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ORIGINAL ARTICLE

Studies on the Effect of Amino Acids/Peptide on Micellization of SDS at Different Temperatures

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Abstract Conductivities of (0.001–0.012) m sodium dodecyl sulfate have been determined in water and in the presence of 0.10 m aqueous glycine/alanine/glycylglycine at 298.15, 303.15, 308.15, and 313.15 K. From the specific conductivity data, the critical micellar concentration, degree of counter ion association, degree of counterion dissociation, free energy of transfer of hydrophobic chain from the medium to interior of the micelle, and surface contribution, standard free energy of micellization, standard enthalpy of micellization, and standard entropy of micellization of sodium dodecyl sulfate have been computed. The thermodynamic parameters of micellization and the effect of additives on these parameters have been used to study the interactions present in the micellar systems.

Keywords Micellization electrical conductivity · Sodium dodecyl sulfate · Amino acids/peptide

Introduction

The monomers of a surfactant in aqueous solutions self-associate to form structures called micelles. At a broader threshold of monomer concentration called the critical micelle concentration (CMC), self association occurs and micelles form. Ideally, the concentration of surfactant monomers remains constant above the CMC and is equal to the CMC value as more surfactant is added to the solution; only the concentration of micelles increases [1, 2]. It is a well established fact that the CMC of a surfactant is an extremely important parameter in view of its importance in the determination and optimization of various characteristic properties of micelles used in many pharmaceutical, biotechnological, and chemical processes [3]. As a result, detailed investigation of their behavior in aqueous and in presence of additives has recently attracted the attention of several investigators [4–6]. Such a wide application of surfactants is possible because of their unique character of having both hydrophilic and hydrophobic groups in the same molecule. The aggregation phenomena of amphiphilic molecules involve contributions from both repulsive and attractive interactions. Especially in ionic surfactants, the repulsive forces originated primarily from electrostatic repulsion between the polar head groups [7], whereas, attractive interactions have generally been attributed to hydrophobic interactions [8] between the nonpolar tails of the surfactant monomers. The interactions of these two moieties with water and additives are an important cause for surfactants to aggregate into micelles and other nanometer scale structures in aqueous solution [6]. The study of specific and nonspecific interactions of surfactants with proteins has been a subject of extensive research due to its diverse importance [9]. However, in order to have fine details, the interactions of basic structural units of proteins (i.e., amino acids) with surfactants must be studied owing to the complex structure of the biological macromolecules [10]. The side chains of these building blocks differ in size, shape, charge, hydrogen-bonding capacity, hydrophobicity, and chemical reactivity. Individually and collectively, these side chains contribute to the structure and function of proteins [7]. Amino acids like glycine and alanine are considered to be strong structure-breakers in aqueous solutions due to the presence of peripheral charges [8]. And a peptide like glycylglycine is an important biomolecule due to its wide range of applications in drug production.

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This is due to its ability to act as a hormone and its role as a signal transmitter in cell communications [11]. On the other hand, the commonly used surfactant sodium dodecyl sulfate (SDS) is reported to act as a more potent protein denaturant than urea and guanidine hydrochloride [12]. It is commonly used to solubilize biological membranes and to isolate and purify membrane proteins and membrane lipids. In continuation of our studies on thermodynamic and transport properties of amino acids in aqueous surfactant solutions [13–15], we report here the effect of amino acids, glycine and alanine and the peptide glycylglycine on the micellization of sodium dodecyl sulfate in aqueous medium.

Additives, on the basis of their influence on the micellization process, can be classified in two main categories—electrolytes and non-electrolytes [16]. Electrolytes generally facilitate the formation of ionic micelles, primarily by lowering the coulombic free energy of the interface, resulting in a decrease in critical micelle concentration and an increase in the micellar aggregation number, so that at high ionic strength huge surfactant aggregates are formed [17]. On the other hand, non-electrolyte organic additives, which can be further classified as polar and non-polar, affect micellization in different ways depending on the nature of the additives as well as its quantity [17]. Therefore, the properties of surfactant solutions are differently affected in presence of additives. The present work becomes interesting because the behavior of amino acids/peptide in aqueous solutions is somewhere between strong electrolytes and non-electrolytes [18].

