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Interionic interaction of some amino acids in aqueous K_2SO_4 solution at 303.15K

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ABSTRACT

Ultrasonic velocity (U), density (ρ) and viscosity (η) have been measured for three amino acids viz., L-asparagine, L-histidine and L-lysine in aqueous K_2SO_4 solution (0.5M) at 303.15K. Using the experimental values, the 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 B-coefficient of Jones-Dole equation were calculated. The results of the parameters have been discussed in terms of ion-ion and ion-solvent interactions.

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

INTRODUCTION

Ultrasonic investigation in aqueous solutions of 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, considerable 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[1,2]. 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[3,4] and biomolecules[5] have been carried out in pure and mixed aqueous solutions. Amino acids are the fundamental structural units of protein. The investigation of

volumetric and thermodynamic properties of amino acids in aqueous and mixed aqueous solvents have been the area of interest of a number of researchers[6-8].

It is well known that electrolytes can influence the solubility behaviour of aminoacids. Consequently, study of the volumetric properties of amino acids in aqueous salt solutions is very useful to obtain information about various types of interactions in the solutions. Owing to these considerations, an attempt has been made to elucidate the interionic interactions of L-asparagine, L-histidine and L-lysine in aqueous K_2SO_4 solution at 303.15K. In this work, we report 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 volumes (ΔV_φ^0) and viscosity A and B coefficient of Jones-Dole equation have been obtained to shed more light on such information. These results are expected to high light the occurrence of native and relative strength of various types of interaction between amino acid and aqueous potassium sulphate solution.

In the present work, we report the values of density, viscosity and ultrasonic velocity of 0.02 to 0.1 molarity of L-asparagine, L-histidine and L-lysine in aqueous K_2SO_4 solution (0.5M) at 303.15K. Various physical and thermodynamical parameters like adiabatic compressibility (β), 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 adiabatic compressibility ($\Delta\varphi_K^0$), transfer volume ($\Delta\varphi_V^0$)and viscosity A and B coefficients of Jones-Dole equation[18] were calculated from the measured experimental data. All these parameters are discussed in terms of ion-ion and ion-solvent interactions occurring between amino acids and aqueous K_2SO_4 solutions.

MATERIALS AND METHODS

Analytical reagent (AR) and spectroscopic reagent (SR) grades with minimum assay of 99.9% of L-asparagine, L-histidine, L-lysine and K_2SO_4 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 K_2SO_4 (0.5 mol·dm^{-3}) 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 thermo dynamical 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,

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

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[9] from Debye Huckel theory[10] and is given by

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

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

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

The apparent molar volume φ_V has been found to differ with concentration according to Masson[11] empirical relation as

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

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 K_2SO_4 solution have been calculated by the equation

$$\Delta\varphi_V^0 = \varphi_V^0 \text{ (in aqueous } K_2SO_4 \text{ solution)} - \varphi_V^0 \text{ (in water)} \qquad \ldots(7)$$

where φ_V^0 denotes limiting apparent molar volume.

The viscosity A and B coefficients for the amino acids in aqueous K_2SO_4 solutions were calculated from the Jones-Dole equation[12].

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

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[13] B or Jones-Dole coefficient is an empirical constant determined by ion-solvent interactions.

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity and ultrasonic velocity (U) for different molarity of the three amino acids in aqueous K_2SO_4 solution (0.5M) at 303.15K are shown in Table-1. Further, 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 volumes at infinite dilution ($\Delta\varphi_V^0$) and viscosity A and B-coefficients of Jones-Dole equation are shown in Tables 2-3.

Table–1. Values of density (ρ), viscosity (η) and ultrasonic velocity (U) of some amino acids in aqueous K_2SO_4 solutions (0.5M) at 303.15 K for

M/(mol·dm^{-3})	ρ/(kg.m^{-3})	η/(×10^{-3} Nsm^{-2})	U/(ms^{-1})
System – I L-asparagine + Water + K_2SO_4			
0.00	1033.3	0.8838	1519.8
0.02	1034.3	0.8918	1529.4
0.04	1035.5	0.9017	1545.0
0.06	1036.7	0.9020	1557.5
0.08	1038.0	0.9131	1585.2
0.10	1039.0	0.9142	1598.4
System – II L-histidine + Water + K_2SO_4			
0.00	1033.3	0.8838	1519.8
0.02	1035.0	0.8868	1535.2
0.04	1036.6	0.8896	1558.8
0.06	1038.0	0.8975	1584.6
0.08	1038.8	0.8998	1609.2
0.10	1040.9	0.9096	1625.0
System – III L-lysine + Water + K_2SO_4			
0.00	1033.3	0.8838	1519.8
0.02	1036.2	0.8842	1548.8
0.04	1037.5	0.8885	1570.8
0.06	1038.4	0.8935	1589.2
0.08	1039.4	0.8965	1620.6
0.10	1042.1	0.8993	1649.8

In all the three systems (Table – 1) the values of density and ultrasonic velocity increases with increase in molar concentration of amino acids. Generally, the values of ultrasonic velocities are smaller in L-asparagine than other two amino acids. Molecular association is thus responsible for the observed increase in ultrasonic velocity in these mixtures. The factors apparently responsible for such a behaviour may be the presence of interactions caused by the proton transfer reactions of amino acids in aqueous potassium sulphate. The increasing trend suggests a strong electrolytic nature in which the solute tends to attract the solvent molecules. The increase in ultrasonic velocity in these solutions may be attributed to the cohesion brought about by the ionic hydration.

