INTERMOLECULAR INTERACTIONS OF SOME AMINO ACIDS IN AQUEOUS 1,4-DIOXANE SOLUTIONS AT 298.15K

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ABSTRACT

Ultrasonic velocity (U), viscosity (η) and density (ρ) have been measured for three amino acids viz., L-serine, L-proline, L-histidine in aqueous 1,4-dioxane mixtures (0.6m) at 298.15K. Using the experimental values, the adiabatic compressibility (β), molal hydration number (n_H), apparent molal compressibility (φ_K), apparent molal volume (φ_V), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0), their constants (S_K, S_V), and viscosity coefficients of A and B parameters of Jones-Dole equation were calculated and the results of these parameters have been discussed in terms of solute –solvent and solute-co-solute interactions.

Keywords: *ultrasonic velocity, apparent molar volume, hydration number.*

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 of intermolecular and intramolecular 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 volumetric and ultrasonic measurements, since these properties are sensitive to the degree and nature of hydration[1-6]. 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[7-9] and biomolecules[10-11] 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[12-16]. Mixed aqueous solvents are used extensively in chemistry and other fields to control factors like stability, reactivity and stability of systems. 1,4-dioxane is a widely used solvent because it is a non-hydrogen bonded cyclic ether, miscible with water in all proportions with a boiling point close to that of water. Moreover, its dipole moment is close to zero (0.45 D) and the dielectric constant can be raised over a wide range of (2.2-7.8) in its mixtures with water. Since volumetric, compressibility and viscosity studies are lacking in aqueous mixtures of amino acids, an attempt has been made to understand the behaviour of L-serine, L-proline and L-histidine in aqueous 1,4-dioxane mixture of 0.6m concentration at 298.15K 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), hydration number (n_H), limiting apparent molal compressibility (φ_K^0), limiting apparent molal volume (φ_V^0) and their constants (S_K, S_V) and viscosity A and B coefficient have been obtained to shed more light on such interactions.

EXPERIMENTAL

Analytical reagent (AR) grade and spectroscopic reagent (SR) grade with minimum assay of 99.9% of L-serine, L-proline, L-histidine and 1.4-dioxane were obtained from E-Merck, Germany and SdFine chemicals, India was used as such without further purification. Water used in the experiments was deionised, distilled and degassed prior to making solutions. Aqueous solutions of 1.4-dioxane (0.6 mol·kg^{-1}) were prepared by mass and used on the day they were prepared. Solution of amino acids in the concentration range of 0.02-0.1 mol·kg^{-1} were made by mass on the molality concentration scale with a precision of $\pm 1 \times 10^{-4}$g on a electronic digital balance (Model: SHIMADZU AX200). The density was determined using a specific gravity bottle by relative measurement method with an accuracy of ± 0.01 kg·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 $\pm$ 0.01s. An ultrasonic interferometer having the frequency 3MHz (MITTAL ENTERPRISES, NEW DELHI, MODEL F-81) with an overall accuracy of $\pm$ 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 $\pm$ 0.1 K.

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

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

Molal hydration number has been computed using the relation

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

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 molal 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 molal concentration of the solute, and M the molecular mass of the solute. φ_K is the function of m as obtained by Gucker [17] from Debye Huckel theory[18] and is given by

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

where 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 (4) have been evaluated by the least square method.

The apparent molal volume φ_v has been calculated using the relation

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

The apparent molal volume φ_v has been found to differ with concentration according to Masson[19] empirical relation as

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

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 for the amino acids in aqueous 1,4-dioxane solutions were calculated from the Jones-Dole equation[20,21].

$$\frac{\eta}{\eta_0} = 1 + Am^{1/2} + Bm \qquad \ldots(7)$$

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

RESULTS AND DISCUSSION

The experimental values of density (ρ), viscosity (η), ultrasonic velocity (U), for different molal composition of each of the three amino acids viz., L-serine, L-proline and L-histidine in aqueous 1,4-dioxane mixtures (0.6 mol·kg^{-1}) are shown in Table 1. The values of adiabatic compressibility, hydration number, apparent molal compressibility, apparent molal volume, limiting apparent molal compressibility, limiting apparent molal volume, constants S_K and S_V, and viscosity coefficients of A and B parameters of Jones-Dole equations are given in Tables2-3.

