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Ion association of glycine, α-alanine and β-alanine in water and water+ D-glucose mixtures at different temperatures

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ABSTRACT

The conductance of glycine, α-alanine and β-alanine has been measured in the concentration range of 1×10^{-2} to 8×10^{-2} mol dm^{-3} in aqueous and aqueous binary mixtures containing D-glucose (5,10,15,20% (w/w)) at different temperatures (298.15-313.15 K). The conductance data in all cases have been computed by Shedlovsky equation to obtain Λ^0_m and K_A . Based upon the composition dependence of Walden product, the influence of the D-glucose mixtures on the solvation of ions has been discussed. The values of the association constants, K_A, are used to obtain various thermodynamic parameters for the association process in the solution.

INTRODUCTION

The interaction of proteins with carbohydrates plays a key role in a wide range of biochemical processes. Most of these interactions, such as hydrogen bonding and electrostatic interactions, have non-covalent nature. Due to the structural complexity of proteins, direct thermodynamic study is quite difficult. So the low molecular weight model compounds such as amino acids are studied. An extensive literature survey indicates that remarkable experimental work has been reported on thermodynamics of amino acids in aqueous alkali metal salts (Lilley et al. 1980; Lilley and Tasker, 1982; Bhat and Ahluwalia, 1985; Wadi and Goyal, 1992; Soto et al. 1998; Palecz, 2000; Shen et al., 2000; Badarayani and Kumar, 2002). However, few studies on the thermodynamic properties of the amino acids, especially conductivity properties have been carried out in sugar solutions. Amino acids are compounds that contain both carboxylic group (-COOH) and amine group ($-NH_2$) and the side chain is unique for each and every amino acid. The elements present in amino acids are carbon, hydrogen, nitrogen and oxygen. Amino acid plays an important role in bio-chemistry. Glucose, also called dextrose, is the most widely distributed sugar in the plant and animal kingdoms. The chain form of glucose is a polyhydric aldehyde. It has multiple hydroxyl groups and an aldehyde group. This article reports the electrical conductances measured for glycine, α-alanine and β-alanine in water and water+ D-glucose(5,10,15,20%(w/w)) at 298.15, 303.15, 308.15 and 313.15 K as a function of concentration of these amino acids with a view to unravel their association and solvation behaviour.

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MATERIALS AND METHODS

All chemicals used were of GR or BDH., Anala R grades. Conductivity water (Specific conductance ~ 10^{-6} S cm^{-1}) was used for preparing water with D-glucose (0, 5, 10, 15 and 20% (w/w) mixtures .The D-glucose content in the mixed solvents was accurate to within ±0.01%. The solutions of amino acids were prepared on the molal basis and conversion of molal to molar was done by using the standard expression considering the density differences at the respective temperatures (Robinson and Stokes, 1955). The conductance measurements were made on a digital reading conductivity meter with a sensitivity of 0.1% and giving the conductance value of three digits. A dipping type conductivity cell with a platinised electrode (cell constant 1S cm^{-1}) was used.

The measurements were made over the temperature range of 298.15-313.15 K (±0.05K). The specific and molar conductances were expressed in terms of S cm^{-1} and S cm^2 mol^{-1}, respectively. The ionic strengths of the solutions were kept as low as possible (~10^{-4} to 10^{-2} M). The experiment was carried out with different concentrations of solutions ranging from 1×10^{-2} to 8×10^{-2} M in water and 5, 10,15 and 20 wt% D-glucose in water. The conductance of different concentrations of glycine, α-alanine and β-alanine were measured making appropriate corrections for the conductance of the solvents concerned.

RESULTS AND DISCUSSION

The experimental data of conductance measurements of glycine, α-alanine and β-alanine in water and water+ D-glucose mixtures after solvent correction were analysed using Shedlovsky and Fuoss-Kraus extrapolation techniques (Shedlovsky and Kay,1956;Fuoss,1975).As the Λ_m^0 values obtained by the two methods are very close to each other as in our previous studies(Dash and Supkar,1995)the Λ_m^0 and K_A values obtained by Shedlovsky method are recorded in Table 1 for a_0=q only. As observed, for all the amino acids in water the Λ_m^0 values increase with increase in temperature indicating less solvation or higher mobility of ions. This is due to the fact that the increased thermal energy results in greater bond breaking and variation in vibrational, rotational and translational energy of molecules that leads to higher frequency and hence the higher mobility of ions. The variation of Λ_m^0 values of glycine, α-alanine and β-alanine in water with D-glucose mixed solvents are found to be irregular. This indicates the variations in the ionic radii and mobility of ions due to varying degree of the ion solvation in solution. However, the magnitude of variation in Λ_m^0 values differs from one amino acid to the other in different solvents depending on the nature of the amino acids studied. The association constant, K_A, values of all the amino acids mentioned above show an irregular variation with increase in temperature as well as with increase in D-glucose content. This may be attributed to the varying degree of exothermic ion-pair association caused due to difference in ionic stability, specific ion-solvent and solvent-solvent interactions. Appreciable variation of the Walden product as a function of the solvent is generally regarded as an index of specific ion-solvent interactions including structural effects. The variation of the Walden product (Λ_m^0 η_0) with composition of D-glucose at various temperatures are shown in Figure 1(a,b,c,d).

