad ... (3)$$

wheβre φ_K^0 is the limiting apparent molal compressibility at infinite dilution and S_K is a constant. φ_K^0 and S_K of equation (3) have been evaluated by least square method.

The apparent molal volume φ_V has been calculated using the relation

$$\varphi_V = \left(\frac{M}{\rho}\right) - \frac{1000\left(\rho - \rho_0\right)}{m\rho\rho_0} \qquad ...(4)$$

The apparent molal volume φ_V has been found to differ with concentration according to Masson's[6] empirical relation as

$$\varphi_V = \varphi_V^0 + S_V m^{1/2} \qquad ...(5)$$

where φ_V^0 is the limiting apparent molal volume at infinite dilution and S_V is a constant and these values were determined by least square method.

The viscosity A and B coefficients of arginine in aqueous disaccharide solutions were calculated from the Jones-Dole equation[7-8].

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \qquad ...(6)$$

where, η and η_0 are the viscosities of the solution and solvent respectively and m is the molal concentration of the solute. A is determined by the ionic attraction theory of Falkenhagen-Vernon and therefore also called Falkenhagen coefficient, B or Jones-Dole coefficient is an empirical constant determined by ion-solvent interactions.

The molal hydration number has been computed using the relation.

$$n_H = \left(\frac{n_1}{n_2}\right)\left(1 - \frac{\beta}{\beta_0}\right) \qquad ...(7)$$

where β and β_0 are adiabatic compressibilities of solution and solvent respectively, n_1 and n_2 are number of moles of solvent and solute respectively.

Table 1 Values of density (ρ), Viscosity (η) and ultrasonic velocity (U) of arginine in aqueous disaccharides at 298.15K

Molality m/(mol.kg^{-1})	Density ρ/(kg.m^{-3})	Viscosity η/(× 10^{-3}Nsm^{-2})	Ultrasonic velocity U/(ms^{-1})
System I : Arginine + aqueous galactose			
0.00	1017.5	1.0033	1512.6
0.02	1013.1	1.0099	1526.4
0.04	1027.6	1.0451	1527.9
0.06	1034.1	1.0748	1530.9
0.08	1036.3	1.0972	1533.0
0.10	1036.9	1.1308	1536.0
System II : Arginine + aqueous maltose			
0.00	1031.2	1.0830	1542.6
0.02	1033.8	1.0959	1562.4
0.04	1035.0	1.1051	1551.3
0.06	1036.2	1.1125	1544.4
0.08	1037.8	1.1362	1539.6
0.10	1038.2	1.1481	1536.6
System III : Arginine + aqueous lactose			
0.00	1031.2	1.0832	1542.6
0.02	1034.9	1.0999	1563.0
0.04	1035.1	1.1080	1551.4
0.06	1036.2	1.1125	1545.0
0.08	1037.8	1.1365	1541.2
0.10	1038.2	1.1481	1539.3

Results and Discussion

The experimental values of density, viscosity and ultrasonic velocity for different molality of arginine in each of the three aqueous disaccharides viz., galactose, maltose and lactose at 298K are shown in Table 1. The values of adiabatic compressibility (β), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their constants (S_K, S_V), hydration number (n_H)and the values of A and B coefficients of Jones - Dole equation are given in Tables 2-3.

In all the systems (Table 1) the values of density increases with increase in molal concentration of arginine. This increasing behaviour suggests Sa moderate strong electrolytic nature in which the solute tends to attract the solvent molecules. The ultrasonic velocity (Table 1) increases with increase in the concentration of solute in aqueous galactose, but however it found to be decreases in aqueous maltose and lactose systems. Generally the values of ultrasonic velocities are smaller in aqueous galactose than the other systems. Molecular association is thus responsible for the observed increase in ultrasonic velocity in these mixtures. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration.

The decrease in adiabatic compressibility (Table 2) observed in aqueous galactose with arginine in the present study generally confirms that conclusions drawn from the velocity data. However these values are found to be increase with increase in molal concentration of arginine in aqueous maltose and lactose mixtures. The adiabatic compressibility values are larger in galactose mixtures compared to maltose and lactose mixtures which show molecular associations/ interactions greater in galactose mixtures than that of other two mixtures. The decrease in compressibility imply that there is enhanced molecular associations in these system on increase in solute content, as the new entities (formed due to molecular association) become compact and less compressible.[9] The positive values of hydration (Table 2) number indicates an appreciable solvation of solutes[10]. This is an added support for the structure promoting nature of the solutes as well as the presence of a appreciable dipole-dipole interaction between solute and water molecules. This also suggests that compressibility of the solution will be less than that of the solvent. As a result, solutes will gain mobility and have more probability of contacting solvent molecules. This may enhance the interaction between solute and solvent molecules. Further, decreasing behaviour of n_H shows that galactose, maltose and lactose have a dehydration effect on the arginine.

