Effect of Temperature on the Interactions of Glycyl Dipeptides with Sodium Dodecyl Sulfate in Aqueous Solution: A Volumetric, Conductometric, and Fluorescence Probe Study

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The interactions of glycyl dipeptides (2-[(2-aminoacetyl)amino]acetic acid (commonly known as glycylglycine), 2-[(2-aminoacetyl)amino]-3-methylbutanoic acid (commonly known as glycyl-L-valine), and (2*S*)-2-[(2-aminoacetyl)amino]-4-methylpentanoic acid (commonly known as glycyl-L-leucine)) with sodium dodecyl sulfate (SDS) as a function of temperature in aqueous solution have been investigated by a combination of density, conductivity, and fluorescence methods. The standard partial molar volume ($V^{o}_{2,\phi}$), standard partial molar volumes of transfer for dipeptide from water to aqueous SDS solutions ($\Delta_t V^{o}$), partial molar expansibility (E^{o}_{ϕ}), and Hepler's constant have been calculated from density data. Electrical conductivity was used to estimate the critical micellar concentration (cmc) and the thermodynamic parameters of micellization of SDS in aqueous peptide solutions. The change of micropolarity produced by the interaction was monitored by the measurement of emission intensity ratio between the first and the third bands (I_1/I_3) of pyrene fluorescence. The obtained data have been discussed in light of various interactions operating in the ternary system of peptide, water, and SDS.

Introduction

In recent years, there has been growing interest in the interactions between protein and surfactant due to their many applications in biosciences, foods and cosmetics, drug delivery, detergency, and biotechnological processes.[1,2] Using various numbers of tools and techniques, these interactions have been studied and published in the past few years.[3−16] It has been proposed that hydrophobic and electrostatic interactions are the two main driving forces for the association between surfactants and proteins in aqueous solution. However, the study of protein−surfactant interactions is difficult because of the complexity of interactions in such a large molecule. Several details in the mode of these interactions remain unanswered. Therefore, it is very important to understand the origin and nature of these interactions both qualitatively and quantitatively. To understand the fine details, the interactions of the building blocks of the protein with surfactants must be studied. There have been some investigations on the interaction of surfactants with amino acids.[17−24] However, to the best of our knowledge, no report is available in the literature on the thermodynamic properties of some small peptides in aqueous surfactant solutions at different temperatures, except for the work of Singh et al.,[19] who have reported only volumetric properties of some amino acids and two peptides (diglycine and triglycine) in aqueous surfactant solutions at $T = 298.15$ K.

Peptides are important molecules because of their wide application in drug production and their roles as signal transmitters in cell communications.[25] Moreover, small peptides have been widely used as a protein model compound recently in the studies of the thermodynamic properties of protein because they contain more complex structures and more components of protein than amino acids. The systematic study of peptide−surfactant interactions can provide valuable information about peptide's behavior and insight into the conformational stability of proteins in surfactant solutions. Such an investigation can also obtain the information about the role of the presence of peptides in the micellization process.

Keeping these considerations in mind, in this paper, we report studies on the interactions of sodium dodecyl sulfate (SDS) with glycyl dipeptides (2-[(2-aminoacetyl)amino]acetic acid (commonly known as glycylglycine), 2-[(2-aminoacetyl)amino]-3-methylbutanoic acid (commonly known as glycyl-L-valine), and (2*S*)-2-[(2-aminoacetyl)amino]-4-methylpentanoic acid (commonly known as glycyl-L-leucine)) by densimetry, conductometry, and fluorescence spectroscopy. The ionic surfactant SDS has been chosen because of the strong interaction with protein and regular use in industry. The resulting data are discussed in terms of the interactions operating in SDS−dipeptide−H_2O systems including the effect of SDS on the volumetric properties of dipeptides and the effect of dipeptides on the micellization as well as microenvironmental properties of SDS micelles.