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 K_2SO_4 solution (0.5M) 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-asparagine + Water + K_2SO_4				
0.00	4.1899	-	-	-
0.02	4.1334	34.34	2.98	46.64
0.04	4.0457	43.99	3.82	53.87
0.06	3.9764	43.37	3.78	52.75
0.08	3.8338	54.37	4.69	54.63
0.10	3.7672	51.70	4.46	52.95
System – II L-histidine + Water + K_2SO_4				
0.00	4.1899	-	-	-
0.02	4.0995	55.04	7.08	79.33
0.04	3.9197	82.22	4.86	76.87
0.06	3.8367	71.81	6.20	72.88
0.08	3.7175	72.09	6.18	63.90
0.10	3.6382	67.45	5.82	70.51
System – III L-lysine + Water + K_2SO_4				
0.00	4.1899	-	-	-
0.02	4.0231	101.63	8.93	135.24
0.04	3.9063	86.53	7.51	97.77
0.06	3.8131	76.61	6.62	79.04
0.08	3.6632	80.31	6.89	70.82
0.10	3.5255	81.17	7.00	81.55

The decrease in adiabatic compressibility (Table-2) observed in aqueous K_2SO_4 with amino acids in the present study generally confirms that conclusion drawn from the velocity data. The decrease in adiabatic compressibility is attributed to the influence of the electrostatic field of ions (K^+ and SO_4^{2-}) on the surrounding solvent molecules so called electrostriction. 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 decrease in compressibility values on addition of amino acids in to the salt solution may be due to : (i) an increase in the number of incompressible amino acid molecules, which essentially behave as

Zwitterions in aqueous solutions; (ii) Zwitterions terminal groups (NH_3^+ / COO^-) – ions (K^+, SO_4^{2-}) interactions and (iii) NH_3^+/COO^- water dipole interactions in solutions.

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 K_2SO_4 solutions (0.5M) at 303.15K

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-asparagine+ Water + K_2SO_4	-1.83	-8.92	-44.10	35.32	-0.03	0.040	0.221
L-histidine+ Water + K_2SO_4	-7.72	7.16	-89.77	30.63	0.07	-0.035	0.304
L-lysine + Water + K_2SO_4	-10.04	11.16	-170.90	59.48	0.33	-0.036	0.380
Experimental values of φ_v^0 /(×10^{-3} m^3.mol^{-1}) of amino acids in water: L.asparagine: -79.42; L-histidine: -120.40; L-lysine: -230.38							

The interaction between the solute and water molecules present in the solvent is termed as hydration. From the Table-2, it is observed that the values of n_H are positve in all systems studied and it indicates an appreciable solvation of solutes. The values of n_H are found to increases non-linearly with increasing the content of L-asparagine and L-histidine but where as it found to be decrease in L-lysine indicating that interaction involving (K^+, SO_4^{2-}) ions with the charged centres of amino acids becomes weaken which further enhanced the electrostriction of the charged centres with water molecules and weakening the interaction between ion and the charged centres of amino acid. The increasing behaviour of n_H suggests that the decrease in solute-co-solute interactions and vice-versa.

The values of φ_K and φ_V (Table-2) are all negative over the entire range of molarity. The values of φ_K and φ_V are decreases non-linearly with increasing the concentration of L-asparagine but where as it found to be increases in L-histidine and L-lysine mixtures. The maximum value of φ_V obtained in all the three systems is in the order: L-asparagine > L-histidine > L-lysine. The negative values of φ_K and φ_V for all the amino acids indicating the existence of ionic and hydrophilic interactions occurring in these systems. The negative values of φ_V indicate electrostrictive solvation of ions[14]. The non-linear variation of φ_K and φ_V in all the three systems reveals that existence of ion-solvent interaction between the components in the mixtures. From the magnitude of φ_V it can be concluded that strong

molecular association is found in L-lysine than the other two amino acids and hence L-lysine is a more effective structure maker.

φ_K^0 provides information regarding ion–solvent interactions and S_K that of ion-ion interaction in the solution. From the Table-3, φ_K^0 values are negative in all the three systems studied. The appreciable negative values of φ_K^0 for all the systems reinforce our earlier view that the existence of ion-solvent interaction in the present systems. The values of S_K is negative in (Table-3) L-asparagine but it found to be positive for other two amino acids. The negative values of S_K indicates weakening of ion-ion interactions and suggest the structure breaking effect of the amino acids. It is well known that solutes causing electrostriction lead to decrease in compressibility of the solution. This is reflected by the negative values of φ_K of the amino acids.