Table 2 Values of adiabatic compressibility (β), hydration number (n_H), apparent molal compressibility φ_k, apparent molal volume φ_v of arginine in aqueous disaccharides at 298.15K

Molality $m/(mol.kg^{-1})$	Adiabatic compressibility $\beta/(\times 10^{-10}\ m^2\ N^{-1})$	Hydration number (n_H)	Apparent molal compressibility $(-\varphi_k/(\times 10^{-8}\ m^2\ N^{-1})$	Apparent molal volume $-\varphi_v/(m^3 mol^{-1})$
System I : Arginine + aqueous galactose				
0.00	4.2950	----	----	----
0.02	4.2132	58.0	43.43	58.96
0.04	4.1685	43.0	42.28	248.15
0.06	4.1259	35.9	40.01	271.90
0.08	4.1061	30.5	33.53	230.95
0.10	4.0874	26.2	28.87	190.66
System II : Arginine + aqueous maltose				
0.00	4.0783	----	----	----
0.02	3.9625	79.3	63.04	126.06
0.04	4.0148	21.6	19.54	92.12
0.06	4.0461	6.7	8.66	80.81
0.08	4.0650	2.5	4.92	79.99
0.10	4.0760	0.5	3.27	74.66
System III : Arginine + aqueous lactose				
0.00	4.0752	----	----	----
0.02	3.9553	82.1	67.30	179.23
0.04	4.0139	21.6	19.12	94.38
0.06	4.0429	6.7	8.79	80.64
0.08	4.0566	3.1	5.63	79.83
0.10	4.0651	1.5	3.74	67.71

From the Table 2, the following observations have been made on φ_K and φ_V

i. The values of φ_K are all negative over the entire range of molality and the same increases with increase in concentration of solute in all the three systems.

ii. The values of φ_V are all negative over the entire range of molality. Further these values are increases with increase in concentration of arginine in aqueous maltose and lactose mixtures, but however a reverse trend has been obtained for galactose mixtures.

iii. The maximum value of φ_V obtained in all the systems is in the order: maltose > lactose > galactose.

The increasing values of φ_K reveals that strengthening of the solute – solvent interactions exist in these mixtures. Further, the negative values of φ_V in all the systems indicate the presence of solute-solvent interactions. The decrease in φ_V is due to strong ion-solvent interaction and vice-versa. The negative values of φ_V indicate electrostrictive solvation of ions.[11] From the magnitude of φ_V, it can be concluded that, strong molecular association is found in galactose mixture and hence galactose mixture is a more effective structure maker than others.

φ_K^0 provides information regarding ion-solvent interactions and S_k, that of solute-solute interactions in the mixtures. φ_K^0 and φ_V^0 values (Table 3) are negative in all the systems studied. Appreciable negative value of φ_K^0 for all the systems reinforce our earlier view that existence of solute-solvent interaction in the present systems. The magnitude is in the order: maltose>lactose > galactose. Further, the negative values of S_k and S_v which indicates the existence of ion - ion / solute-solute interactions. The negative values of φ_V^0 indicate smaller solute-solvent interactions present in these systems. The magnitude of φ_V^0 is in the order: galactose < lactose < maltose.

From the Table 1 it is observed that the values of viscosity increases with increasing concentration of arginine in aqueous disaccharides mixtures. This increasing trend indicates the existence of molecular interaction occurring in these systems.

Table 3 Values of limiting apparent molal compressibility (φ_k^0), Limiting apparent molal Volume (φ_v^0), constants S_K and S_v and A and B coefficients of Jones-Dole equation of arginine in aqueous disaccharides at 298.15K

Systems	**Limiting apparent molal compressibility** $-\varphi_k^0$ **/($\times 10^{-8}$ m^2 N^{-1})**	**Constant -S_k/($\times 10^{-8}$N^{-1}m^{-1}.mol^{-1})**	**Limiting apparent molal volume** $-\varphi_v^0$**/(m^3.mol^{-1})**	**Constant -S_v/(m^{3}lt$^{1/2}$.mol$^{-3/2}$)**	**A coefficient A/(dm$^{3/2}$.mol$^{-1/2}$)**	**B coefficient B/(dm^3.mol^{-1})**
arginine + aqueous galactose	0.039	0.228	117.20	525.55	0.1423	0.7632
arginine + aqueous maltose	0.016	0.095	63.15	174.81	0.0745	0.3572
arginine + aqueous lactose	0.017	0.097	74.50	163.91	0.0832	0.3481

In order to shed more light on this the role of Viscosity B - coefficient has also been obtained. From Table 3, it is observed the values of A and B are positive in all systems studied. Since A is a measure of ionic interaction[12] it is evident that there is a weak ion-ion interaction in the mixtures studied, which is indicated by the smaller magnitude of A values. B coefficient is also known as measure of order or disorder introduced by the solute in to the solvent. It is also a measure of solute-solvent interaction and the relative size of the solute and solvent molecules. The behaviour of B-coefficient in all the three systems suggest the existence of strong ion-solvent interactions. The magnitude of B values is in order of galactose> maltose> lactose. This conclusion is in excellent agreement with that drawn from S_v and φ_V^0 data and the larger values of B indicate structure making capacity of the solute.

Conclusion

In the light of the above observations, it may be concluded that existence of ion-solvent interactions resulting in attractive forces promote the structure making tendency while solute-solute interactions resulting in dipole-dipole, dipole-induced dipole and electrostrictive forces enhance the structure breaking properties of aminoacid. The existence of molecular interaction is in order of galactose > maltose > lactose. This suggests arginine in aqueous galactose mixture is a strong structure maker than the other two mixtures.

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