Experimental Section

Chemicals. All of the used dipeptides, 2-[(2-aminoacetyl)-amino]acetic acid (commonly known as glycylglycine with CAS # 556-50-3), 2-[(2-aminoacetyl)-amino]-3-methylbutanoic acid (with CAS # 1963-21-9 and commonly known as glycyl-L-valine), and (2*S*)-2-[(2-aminoacetyl)amino]-4-methylpentanoic acid (commonly known as glycyl-L-leucine with CAS # 869-19-2), were supplied by Sigma with a mass fraction purity of 0.99. Each sample was recrystallized twice from aqueous ethanol solutions and dried for 24 h under vacuum at room temperature. They were then stored over P_2O_5 in a desiccator before use. The surfactant SDS (mass fraction purity > 0.99, Fluka) and

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Table 1. Standard Partial Molar Volumes $V^{o}_{2,\phi}$/(cm^3·mol^{-1}) for the Dipeptides in Water and 0.05 mol·kg^{-1}Aqueous SDS Solution at Different Temperatures

	$V^{o}_{2,\phi}$/cm^3·mol^{-1}			
	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
	Water			
glycylglycine	76.29 ± 0.07 76.29[a], 76.27[b], 76.23[c], 76.39[d]	76.55 ± 0.09	76.89 ± 0.12 77.11[c], 77.12[d]	77.56 ± 0.09 77.59[a]
glycylvaline	122.25 ± 0.05 122.25[a], 122.34[c]	122.49 ± 0.06 122.96[c]	123.01 ± 0.07 123.64[c]	124.02 ± 0.08 124.06[a]
glycylleucine	139.69 ± 0.10 139.69[a], 139.62[c]	140.12 ± 0.05	140.47 ± 0.10 140.97[c]	141.70 ± 0.09 141.72[a]
	0.05 mol·kg^{-1} SDS Solution			
glycylglycine	76.40 ± 0.07	76.73 ± 0.08	77.78 ± 0.05	78.85 ± 0.09
glycylvaline	122.96 ± 0.06	123.53 ± 0.07	124.07 ± 0.04	125.21 ± 0.06
glycylleucine	140.11 ± 0.04	140.69 ± 0.06	141.25 ± 0.06	142.55 ± 0.06

[a] Ref 27. [b] Ref 28. [c] Ref 29. [d] Ref 30.

pyrene (mass fraction purity ≥ 0.99, Sigma) were used without further purification. Potassium chloride (mass fraction purity of 0.99999, Aldrich Chem. Co.) was dried for 48 h at T = 373 K and was used to determine the conductance cell constant. Water with a conductivity of (0.8 to 1.0)·10^{-4} S·m^{-1} was obtained by distilling deionized water. In densimetry, all of the solutions were prepared gravimetrically with a Shimadzu AY 120 balance with an uncertainty of ± 0.1 mg. The uncertainty in molality was ± 0.0002 mol·kg^{-1}. In the conductometric experiment, all of the mass determinations were done on a Satorius BP 211D digital balance having an uncertainty of ± 0.01 mg, and the molalities calculated were found to be uncertain to ± 0.00002 mol·kg^{-1}.

Apparatus and Procedures. Solution densities were measured to ± 1·10^{-6} g·cm^{-3} with an Anton Paar DMA 60/602 vibrating-tube digital densimeter that was calibrated daily at T = 298.15 K using dry air and water with a conductivity of (0.8 to 1.0)·10^{-4} S·m^{-1}. The uncertainty of density measurement was ± 3·10^{-6} g·cm^{-3}. The densimeter was thermostatted using Schott thermostat units, which have a thermal stability of ± 0.005 K.

The electrical conductivity of each sample was measured with a conductivity meter (model 145A+, Thermo Orion), using a conductivity cell (model 011510, Thermo Orion). The conductance cell was equipped with a water circulating jacket, and the temperature was controlled within ± 0.02 K with a low temperature thermostat (model DC-2006, Shanghai Hengping Instrument Factory). The cell constant is 1.092 cm^{-1}, which was calculated by repeated measurements of KCl solutions. The uncertainty of the conductivity measurements was estimated to ± 0.5 %. All data were corrected with the specific conductivity of the solvent.