In all the three system (Table 1) the values of density and ultrasonic velocity increases with increase in molal concentration of amino acids. This increasing trend suggest, a molecular interaction exist between solute and solvent molecules. Generally the values of ultrasonic velocities are smaller in L-histidine 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. It is known that aqueous 1,4-dioxane mixture of L-serine, L-proline and L-histidine contain in addition to the uncharged molecules NH_2CH_2COOH, an electrically neutral molecule, Viz., $^+NH_3CH_2COO^-$ dipolar ions (Zwitterions). When the amino acids are dissolved in aqueous 1,4-dioxane mixtures, the cations NH_3^+ and anions COO^- are formed.

The water molecules are attached to the ions strongly by the electrostatic forces, which introduce a greater cohesion in the solution. Thus the cohesion increases with the increase of amino acid concentration in the solution. The increased association, observed in these solutions, may also be due to water structure enhancement brought about by the increase in electrostriction effect which brings about the shrinkage in the volume of solvent, caused by the Zwitterionic portion of the amino acid, is increased in mixed solvents as compared to that in pure water. This effect is similar to the results of Dash et. al.[22] and Ragouramane et. al.[23].

From Table 2, it was observed that the adiabatic compressibility values are larger in L-histidine compared to L-proline and L-serine which shows molecular association/interaction is greater in L-histidine than that of other two amino acids.

Table-1: Values of density (ρ) viscosity (η) and ultrasonic velocity (U) of some amino acids in aqueous 1,4-dioxane (0.6m) mixtures at 298.15 K

m/(mol. kg⁻¹)	ρ/ (kg m⁻³)	η/(×10⁻³ Nsm⁻²)	U/(m.s⁻¹)
$m/(\text{mol. kg}^{-1})$	$\rho/(\text{kg m}^{-3})$	$\eta/(\times 10^{-3}\,\text{Nsm}^{-2})$	$U/(\text{m.s}^{-1})$
System 1: aqueous 1,4-dioxane (0.6m) + L-serine			
0.00	997.24	0.9944	1527.6
0.02	997.36	0.9952	1536.8
0.04	997.53	1.0000	1537.1
0.06	998.46	1.0078	1540.7
0.08	999.55	1.0139	1541.1
0.10	1000.03	1.0265	1543.8
System II : aqueous 1,4-dioxane (0.6m) + L- proline			
0.00	997.24	0.9944	1527.6
0.02	997.44	1.0087	1535.5
0.04	997.65	1.0130	1536.2
0.06	998.64	1.0248	1538.7
0.08	1000.63	1.0259	1539.3
0.10	1001.57	1.0318	1541.1
System III : aqueous 1,4-dioxane (0.6m) + L-histidine			
0.00	997.24	0.9944	1527.6
0.02	1002.23	1.0095	1530.2
0.04	1004.21	1.0190	1532.8
0.06	1006.11	1.0328	1534.7
0.08	1007.06	1.0394	1537.8
0.10	1019.7	1.0450	1539.9

Table-2: Values of adiabatic compressibility (β), hydration number (n_H), apparent molal compressibility (φ_K) and apparent molal volume (φ_V) of some amino acids in aqueous 1,4-dioxane (0.6m) mixtures at 298.15 K

m/(mol. kg⁻¹)	β/(×10⁻¹⁰ m² N⁻¹)	(nH)	− φk/(×10⁻⁷ m² N⁻¹)	− φv/(×10⁻³ m³ mol⁻¹)
$m/(\text{mol. kg}^{-1})$	$\beta/(\times 10^{-10}\,\text{m}^2\,\text{N}^{-1})$	(n_H)	$-\varphi_K/(\times 10^{-7}\,\text{m}^2\,\text{N}^{-1})$	$-\varphi_V/(\times 10^{-3}\,\text{m}^3\,\text{mol}^{-1})$
System 1: aqueous 1,4-dioxane (0.6m) + L-serine				
0.00	4.297	…	…	…
0.02	4.250	31.61	23.86	6.02
0.04	4.244	16.51	13.56	7.27
0.06	4.223	15.63	13.19	20.37
0.08	4.213	13.30	11.74	28.69
0.10	4.196	12.49	11.29	28.91
System II : aqueous 1,4-dioxane (0.6m) + L- proline				
0.00	4.297	…	…	…
0.02	4.252	28.43	22.92	9.98
0.04	4.248	15.22	12.69	10.27
0.06	4.229	14.15	12.33	23.32
0.08	4.218	12.31	11.69	42.48
0.10	4.204	11.49	11.18	43.39
System III : aqueous 1,4-dioxane (0.6m) + L-histidine				

