Available online at www.pelagiaresearchlibrary.com

Pelagia Research Library

Der Chemica Sinica, 2014, 5(1):71-76

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

The structure making and structure breaking properties of amino acids in aqueous glucose solution at different temperatures

Parvinder Khanuja[1] and V. R. Chourey[2]

[1]Department of Chemistry, S. N. P. G. College, Khandwa (M.P.), India
[2]Department of Chemistry Holkar Science College, Indore (M.P.), India

---

ABSTRACT

The volumetric and viscometric studies of amino acid-have been determined in 0.05- 0.25 M aqueous glucose at 293.15, 303.15 and 313.15 K. The apparent molar volume values vary linearly with square root concentration of glucose solution. The $\emptyset_{v0}$ values vary with Temperatures and can be represented as power series of structure making and structure breaking capacity of Amino Acids in Aqueous Glucose Solution is obtained from the sign of dB/dT values .the partial molar volume expansibility has also been determined. The results found that amino acids shows structure making ability in aqueous glucose solution.

Keywords: Jones dole, Masson equation, Glucose.

INTRODUCTION

With continuation of our studies[1] which has been concluded that carbohydrates are structure makers in aqueous solution. Interaction of amino acids in aqueous glucose solution at different temperature plays an important role to understand biochemical process in living cells[2].

Amino acids, particularly important in biochemistry, are critical to life, and have many functions in metabolism and serve as a building block of proteins[3-4]. The effect of amino acids in carbohydrate solution and other mixed aqueous solvents[5-8] has been subject of interest.

The objective of this work was to measure density and viscosity of (0.05-0.15m) amino acids (glycine L-alanine and valine) in (0.05 - 0.25 m) aqueous glucose solution at 293.15, 303.15 and 313.15K.Attempts has been made to correlate solute–solvent interaction and structure making and breaking properties of amino acids in this temperature range .

MATERIALS AND METHODS

All the Chemicals were used are of Analar grade. Water used for preparing solution was double distilled had specific conductance of ~$10^{-6}\Omega$ cm^{-1}. He solution of different molarities of amino acids were prepared by dissolving accurately weighed amount of amino acids in aqueous (0.05-0.25 M) glucose solution. The densities and viscosity measurement were carried out by using density bottle and Ostwald viscometer respectively at 293.15, 303.15, and 313.15 k.

The mass measurement was done on digital electronic balance (Sartorius GC103). Temperature was controlled by thermostatic water-bath with $\pm 0.1^0$c accuracy. The viscosities were calculated[9-10] by using the formula $\eta / \eta_{0=} t\, d\, / t_0 d_0$ where η, t & d are the absolute viscosity, time of flow and density of solution, while η_0 ,t_0 & d_0 are same quantities for the solvent water. The absolute viscosities of water at 293.15, 303.15 and 313.15K were taken as 1.005, 0.8007 and 0.656 centi- poise respectively .The densities of water were taken as 0.9982, 0.99565 and 0.9922 $g.cm^{-3}$ respectively [9-10]

RESULTS AND DISCUSSION

Volumetric study

The apparent molar volumes ($\emptyset_v$) of amino acids in aqueous glucose solution were calculated from density data by using the following equation[11]:

$$\emptyset_{v=} M/d_0 - 1000(d-d_o)/d_{0C}$$

Where d_0 and d are the densities of solvent and solution respectively, C is the molar concentration and M is molecular weight of solute.

For each system $\emptyset_v$ with $\sqrt{c}$ were found to be linear thus the data are fitted to Masson[12]equation, these were used to calculate limiting partial molar volume and experimental slope by least square method.

$$\emptyset_v = \emptyset_{v0} + Sv\sqrt{c}$$

In these Sv is the experimental slope or volumetric pair wise interaction coefficient provides information regarding solute-solute interaction. While Φv_0 provides information regarding solute–solvent interaction .The values of Φv_0 and Sv for the amino acids in aqueous glucose solution at different temperatures are presented in **Table 1 and 2**. It is found that value of S_v is positive and decrease with increasing temperature for all amino acids.