Fluorescence spectra were recorded on a F4500 Hitachi fluorescence spectrometer at room temperature using emission and excitation slit widths of (2.5 and 5) nm, respectively, with a scan rate of 60 nm·min^{-1}. All systems were examined in a solution of 2.0·10^{-6} mol·dm^{-3} pyrene used as a probe. The excitation wavelength was 335 nm. The molality of dipeptides was kept to 0.04 mol·kg^{-1}.

Results and Discussion

The density data measured for glycyl dipeptides in water and 0.05 mol·kg^{-1} aqueous SDS solution at T = (298.15, 303.15, 308.15, and 313.15) K are listed in Tables S1 and S2 of Supporting Information. The apparent molar volumes ($V_{2,\phi}$) were calculated from the solution densities, ρ, using the following equation

$$V_{2,\phi} = M/\rho - 10^3(\rho - \rho_o)/m_p\rho\rho_o \quad (1)$$

where M is the molar mass of the glycyl dipeptides in g·mol^{-1}, ρ_o is the density of solvent in g·cm^{-3}, and m_p is the molality of the dipeptide in mol·kg^{-1} in SDS−water mixtures. The reported apparent molar volume data (Tables S1 and S2, Supporting Information) for the peptides were found to be adequately presented by the linear equation

$$V_{2,\phi} = V^{o}_{2,\phi} + S_v m_p \quad (2)$$

where $V^{o}_{2,\phi}$ is the infinite dilution apparent molar volume that equals the standard partial molar volume and S_v is an experimentally determined parameter. Values of $V^{o}_{2,\phi}$ have been evaluated by weighted least-squares regression analysis. The standard partial molar volumes for the glycyl dipeptides in water and in aqueous SDS solutions are represented in Table 1 along with their standard deviations. In those cases, where there was no dependence on m_p, $V^{o}_{2,\phi}$ was calculated by taking an average of all data points. The standard deviations pertain to the mean value.

It is mentioning here that the dipeptides can exist in different ionic forms depending on the environment. There are several forms of dipeptide, namely, the fully protonated dipeptide, the zwitterionic form, and the fully deprotonated dipeptide, and the relative concentrations of these different forms depend strongly on the pH of the medium. The pH value of the 0.05 mol·kg^{-1} aqueous SDS solution is 5.73. The isoelectric points of the studied three dipeptides are about 5.6 to 5.7.[26] So the studied dipeptides are almost the zwitterionic forms in 0.05 mol·kg^{-1} aqueous SDS solution.

It can be seen from Table 1 that the obtained $V^{o}_{2,\phi}$ values for glycyl dipeptides in aqueous solution at different temperatures fit very well with those available in literature.[27−30] The temperature dependence of $V^{o}_{2,\phi}$ for the dipeptides can be expressed in polynomical form with (T − 273.15) K as a variable, as follows:

$$V^{o}_{2,\phi}/\text{cm}^3\cdot\text{mol}^{-1} = A_1 + A_2((T/\text{K}) - 273.15) + A_3((T/\text{K}) - 273.15)^2 \quad (3)$$

A_1, A_2, and A_3 are coefficients. The standard deviation of the fits are 0.14 to 0.16. To obtain the qualitative information on the hydration of dipeptide, the values of Hepler's constant ($\partial^2 V^{o}_{2,\phi}/\partial T^2$) have been calculated and are included in Table 2.

