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Theoretical study of molecular interactions of amino acids in aqueous carbohydrate solutions by scaled particle theory

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The scaled particle theory (SPT) has been applied to study solvation thermodynamics of some polar and non-polar amino acids (*l*-serine, *l*-threonine, *l*-asparagine, *l*-glutamine, glycine, *l*-alanine, *l*-valine, *l*-methionine) in water and in aqueous-glucose (5% *d*-glucose, *w/v* in water) at 298.15 K. The solvation free energy (ΔG_{Solv}), enthalpy (ΔH_{Solv}) and entropy (ΔS_{Solv}) of amino acids in aqueous-glucose have been calculated using SPT from various contributions. The results show that the major contribution to thermodynamic parameters is from the interactions between the participating components. While the cavity formation for accommodation of amino acid molecules in aqueous-glucose molecules does not dependent solely on contributions from enthalpy, there is specific contribution from entropy terms. The results also indicate that the interactions in the studied systems follow the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine in the case of polar amino acids; and glycine < *l*-alanine < *l*-valine < *l*-methionine in case of non-polar amino acids.

Keywords: Solution chemistry, Scaled particle theory, Amino acids, Carbohydrates, Solvation thermodynamics

Proteins are essential components of living organisms. Proteins stimulate various biological reactions. However, the direct study of interactions of protein in solution is too difficult because of their complex structure. Generally, the functioning of proteins is monitored by studying their components molecules, amino acids. One of the most useful approach is to study the proteins in the presence of fluids which are generally present around it in biological systems, i.e. water and carbohydrates[1–5]. Polyhydroxy compounds are known to stabilize the native globular structure of proteins by preferentially hydrating[6]. Our aim is to study the protein-carbohydrate interactions that lead to this stabilization. These interactions find their applications in immunology, pharmacology, biosynthesis, medicine and cosmetic industries[7,8]. The physicochemical properties of solutions depend upon the interactions in the system. The variations in these properties with concentration and temperature indicate the changing nature of protein in these solutions. Hence, the study of interactions of amino acids in water + carbohydrate solutions will be important from biological point of view.

Herein, an attempt has been made to study the solvation thermodynamics of some polar and non-polar amino acids (*l*-serine, *l*-threonine, *l*-asparagine, *l*-glutamine, glycine, *l*-alanine, *l*-valine, *l*-methionine) in water and in aqueous-glucose (5% *d*-glucose, *w/w* in water) at 298.15 K using the well known Scaled Particle Theory, put forward by Reiss[9,10]. Scaled Particle Theory gives an expression for calculating the reversible work which must be performed to create a cavity in hard sphere fluid and obtain the resulting solvation free energy. We have used Pierotti's[11] approach to obtain various thermodynamics parameters of solvation of amino acid in water and in aqueous glucose at 298.15 K. The findings of the present work may help in investigating the role of glucose in stabilizing macromolecules like proteins in aqueous solutions.

Theory

According to the Scaled Particle Theory[11], the process of solvation of a solute mainly consists of two steps (i) formation of cavity of appropriate size to accommodate the solute, and, (ii) interaction of solute in the cavity with the solvent. The free energy of solvation is combination of free energy of cavity formation (ΔG_{cav}), the interaction term (ΔG_{int}) and free energy of volume formation due to standard state conversion[11] can be represented as Eq. (1),

$$\Delta G_{solv} = \Delta G_{cav} + \Delta G_{int} + RT \ln\left(\frac{RT}{V}\right) \quad \ldots(1)$$

where R is the gas constant and T is the temperature in Kelvin. V (=M/d) is the molar volume of the solvent, $M = z_1 M_1 + z_2 M_2$, where 1 is the subscript for water and 2 for cosolute. Following Pierotti[11], ΔG_{cav} is given by the relation (2),

$$\Delta G_{cav} = RT[-\ln(1-Y_3) + 3Y_2\sigma_s/(1-Y_3) + 3Y_1\sigma_s^2/(1-Y_3) + 9Y_2^2\sigma_s^2/(1-Y_3)^2] \quad \ldots (2)$$

