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Acoustical and transport behavior of some amino acids in aqueous DMSO solutions at 303.15K

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ABSTRACT

Ultrasonic velocity (U), Viscosity (η) and density (ρ) have been measured for three amino acids viz., L-glutamine, L-arginine, L-lysine in aqueous DMSO solutions at 303.15K. Using the experimental values, the adiabatic compressibility (β), hydration number (n_H), apparent molar compresiblility (φ_K) apparent molar volume (φ_V), limiting apparent molar compressibility (φ_K^0), limiting apparent molar volume (φ_V^0) and their constants (S_K, S_V), transfer volume ($\Delta\varphi_V^0$) and viscosity A and B coefficients of Jones-Dole equation were calculated. The experimental results have been discussed in terms of ion-solvent and solute–co-solute interactions on the basis of cosphere over lap model.

Keywords: Ultrasonic velocity, apparent molar compressibility, apparent molar volume and transfer volume.

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 intermolecular and intra molecular association, complex formation and related structural changes affect the compressibility of the system which in turn produces corresponding variation in the ultrasonic velocity. During the last two decades, the ultrasonic study has been carried out to investigate hydration of proteins through volume and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration [1-3].

Amino acids belong to an important family of bio-molecules which serve primarily as basic building block of proteins. Mixed aqueous solvents are used extensively in chemistry and other fields to control factors like stability, reactivity and stability of systems. DMSO is an aprotic polar solvent strongly associated due to a highly polar S = O group in the molecule and large dipole moment. DMSO is called super solvent due to its wide range of applicability as solvent in

biological process and chemical intermediates. The study of DMSO is important because of its utilization in a broad range of applications in medicine.

Since volumetric, compressibility and viscosity studies are lacking in aqueous non-electrolytic mixtures of amino acids, an attempt has been made to understand the behaviour of L-glutamine, L-arginine and L-lysine in aqueous DMSO solutions 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 inter ionic interaction between the components. Hence their derived parameters such as adiabatic compressibility (β), apparent molar compresiblility (φ_K) , apparent molar volume (φ_V), limiting apparent molar compressibility (φ_K^0), limiting apparent molar volume (φ_V^0) and their constants (S_K, S_V), hydration number (n_H) and the value of A and B co-efficient of Jones-Dole-equation have been obtained to shed more light on such interactions.

MATERIALS AND METHODS

Analytical reagent (AR) and spectroscopic reagent (SR) grades which minimum assay of 99.9% of L-glutamine, L-arginine, L-lysine and DMSO were obtained from E-Merck, Germany and SdFine chemicals, India, which are used as such without further purification. Water used in the experiment was deionised, distilled and was degassed prior to making solutions. Aqueous solutions of DMSO (3:1) were prepared by volume and used on the day they were prepared. Solution of amino acids in the concentration range of 0.02-0.1 mol·dm^{-3} were made by volume on the molarity concentration scale with precision of ± 1 × 10^{-4}g on 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 kgm^{-3}. An Ostwald's viscometer (10 ml) was used for the viscosity measurement. Efflux time was determined using a digital chronometer within ±0.01s. An ultrasonic interferometer having the frequency of 3 MHz (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

Various acoustical and thermodynamical parameters are calculated from the measured data such as

Adiabatic compressibility

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

The molar hydration number has been computed using the relation,

$$n_H = \left(\frac{n_1}{n_2}\right)\left(1 - \frac{\beta}{\beta_0}\right) \qquad \ldots(2)$$

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.