Table 2. Hepler's Constant ($\partial^2 V^o_{2,\phi}/\partial T^2$) and Partial Molar Expansibility E^o_ϕ for Glycyl Dipeptides in Water and 0.05 mol·kg^{-1} Aqueous SDS Solution

	$\partial^2 V^o_{2,\phi}$	E^o_ϕ/cm^3·mol^{-1}·K^{-1}			
	∂T^2	T/K = 298.15	T/K = 303.15	T/K = 308.15 K	T/K = 313.15 K
		Water			
glycylglycine	0.0082	0.0215	0.0625	0.104	0.144
glycylvaline	0.0154	0.0011	0.0781	0.155	0.231
glycylleucine	0.0160	0.0076	0.0876	0.168	0.248
		0.05 mol·kg^{-1} SDS Solution			
glycylglycine	0.0106	0.0687	0.122	0.175	0.228
glycylvaline	0.0114	0.0603	0.117	0.174	0.231
glycylleucine	0.0144	0.0496	0.122	0.194	0.266

Table 3. Standard Partial Molar Volumes of Transfer $\Delta_t V^o$/(cm^3·mol^{-1}) for the Dipeptides from Water to 0.05 mol·kg^{-1} Aqueous SDS Solution at Different Temperatures

	$\Delta_t V^o$/cm^3·mol^{-1}			
	T/K = 298.15	T/K = 303.15	T/K = 308.15	T/K = 313.15
glycylglycine	0.11 ± 0.10	0.18 ± 0.12	0.89 ± 0.13	1.29 ± 0.13
glycylvaline	0.71 ± 0.08	1.04 ± 0.09	1.06 ± 0.08	1.19 ± 0.10
glycylleucine	0.42 ± 0.11	0.57 ± 0.08	0.78 ± 0.12	0.85 ± 0.11

Using the eq 3 the partial molar expansibility E^o_ϕ can be obtained by the relation

$$E^o_\phi = (\partial V^o_{2,\phi}/\partial T)_p = A_2 + 2A_3((T/\mathrm{K}) - 273.15) \quad (4)$$

The results are also given in Table 2. From Table 2, we note that Hepler's constants are positive. According to the criteria proposed by Hepler,[31] the structure-breaking solutes are accompanied by the negative ($\partial^2 V^o_{2,\phi}/\partial T^2$) values. Correspondingly, the positive values of ($\partial^2 V^o_{2,\phi}/\partial T^2$) are associated with the structure-making solutes. In the present investigation, the positive values suggest that the three peptides are structure makers in SDS aqueous solution. The E^o_ϕ values are positive, and the increase with an increase of temperature may be ascribed to the presence of caging effect.[32] On heating, some water molecules may be released from the hydration layers of dipeptides. The E^o_ϕ values in aqueous SDS solution are larger than those in water. It indicated that with the increase of temperature, the ternary solution volume increases a little more rapidly than that of aqueous dipeptide solutions owing to the interaction between the dipeptide and the SDS.

The standard volumes of transfer for the glycyl dipeptides from water to aqueous solutions of SDS were calculated by

$$\Delta_t V^o = V^o_{2,\phi}(\text{in aqueous SDS}) - V^o_{2,\phi}(\text{in water}) \quad (5)$$

where $V^o_{2,\phi}$ (in water) is the standard partial molar volume for the glycyl dipeptides in water. The results are presented in Table 3. As seen from Table 3, $\Delta_t V^o$ values of dipeptides from water to aqueous SDS are positive. The cosphere overlap model[33] can be utilized to rationalize this phenomenon in terms of solute−solvent interactions. The following type of interactions can occur in the ternary system of peptide−SDS−water:[19] (a) ion−ion interactions between the SO_4^{2-}/Na^+ of SDS with the NH_3^+/COO^- group of peptide, respectively; (b) ion−peptide group interactions between ions of SDS and the peptide backbone unit (−CH_2CONH) of dipeptides; (c) ion−nonpolar (hydrophobic) group interactions between ions of SDS and nonpolar groups of the dipeptides or between charged ends of dipeptides and nonpolar groups of SDS; (d) hydrophobic−hydrophobic interactions between the alkyl chain of the SDS and the hydrophobic group of the peptides. Because of the interactions of the ions of SDS with the NH_3^+/COO^- group and the peptide group of peptide, the electrostriction of water molecules lying in the vicinity of these charged centers and polar group of the peptides will be reduced, which gives rise to a positive $\Delta_t V^o$.[19,21] Further the interactions (c) and (d) contribute negatively to $\Delta_t V^o$ due to a structure break to the water structure on the hydrophobic hydration sphere of nonpolar side chains. The presently observed positive $\Delta_t V^o$ values for all of the dipeptides suggest that ion−ion and ion−peptide group interactions are stronger than ion−nonpolar and hydrophobic−hydrophobic group interactions.