where

$$Y_3 = \pi N_A\left(z_1\sigma_w^3 + z_2\sigma_a^3\right)/6V \quad \ldots (3)$$

$$Y_2 = \pi N_A\left(z_1\sigma_w^2 + z_2\sigma_a^2\right)/6V \quad \ldots (4)$$

$$Y_1 = \pi N_A\left(z_1\sigma_w + z_2\sigma_a\right)/6V \quad \ldots (5)$$

N_A is Avogadro's number and σ_w, σ_a and σ_s are the hard sphere diameters of water, glucose and amino acid respectively. The value of hard sphere diameter of water at 298.15 K was taken from literature[11–15]. The hard sphere diameter for glucose was calculated by isothermal compressibility method suggested by Mayer[16] where binary mixtures are assumed to be pure 'uniform' solvent that can be characterized by a single mean hard sphere diameter[13]. Isothermal compressibility values were obtained from ultrasonic speeds of solvent[17]. The physical parameters required in evaluating the various contributions of the Gibbs free energy, enthalpy and entropy of solvation for amino acids in water and aqueous glucose at 298.15 K are listed in Table 1.

The Gibbs free energy of interaction is given by the relation[11]:

$$\Delta G_{int} = -(32/9)\sum_{j=1}^{m}\rho_j\varepsilon_{sj}\sigma_{sj}^3 - (4/3)\sum_{j=1}^{m}\rho_j\mu_j^2\alpha_s/\sigma_{sj}^3 - (4/3)\sum_{j=1}^{m}\rho_j\alpha_j\mu_s^2/\sigma_{sj}^3 \quad \ldots(6)$$

where 's' is for solute and 'j' is for the j[th] component in a fluid mixture of solvent containing 'm' components. ρ is the number density, ε the energy parameter, μ is the dipole moment and α is the polarizability. The density values of various amino acids in glucose were taken from literature[18-22]. The values of μ were also taken from literature[23-27]. ε_{sj} and σ_{sj} were evaluated by the mixing rule[18].

$$\varepsilon_{sj} = \left((\varepsilon/\kappa)_s.(\varepsilon/\kappa)_j\right)^{(1/2)} \quad \ldots (7)$$

$$\sigma_{sj} = (\sigma_s + \sigma_j)/2 \quad \ldots (8)$$

The ε/κ and σ_s for amino acids were calculated by using the relations proposed by Tiepel and Gubbins[29].

$$\varepsilon/k = T_C[0.7500 - 0.5709w] \quad \ldots (9)$$

$$\sigma_s = (T_c/P_c)^{(1/3)}[2.4380 + 1.7282w] \quad \ldots (10)$$

The ε/κ for amino acid were also calculated by using Eq. (9). The values of critical properties required for glucose and amino acids were calculated by the group contribution method known as "modified Lyderson-Joback-Reid"[30]. W, the acentric factor was computed using the equation proposed by Kontogeorgis[31],

$$\ln w = -4.9112 + 0.8953\ln V_w \quad \ldots (11)$$

where V_w is the van der Waal volume computed from the group contribution method as suggested by Bondi[32].

The polarizability, α for water was taken from the literature[33], and for amino acids and glucose calculated from experimentally measured refractive indices of their aqueous solutions by using the following relation,

$$(n^2 - 1/n^2 + 2).(M_s/\rho) = (4\pi N_A/3).(x_1\alpha_1 + x_2\alpha_2) \quad \ldots(12)$$

where M_s is the molar mass of solute, ρ is the density

Table 1 – Values of some physicochemical parameters at 298.15 K used in the calculation of thermodynamic parameters