The volume of transfer $_{\Delta}\Phi v_{0tr}$ of amino acids from water to aqueous glucose solution was calculated by using given relation at different temperatures and is summarized in **Table 3**.

$_{\Delta}\Phi v_{0tr}$ = Φv_0 (amino acid in aq. glucose) – Φv_0 (amino acid in pure water.)

It is found that value of $_{\Delta}\Phi v_{0tr}$ is negative for all selected amino acids in aqueous glucose solution at all studied temperatures. The negative $_{\Delta}\Phi v_{0tr}$ values are decreasing continuously with increasing concentration and temperature of glucose. Similar observation has been obtained by Gupta[13] et al and Zhuo[14]et al in their studies.

The partial molar volume of transfer of amino acids from water to aqueous glucose solutions can be further simplified by the co-sphere overlap model[15-16].

Various types of interaction between amino acids and glucose are classified as follows.

- Hydrophilic – ionic interaction; interaction between the OH group of the glucose and the zwitter ionic centers of the amino acids.
- Hydrophilic –Hydrophilic interaction: interaction between the OH group of the glucose and the $–NH_2$ group of the amino-acid (glycine/alanine) mediated through Hydrogen bonding.
- Hydrophobic- Hydrophobic interaction: interaction between the non polar sides group of the glucose, and the non polar group of the amino-acid.
- Hydrophobic- Hydrophilic interaction: interaction between the OH group of the glucose molecules, and the non-polar group of amino-acid.

The interactions of type (1) & (2) contribute positive transfer volume, while type (3) & (4) contribute negatively. The introduction of a CH_3 group in alanine in CH $(CH_3)_2$group in valine provides additional tendency of hydrophilic–hydrophobic as well as hydrophobic–hydrophobic interaction.

The temperature dependence of limiting apparent molar volume, Φ_{v0} for amino acids in aqueous glucose solution can be given by following expression[13].

$\Phi_{v0}=a_0+a_1T+a_2T^2$

The partial molar expansibilities of amino acids in aqueous glucose were calculated and recorded in **Table 4**.

$\Phi_{E0}= (\partial\Phi_{v0}/\partial T)_{p=} a_1+2a_2T$

The structure making and breaking capacity of amino acids in aqueous glucose may be interpreted with the help of Hepler's [17]reasoning i.e. on the basis of sign of giving expression, it has been assumed that structure making solute have positive and structure breaking solute has negative value.

$(\partial\Phi_{E0}/\partial_T)_p = (\partial^2\Phi_{v0}/\partial_T^2)_{p=} - a_2$

Table 1. Partial molar volume at infinite dilution Φv_0 (cm^3mol^{-1})of Glycine ,L Alanine and Valine in aqueous Glucose solution at different temperatures (293.15,303.15and 313.15K)

Conc.	Glycine			L-Alanine			Valine		
	293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
0.25m	41.83	42.65	43.62	58.68	59.69	60.71	91.48	91.97	92.47
0.20m	41.77	42.62	43.57	58.65	59.66	60.69	91.45	91.94	92.45
0.15m	41.72	42.60	43.52	58.60	59.61	60.65	91.39	91.88	92.39
0.10m	41.67	42.55	43.44	58.53	59.53	60.57	91.33	91.81	92.30
0.05m	41.63	42.50	43.39	58.49	59.48	60.53	91.28	91.75	92.25

Table 2. Experimental slope Sv (cm^3 lit ^{½} $mol^{-3/2}$) of Glycine ,L- Alanine and Valine in aqueous Glucose solution at different temperature (293.15,303.15and 313.15K)