Furthermore, it can be seen from Table 3 that although glycylvaline and glycylleucine are more hydrophobic that glycylglycine, their $\Delta_t V^o$ values are generally higher than that of glycylglycine, except for the data at higher temperatures (especially 313.15 K). This suggests that, even for glycylvaline and glycylleucine, the ion−ion interactions between the dipeptides and the SDS dominate over the other interactions. A similar conclusion has been obtained by Singh et al. for some α-amino acids in aqueous SDS solutions.[19]

The specific conductivities κ of SDS in water and (0.02, 0.03, 0.04, 0.05, and 0.06) mol·kg^{-1} aqueous dipeptide solutions are measured at T = (288.15, 293.15, 298.15, 303.15, and 308.15) K. The obtained specific conductivities are listed in Tables S3 to S6 of Supporting Information. For all temperatures, the concentration dependence of the specific conductivity shows a monotonic increase with a gradual decrease in slope (see Figure S1, Supporting Information, taking SDS in 0.02 mol·kg^{-1} glycylglycine solution as an example). The values of critical micellar concentration, cmc, and the degree of counterion dissociation (β) values at each solvent composition were estimated from these plots using the second derivative treatment reported by Aguiar et al.[34,35] The obtained cmc and β values are listed in Table 4. Table 4 shows that the values of cmc and β of SDS at different temperatures in aqueous solution are in good agreement with those reported elsewhere.[36−38]

It is important to mention here that the dipeptides exist mostly in the zwitterionic forms in our studied systems. Some workers[39−41] studied the ionic forms of many amino acids in the aqueous salts of weak acids and strong bases solution (pH ≈ 9) and found that the amino acids exist mostly in the zwitterionic forms and the fraction of the other forms are very small and can be neglected. Because the peptide bond of the peptide does not dissociate, the dissociation of the dipeptide is same as the amino acids. In the conductometric study, since the concentration of SDS is small, the pH of the solution of SDS is about 6 to 7. Following the calculations of literature,[39−41] we found that there is a very small fraction of fully deprotonated dipeptides and there are electrostatic interactions between the peptide and the SDS.

The variation of cmc with temperature is shown in Figure 1. Each plot appears to follow a curve concave downward with a minimum at a certain temperature. Similar observations were reported for aqueous solutions of other surfactants.[42−45] This behavior may be related to two competitive effects. First, an increase in temperature disrupts the water surrounding the

Table 4. Critical Micelle Concentration cmc and Degree of Counterion Dissociation β of SDS in Aqueous Solution in the Presence and Absence of Dipeptides at Different Temperatures

