STUDY OF DENSITY (ρ), VISCOSITY (η) AND MOLAR VOLUME (φ_v) OF AMINO ACIDS SERINE AND CYSTEIN IN MIXED AQUEOUS SOLVENT SYSTEM

Ruchi Tyagi[1], Fazlur Rehman[2], Man Singh[3], U K Jetley[4]

[1,4]R S S (PG) College, Ghaziabad,[2]Faiz-E-Am Degree College, Meerut

[3]Central University of Gujarat, Gandhi nagar(India)

ABSTRACT

Density (ρ),viscosity (η) and molar volume(ϕ_v) have been determined in aqueous and mixed aqueous solutions of concentration ranging from 0.025 to 0.402 for serine and 0.00006 to 0.00201 for cystein at 301.15 K. These experimental values have been performed to evaluate apparent molar volume (ϕ_v), limiting apparent molar volume (ϕ°_v), viscosity coefficients A and B of Jones-Dole equation, relative viscosity, and excess Gibbs free energy of activation .These parameters have been used to interpret the solute-solvent and solute-solute interactions in the given mixed solution.

Key Words : Density, Viscosity, Molar Volume, Cystein, Serine

I INTRODUCTION

Amino acids play a central role both as building blocks of protein and as intermediates in metabolism. Besides 20 amino acids,, mostly α- amino acids, obtained as hydrolysis products of proteins, over 150 other amino acids are known to occur biologically in free and combined form but never found in proteins, some of them function as precursors or intermediates in metabolism[1-3].The chemical properties of the amino acids of proteins particularly determine the biological activity of protein, and depend on size, shape, charge, capacity of hydrogen bonding, hydrophobic interactivity and chemical reactivity. Only hydrophilic amino acids do interact in aqueous environment due to their polar nature. Serine and cystein are polar amino acids. Cystein, in particular, is highly reactive due to the presence of nucleophilic thiol group which is capable of inactivation of insulin in blood stream by breaking one of the three disulphide bonds in insulin structure. As such cystein is used to treat hypoglycemic attack and promotes iron production to make up iron deficiency in anemic condition. Serine, on the other hand, is involved in fat and fatty acid formation, muscle synthesis, and also plays a key role in stabilizing extracellular proteins due to the formation of disulfide bond.

Literature revealed that different physico-chemical and thermodynamic properties of amino acids (and peptides) depend upon the molecular interactions (hydrogen bonding, ion–ion, ion–solvent, solute–solvent, etc) of different amino acid molecules and the other entities present in aqueous and mixed aqueous medium at different temperatures and concentrations in the living cells [4-14], which eventually exhibit the behaviour of structure-making and breaking of amino acids in the mixed solvent system. The ionic solvents drastically affect the behaviour of amino acids in solution which can be used for their separation and purification [15-16]. Recently, a useful study has been carried out to investigate the hydration of protein through different measurements which are sensitive to the degree and nature of hydration [17-18]

Several investigations have, so far, been carried out by the different investigators on the partial molar volumes, adiabatic compressibilities, heat capacity, Gibbs free energy of transfer volume ,and the viscosity-β-coefficient measurements on amino acids with organic salts and mixed aqueous solvents at different temperatures, concentrations, and pH to get different types of information [19-23].

In the present study, density (ρ) and viscosity (η) and molar volume($\varphi_{v)}$ of different concentrations of serine and cystein in aqueous DTE were measured at 301.15K. These experimental values have been used to evaluate apparent molar volume (φ_v), limiting apparent molar volume ($\varphi^{\circ}_{v),}$ viscosity coefficients A and B of Jones-Dole equation, relative viscosity and excess Gibbs free energy of activation.

II EXPERIMENTAL

Amino acids serine and cystein (Emerck Germany) were extra pure and used without further purification).Aqueous dithioerythritol (Emerck Germany) solution was taken as a solvent for the preparation of amino acid solution of different concentrations. The serine and cystein concentration in these mixture ranged from (from 0.025 to 0.402 for serine and 0.00006 to 0.00201 for cystein) mol dm-3.

Viscosity (η) measurement has been made with a Borosil MS Survismete[24], which was calibrated with distilled water. The time of fall was recorded with a stop watch of least count 0.1 second and viscosity value calculated by using poi Seuilles equation noted below.

$$\eta = \pi \rho h g r4 t / s l v = \rho\beta t$$

The terms h, g, r, ρ and v in the above expression are constant for a given viscometer and, therefore, have been replaced by single term β.