Comp.	σ (Å)	ρ (g cm^{-3})	ε/κ (K)[a]	μ (D)	α (10^{-24} cm^3)[b]
Water	2.76[11-15]	0.99707[18]	79.30	1.84[26]	1.47
Glycine	5.95[16]	1.00011[20]	448.02	13.3[24]	5.59
l-Alanine	6.51[16]	0.99983[20]	449.46	16.3[23]	8.53
l-Valine	7.61[16]	0.99962[19]	435.51	16.0[27]	24.00
l-Methionine	8.23[16]	0.99961[21]	434.45	13.8[21]	13.60
l-Serine	6.49[16]	1.00146[20]	486.50	18.0[23]	8.49
l-Threonine	7.18[16]	1.00125[18]	451.49	13.6[23]	9.81
l-Asparagine	8.04[16]	1.00251[22]	546.35	17.6[22]	1.73
l-Glutamine	9.29[16]	1.00239[22]	644.65	15.1[30]	8.58
d-Glucose	4.99[16]	1.01469[18]	517.90	14.1[25]	14.90

[a]Eq (9); [b]Eq (12). Superscripts in Cols 2, 3 and 5 are reference nos.

of the solution and x_1 and x_2 are the mole fractions of the solute and solvent. Dipole moment values were collected from literature[27,33-35]. The enthalpy of solvation was calculated by the relation:

$$\Delta H_{solv} = \Delta H_{cav} + \Delta H_{\text{int}} + RT\left(\alpha_o T - 1\right) \quad \ldots (13)$$

where ΔH_{cav} and ΔH_{int} are enthalpy of creation of cavity and interaction. α_{o} is the coefficient of thermal expansion. The value of α_{o} were taken from literature and for others calculated by Eq. (14).

$$\alpha\left(T;m\right) = -\left(\frac{\partial \ln \rho}{\partial T}\right)_{\text{P,m}} \quad \ldots (14)$$

The enthalpy of cavity creation is given by the expression:

$$\Delta H_{\text{cav}} = \left(\alpha_{\text{o}} RT^2 / \left(1 - Y_3\right)\right)[Y_3 + 3Y_2\sigma_{\text{s}} / \left(1 - Y_3\right) + 3Y_1\sigma_{\text{s}}^2 / \left(1 - Y_3\right) + 9Y_2^2\sigma_{\text{s}}^2 / \left(1 - Y_3\right)^2] \quad \ldots (15)$$

The enthalpy of interaction, ΔH_{int}, was assumed to be equal to ΔG_{int}[11] and therefore, ΔS_{int} becomes zero. The entropy of solution is given by the relation:

$$\Delta S_{\text{solv}} = \Delta S_{\text{cav}} + \Delta S_{\text{int}} - R\ln\left(RT/V\right) + \alpha_{\text{o}} RT \quad \ldots (16)$$

where ΔS_{cav} and ΔS_{int} are the entropies of cavity formation and interaction respectively. ΔS_{cav} is calculated from Eq. (17).

$$\Delta S_{\text{cav}} = \left(\Delta H_{\text{cav}} - \Delta \text{G}_{\text{cav}}\right) / \text{T} \quad \ldots (17)$$

Results & discussion

According to SPT, the value of ΔG_{cav} depends on the hard sphere diameter, σ of component molecules. In Tables 1, 2 and 3, it is observed that for polar amino acids, ΔG_{cav} follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine and in non-polar amino acids, glycine < *l*-alanine < *l*-valine < *l*-methionine. The order can be explained by the variation in hard sphere diameter. As the size of solute molecule increases, the cavity of greater dimensions is required to accommodate the larger molecule. A greater amount of work needs to be done to create cavity of larger size. Hence, a greater amount of ΔG_{cav} is required for accommodating a molecule with larger σ. In both the cases (polar and non-polar amino acids), ΔG_{cav} follows the trend in σ, i.e., it increases with increase in *σ*.