Although numerous studies on the effects of additives of varied natures on micellization have been reported in the literature [17, 19–26], relatively very few studies are available on the effect of amino acids/peptide on the micellization of SDS at different temperatures. The conductometric technique has been found to be highly useful for studying the solution behavior of various systems, including surfactants [6, 20, 25, 27–30]. However, Bakshi et al. [31] had studied the effect of glycine, alanine, valine and methionine on the CMC of SDS at a single temperature. To the best of our knowledge no work has been reported on the study of SDS in aqueous amino acids/peptide at different temperatures.

These considerations led us to investigate the effects of the zwitterionic molecules, i.e., amino acids/peptide on the micellization of anionic surfactant SDS in aqueous solutions at a wider range of temperature and surfactant concentration using conductivity method. Moreover, various important thermodynamic parameters such as the standard free energy of micellization ΔG^0_m, the standard enthalpy of micellization ΔH^0_m, the standard entropy of micellization ΔS^0_m, the free energy of transfer of hydrophobic chain from the medium to interior of the micelle ΔG^0_{HP}, the surface contribution ΔG^0_S, and $\Delta G^0_{HP,tr}$, $\Delta G^0_{S,tr}$, the effect of side groups of amino acids/peptide on these parameters.

Experimental

Glycine (Merck, mass fraction > 0.99), dl-alanine (Loba Chemie, mass fraction > 0.98), and glycylglycine (Merck, mass fraction > 0.99) were recrystallized from aqueous-ethanol solution and dried under vacuum over P_2O_5 at 338 K for 10 h before use. Sodium dodecyl sulfate (Central Drug House Ltd., Mumbai, mass fraction > 0.99) was used after recrystallization from ethanol and was dried in a vacuum over P_2O_5. Water, with conductivity 1.05×10^{-6} S cm^{-1} at 298.15 K was used for preparation of solutions and was obtained by distilling deionized water from alkaline $KMnO_4$ to remove organic matter, if any. Stock solutions of 0.10 m (mol kg^{-1}) of each Gly, Ala and Gly–Gly in water were prepared and used as solvents to prepare thirty-nine solutions of 0.000, 0.001, 0.002, 0.003, 0.004, 0.005, 0.006, 0.007, 0.008, 0.009, 0.010, 0.011, and 0.012 m SDS in order to cover the pre- and post-micellar concentration range of SDS. The weighings were done on a Precisa XB-220A, Swiss make electronic balance with a precision of ±0.0001 g. All necessary precautions were taken to prepare solutions. The solutions were stored in special airtight bottles to minimize absorption of atmospheric moisture and carbon dioxide. Conductivities of the solutions were measured with a Control Dynamics Conductivity Meter, India, having a cell constant 1.007 cm^{-1}. The conductivity meter was calibrated by measuring the conductivities of the solutions of potassium chloride (Merck, purity > 99%) of different concentrations (0.01 and 0.1 N). The solution and the measuring cell were immersed in an electronically controlled thermostated water bath (Julabo, Model MD, Germany), maintaining the temperature within ±0.02 K.

Results and Discussion

The experimental values of the conductivity (κ) of SDS in 0.10 m aqueous Gly, Ala, and Gly–Gly as a function of surfactant concentration at 298.15, 303.15, 308.15, and 313.15 K are listed in Table 1. The values of CMC of SDS in aqueous and in aqueous amino acids/peptide, obtained from the intersection of the fitting lines of the conductivity versus concentration plots above and below the break point, as a function of temperature are reported in Table 2. The dependence of κ on [SDS] and temperature in presence of amino acids is graphically shown in Fig. 1. The observed CMC values of SDS in aqueous solution are 8.1, 8.3, 8.5, and 8.9×10^{-3} mol kg^{-1} at 298.15, 303.15,

Table 1 Values of the conductivities, κ, of SDS in 0.10 m aqueous glycine, alanine, and glycylglycine as a function of surfactant concentration at different temperatures