The apparent molar compressibility has been calculated from relation,

$$\varphi_K = \frac{1000}{m\rho_0}\left(\rho_0\beta - \rho\beta_0\right) + \left(\frac{\beta_0 M}{\rho_0}\right) \quad \ldots(3)$$

where β, ρ and β_0, ρ_0 are the adiabatic compressibility and density of solution and solvent respectively, m is the molar 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

$$\varphi_K = \varphi_K^{\,0} + S_K m^{1/2} \quad \ldots(4)$$

where $\varphi_K^{\,0}$ is the limiting apparent molar compressibility at infinite dilution and S_K is a constant. $\varphi_K^{\,0}$ and S_K of equation (4) have been evaluated by the least square method.
The apparent molar volume φ_V has been calculated using the relation

$$\varphi_V = \left(\frac{M}{\rho}\right) - \frac{1000\left(\rho - \rho_0\right)}{m\rho\rho_0} \quad \ldots(5)$$

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

$$\varphi_V = \varphi_V^0 + S_V m^{1/2} \quad \ldots(6)$$

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

Transfer volumes ($\Delta\varphi_v^0$) of each amino acid from water to aqueous DMSO solution have been calculated by the equation

$$\Delta\varphi_V^0 = \varphi_V^0 \text{ (in aqueous DMSO solution)} - \varphi_V^0 \text{ (in water)} \quad \ldots(7)$$

where φ_V^0 denotes limiting apparent molar volume.

The viscosity A and B coefficients for the amino acids in aqueous DMSO solutions were calculated from the Jones-Dole equation[7].

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \quad \ldots(8)$$

where, η and η_0 are the viscosities of the solution and solvent respectively and m is the molar concentration of the solute. A is determined by the ionic attraction theory of Falkenhagen-Vernon and therefore also called Falkenhagen coefficient[8] B or Jones-Dole coefficient is an empirical constant determined by ion-solvent interactions.

RESULTS AND DISCUSSION

The values of density (ρ), Viscosity (η) and ultrasonic velocity (U) of three amino acids in aqueous DMSO mixtures (Volume ratio 3:1) are presented in Table-1. The values of adiabatic compressibility (β), hydration number (n_H), apparent molar compressibility (φ_K), apparent molar volume (φ_V), limiting apparent molar compressibility (φ_K^0), limiting apparent molar volume (φ_v^0) and their constants (S_K, S_V), transfer volume ($\Delta\varphi_v^0$) and viscosity co-efficients of

A and B of Jones-Dole equations are given in the Tables 2-3.

Table–1. Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of some amino acids in aqueous DMSO solutions (3:1) at 303.15 K for

M/(mol·dm^{-3})	ρ/(kg.m^{-3})	η/(×10^{-3} Nsm^{-2})	U/(ms^{-1})
System – I L-glutamine + water + DMSO			
0.00	1024.1	1.4021	1522.2
0.02	1025.3	1.4169	1526.3
0.04	1026.6	1.4372	1528.8
0.06	1029.0	1.4803	1531.2
0.08	1030.3	1.5552	1535.3
0.10	1032.2	1.6324	1540.6
System – II L-arginine + water + DMSO			
0.00	1024.1	1.4021	1522.2
0.02	1026.3	1.4069	1524.9
0.04	1027.9	1.4218	1526.2
0.06	1030.0	1.4448	1528.7
0.08	1031.3	1.5054	1531.8
0.10	1033.1	1.6024	1536.5
System – III L-lysine + water + DMSO			
0.00	1024.1	1.4021	1522.2
0.02	1026.8	1.4035	1523.5
0.04	1028.3	1.4186	1525.4
0.06	1030.2	1.4301	1526.8
0.08	1031.8	1.5008	1529.3
0.10	1033.7	1.5192	1534.6

Table–2. Values of adiabatic compressibility (β) and hydration number (n_H), apparent molar compressibility (φ_K) and apparent molar volume (φ_V) of some amino acids in aqueous DMSO solutions (3:1) at 303.15 K for