Table 2 – Contributions of various thermodynamic parameters of solvation for amino acids (polar) in water and aqueous-glucose solutions at 298.15 K

System	ΔG_{cav} (kJ mol^{-1})	ΔG_{int} (kJ mol^{-1})	ΔG_{solv} (kJ mol^{-1})	ΔH_{cav} (kJ mol^{-1})	ΔH_{solv} (kJ mol^{-1})	ΔS_{cav} (kJ mol^{-1} k^{-1})	ΔS_{solv} (kJ mol^{-1} k^{-1})
Amino acid+water							
l-Serine	55.85	-127.79	-25.49	9.2447	-120.83	-0.1563	-0.3115
l-Threonine	66.99	-152.97	-39.53	11.159	-144.10	-0.1873	-0.3424
l-Asparagine	82.15	-215.67	-87.07	13.773	-204.18	-0.2293	-0.3848
l-Glutamine	107.08	-325.53	-172.00	18.084	-309.73	-0.2985	-0.4536
Amino acid+d-glucose+water							
l-Serine	54.47	-125.68	-24.82	10.95	-116.98	-0.1460	-0.3023
l-Threonine	65.32	-150.39	-38.69	13.21	-139.43	-0.1748	-0.3311
l-Asparagine	80.08	-211.95	-85.48	16.30	-197.90	-0.2139	-0.3703
l-Glutamine	104.36	-319.77	-169.03	21.40	-300.61	-0.2782	-0.4346

Table 3–Contributions of various thermodynamic parameters of solvation for amino acids (non-polar) in water and aqueous-glucose solutions at 298.15 K

System	ΔG_{cav} (kJ mol^{-1})	ΔG_{int} (kJ mol^{-1})	ΔG_{solv} (kJ mol^{-1})	ΔH_{cav} (kJ mol^{-1})	ΔH_{solv} (kJ mol^{-1})	ΔS_{cav} (kJ mol^{-1} k^{-1})	ΔS_{solv} (kJ mol^{-1} k^{-1})
Amino acid+water							
Glycine	47.95	-102.52	-8.12	7.89	-96.92	-0.1344	-0.2895
l-Alanine	56.12	-123.54	-20.97	9.29	-116.54	-0.1571	-0.3122
l-Valine	74.36	-170.47	-49.67	12.4	-160.33	-0.2077	-0.3629
l-Methionine	85.76	-202.78	-70.57	14.40	-190.67	-0.2394	-0.3945
Amino acid+d-glucose+ water							
Glycine	46.78	-100.86	-7.70	9.34	-93.77	-0.1255	-0.2819
l-Alanine	54.74	-121.5	-20.38	11.00	-112.75	-0.1467	-0.3030
l-Valine	72.50	-167.57	-48.69	14.71	-155.10	-0.1938	-0.3501
l-Methionine	83.60	-199.27	-69.28	17.04	-184.48	-0.2232	-0.3796

The Gibbs free energy of interaction (ΔG_{int}) values are large and negative as observed in Tables 2 and 3. This indicates that interactions between amino acids and water/ aqueous glucose are favourable. Glucose, a polyol with six –OH group, when added to water partially breaks its H-bonded structure, releasing water dipoles which form glucose-water hydrogen bonds having statistically favoured configuration, with release of energy in terms of ΔG_{int}. The magnitude of ΔG_{int} in water is higher than that in aqueous-glucose solutions indicating stronger interactions of solute in water. There is a possibility of mainly following three types of interactions occurring between amino acid and glucose molecules:

(i) The hydrophilic-ionic interaction between OH groups of glucose and zwitterions of *l*-histidine.
(ii) Hydrophilic-hydrophilic interaction the OH groups of glucose and polar groups in the side chain of polar amino acids mediated through hydrogen bonding.
(iii) Hydrophilic-hydrophobic interaction between the OH groups of glucose molecule and non-polar ($-CH_2$) in side chain of non-polar amino acid molecules.
(iv) Hydrophobic-hydrophobic group interactions between the non-polar groups of glucose and non-polar ($-CH_2$) in side chain of amino acid molecule.