m (mol kg^{-1})	T (K)			
	298.15	303.15	308.15	313.15
SDS + 0.10 m aqueous glycine κ (mS cm^{-1})				
0.000	0.06	0.06	0.06	0.12
0.001	0.15	0.17	0.18	0.23
0.002	0.23	0.26	0.28	0.35
0.003	0.33	0.35	0.38	0.47
0.004	0.40	0.44	0.48	0.57
0.005	0.48	0.53	0.59	0.69
0.006	0.56	0.62	0.68	0.79
0.007	0.64	0.70	0.78	0.87
0.008	0.70	0.80	0.87	0.95
0.009	0.75	0.84	0.95	1.04
0.010	0.77	0.88	0.99	1.12
0.011	0.81	0.92	1.04	1.16
0.012	0.84	0.95	1.08	1.19
SDS + 0.10 m aqueous alanine κ (mS cm^{-1})				
0.000	0.06	0.06	0.07	0.08
0.001	0.16	0.18	0.20	0.24
0.002	0.24	0.28	0.32	0.37
0.003	0.33	0.38	0.45	0.51
0.004	0.42	0.49	0.55	0.63
0.005	0.50	0.59	0.67	0.76
0.006	0.58	0.67	0.78	0.90
0.007	0.64	0.79	0.88	1.03
0.008	0.67	0.83	0.96	1.13
0.009	0.71	0.87	1.02	1.20
0.010	0.76	0.92	1.07	1.26
0.011	0.79	0.97	1.13	1.33
0.012	0.83	1.02	1.18	1.40
SDS + 0.10 m aqueous glycylglycine κ (mS cm^{-1})				
0.000	0.05	0.07	0.07	0.09
0.001	0.15	0.17	0.20	0.23
0.002	0.26	0.29	0.31	0.36
0.003	0.35	0.39	0.43	0.48
0.004	0.44	0.49	0.54	0.61
0.005	0.52	0.58	0.64	0.74
0.006	0.58	0.65	0.71	0.83
0.007	0.64	0.73	0.79	0.92
0.008	0.70	0.80	0.86	1.01
0.009	0.77	0.86	0.94	1.09
0.010	0.83	0.93	1.02	1.18
0.011	0.89	1.00	1.10	1.27
0.012	0.94	1.05	1.16	1.36

308.15, and 313.15 K, respectively, which compare well with the literature values 8.0 and 8.5 $\times$ 10^{-3} mol dm^{-3} [24] at 298.15 and 308.15 K; 8.2 and 8.7 $\times$ 10^{-3} mol L^{-1} [32] at 303.15 and 313.15 K; 8.15, 8.40, and 8.80 mol L^{-1} [33] at 298.15, 303.15, and 308.15 K, respectively. The CMC of SDS both in aqueous and in amino acids/peptide (Table 2) increases with increase in temperature. The effect of temperature on the CMC of surfactant in aqueous medium is complex [34]. In general, the effect of temperature on the CMC of surfactants in aqueous medium is analyzed in terms of two opposing effects [22, 30, 34]:

(i) Cmc first tends to decrease with increase in temperature, as temperature increase causes decrease in

Table 2 Values of critical micelle concentration, CMC and degree of ionization β of SDS in water and in 0.10 m aqueous glycine, alanine, and glycylglycine at different temperatures

T (K)	Water	Aqueous glycine	Aqueous alanine	Aqueous glycylglycine
CMC (mol kg^{-1})				
298.15	**0.0081**	0.0076	0.0065	0.0045
303.15	0.0083	0.0079	0.0069	0.0047
308.15	0.0085	0.0081	0.0072	0.0050
313.15	0.0089	0.0083	0.0075	0.0052
β				
298.15	0.33	0.39	0.42	0.60
303.15	0.38	0.42	0.45	0.63
308.15	0.42	0.44	0.48	0.66
313.15	0.45	0.47	0.51	0.69

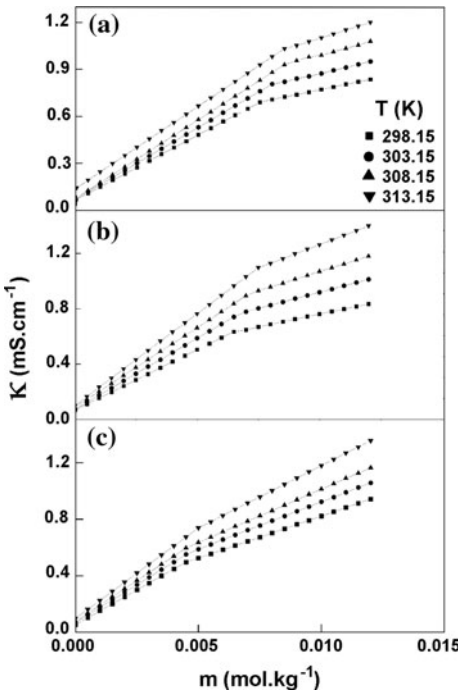

Fig. 1 Variation of specific conductivity κ on [SDS] in 0.10 m aqueous. **a** glycine, **b** alanine, and **c** glycylglycine at different temperatures