As observed, the values in case of all the amino acids pass through a maximum, which is prominent in case of β-alanine and glycine. The existence of maximum in Walden product, can be explained on the basis of hydrophobic hydration of cation due to the presence of co-solvent in water rich region. After this maximum cation and anion get solvated leading to increase in ion-solvent interaction. The variation of the Λ_m^0 η_0 value with the solvent compositions is due to an electrochemical equilibrium between the cations of different amino acids with the solvent molecules on one hand and the selective solvation of ions on the other with the change of the composition of the mixed solvents and temperature of the solution.

It is of interest to derive the value of the ratio R_X defined by

$$R_X= \Lambda_m^0\ \eta_0(\text{mixed solvent})/\ \Lambda_m^0\ \eta_0(\text{water})$$

for the amino acids in the mixed solvents(Bishop and Jennings,1958).

The values of R_X are recorded in Table-2 .As observed, the R_x values in case of α-alanine are less in comparison to glycine and β-alanine. A structure breaking ion, in general possesses high mobility and decreases the local viscosity leading to a high value of Λ_m^0 η_0.So the higher values of Λ_m^0 η_0 for glycine and β-alanine support this view.

Using the relation

$$\Lambda_m^0\ \eta_0 = 1/6\pi rT$$

where r is the effective radius of the concerned ion, it has been possible to derive the values of r for the cations of the amino acids. As evident from Table-3 the values of r in case of α-alanine is more as compared to glycine and β-alanine. In α-alanine as the effective radius is large it leads to increase in the local viscosity. So Λ_m^0 η_0 value is less.

The mobility of molecular species, $U= \Lambda_m^0 / F$

The perusal of Table 3 shows that the mobility of α-alanine is the least. The mobility of β-alanine is higher than glycine except at 15 wt% D-glucose solution. The mobility of α-alanine is more in water and for β-alanine it is in lower wt% of D-glucose (i.e, 5wt%).But for glycine it is highest in 15wt% D-glucose. In case of glycine, mobility increases with increase in temperature as well as with increase in wt% of D-glucose upto 15wt%.But irregular variation of mobility is observed for α-alanine and β-alanine. Since conductance of an ion depends on its rate of movement, it is quite reasonable to treat conductance similar to the one employed for the process taking place at a definite rate which increases with temperature. The energy of activation(E_s) of the conducting process may be obtained from the Arrhenius equation(Bockris and Reddy,1998),

$$\Lambda_m^0 = A_f\ e^{-Es/RT}$$

where A_f is the frequency factor, R is the gas constant ,T is the temperature and E_s is the Arrhenius activation energy of the transport process. The energy of activation E_s , of the rate process was calculated from the slope of the linear plot of log Λ_m^0 versus 1/T (Corradini et al.,1993)and resulted values are included in Table 4. E_s values for all the amino acids in all the solvents are found to be positive.

The free energy change (ΔG^0)for the association process was calculated from relation(Coetzee and Kalvin,1976)

$$\Delta G^0= - RT \ln K_A$$

The heat of association (ΔH^0) was obtained from the slope of the plot of ln K_A vs 1/T and the entropy change (ΔS^0) associated with the process from the Gibbs-Helmholtz equation

$$\Delta G^0= \Delta H^0- T\ \Delta S^0$$

The positive values of ΔH^0 and ΔS^0 (Table 4) indicate that the association process is endothermic in nature and more energy consuming. However, in some cases the association process is accompanied by release of energy.

Table. 1: Values of Λ^0_m (s m^2 mol^{-1}) , K_A (dm^3 mol^{-1}) and Walden product (Λ_0 η_0) obtained by Shedlovsky technique (a^0 = q) for glycine, α-alanine and β-alanine in water and water+ D-glucose mixtures at different temperatures.