0.00	4.297	…	…	…
0.02	4.262	21.92	28.50	250.19
0.04	4.239	17.88	22.00	174.73
0.06	4.220	15.83	19.19	148.11
0.08	4.199	15.10	17.51	122.99
0.10	4.181	14.42	16.60	115.52

Table-3: Values of limiting apparent molal compressibility (φ_k^0), limiting apparent molal volume (φ_v^0), constants S_K, S_V and viscosity A and B coefficients of Jones-Dole equation of some amino acids in an aqueous 1,4-dioxane (0.6m) mixtures at 298.15 K

Amino acids	— φ_k^0 /(×10⁻⁸m²N⁻¹)	S_k/(×10⁻⁸N⁻¹ m⁻¹.mol⁻¹)	– φ_v^0 /(m³.mol⁻¹)	S_v/(m³lt½. mol⁻³/²)	A Coefficient A/(dm³/². mol⁻¹/²)	B Coefficient B/(dm³. mol⁻¹)
Serine+aqueous 1,4- dioxane	31.42	45.48	8.12	- 112.6	-0.8568	1.2606
Proline+aqueous 1,4- dioxane	29.03	54.96	60.54	-162.2	-0.1842	2.8436
Histidine+aqueous 1,4- dioxane	31.35	45.18	- 285.24	524.9	-0.5231	3.8850

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 implies that there is an enhanced molecular association in these systems on increase in solute content, as the new entities (formed due to molecular association) become compact and less compressibility.

The interaction between the solute and the water molecules in the solvent is termed as hydration. The positive values of hydration number increases as appreciable solvation of solutes[24]. This is an added support for the structure promoting nature of the solutes as well as the presence of dipolar 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 of solvent molecules. From the Table 2, it is observed that the values of hydration number decreases with increasing the concentration of solute in all the three system studied. This shows that L-serine, L-proline and L-histidine have a dehydration effect on aqueous 1,4-dioxane mixtures at 298.15K.

The following observations have been made on φ_K and φ_V (Table 2) of the L-serine, L-proline and L-histidine in aqueous 1,4-dioxane mixture.

1. The values of φ_K and φ_V are all negative over the entire range of molality.

2. φ_K values are increasing with increase in concentration of solute in all the three systems studied.

3. The φ_V values decreases with increase in concentration of L-serine and L-proline, whereas reverse trend was obtained in L-histidine.

4. The maximum value of φ_V obtained in all the three system is in order L-serine > L-proline > L-histidine.

All the above observations clearly suggest that the negative values of φ_K indicate ionic, dipolar and hydrophobic interactions occurring in these systems. The increasing values of φ_K in all the three system reveals that less strengthening the solute–solvent interactions exist in these mixtures. Further the negative values of φ_V in all the system 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 indicates electrostrictive solvation of ions[25]. From the magnitudes of φ_V it can be concluded that, strong molecular association is found in L-histidine mixtures than the other two and hence L-histidine mixture is a more effective structure maker than others.

The limiting apparent molal compressibility due to Masson[19] φ_K^0 have been computed using least square method. φ_K^0 provides information regarding solute–solvent interactions and S_K provided that of solute–solute interaction in the mixtures. One can notice from Table 3 that φ_K^0 values are negative in all the systems studied. Appreciable negative values of φ_K^0 for all systems reinforce our earlier view that existence of solute-solvent interaction in the present systems. The positive values of S_K shows the existence of ion-ion/solute-solute interaction in all systems studied.

It is clear from Table 3 that the values of φ_V^0 are negative in L-serine and L-proline but it found positive in L-histidine mixtures.

Depending upon the behaviour of φ_V^0 the following types of interactions are possible:

1. Ion-dipolar interactions occurring between Zwitterionic centres of amino acids and dipolar parts of 1,4-dioxane
2. hydrophobic-dipolar interaction between non-polar parts of amino acids and dipolar part of 1,4-dioxane , and
3. hydrophobic-hydropobic interactions occurring between non-polar parts of amino acids and hydrophobic parts of 1,4-dioxane .

The first type of interactions results in positive contribution where as the other two result in negative contribution. Therefore, the presently obtained positive value for L-histidine mixture show that the first type of interactions (due to ion-dipolar) dominate over the other two types. The negative values for L-serine and L-proline mixtures suggest that second and third types of interactions overweight the effect of the first.

It is evident from the Table 3 that the negative values of S_V in L-serine and L-proline mixtures indicate the presence of weak solute-solute interaction where as the positive values of S_V in L-histidine predicts strong solute-solute interaction. Further, these values indicates the 1,4-dioxane induced effect on the solute-solute interaction which have the bearing of both the increasing non-polar part of the amino acids and the dependence of the behaviour of 1,4-dioxane on the concentration in aqueous medium.