Conc.	Glycine			L-Alanine			Valine		
m	293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
0.25	2.36	2.1	1.69	2.02	1.82	1.79	2.78	2.21	1.87
0.20	2.3	2.05	1.67	1.82	1.76	1.78	2.57	2.20	1.59
0.15	2.28	1.92	1.56	1.75	1.65	1.48	2.40	2.15	1.43
0.10	2.26	1.81	1.50	1.72	1.57	1.53	2.23	2.31	1.34
0.05	2.17	1.83	1.44	1.60	1.54	1.42	2.07	2.05	1.28

Table.3 $_{\Delta}\Phi v_{0tr}$ (cm^3mol^{-1})of Glycine ,L- Alanine and Valine in aqueous Glucose solution at different temperature (293.15,303.15and 313.15K)

Conc.	Glycine			L-Alanine			Valine		
	293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
0.25	-0.95	-0.63	-0.38	-0.41	-1.03	-0.49	-0.04	-0.075	-0.185
0.20	-1.01	-0.66	-0.43	-0.44	-1.06	-0.51	-0.07	-0.105	-0.205
0.15	-1.06	-0.68	-0.48	-0.49	-1.11	-0.55	-0.13	-0.165	-0.265
0.10	-1.11	-0.73	-0.56	-0.56	-1.187	-0.63	-0.19	-0.235	-0.355
0.05	-1.15	-0.77	-0.61	-0.60	-1.24	-0.67	-0.24	-0.295	-0.405
Φv_0 in (Water	42.78	43.28	44.00	59.909	60.72	61.2	91.52	92.045	92.655

Viscometric properties

Viscosity data has been analyzed with the help of Jones-Dole[18] equation using linear relation of $[(\eta/\eta_{0)-1}]/ c^{1/2}$ with $c^{1/2}$ by least square method. The viscosity *A* and *B* coefficients[19] were obtained from the intercepts and slopes and are given in **Table 5**.

$\eta/ \eta_0= \quad \eta r =1+A\ c^{1/2}+BC$

The values of (dB/dT) [20]were calculated from the slope of the curve obtained with B- coefficient value against temperatures and recorded in **Table 6**. The sign of (dB/dT) value was found to provide information regarding the structure making and breaking ability of solute in solvent media. In general (dB/dT) was negative for structure making and positive for structure breaking. These are in identical agreement with the conclusion drawn from Hepler equation.

Determination of the free energy of activation of viscous flow of per mole of solute and solvent at different temperatures to obtained additional information, evaluated by the Erying viscosity relation[21-22].

$\Delta G = RT \ln (\eta_0 V_1 / h N)$

Where h is the Plank constant, N is the Avogadro number; η is the viscosity of the solvent and **Δ**G is the contribution per mole of the solute to the free energy of activation for viscous flow of the solution at infinite dilution, V is the **molar volume**[23]of solution which obtained from the relation-

$V = (10^3 + mM_2) / d (10^3 / M_1 + m)$

Where M_1 and M_2 are molecular weight for solvent and solute respectively, and the other symbol has their usual meanings.

The values of Δ S[24]and Δ H was calculated by least square method using temperature dependant data of ΔG. The Values of Δ**G** were found to be positive at all studied temperatures.

Table 4. ϕ_{E0} ($cm^3 mol^{-1} K^{-1}$) of Glycine, L- Alanine and Valine in aqueous Glucose solution at different temperature (293.15, 303.15and 313.15K)

Conc.	Glycine			L-Alanine			Valine		
	293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
0.25m	0.0745	0.0895	0.1045	0.1005	0.1015	0.1025	0.0485	0.0495	0.0505
0.20m	0.0800	0.0900	0.1000	0.100	0.102	0.104	0.0480	0.0500	0.0520
0.15m	0.0865	0.0895	0.0925	0.0995	0.1025	0.1055	0.0480	0.0500	0.0520
0.10m	0.0875	0.0885	0.0895	0.0986	0.102	0.105	0.0472	0.0484	0.0496
0.05m	0.087	0.0880	0.0890	0.096	0.102	0.108	0.0440	0.0480	0.0520