hydration of hydrophilic group, which favors micellization. (ii) However, at relatively higher temperature range disruption of the structured water surrounding the hydrophobic group occurs, this disfavors micellization [22, 35], thereby, increasing the CMC of the surfactant. It is clear from the Table 2 that the second effect seems to be dominant over the first one for the present system, in the temperature range studied. Our finding is supported by the fact that for ionic surfactants, minimum in the CMC-temperature curve appears around 298 K [34], and then CMC tends to increase, as for SDS in this case, with increase in the temperature. Furthermore, Table 2 exhibits the effect of additives on the CMC of SDS, it decreases in the sequence: in water >Gly > Ala > Gly–Gly at each investigated temperature. It is well known that the micellization process occurs due to the hydrophobic interactions and that dispersion force is the attractive force in the micellization [35, 36]. Thus, as the number of carbon atoms increases from Gly to Gly–Gly so does the hydrophobic character of the molecules. The increase in hydrophobic interaction requires a lower addition of surfactant molecules for micellization [36], resulting in a decreased CMC in the presence of amino acids and follows the sequence as given above. This may also be explained by considering the zwitterionic nature of amino acid additives, which interact with the water molecules, causing dehydration of the hydrophilic head of the surfactant micelles [35]. This, in turn, favors micellization, thereby, leading to a decrease in CMC of SDS in the presence of amino acids. A similar decrease in CMC of SDS upon addition of amino acids in aqueous medium has also been reported by others [31].

The degree of ionization (β) of the micelles can be estimated conductometrically from the ratio of the slopes of the two linear segments above and below CMC of specific conductivity versus surfactant concentration [30, 37, 38] and, hence, the degree of counterion association, is given as $\alpha = 1 - \beta$. This simple method is quite satisfactory in providing quantitative estimation of β, as reported by Buckingham and co-workers [39]. Further, the goodness of the method was verified by Kale et al. [40] and also by Bandyopathyay and Moulik [41] who have estimated β by using ion-selective membrane electrode and found that the values of β thus obtained are in good agreement with those obtained conductometrically. However, in fact, like CMC [30, 42], the degree of counterion dissociation β or, in turn, counterion association α is experimental technique dependent [43]. As a result, the values of α for Na^+ ions bound to SDS micelles are reported to lie in the range 0.46–0.86 [44] in aqueous medium, depending on the experimental technique employed (electromotive force, light scattering, mass-action model, equilibrium dialysis, osmotic coefficient, electrophoresis, and zeta-potential). Our value 0.67 of α for

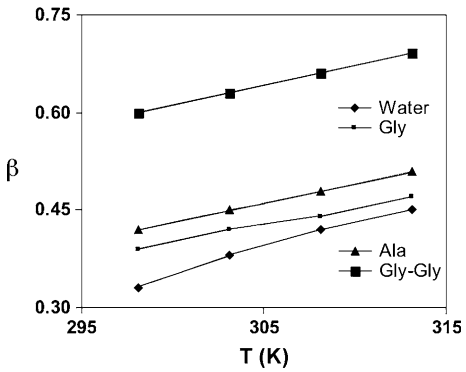

Fig. 2 Variation of degree of ionization β with temperature in the presence of water and in 0.10 m aqueous glycine, alanine, and glycylglycine

Na^+ ions bonded to SDS micelles (Table 2) in aqueous medium determined conductometrically at 298.15 K is fairly good and lies in the reported range. The values of β are included in Table 2 and its variation with temperature is shown in Fig. 2. It is evident from Table 2 that both CMC and β for the investigated systems increase with an increase in the temperature. The increase in thermal energy due to the rise in temperature enhances the ionization of the ionic surfactant SDS and, thereby, an increase in β with temperature is obvious. Similar results have also been reported for the variation of CMC and β for SDS in presence and absence of additives in aqueous medium by others [22, 30]. In the presence of the additives amino acids/peptide, the values of degree of ionization, β are found to increase from Gly to Gly–Gly.