M/(mol·dm^{-3})	β/(×10^{-10} m^2 N^{-1})	n_H	$-\varphi_K$ /(×10^{-7} m^2 N^{-1})	$-\varphi_V$ /(10^{-3} m^3 mol^{-1})
System – I L-glutamine + water + DMSO				
0.00	4.2141	--	-	-
0.02	4.1866	14.7	1.6450	56.9
0.04	4.1677	12.4	1.4158	59.2
0.06	4.1449	12.3	1.4906	77.2
0.08	4.1192	12.7	1.5245	73.3
0.10	4.0818	14.1	1.6559	76.4
System – II L-arginine + water + DMSO				
0.00	4.2141	--	-	-
0.02	4.1902	2.6	1.6501	104.4
0.04	4.1766	19.9	1.3278	90.0
0.06	4.1544	15.9	1.3994	93.0
0.08	4.1324	14.5	1.3925	85.0
0.10	4.1000	15.2	1.5105	84.8
System – III L-lysine + water + DMSO				
0.00	4.2141	--	-	-
0.02	4.1959	1.9	1.4646	128.1
0.04	4.1793	18.6	1.2936	99.5
0.06	4.1640	13.3	1.2531	96.1
0.08	4.1430	12.7	1.2938	90.9
0.10	4.1078	14.2	1.4645	90.4

In all the three systems (Table-1) the values of density and ultrasonic velocity increases with increase in molar concentration of amino acids. This increasing trend suggests a strong molecular interaction exist between solute and solvent. Generally, the values of ultrasonic velocities are smaller in L-lysine than other two amino acids. 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.

Table-3 Values of limiting apparent molar compressibility (φ_k^0), constant (S_K), limiting apparent molar volume (φ_v^0), transfer volume ($\Delta\varphi_v^0$), constant (S_V) and A and B coefficients of Jones-Dole equation of some amino acids in aqueous DMSO solutions (3:1) at 303.15 K for

Systems	φ_k^0 /(×10^{-7} m^{2}N^{-1})	S_k/(×10^{-7}N^{-1} m^{-1}.mol^{-1})	φ_v^0 /(×10^{-3} m^3.mol^{-1})	$\Delta\varphi_v^0$ /(×10^{-3} m^3.mol^{-1})	S_v/(× m^{3}lt^{½}. mol$^{-3/2}$)	A / (dm$^{3/2}$ mol$^{-1/2}$)	B / (dm^3 mol^{-1})
L-glutamine+ water + DMSO	1.5194	1.1371	0.0414	0.1147	-0.5625	0.3408	2.5616
L-arginine+ water + DMSO	1.6350	7.5473	0.1191	0.1166	-0.1471	0.3582	2.2960
L-lysine + water + DMSO	1.4003	1.9562	0.1517	0.2138	0.3216	0.2423	2.5788
Experimental values of φ_v^0 /(×10^{-3} m^3.mol^{-1}) of amino acids in water: L-glutamine: 521.1; L-arginine: 28.0; L-lysine: -473.3							

Table-2 shows the variations of adiabatic compressibility with molar concentration of amino acids at 303.15K. The decrease in adiabatic compressibility, observed in DMSO-water mixtures with amino acids in the present study generally confirms that conclusions drawn from the velocity data. The adiabatic compressibility values are greater in L-lysine compare to L-glutamine and L-arginine which shows molecular association / interaction is greater in L-lysine than that of other two amino acids. Amino acid molecules in the neutral solution exist in the dipolar form and thus have stronger interaction with the surrounding water molecules. The increasing electrostrictive compression of water around the molecules results in a large decrease in the compressibility of solutions.

The interaction between the solute and the water molecules in the solvent is said to be hydration. From the Table-2, it is observed that the values of n_H are positive in all systems studied and such positive values of n_H indicate an appreciable solvation of solutes. The values of n_H are found to increase non-linearly with increasing the content of L-arginine and L-lysine but it decreases in L-glutamine. A decreasing values of n_H which indicates the strength of interaction gets weakened in the solute-solvent molecules.