The densities of serine and cystein solution of different concentration were measured by a calibrated Pykometer of 50ml capacity at 301.15K(Table-1). The precision in the measurement of density was approximately +_ 0.1% and, on this behalf the error limit in the calculation of viscosity by Poi Seuilles equation was approximately +_0.2%

The apparent molar volume (φv) of serine and cystein in aqueous dithierythritol has been calculated at 301.15K using the following equation[25].

$$\varphi_V = \left[\frac{M}{\rho}\right] - \frac{1000(\rho - \rho_o)}{m \rho \rho_o}$$

where, ρ and ρ_o are the densities of solution and solvent respectively, and M is molecular weight of solute and [m] is the molality of solution.

The apparent molar volume (Φv), has been found to differ with concentration according to Masson [26] empirical relation as

$$\varphi_v = \varphi_v^0 + S_v m^{1/2}$$

Where, φ_v^0 = the limiting apparent molar volume at infinite dilution.

S_v = A constant and determined by least- square method

The viscosity data have been analyzed in the light of Jones-Dole Semi empirical equation [27]

$$\frac{\eta}{\eta^\circ} = 1 + Am^{1/2} + Bm$$

Where, η and η° are the viscosities of the solution and solvent respectively.

And M = The molar concentration of the solute-solvent system.

A and B are constants which are definite for a solute- solvent system, A is known as the Falkenhagen coefficient which characterizes the ionic interaction and B is the Jones- Dole or Viscosity B-coefficient which depends on the size of the solute and the nature of solute-solvent interaction.

III RESULTS AND DISCUSSION

From the experimental values of density and viscosity, some parameters such as apparent molar volume (φ_v),limiting apparent molar volume (φ°_v) and their constant, and viscosity B-Coefficient of Jones-Dole equation were calculated (Table-1).

The above observations clearly suggest that the negative values of apparent molar volume(φ_v) in the given systems indicates the electrostrictive solvation of ions due to solute-solvent-ions interaction.

From the magnitude of φ_v, it can be concluded that stronger molecular association is found in the cystein than serine; hence cystein is a more effective structure making.

The volume behaviour of a solute at infinite dilution is satisfactorily represented by (φ°_v), which is independent of the solute-solute interactions and provides information concerning solute-solvent interaction.

The result reveals that the larger positive values of φ°_v suggest the presence of strong solute-solvent interaction and vice versa in the given media. The decrease in φ_{v° may be attributed to the increased hydrophilicity of the amino acid. The $\Delta\varphi^\circ_v$ values can also be explained on the basis of co-sphere overlap model in terms of solute – co- solute interaction. According to this model, hydrophilic-ionic group interactions contribute positively whereas hydrophilic-hydrophobic group interactions contribute negatively to the φ°_v values

The values (Table-1) of the A coefficient(either negative or positive) for serien and cystein over the entire composition range of aqueous dithioerythritol at 301.15K, indicate the presence of solute-solute interactions.The

value of the B-coefficient for the amino acids in aqueous dithioerythritol solutions are positive indicating that the ion-solvent interactions are stronger. Further, the values of B-coefficient increase with increasing dithioerythritol percentage in solution which suggests that solute-solvent interactions are stronger in cystein than serine.

The results of Φv shows that the value of Φv decreases with the increase in the concentration of amino acids and increases with increase in the concentration of dithioerythritol in solution suggesting that the solute-solvent interaction increase with the increase dithioerythritol percentage.Result reveals that φ°_{v} are positive, which indicates the presence of solute-solvent interactions.

The value of φ°_{v} increases, with the increase in concentration of dithioerythritol aqueous solution which exhibits the increasing trends of solute-solvent interaction increases. All the values of S_v being negative indicate the presence of weak solute- solute interactions in solution. Moreover, the values of S_v become more negative with increase of dithioerythritol percentage suggesting that the solute- solute interaction decreases with the concentration of dithioerythritol.

The increase in concentration of solute in solution contributes positively to the viscosity B-coefficient. On the other hand, the breaking of the solvent structure by solute causes a decrease in the viscosities. This contributes negative to the B-coefficient. Thus, B-coefficient is the resultant of these two opposite forces [28].Therefore, the molecules / ions exhibiting negative B- coefficient have been assumed to exert a structure breaking effect on the solvent while the ions with positive B-coefficient exert a structure making effect on the solvent.

On comparing the data, it was found that in determining viscosity of amino acids, the charge distribution is less important than the size and structure of the hydrocarbon chain due to the large size and non-electrolytic nature of amino acids, irrespective of the structure, and show significant positive core contribution to the B-coefficient, which exceed any negative contribution.

IV CONCLUSION

From the magnitude of φ_v and the values of B-coefficient it can be concluded serine possess greater molecular association than cystein in aqueous DTE solution. From φ°_{v} suggest increase in hydrophilic and hydrophobic group interaction with increase of the bulk of side chain length of amino acid.