The total free energy per surfactant molecule associated with forming the micelle is given by the relation [45, 46]:

$$\Delta G_{\mathrm{M}}^{0} = RT \ln X_{\mathrm{CMC}}. \quad (1)$$

In presence of an additive, the free energy, $\Delta G_{\mathrm{M}}^{0}$, consists of the interactions SDS–SDS, additive-SDS, and additive–additive. The energies associated with these interactions can be divided into three types of contributions [25, 31, 45, 46]:

$$\Delta G_{\mathrm{M}}^{0} = \Delta G_{\mathrm{HP}}^{0} + \Delta G_{\mathrm{el}}^{0} + \Delta G_{\mathrm{all\ other}}^{0} \quad (2)$$

where $\Delta G_{\mathrm{HP}}^{0}$ is the hydrophobic free energy associated with transferring the surfactant hydrocarbon chain from the medium to the interior of the micelle, this derives micellization, $\Delta G_{\mathrm{el}}^{0}$ is associated with the electrostatic interactions between the head groups and counterions, this opposes micellization, and all other contributions arising from specific interactions, $\Delta G_{\mathrm{all\ other}}^{0}$. Furthermore, the last two interaction energies $\Delta G_{\mathrm{el}}^{0}$ and $\Delta G_{\mathrm{all\ other}}^{0}$ can be combined [25, 31] to yield the energy associated with the surface contributions, $\Delta G_{\mathrm{S}}^{0}\left(= \Delta G_{\mathrm{el}} + \Delta G_{\mathrm{all\ other}}^{0}\right)$. The values of $\Delta G_{\mathrm{HP}}^{0}$ and $\Delta G_{\mathrm{S}}^{0}$ can be estimated by considering

the equilibrium model [46, 47] which relates the degree of counterion binding to the electrostatic interactions between surfactant head groups and counterions. Moreover, this provides an estimation of the free energy of transferring the surfactant hydrocarbon chain from water into the interior of the micelle. The equilibrium between counterions C^+, surfactant monomers S^-, and monodispersed micelles M^{P-}, can be represented as

$$(N-P)C^+ + NS^- \rightleftharpoons M^{P-}. \quad (3)$$

Thus, the equilibrium constant for Eq. 3 can be related to the standard free energy of micelle formation per monomer unit by

$$\Delta G^0_M/RT = -(1/N)\ln C_{M^{P-}} + \ln C_{S^-} + (1-P/N)\ln C_{C^+}. \quad (4)$$

In the case of typical micelles, as SDS, ($N = 50$–100), the value of $C_{M^{P-}}$ is small and insensitive to large errors in the evaluated $C_{M^{P-}}$ values, and the values of C_{C^+} and C_{S^-} can be replaced by the value of CMC in the second and third terms in the above equation to give

$$\Delta G^0_{HP} = RT\ln X_{CMC} + RT(1-P/N)\ln X_{CMC} \quad (5)$$

where P/N ($=\beta$) is the degree of ionization of counterions from the micelles and X_{CMC} is the CMC value expressed in the mole fraction. Combining Eq. 5 with Eq. 2, the equilibrium model yields

$$\Delta G^0_S = -\alpha RT\ln X_{CMC}. \quad (6)$$

From the computed values of ΔG^0_{HP} and ΔG^0_S, using Eqs. 5 and 6, the corresponding transfer values, $\Delta G^0_{HP,tr}$ and $\Delta G^0_{S,tr}$ of micelles from water to aqueous amino acids/peptide solutions can be evaluated by the relation

$$\Delta Y^0_{HP/S,tr} = \Delta Y^0_{HP/S}(\text{in aqueous amino acids/peptide}) - \Delta Y^0_{HP/S}(\text{in water}) \quad (7)$$

where $\Delta Y^0_{HP/S}$stands for ΔG^0_{HP} or ΔG^0_S. The values of $\Delta G^0_{HP,tr}$ and $\Delta G^0_{S,tr}$, thus obtained, together with the values of ΔG^0_{HP} and ΔG^0_S at investigated temperatures are presented in Table 3.