For non-polar amino acids, the magnitude of ΔG_{int} values follows the order: glycine < *l*-alanine < *l*-valine < *l*-methionine. This trend can be explained by considering the hydrophilic/hydrophobic nature of amino acids. As the hydrogen atom of glycine is replaced with $-CH_3$ group in *l*-alanine, $-CH(CH_3)_2$ group in *l*-valine and $-CH_2CH_2SCH_3$ in *l*-methionine, there is appreciable increase in hydrophobic character in the side chain of amino acids. Due to this, the interactions of the type (iii) and (iv) become increasingly significant leading to such trend. As the size of hydrophobic group increases, the N-terminal is highly shielded for electrostriction, allowing solute molecule to interact strongly with the solvent. Similar trend for limiting apparent molar volume, ϕ_v^o has been reported by Ali *et al.*[26] for α-amino acids (glycine, DL-alanine, L-serine and DL-valine) in 0.2 *M* aqueous-D-glucose solution.

In polar amino acids, the magnitude of negative ΔG_{int} values follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine. Major types of interactions that may occur in these systems are of type (i) and (ii), i.e., the hydrophilic-ionic group and hydrophilic-hydrophilic group interactions dominate in these systems. The molecular interactions in *l*-serine and *l*-threonine solutions are weaker than those in *l*-asparagine and *l*-glutamine[36]. The amino group present in *l*-asparagine and *l*-glutamine may interact more strongly with the solvent as compared to hydroxyl group in *l*-serine and *l*-threonine which is reflected in ΔG_{int} values.

From Tables 2 and 3, it is observed that ΔG_{Solv} values are negative for amino acids in water and aqueous-glucose solvent (Figs 1 and 2). This shows that the solvation of amino acid molecules in water and aqueous-glucose is a thermodynamically favourable process. The more negative values of ΔG_{Solv} in water than those in aqueous-glucose supports our conclusion that interactions of amino acids in water are stronger as compared to those in aqueous-glucose solutions. The magnitude of negative ΔG_{Solv} values for these system follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine in case of polar amino acids and glycine < *l*-alanine < *l*-valine < *l*-methionine in case of non-polar amino acids, which indicates that solvation of amino acid molecules becomes more favourable as the size of the molecule increases.

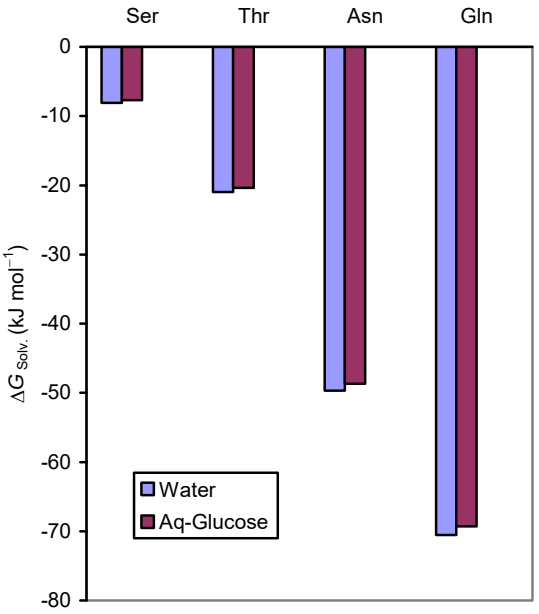

Fig. 1 – Gibbs solvation energy (ΔG_{Solv}) for *l*-serine (Ser), *l*-threonine (Thr), *l*-asparagine (Asn) and *l*-glutamine (Gln) in water and in aqueous-glucose solutions at 298.15 K.