TABLE-1

Values of Molality, Viscosity, Relative Viscosity, Apprent Molal Volume,Limiting apparent molar volume, Cofficients of Jones-Dole equation,Gibbs free energy of serine & cystein in aqueous DTE solutions

Amino acids	Molality (m)[mol kg^{-1}]	Density(ρ) [$gmcm^{-3}$]	Apprent Molal Volume(φ_v)[$cm^{-3}mol^{-1}$]	Viscosity ($\eta\pm3x10^{-4}$) [10g $cm^{-1}s^{-1}$]	Relative Viscosity (ηrel) [10 cm^{-1} s^{-1}]	Coefficient of Jones-Dole equation		Gibbs free energy
						A $L^{1/2}_{1/2}mol^{-1/2}$	B $Lmol^{-}$	Kj mol^{-1}

L-serine	0.025	0.990919024	285.8231	0.788272938	1.000296634	-0.0523 1.035	0.82948545
	0.050	0.997002377	55.9907	0.790652870	1.003316701		-1.012187248
	0.101	0.999747785	53.0181	0.794613006	1.008342004		-4.020437329
	0.201	1.000816406	73.6486	0.791187019	1.003994522		-1.418825869
	0.302	1.008207396	59.0489	0.786994378	0.998674175		-780332546
	0.402	1.010875301	63.5635	0.821359428	1.042282476		-23.953606390
L-Cystein	0.00006	0.992865287	32267.8596	0.758775571	0.962865287	-0.00152 0.0043	23.766373943
	0.00013	0.994830488	-2224.1840	0.761884633	0.99810601		21.304289394
	0.00025	0.993831163	2969.8561	0.761613928	0.966467084		21.518263292
	0.00050	0.994991875	-7829.0276	0.765309558	0.971156736		18.603677047
	0.00101	0.994171262	491.5202	0.768636699	0.975378787		15.991717891
	0.00201	0.994646305	67.7484	0.769664012	0.976682419		15.187513197

REFERENCES

1) Meister A, *Biochemistry of amino acids*, II Edn.Acadamic press Inc New York,1965.
2) 2. Jeremy M Berg, John L Tymoczko and Lubert Stryer, *Biochemistry* V Edn,WH Freeman Co,New York,2003.
3) Lehninger, *Principles of Biochemistry*, IV Edn, David L Nelson,Micheal M Cox,Freeman W H and Co.New york,2005.
4) Bhat R and Ahluwalia J C, *J. Phys. Chem*,89, 1099-1105,1985.

5) Wadi R K and Goyal R K, *J.Solution Chem*. 21,163-170,1992.
6) Ogawa T and Suji T T, *Annu.Rev.Biochem*,56,21-40,1987.
7) Dewine W and Lowe B M, *J. Chem Soc*2113,1971.
8) Ali A and Shahjahan Z, *Phys, Chem.* 222,1519,2008.
9) Duke M M,HakimA W, McKay R M, Preuss K E, *Can J.Chem*,72,1489-1499,1994.
10) Hedwig G R, Hoiland H, *Biophys.Chem*,49,175-183,1994.
11) Santosh M S, Bhat D K, Bhat A S, *J. Chem Eng Data*,54,2813-2818,2009.
12) Riyazudden and Basharat R, *J.Chem Thermodynamics*,38,1684-1695,2006.
13) Banipal T S ,Singh K and Banipal P K, *J. Solution Chem*,36,1635-1667,2007b.
14) Thirumaran S and Kannappam A, *Global J. Mol Sci*,4,160-166,2009.
15) Pal A and Kumar S, *J. Mol Liquids* 121,148-155,2005.
16) Ferreira L A,Maced E A and Pinho S P, *J. Chem. Thermodynamics*, 41,193-196,2009.
17) Wang J, Yan Z and Lu, *J Chem Thermodynamics*,36,281-288,2004.
18) Sadeghi S and Goodarzi B, *J. Mol Liquids*,141, 62-68,2008.
19) Kumar A and Badarayani R, *J. Chem Thermodyn*. 35,897-908,2003.
20) Nain A K and Chand D , *J Chem Thermodynamics*,41,243-249,2009.
21) Palani R, Geetha A, *Research Journal of Physics*,1(2), 82-89,2007.
22) AL-Dulaimy Z A, AL-Amel Z W, AL-Khulisy R S, Hussein Z H, *Ibn-Haitham Journal of Pure Applied Science*,25(1), 2012.
23) Ksnnappan V and Chidambara Vinayagam S, *Indian Journal of Pure and Applied Physics*,51,471-478,2013.
24) Singh M, *J Biochem.Biophys. Methods*, 67(2-3), 151-161, 2006.
25) Pal A,and Kumar S ,*J. Chem.Soc*, 117(3),267, 2005.
26) Masson D O,*Philos Mag*,8,218,1929.
27) Jones G and Dole M , *J.Am. Chem. Soc*,51,2950-2964,1929.
28) Mason L S, Kompmeyer P M and Robinson A L, *J Am Chem Soc*,74,1287,1952.