The values of ΔG^0_{HP} and ΔG^0_S for SDS in water are found to be -36.57 and 14.65 kJ mol^{-1} at 298.15 K, respectively, which are in excellent agreement with the values reported in the literature [25]. Furthermore, it is clear from Table 3 that the values of ΔG^0_S for SDS in water + amino acids/peptide are lower than that of SDS in pure water and the values of ΔG^0_{HP} are less negative in presence of additives than in pure water at all studied temperatures. The values of ΔG^0_S decrease while those of ΔG^0_{HP} increase with increase in temperature. Similar results on the variations of ΔG^0_S and ΔG^0_{HP} with the increasing amount of amino acids have also been reported in aqueous SDS [31]. Here, it is interesting to note that an increase in temperature acts in the same way as the addition of non-polar substances [48]. Thus, our finding regarding the variations of ΔG^0_S and ΔG^0_{HP} with temperature truly endorses the results reported for similar variations in these parameters with increases in the concentrations of Gly, Ala, Val, and methionine [31], due to increased non-polar character from Gly to methionine. From the thermodynamic point of view, the decrease in ΔG^0_S can be ascribed to the energy associated with the non-availability of Na^+ counterions, as a result of increased temperature, for electrostatic interactions with the head groups on the surface of the micelle due to interactions between dipolar zwitterionic amino acids/peptide molecules with the counterions. The electrostatic repulsion between the head groups is increased due to removal of counterions from the micellar surface. This, in turn, increases the electrostatic repulsions between the head groups, which consequently destabilizes the micelles, thus, ΔG^0_{HP} becomes less negative. At a given temperature, ΔG^0_{HP} becomes less negative as we move from Gly to Gly–Gly (Table 3). This may be attributed to the solubilization of some portions of the amino acids/peptide in the palisade layer of the micelle, and the solubilization becomes more significant as the hydrophobic character increases from Gly

Table 3 Values of, ΔG^0_{HP}, ΔG^0_S, $\Delta G^0_{HP,tr}$ and $\Delta G^0_{S,tr}$ of SDS in water and in 0.10 m aqueous glycine, alanine, and glycylglycine at different temperatures

T (K)	ΔG^0_{HP} (kJ mol^{-1})	ΔG^0_S (kJ mol^{-1})	$\Delta G^0_{HP,tr}$ (kJ mol^{-1})	$\Delta G^0_{S,tr}$ (kJ mol^{-1})
SDS + water				
298.15	−36.57	14.65	–	–
303.15	−36.00	13.80	–	–
308.15	−36.63	13.13	–	–
313.15	−35.29	12.54	–	–
SDS + 0.10 m aqueous glycine				
298.15	−35.53	13.49	1.04	−1.16
303.15	−35.29	12.98	0.71	−0.83
308.15	−35.24	12.63	0.39	−0.50
313.15	−35.05	12.14	0.23	−0.40
SDS + 0.10 m aqueous alanine				
298.15	−35.43	13.01	1.14	−1.64
303.15	−35.03	12.39	0.97	−1.42
308.15	−34.80	11.89	0.83	−1.24
313.15	−34.59	11.42	0.69	−1.12
SDS + 0.10 m aqueous glycylglycine				
298.15	−35.57	9.24	4.01	−5.40
303.15	−32.42	8.81	3.58	−4.99
308.15	−31.99	8.15	3.64	−4.97
313.15	−31.61	7.49	3.68	−4.05

to Gly–Gly, making ΔG^0_{HP} less negative. It can also be seen that more hydrophobic additives have subsequently stronger energetic effects, as reflected from the change of $\Delta G^0_{HP,tr}$ and $\Delta G^0_{S,tr}$ (Table 3). As mentioned above, the hydrophobic character increases in the order Gly < Ala < Gly–Gly, it would also be the order of interaction between the hydrophobic group of SDS and the hydrophobic part of additives. Accordingly, the value of $\Delta G^0_{HP,tr}$ in transferring the hydrophobic chain of SDS from the medium to the interior of the micelle follows the above sequence (Table 3).

The CMC values, determined at various temperatures, were used for calculating the thermodynamic parameters of micellization. The standard free energy of micelle formation per mole of the monomer ΔG^0_m were calculated using mass action model [22, 49]:

$$\Delta G^0_m = (2-\beta)\, RT \ln X_{CMC} \quad (8)$$

where R is the gas constant, T, the temperature in Kelvin scale and X_{CMC} is the CMC value expressed in terms of mole fraction.