Table 5. Viscosity B coefficient ($m^3 mol^{-1}$) of Glycine, L- Alanine and Valine in aqueous Glucose solution at different temperatures (293.15, 303.15and 313.15K)

Conc.	Glycine			L-Alanine			Valine		
	293.15	303.15	313.15	293.15	303.15	313.15	293.15	303.15	313.15
0.25m	0.1308	0.1046	0.0953	0.149	0.1229	0.127	0.3074	0.3088	0.3051
0.20m	0.1346	0.1189	0.1031	0.1503	0.1285	0.1308	0.3012	0.275	0.2974
0.15m	0.1411	0.1228	0.1131	0.151	0.1326	0.1345	0.2683	0.269	0.265
0.10m	0.1444	0.1237	0.1167	0.154	0.134	0.139	0.246	0.247	0.244
0.05m	0.1464	0.1266	0.1195	0.155	0.1366	0.141	0.217	0.218	0.215

Results shows density and viscosity increases with concentration of amino acids and decreases with increasing in temperature. Increasing values of density and viscosity shows that there is moderate attraction with solute and solvent molecules and decreased value with increasing temperature shows decrease in intermolecular forces due to increasing thermal energy of the system.

It is found that value of $\mathbf{\Phi v_0}$ for all amino acids **(Table 1)** is Positive and their trend in solute-solvent interaction is in order of glycine < L-alanine<valine . This shows that solute solvent interaction increases with increase in number of carbon atoms. Similar conclusion has been reported for glycine in aqueous NH_4Cl[25], NaCl- KCl [26], methanoic acid [27] and glycerol[28]solution as Φv_0 increases with increasing temperature. It can be observed that Φv_0 increase with temperature showing that the reduction of electrostriction occurs at higher temperature. The $\mathbf{\Phi_{v0}}$ values are high in comparison to Sv for all concentration range, which suggests the primacy of solute-solvent interaction.

It is found that values of $\mathbf{S_v}$ for all selected amino acids are positive in aqueous glucose solution. It suggests that in system having more solute– solvent interactions in comparison to solute–solute interactions

The negative $\Delta\mathbf{\Phi v_{0tr}}$ **(Table 3)** value due to the enhancement of electrostricted hydrated zone around zwitter ionic ends. Hydrophobic hydration generate around the carbon skeleton in the presence of co-solvents. The electrostriction of neighboring water due to this charged centre will be increase in the presence of amino acids this will be lead to increase in shrinkage.

In case of glycine continuous decrease in negative $\Delta\mathbf{\Phi v_{0tr}}$ values exhibit that the electrostriction first increase and then decrease on increasing temperature. It brings about decrease in volume of the solvent thereby increasing the strong interaction between glucose and water. In glycine-glucose system, hydrophobic interactions are leading at lower concentration, while at higher concentration hydrophilic interactions are leading. This behavior is consistent with the studied of amino acid in Tetra-propyl ammonium bromide[29] silver sulphate[30].Opposite behaviour has been reported by Pal[31] in higher concentration of sucrose solution.

It was founded that in case of alanine negative $\Delta\mathbf{\Phi v_{0tr}}$ value increase up to 303.15 and then decrease on 313.15K .In valine negative $\Delta\mathbf{\Phi v_{0tr}}$ values increases with increasing temperature .The increasing in negative $\Delta\mathbf{\Phi v_{0tr}}$ value In case of alanine- glucose system in comparison to glycine and valine suggests hydrophobic- hydrophobic interactions is dominating over hydrophilic-hydrophilic interactions. In case of valine less negative $\Delta\mathbf{\Phi v_{0tr}}$ value with increasing concentration and temperature suggests that reduction in shrinkage.