	T/K = 288.15		T/K = 293.15		T/K = 298.15		T/K = 303.15		T/K = 308.15	
m_p	10^3 cmc		10^3 cmc		10^3 cmc		10^3 cmc		10^3 cmc	
mol·kg^{-1}	mol·dm^{-3}	β	mol·dm^{-3}	β	mol·dm^{-3}	β	mol·dm^{-3}	β	mol·dm^{-3}	β
0	8.31 ± 0.03	0.351	8.11 ± 0.04	0.361	8.09 ± 0.04	0.369	8.19 ± 0.03	0.395	8.33 ± 0.03	0.403
	8.14[a]	0.375[a]	8.03[a]	0.395[a]	7.75[a]	0.410[a]	7.50[a]	0.430[a]	7.40[a]	0.467[a]
					8.16[b]	0.39[b]	8.37[b]	0.40[b]		
			8.4[c]		8.1[c]		8.4[c]		8.6[c]	
					Glycylglycine					
0.0200	8.07 ± 0.03	0.337	7.99 ± 0.06	0.374	7.87 ± 0.03	0.388	7.93 ± 0.04	0.406	8.12 ± 0.04	0.410
0.0300	8.02 ± 0.04	0.364	7.90 ± 0.03	0.380	7.85 ± 0.04	0.394	7.89 ± 0.05	0.408	8.08 ± 0.03	0.416
0.0400	7.82 ± 0.05	0.366	7.78 ± 0.04	0.383	7.73 ± 0.04	0.399	7.76 ± 0.05	0.413	7.95 ± 0.04	0.423
0.0500	7.79 ± 0.03	0.371	7.71 ± 0.04	0.388	7.65 ± 0.05	0.405	7.69 ± 0.05	0.416	7.85 ± 0.05	0.431
0.0600	7.61 ± 0.04	0.378	7.55 ± 0.03	0.396	7.52 ± 0.04	0.410	7.61 ± 0.05	0.425	7.75 ± 0.03	0.435
					Glycylvaline					
0.0200	7.89 ± 0.05	0.360	7.79 ± 0.04	0.373	7.76 ± 0.05	0.395	7.80 ± 0.04	0.407	7.90 ± 0.03	0.424
0.0300	7.81 ± 0.02	0.384	7.75 ± 0.03	0.390	7.71 ± 0.05	0.407	7.72 ± 0.04	0.423	7.86 ± 0.04	0.438
0.0400	7.47 ± 0.04	0.391	7.31 ± 0.04	0.407	7.30 ± 0.03	0.415	7.36 ± 0.05	0.429	7.45 ± 0.03	0.440
0.0500	7.30 ± 0.02	0.390	7.26 ± 0.07	0.411	7.15 ± 0.04	0.424	7.16 ± 0.06	0.436	7.26 ± 0.03	0.453
0.0600	7.17 ± 0.03	0.416	7.00 ± 0.04	0.413	6.98 ± 0.05	0.430	7.00 ± 0.03	0.442	7.13 ± 0.05	0.457
					Glycylleucine					
0.0200	7.49 ± 0.02	0.374	7.39 ± 0.03	0.381	7.34 ± 0.06	0.394	7.32 ± 0.06	0.410	7.58 ± 0.08	0.437
0.0300	7.37 ± 0.05	0.391	7.26 ± 0.05	0.410	7.14 ± 0.05	0.429	7.15 ± 0.08	0.440	7.25 ± 0.06	0.455
0.0400	7.12 ± 0.05	0.410	6.96 ± 0.03	0.419	6.88 ± 0.04	0.442	6.85 ± 0.05	0.456	6.94 ± 0.06	0.468
0.0500	6.90 ± 0.06	0.427	6.74 ± 0.06	0.440	6.66 ± 0.07	0.454	6.61 ± 0.06	0.475	6.66 ± 0.08	0.482
0.0600	6.53 ± 0.07	0.437	6.30 ± 0.09	0.451	6.20 ± 0.09	0.461	6.15 ± 0.09	0.476	6.12 ± 0.09	0.484

[a] Ref 36. [b] Ref 37. [c] Ref 38.