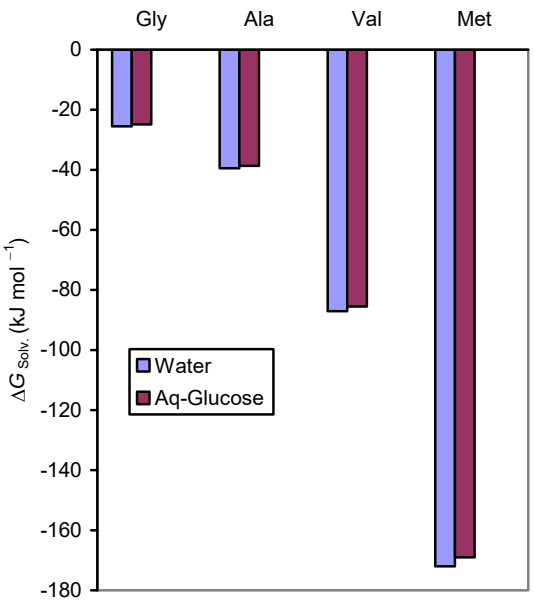

Fig. 2 – Gibbs solvation energy (ΔG_{Solv}) for glycine (Gly), *l*-alanine (Ala), *l*-valine (Val) and *l*-methionine (Met) in water and in aqueous-glucose solutions at 298.15 K.

The values of ΔG_{cav} for amino acids are positive in water as well as in aqueous-glucose solvent, suggesting that the cavity creation is an endothermic process, i.e., the energy is supplied to solvent molecules to create cavity of appropriate size. The magnitude of ΔG_{cav} values for these system follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine in the case of polar amino acids, and, glycine < *l*-alanine < *l*-valine < *l*-methionine in the case of non-polar amino acids, which indicates that cavity formation becomes less favourable as the size of the amino acid molecule increases. Furthermore, it has also been observed that for the systems under study the values of ΔG_{cav} are much larger than ΔH_{cav}, indicating that process of cavity formation for amino acids in aqueous-glucose is not entirely enthalpy dominated. There is significant contribution from entropy term towards ΔG_{cav}.

The ΔH_{Solv} values for amino acid in water are negative and further becomes more negative for amino acid in aqueous-glucose solutions and follows similar trend as those of ΔG_{Solv}: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine in case of polar amino acids and glycine < *l*-alanine < *l*-valine < *l*-methionine in case of non-polar amino acids. This indicates that the hydrophilic-ionic groups and hydrophilic-hydrophilic group interactions (in case of polar amino acids) increase while the hydrophilic-hydrophobic and hydrophobic-hydrophobic group interactions in (in case of polar amino acids) increase in presence of glucose.

The ΔS_{cav} values are negative for all the systems considered, implying that all the systems show certain degree of orderliness. The values of ΔS_{cav} for amino acids in water suggest that solvent in solvation shell of amino acid is more structured in water as compared to that in aqueous-glucose. For ternary system, the order of magnitude of negative ΔS_{cav} values follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine for polar amino acids, and, glycine < *l*-alanine < *l*-valine < *l*-methionine in the case of non-polar amino acids. The lesser value of ΔS_{cav} in aqueous-glucose solutions can be explained by the fact that when the cavities are large, it cannot maintain its H-bonding network, and acts like a flat surface. A small fraction of H-bonds are broken, increasing the randomness in solution and hereby increasing the entropy.

The magnitude of negative ΔS_{Solv} values follows the same trend as ΔS_{Solv} and follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine in case of polar amino acids and glycine < *l*-alanine < *l*-valine < *l*-methionine in case of non-polar amino acids. Overall entropy is increased when amino acids are added to aqueous-glucose supporting our claim that the interactions are stronger in pure water as compared to that in aqueous-glucose.

The results of present study indicate that there are significant interactions of the investigated amino acids in pure water as well as in aqueous-glucose solution. The magnitude of negative ΔG_{int} values for non-polar amino acids follows the order: glycine < *l*-alanine < *l*-valine < *l*-methionine which is explained by the increasing hydrophobic nature with increasing alkyl groups in the same order. The magnitude of negative ΔG_{int} values for polar amino acids follows the order: *l*-serine < *l*-threonine < *l*-asparagine < *l*-glutamine, which is explained by considering the hydrophilic-hydrophobic and hydrophobic-hydrophobic group interactions present in these amino acids. The results also suggest that the cavity formation for accommodation of amino acid molecules in aqueous-glucose molecules receive contributions from enthalpic as well as entropic factors.

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