The limiting apparent molar expansibilities Φ_{E0} for amino acids in aqueous glucose showed that value decrease with concentration and increase with increasing temperature in case of glycine. In case of alanine and valine it increases with increasing concentration and temperature. Positive increase in Φ_{E0} may indicate the presence of caging effect[32]. Further increase in magnitude with rise in temperature in alanine and valine exhibit the behaviour of solute is just like symmetrical tetra alkyl ammonium salt[33]. The obtained positive sign of $(\partial^2\Phi_{v0}/\partial T^2)_p$ value has suggests structure making nature.

Values of A coefficients are negative for glycine and L-alanine in aqueous glucose at all the investigated temperatures .These results indicate the presence of weak solute–solute interaction.

The value of B-coefficient is positive, which point out the existence of ion-solvent interaction. A decrease in values of B with rising in temperature and concentration in case of glycine showed structure making effect. B value of alanine decreases at 303.15K and that increases at 313.15K suggests that increase in solvation at higher at higher temperature. This behavior suggests that enhancement of water structure by alanine at higher temperature and disruption of water structure at lower temperature it has been founded that glycine behave structure maker and alanine behave as weak structure maker. The value of B-coefficient for valine **is** positive and increases up to 303.15 K and then decrease this may be due to suggests that decrease in solvation at high temperature.

Negative (**dB/dT) (Table 6)** values reveals that structure making capacity of all selected amino acids in aqueous glucose solution. Structure making capacity amino acids decrease with increasing concentration of glucose. These are in identical agreement with the conclusion drawn from Hepler equation as discussed earlier. Such the values of coefficient A and B supports the behaviors of Φv_0 and S_v and Φv_{0tr} which all suggest solute-solvent interaction predominant over solute-solute interaction.

Table 6 Hepler and dB/dT Constant of Amino Acids In Aqueous Glucose Solution At Different Temperatures (293.15, 303.15 AND 313.15 K)

Conc.	Glycine		L-Alanine		Valine	
	Hepler constant	dB/dT constant	Hepler constant	dB/dT constant	Hepler constant	dB/dT constant
0.25	0.0015	-0.0018	0.0001	-0.00252	0.0001	-0.00012
0.20	0.0010	-0.0016	0.0002	-0.00196	0.0002	-0.00019
0.15	0.0003	-0.0014	0.0003	-0.00161	0.0002	-0.00016
0.10	0.0001	-0.0015	0.00034	-0.00189	0.00012	-0.0001
0.05	0.0001	-0.0014	0.0006	-0.00181	0.0004	-0.0001

Positive value of ΔG decreases with the increase in solute concentration and increases with the rise of temperature in case of glycine and alanine, while in case of valine this increase with increase in solute concentration and of temperature. This behavior of ΔG[34]suggests that the positive work is required to create holes for viscous flow and at higher temperature the solute–solvent and solvent–solvent interactions weaken due to thermal agitation. The positive value of **ΔH** irregularly decreases with the increase of solute composition .This indicate that to overcome the energy barrier, more positive work has to be done. Thus the viscous flow is not favored for all the glucose molecules in solution systems. This might be due to the fact that the ground state of the binary and ternary systems is more organized than the transition states.

CONCLUSION

It has been concluded that glycine behaves as structure-maker and alanine behaves as weak structure-maker in aqueous glucose solutions. The behavior of valine enhances the structure at lower temperature and disrupts water structure at higher temperatures.

Acknowledgement
Author is thankful to UGC New Delhi for award of teacher research fellowship.