Then, the enthalpy of micellization can be obtained by applying the Gibbs–Helmholtz relation [22]:

$$\Delta H^0_m = -(2-\beta)RT^2\left(\frac{\partial \ln X_{CMC}}{\partial T}\right). \quad (9)$$

The values of entropy of micellization, ΔS^0_m, can be estimated from the calculated enthalpy and free energy values, as:

$$\Delta S^0_m = \frac{\Delta H^0_m - \Delta G^0_m}{T}. \quad (10)$$

The thermodynamic parameters of micellization for SDS in water and in presence of additives, Gly/Ala/Gly–Gly at different temperatures are summarized in Table 4. For amphoteric and ionic surfactants, ΔG^0_m has been reported to be between −23 and −42 kJ mol^{-1} at 298.15 K [50]. The free energy values for SDS in water and in presence of aqueous Gly/Ala/Gly–Gly fall within this range. Figure 3 shows the increase in free energy with temperature for SDS in water and in presence of additives, suggesting that an increase in temperature disfavors micellization. This supports the change in CMC with temperature. At a given temperature, ΔG^0_m is found to increase from Gly to Gly–Gly (Table 4). This can be explained by considering the degree of ionization, β of SDS in presence of amino acids and peptide. As the value of β tends to increase from Gly to Gly–Gly (Table 2), the availability of counterions, Na^+ for interaction with the surfactant head group decreases. This would cause increased electrostatic repulsion between the head groups, thereby, increasing the free energy of micellization, ΔG^0_m in the sequence: Gly < Ala < Gly–Gly at a given temperature. Negative values of ΔG^0_m are mainly attributed to the large positive values of $T\Delta S^0_m$ than ΔH^0_m. Therefore, the micellization process is governed primarily by the entropy gain and the driving force for the process is the tendency of the hydrophobic group of the SDS to transfer from the solvent environment to the interior of the micelle [34]. At higher temperatures, disruption of the structured water surrounding the hydrophobic group may be responsible for the entropy increase, while at lower temperature ΔH^0_m seems to be significant. As ΔG^0_m is the sum of the enthalpic, ΔH^0_m, and entropic, $-T\Delta S^0_m$, contributions, their contributions to ΔG^0_m for the studied systems are shown in Fig. 4. It reveals that in presence of amino acids, Gly and Ala, the entropic contribution

Table 4 Values of, ΔG^0_m, ΔH^0_m and ΔS^0_m of SDS in water and in 0.10 m aqueous glycine, alanine, and glycylglycine at different temperatures

	T (K)			
	298.15	303.15	308.15	313.15
SDS + water				
ΔG^0_m (kJ mol^{-1})	−36.57	−36.00	−35.63	−35.29
ΔH^0_m (kJ mol^{-1})	−6.77	−7.94	−9.16	−10.44
ΔS^0_m (kJ mol^{-1} K^{-1})	0.100	0.093	0.086	0.079
SDS + 0.10 m aqueous glycine				
ΔG^0_m (kJ·mol^{-1})	−35.53	−35.29	**−35.24**	−35.05
ΔH^0_m (kJ·mol^{-1})	−9.45	−7.86	−6.24	−4.54
ΔS^0_m (kJ mol^{-1} K^{-1})	0.087	0.090	0.094	0.097
SDS + 0.10 m aqueous alanine				
ΔG^0_m (kJ mol^{-1})	−35.43	−35.03	−34.80	−34.59
ΔH^0_m (kJ mol^{-1})	−14.35	−12.28	−10.17	−8.01
ΔS^0_m (kJ mol^{-1} K^{-1})	0.071	0.075	0.080	0.085
SDS + 0.10 m aqueous glycylglycine				
ΔG^0_m (kJ mol^{-1})	−32.57	−32.42	−31.99	−31.61
ΔH^0_m (kJ mol^{-1})	−10.89	−10.62	−10.28	−9.91
ΔS^0_m (kJ mol^{-1} K^{-1})	0.073	0.072	0.070	0.069

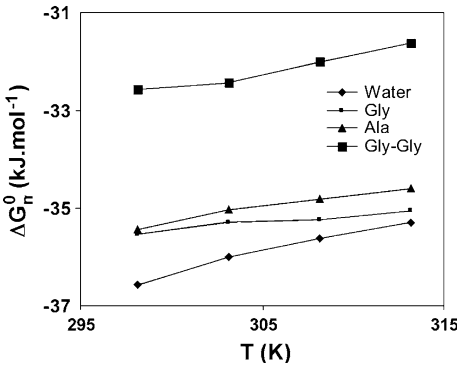

Fig. 3 Variation of free energy of micellization ΔG^0_m for SDS with temperature in presence of water and in 0.10 m aqueous glycine, alanine, and glycylglycine