Wt% D-glucose	temp	Λ^0_m	K_A	Λ^0_m	K_A	Λ^0_m	K_A
		Glycine		α-alanine		β-alanine	
0	298.15	0.52	21.13	0.37	30.39	0.5483	0.23
	303.15	0.63	29.19	0.64	164.79	0.6531	0.46
	308.15	0.70	33.80	0.66	143.04	0.7234	1.16
	313.15	0.75	28.70	0.66	93.30	0.7955	0.83
5	298.15	0.60	32.13	0.15	62.19	6.9354	62.02
	303.15	0.66	26.25	0.24	93.36	2.9918	64.89
	308.15	0.74	23.08	0.21	64.65	3.4623	70.47
	313.15	0.86	29.08	0.21	58.36	4.0102	78.94
10	298.15	0.62	60.04	0.11	43.89	0.7205	30.99
	303.15	0.70	56.09	0.19	70.63	1.1043	73.06
	308.15	0.77	53.57	0.20	60.76	1.3552	99.46
	313.15	0.89	57.86	0.25	69.11	1.2031	45.92
15	298.15	1.41	122.79	0.24	116.56	0.7044	50.67
	303.15	1.98	179.39	0.21	72.63	0.8406	44.02
	308.15	3.16	344.29	0.20	61.07	1.1302	77.51
	313.15	3.79	386.26	0.12	26.81	1.1345	53.87
20	298.15	0.56	282.13	0.04	13.22	0.7202	69.83
	303.15	0.85	456.49	0.07	21.15	1.0306	122.87
	308.15	0.95	431.86	0.05	13.85	1.0916	94.58
	313.15	1.22	546.02	0.08	16.46	1.1754	84.23

Table. 2 : The values of R_x for glycine, α-alanine and β-alanine in D-glucose mixtures.

wt% D-Glucose	Temp	Rx		
		glycine	α-alanine	β-alanine
5	298.15	1.29	0.46	14.11
	303.15	1.13	0.40	4.90
	308.15	1.14	0.34	5.15
	313.15	1.24	0.35	5.43
10	298.15	1.54	0.39	1.68
	303.15	1.38	0.38	2.09
	308.15	1.34	0.37	2.26
	313.15	1.41	0.44	1.79
15	298.15	4.16	0.98	1.96
	303.15	4.68	0.46	1.90
	308.15	6.58	0.44	2.27
	313.15	7.04	0.26	1.98
20	298.15	1.91	0.19	2.33
	303.15	2.31	0.20	2.69
	308.15	2.20	0.14	2.44
	313.15	2.62	0.18	2.38

Table. 3 : Values of mobility of molecular species U (S m^{2}c^{-1}) and effective radius of the concerned ions r (m) for glycine, α-alanine and β-alanine in water and water+ D-glucose mixtures.

wt% D-Glucose	Temp	U×10^6	r×10^2	U×10^6	r×10^2	U×10^6	r×10^2
		Glycine		α-alanine		β-alanine	
0	298.15	5.39	0.384	3.87	0.534	5.68	0.364
	303.15	6.53	0.351	6.65	0.345	6.76	0.339
	308.15	7.25	0.341	6.85	0.361	7.49	0.330
	313.15	7.77	0.347	6.87	0.393	8.24	0.327
5	298.15	6.27	0.296	1.62	1.149	71.87	0.025
	303.15	6.93	0.309	2.53	0.848	31.00	0.069
	308.15	7.71	0.298	2.19	1.050	35.87	0.064
	313.15	8.96	0.279	2.26	1.106	41.55	0.060
10	298.15	6.49	0.248	1.19	1.344	7.46	0.215
	303.15	7.30	0.253	2.03	0.912	11.44	0.162
	308.15	8.07	0.254	2.11	0.971	14.04	0.145
	313.15	9.31	0.245	2.59	0.881	12.46	0.183
15	298.15	14.70	0.092	2.50	0.542	7.29	0.186
	303.15	20.61	0.075	2.10	0.736	8.71	0.177
	308.15	32.82	0.051	2.09	0.814	11.71	0.145
	313.15	39.34	0.049	1.30	1.491	11.75	0.165
20	298.15	5.81	0.200	0.42	2.758	7.46	0.156
	303.15	8.87	0.151	0.76	1.769	10.68	0.126
	308.15	9.87	0.154	0.61	2.488	11.31	0.135
	313.15	12.64	0.132	0.80	2.076	12.18	0.137