REFERENCES

[1] Khanuja P., Chourey V.R. and Ansari A.A., *Der, Chemica, Sinica*, **2012**, 3(4):948-952.
[2] Metzler D.E, The Chemical Reactions of Living Cells, Academic Press, New York, **1977**, 1.
[3] Kharakoz D. P, *J Phys Chem*., **1991**, 95(14), 5634-5642.
[4] Kharakoz D .P, *Biophysics Chem*., **1989**, 34(2), 115-125.
[5] Wadi R K and Goyal R K, *J Soln Chem*., **1992**, 21(2), 163-170.
[6] Wadi R K and Ramaswami P, *J Chem. Soc Faraday Trans*., **1997**, 93, 243-247.
[7] Ali A, Khan S and Nabi F, *J Serb Chem Soc*., **2007**, 72(1), 495-512.
[8] Ali A, Sabir S, Nain A K, Hyder S, Ahmad S, Tariq M and Patel R, *J Chinese ChemSoc*., **2007**, 54, 659.
[9] Kitchner J A, Findlay's, Practical Physical Chemistry, 8th Edn. Longman, London, **1954**, 70.
[10] Shoemaker D and Garland C, Experiments in Physical Chemistry, McGraw-Hill, New York, **1967**, 131.
[11] Panda B. B, Dixit G and Behera B, *Bull Chem. Soc Japan*, **1936**, 69(2), 301-303
[12] Masson D.O., *Philos. Mag*., 8, 218 (**1929**).
[13] Gupta R. R and Singh M, J Indian Chem *Soc*., **2008**, 85, 176-181.
[14] Zhuo K, Lfu Q, WangY, Yaping Wang, Qiuhe Ren and Jianji Wang Jianji Wang, J,*Chem Eng Data*, **2006**, 51(3), 919-927.
[15] Ali A, Soghra Hyder, Saba Sabirm, Anil Kumar Nain and Chand D, *J Chem.Thermodyn*., **2006**, 38(2), 136-143.
[16] Gurney R W, Ionic Processes in Solution, McGraw-Hill New York, **1953**, 3.
[17] Friedman H and Krishnan L, *J Solution Chem*., **1973**, 2(1), 37-51.
[18] Hepler L, *Canadian J Chem*., **1969**, 47(24), 4613-4617.
[19] Jones G and Dole M, *J Am Chem Soc*., **1929**, 51(10), 2950-2964.
[20] Jenkins B, Donald H and Marcus Y, *Chem Rev*., **1995**, 95(8), 2695-2724.
[21] Feakins D, Canning F M, Waghorne W E and Lawrence K G, *J Chem Soc FaradayTrans*., **1993**, 89, 3381-3389.
[22] Glasstone S, Laidler K J and Eyring H, The Theory of Rate Processes, McGraw- Hill,New York, **1941**.
[23] Habeeb S A, *J Al-Nahrain Univ*., **2011**, 14(4), 45-49.
[24] Uddin F and Saeed R, *Acta Cintifica*, **2001**, 52(3), 186-191.
[25] Natrajan M, Wadi R K and Gaur H C, *J Chem Eng Data*, **1990**, 35(1), 87-93.
[26] Ogawa T, Mizutani K and Yasuda M, *Bull Chem Soc Japan*, **1984**, 57(8), 2064-2068.
[27] Roy M N, Ekka D and Dewan R, *Acta Chim Slov*., **2011**, 58(4), 792-796.
[28] Banipal T S, Gagandeep Singh and Lark B S, *J Soln Chem*., **2001**, 30(7), 657-670.
[29] Ali A, Khan S, Hyder S and Tariq M, *J Chem Thermodyn*., **2007**, 39(4), 613-620.
[30] Sinha B, Roy P K and Roy M N, *Acta Chim Slov*., **2010**, 57(3), 651-659.
[31] Pal A, Ramniwas and Chauhan N, *Indian J Chem*., **2010**, 49A, 1309-1317.
[32] Millero F J, Structure and Transport process in water and aqueous solution, R A.Horne, Wiley Interscience, New York, **1971**.
[33] Shashi Kant and Kumar K, *J Indian Chem Soc*., **2008**, 85, 1093-1101.
[34] Dey P, Muhamman A Motin and Entaazul M Huque, *Monatshefte Fur Chemie*. **2003**, 134, 797-809.