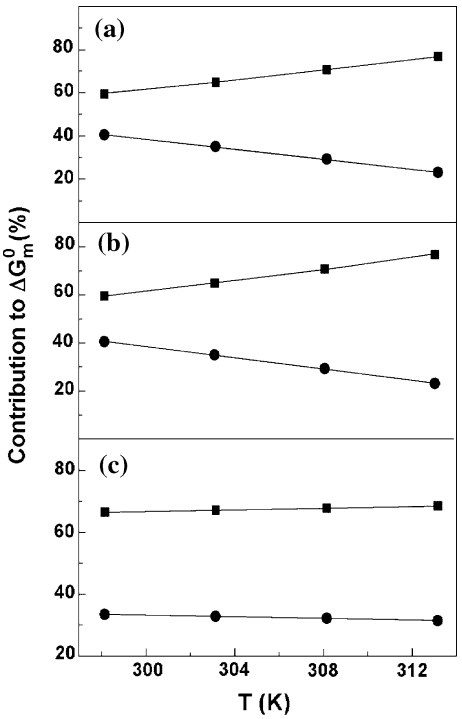

Fig. 4 Enthalpic (*circles*) and entropic (*squares*) contributions to ΔG^0_m at different temperatures in 0.10 m aqueous **a** glycine, **b** alanine, and **c** glycylglycine

$\left(-T\Delta S^0_m\right)$ is increased while enthalpic contribution $\left(\Delta H^0_m\right)$ gets decreased with increase in temperature. In the presence of Gly–Gly, a rise in temperature does not significantly affect the enthalpic and entropic contributions to ΔG^0_m. It is due to the fact that in presence of Gly and Ala, the changes in ΔS^0_m and ΔH^0_m with temperature are quite appreciable, whereas, in the presence of Gly–Gly the changes in these parameters are very small (Table 4) and that, unlike Gly and Ala where ΔS^0_m increases, it slightly decreases with temperature in presence of Gly–Gly. As a result, the entropic $\left(-T\Delta S^0_m\right)$ and enthalpic $\left(\Delta H^0_m\right)$ contributions to ΔG^0_m in presence of Gly–Gly are almost insignificant with increases in temperature.

Conclusion

The effect of Gly, Ala, and Gly–Gly on the micellization of SDS in an aqueous medium has been investigated at different temperatures. The critical micelle concentration of SDS increases with increases in temperature. While it exhibits an opposite trend as the hydrophobic character increases from Gly to Gly–Gly. Using the equilibrium model, the values of ΔG^0_{HP} and ΔG^0_S were calculated and, hence, those of the corresponding transfer values, $\Delta G^0_{HP,tr}$ and $\Delta G^0_{S,tr}$ of micelles from water to aqueous amino acids/peptide were also estimated for the present systems. The observed values of ΔG^0_S decrease while those of ΔG^0_{HP} increase with increase in temperature. The decrease in ΔG^0_S can be attributed to the decreased availability of Na^+ counterions for electrostatic interactions with the polar head groups on the surface of micelles, due to interactions between counterions and dipolar zwitterionic amino acids/peptide molecules. The removal of counterions from the micellar surface enhances the electrostatic repulsion between the head groups of the micelles. This tends to destabilize the micelles, resulting in an increase in ΔG^0_{HP} values. At a given temperature, the observed values of $\Delta G^0_{HP,tr}$ follow the sequence: Gly–Gly > Ala > Gly whereas those of $\Delta G^0_{S,tr}$ exhibit reverse trends, suggesting that more hydrophobic additives have stronger energetic effects. In the presence of amino acids/peptide, ΔG^0_m is found to increase with increases in temperature and that it increases also from Gly to Gly–Gly at a given temperature. Negative values of ΔG^0_m are mainly due to large positive values of $T\Delta S^0_m$ than ΔH^0_m, thereby, suggesting that micellization process is governed primarily by entropy gain. Further, in the presence of Gly and Ala, the entropic contribution $\left(-T\Delta S^0_m\right)$ becomes increased while the enthalpic contribution $\left(\Delta H^0_m\right)$ is decreased with increases in temperature. In the presence of Gly–Gly, the change in enthalpic and entropic contributions to ΔG^0_m with a rise in temperature are too small to be significant. The observed behaviors of these parameters may be attributed to the interactions of amino acids/peptide with water and surfactant molecules, and also due to the possible solubilization of additives in the palisade layer of micelles.

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