Table. 4 : Thermodynamic parameters: ΔG^0(kJ mol^{-1}), ΔH^0(kJ mol^{-1}), ΔS^0(J K^{-1}mol^{-1})and E_s(kJ mol^{-1}) for glycine, α-alanine and β-alanine in water and water+ D-glucose mixtures

wt% D- glucose	ΔG^0	ΔH^0	ΔS^0	Es
	glycine			
0	-7.56	16.78	81.64	19.28
5	-8.60	-6.86	5.848	18.21
10	-10.15	-2.50	25.633	18.32
15	-17.63	63.61	272.52	53.12
20	-13.98	30.01	147.60	37.92
		α-alanine		
0	-8.46	51.11	199.82	27.41
5	-10.23	-8.40	6.151	13.71
10	-9.37	18.98	95.12	36.62
15	-11.79	-70.95	-198.41	30.46
20	-6.40	3.78	34.14	27.06
	β-alanine			
0	3.60	73.75	235.29	18.96
5	-21.65	-95.94	-249.16	23.75
10	-8.51	23.91	108.78	27.33
15	-9.73	11.74	72.04	26.87
20	-10.52	5.01	52.13	23.85

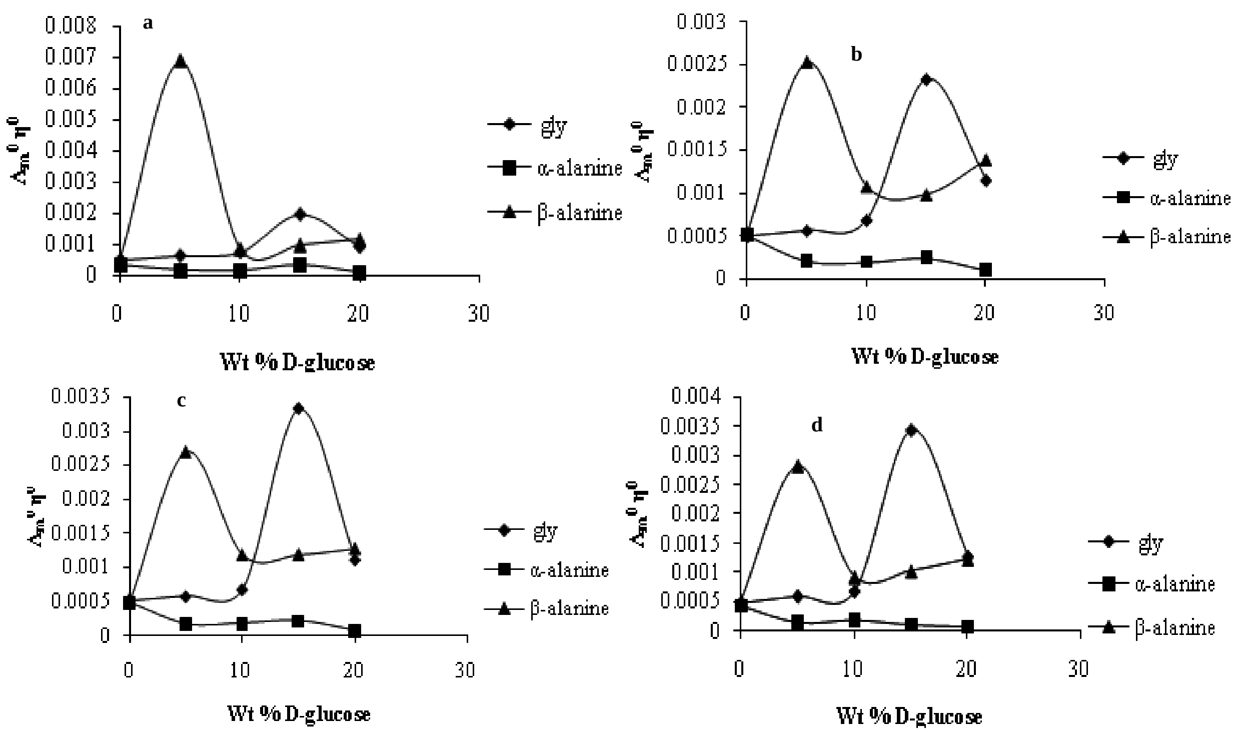

Fig. 1:
(a) : variation of the walden product($\Lambda_m^0\ \eta_0$)with composition of D-glucose at 298.15 K.
(b) : variation of the walden product($\Lambda_m^0\eta_0$)with composition of D-glucose at 303.15 K.
(c): variation of the walden product($\Lambda_m^0\ \eta_0$)with composition of D-glucose at 308.15 K.
(d) : variation of the walden product($\Lambda_m^0\ \eta_0$)with composition of D-glucose at 313.15 K.

CONCLUSION

In this paper the conductance of glycine, α-alanine and β-alanine has been measured in water and water+D-glucose mixtures at various temperatures. The conductance data have been analysed by Shedlovsky extrapolation technique. It has been observed that the Walden product passes through a maxima for glycine and β-alanine.Λ_0 values increase with increase in temperature for all amino acids in water. The effective radius r for α-alanine is large in comparison to the other two amino acids. The E_s values are positive for all the amino acids in all the solvents.

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