In order to shed more light on this, the role of viscosity B-coefficient has also been obtained. From Table 3, it is observed that the values of A are negative in all systems studied and B-coefficient are positive. Since A is a measure of ionic interaction[26] 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 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 amino acids suggests the existence of strong ion-solvent interaction. The larger value of B indicates structure making capacities of the solute. The magnitude of B is in order: L-histidine > L-proline > L-serine.

CONCLUSION

In present study reports experimental data for density, viscosity and ultrasonic velocity at 298.15K for L-serine, L-proline and L-histidine in aqueous 1,4-dioxane mixtures. From these data, some acoustical parameters have been calculated and studied to explain the intermolecular interaction of ionic, diploar and hydrophobic interactions are operating between amino acids and 1,4-dioxane. From the magnitude of φ_V and B-coefficient, it can be concluded that the existence of molecular interaction is greater in L-histidine than that of L-serine and L-proline in aqueous 1,4-dioxane mixtures.

REFERENCES

1. F.J. Millero, A. Surdo and C. Shin, *J. Phys. Chem.*, **82**, 784 (1978).
2. S. Cabani, G. Conti, E. Matteoli, and M.R. Tine, *J. Chem. Soc. Faraday Trans 1*, **77**, 2385 (1981).
3. H. Hoiland, *J. Soln. Chem.*, **9**, 857 (1980).
4. J.V. Leyendekkers, *J. Chem. Soc. Faraday Trans 1*, **84**, 397 (1988).
5. D.P. Kharakoz, *Biophys. Chem.*, **34**, 115 (1989).
6. D.P. Kharakoz, *J. Phys. Chem.*, **95**, 5634 (1991).
7. G.R. Hedwig and H. Hoiland, *J. Chem. Thermodyn.*, **23**, 1029 (1991).
8. R. Bhat and J.C. Awuwalia, *J. Phys. Chem.*, **99**, 1099 (1985).
9. R.K. Wadi and P. Ramaswami, *J. Chem. Soc. Faraday Trans.*, **93**, 243 (1997).
10. V.R. Wadhwani, Y. Akhtar and J.D. Pandey, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **109**, 353 (1997).
11. J.D. Pandey, A.K. Puri, A. Tewari and A.K. Sharma, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **111(6)**, 747 (1999).
12. M.M. Duke, A.W. Hakin, R.M. Mckay and K.E. Preuss, *Can. J. Chem.*, **72**, 1489 (1994).
13. T.V. Chalikan, A.P. Saravazyan, T. Funk and K.J. Breslauer, *Biopolymers*, **34**, 541 (1994).
14. G.R. Hedwig and Hoeil, *Biophys. Chem.*, **49**, 175 (1994).
15. T. Ogawa, M. Yasuda and K. Mizutani, *Bull. Chem. Soc. Jpn.*, **57**, 662 (1984).
16. J.L. Marty, A.W. Hakin, M.M. Duke, and K.E. Preuss, *J. Chem. Soc. Faraday Trans.,* **90**, 2027 (1994).
17. F.T. Gucker, *Chem. Rev.*, **13,** 111 (1933).
18. Debye and Huckel, *Physik., Z.,* **24**, 185 (1923).
19. D.O. Masson, *Philos. Mag.*, **8**, 218 (1929).
20. G. Jones, and M. Dole, *J. Am. Chem. Soc.*, **51**, 2950 (1929).
21. J.D. Pandey, K. Mishra, A Shukla, V. Mushram and R.D. Ravi, *Thermochemica Acta.,* **117**, 205 (1987).
22. U.N. Dash and S. Supkar, *Acoust. Lett.*, **16**, 135 (1992).
23. D. Ragouramane and A. Srinivasa Rao, *Ind. J. Pure & Applied Phys.,* **36,** 777 (1998).

24. Rita Mehra and Hema Sajnami, *Indian Journal of Pure and Applied Physics*, **38,** 762 (2000).
25. A. Dhanalakshmi and E. Jasmine Vasantharani, *J. Pure. Appl. Ultrason.*, **21**, 79 (1999).
26. D.V. Jahagirdar, A.G. Shankarwar, *Ind. J. Pure and Appl. Ultraso.*, **38**, 760 (2000).

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Concerning culture as a process, one would say that it means learning a great many things and then forgetting them; and the forgetting is as necessary as the learning.
-Albert J. Nock