The volume behaviour of the solute at infinite dilution is satisfactorily represented by φ_V^0 which is independent of the ion-ion interactions and provides information concerning ion-solvent interactions. Table-3 reveals that the values of φ_V^0 are negative in all the system studied which indicate the existence of ion-solvent interaction. The magnitude of φ_V^0 is in the order: L-asparagine > L-histidine > L-lysine. The S_V values (Table-3) for all amino acids except L-asparagine are found to be positive, suggesting that ion-ion interactions are weaker than ion-solvent interactions in the systems under study. Generally speaking the types of interaction occurring between the potassium sulphate and Zwitterionic centre of amino acids can be classified as follows:

- Hydrophilic – ionic interactions between the ions of potassium sulphate (K^+, SO_4^{2-}) and Zwitterionic centres of the amino acids.
- Ionic – hydrophobic interactions between the ions of potassium sulphate and the non-polar side group of the amino acids.

The $\Delta\varphi_v^0$ values (Table–3) can also be explained on the basis of co-sphere overlap model[15] in terms of solute-co-solute interactions. According to this model, hydrophilic-ionic group interactions contribute positively, whereas ionic-hydrophobic group interactions contribute negatively to the $\Delta\varphi_v^0$ values. In the present study, the positive $\Delta\varphi_V^0$ values observed for all amino acids suggest that the hydrophilic-ionic type of interactions are dominating over the later.

Viscosity is another important parameter in understanding the structure as well as molecular interactions occurring in the solutions. Viscosity variation is attributed to the structural changes. The structural changes influence the viscosity to a marked extent as compared to density and compressibility. From Table-1, it is observed that the values of viscosity increases with increase in solute concentration. This increasing trend indicates the existence of ion-solvent interaction occurring in these systems.

In order to shed more light on this, the role of viscosity B-coefficient has also been obtained. From the Table-3, it is observed that the values of A-coefficient are positive for

L-asparagine and negative for other two amino acids. Further, B-coefficient are positive in all systems studied. Since A is a measure of ionic interaction[16], it is evident that there is a weak ion-ion interaction in the amino acids 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 into the solvent. It is also a measure of ion-solvent interaction and the relative size of the ion and solvent molecules. The observed behaviour of B-coefficient in all the three systems suggest the existence of strong ion-solvent interaction. The magnitude of B values is in the order : L-lysine > L-histidine > L-asparagine. This conclusion is an 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 summary, acoustical, volumetric and transport parameters have been determined for L-asparagine, L-histidine and L-lysine in aqueous potassium sulphate solutions at 303.15K. The results have been used to explain the ion-solvent interaction between Zwitterionic portion of amino acids and ions of aqueous pottassium sulphate. From the magnitude of φ_v^0 and B-coefficient it can be concluded that the ion-solvent interaction is greater in L-lysine than other two amino acids. Transfer volume $\Delta\varphi_v^0$ suggest hydrophilic-ionic group interactions are dominating over ionic-hydrophobic interaction on the basis of co-sphere overlap model. It can be concluded that ion-solvent interactions are dominating over the solute-co-solute interactions.

REFERENCES

[1] Millero, F.J., Surdo A and Shin, C., *J. Phys. Chem.*, 82 (**1978**) 784.
[2] Cabani, S. Conti. G. Matteoli, E. and Tine, M.R., *J. Chem. Soc. Faraday Trans.1*, 77 (**1981**) 2385.
[3] Hedwig, G.R., and Hoiland, H., *J. Chem. Thermodyn.*, 23 (**1991**) 1029.
[4] Wadi, R.K., and Ramaswami, P., *J. Chem. Soc. Faraday Trans.*, 93 (**1997**) 243.
[5] Wadhwani, V.R., Akhtar, Y., and Pandey, J.D., *Proc. Indian Acad. Sci. (Chem. Sci.)*, 109 (**1997**) 353.
[6] Duke, M.M., Hakin, A.W., Mckay, R.M., and Preuss, K.E., *Can. J. Chem.*, 72, (**1994**) 1489.
[7] Chalikian, T.V., Saravazyan, A.P., Funk, T., and Breslauer, K.J., *Biopolymers*, 34 (**1994**) 541.
[8] Marty, J.L., Hakin, A.W., Duke, M.M., and Preuss, K.E., *J. Chem. Soc. Faraday Trans.*, 90 (**1994**) 2027.
[9] Gucker, B.S., Chauhan, S. and Syal, V.K., *Indian j. Chem.*, 41A (**1933**) 111.
[10] Debye and Huckel, *Physik, Z.*, 24 (**1923**) 185.
[11] Masson, D.O., *Philos. Mag.*, 8 (**1929**) 218.
[12] Jones, G., and Dole, M., *J. Am. Chem. Soc.*, 51 (**1929**) 2950.
[13] Falkenhagen, H. and Vernan, E.L., *Z. Phys.*, 33 (**1932**) 146.
[14] Dhanalakshmi, A. and Jasmine Vasantharani, E, *J. Pure & Appl. Ultrason*, 27 (**1999**) 247.
[15] Gurney, R.W., *Ionic process in solution*, 3 MC Graw Hill, New York (**1953**).
[16] Jahagirdar, D.V., Shankarwar, A.G., *Ind. J. Pure and Appl. Ultraso.*, 38 (**2000**)760.