From the Table-2, it is observed that the values of φ_K and φ_V are all negative over the entire range of molarity and further, these values decreases non-linearly with increasing the content of L-glutamine but is found to be increasing in the case of L-arginine and L-lysine. This observations clearly suggest that the negative values of φ_K and φ_V in all systems indicates the presence of solute-solvent interactions. The negative values of φ_v indicates electrostrictive solvation of ions[9]. The observed increasing behaviour of φ_K and φ_V reveals that the

strengthening of the ion-solvent interaction of L-arginie and L-lysine in aqueous DMSO solutions.

From Table-3, it is observed that the negative values of φ_K^0 for all systems reinforce our earlier view that existence of solute-solvent interactions. The magnitude of φ_K^0 is in order: L-lysine > L-glutamine > L-arginine. Further, the values of S_K, exhibit negative in all systems studied which shows the existence of ion-solute interaction in the solutions.

The volume behaviour of a solute at infinite dilution is satisfactorily represented by $\varphi_v°$ which is independent of the solute-solute interactions and provides information concerning solute-solvent interactions. Table-3 reveals that the values of $\Delta\varphi_v^0$ in all the systems are negative. The negative values of $\Delta\varphi_v^0$ indicate smaller solute-solvent interactions present in these systems. The magnitude of $\Delta\varphi_v^0$ is in order: L-glutamine > L-arginine > L-lysine. It is evident from the Table-3 that S_v exhibits negative values in all the systems, suggesting the presence of stronger ion-ion interaction and less complex ion formation taking place.

DMSO molecules combine mainly with water molecules rather than interact with amino acids molecules. Based on the cosphere overlap model[10], there are three possible types of interactions. (i) Hydrophilic-hydrophilic interaction between the S,O polar group of DMSO and the Zwitterionic centers of amino acids; (ii) Hydrophilic-hydrophobic interaction between the S,O polar group of DMSO and the side chain group of amino acids, (or) between the Zwitterionic centre of amino acids and two methyl groups of DMSO; and (iii) Hydrophobic-hydrophobic interaction between two methyl groups of DMSO and side chain group of amino acids.
The first type of interaction results in a positive transfer volume while the second and third types of interaction result in negative transfer volumes. From the Table-3, the values of $\Delta\varphi_v^0$ of L-glutamine and L-arginine are found to be negative but whereas positive for L-lysine. From the observed values of $\Delta\varphi_v^0$ it can be concluded that second and third type of interaction is dominant over the first type of interaction. Therefore, in DMSO solution, the interaction between polar groups is not dominant. In addition, the two methyl groups in a DMSO molecule have a significant function to construct water structure. Therefore, two methyl groups make a great negative contribution to transfer volume from water to aqueous DMSO.

Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the mixtures. Viscosity variations are attributed to the structural changes. From the Table-1, it is observed that the values of viscosity increases with increasing concentration of three amino acids in aqueous DMSO solutions. This increasing trend indicates the existence of molecular interaction occurring in these systems.

In order to shed more light on this, role of viscosity B-co-efficient has also been obtained. From Table-3, it is observed that the values of A and B are positive in all systems studied. Since A is a measure of ionic interaction[11]. It is evident that there is a strong ion-ion interaction in the mixtures studied. B-co-efficient is also known as measure of order or disorder introduced by the solute in to the solvent. The behaviour of B-co-efficient in all the three system suggests the existence of strong ion-solvent interactions. The larger value of B indicates structure intensifying property of the solute.

CONCLUSION

In summary, volume and compressibility data have been determined for L-glutamine, L-arginine and L-lysine in aqueous DMSO solutions at 303.15K and the results have been used to study the molecular interaction in the solutions. From the magnitude of φ_K^0 and the values of B-coefficient it can be concluded that L-lysine possess strong ion-solvent interaction than other two amino acids in aqueous DMSO solutions. The transfer volume $\Delta\varphi_V^0$ suggests the pre dominance of hydrophilic-hydrophobic interactions over hydrophilic-hydrophilic interactions.

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