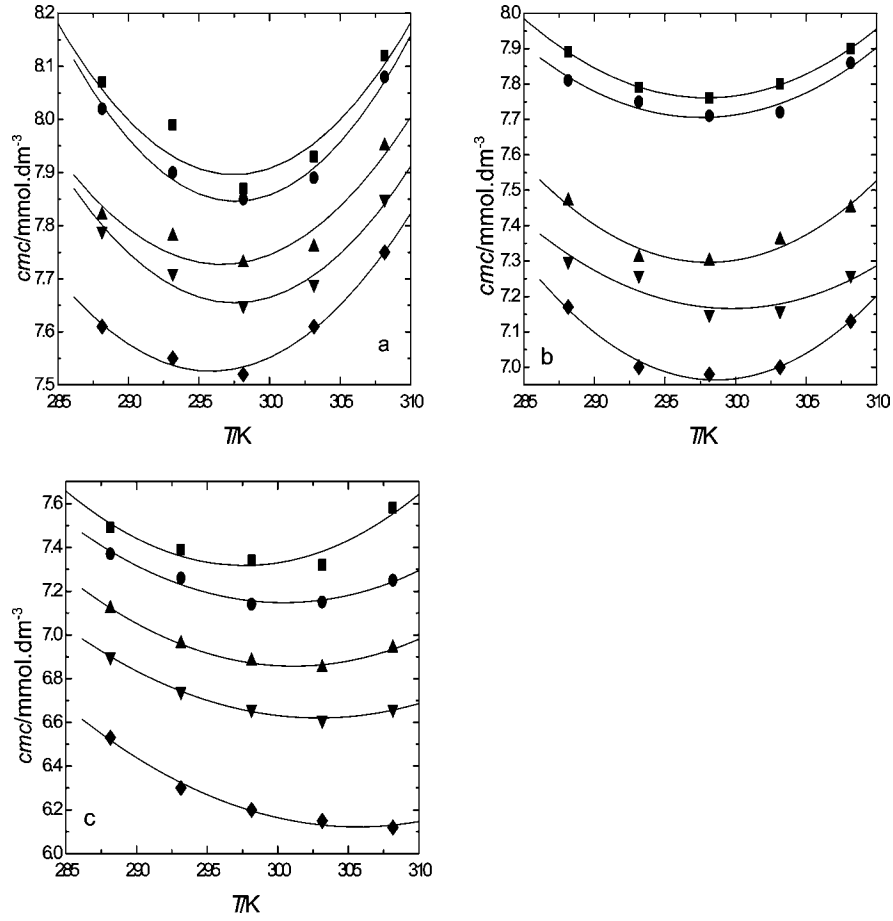

Figure 1. Temperature dependence of the critical micelle concentration of SDS in aqueous glycylglycine (a), glycylvaline (b), and glycylleucine (c) solutions. Symbols indicate dipeptide concentration (mol·kg^{-1}): ■, 0.02; ●, 0.03; ▲, 0.04; ▼, 0.05; ◆, 0.06.

hydration chain, which promotes micelle formation. Second, an increase in temperature also causes a decrease in hydration in the hydrophilic group, and this leads to an increase in repulsion between polar head groups. Thus, the observed minimum reflects the effect of raising the temperature in a balance between these two opposing effects.

As can be seen from Figure 1, the addition of dipeptides decreases the cmc values of SDS at a given temperature. This can be interpreted by the interaction of the dipeptide with SDS. An increase in peptide concentration can cause partial destruction of the hydration shell around the alkyl chain of the SDS monomer. On the other hand, the addition of dipeptide molecules results in decreasing the thickness of the solvation layer around the ionic head of SDS and the electrostatic repulsive interaction between SDS ions. So, the hydrophility of SDS is decreased, that is, its surface activity is enhanced, and its molecules aggregate easily on the surface and in the solution; as a result the value of cmc decreases.

Ionic micelles can bind a considerable amount of counterions. The obtained results in Table 4 show that the degree of counterion binding $(1 - \beta)$ decreases with an increase in the temperature and the concentration of dipeptides. It might be due to the decrease in electrostatic repulsive interaction between SDS ions, which decreases the surface charge density of SDS and will further decrease the counterion association of micelles.

Furthermore, the values in Table 4 show that, in the presence of three dipeptides, the cmc of SDS decreases, whereas the degree of counterion dissociation β increases with the increasing size of alkyl chain length of dipeptides. This observation indicates increased hydrophobicity of the micelle as glycylleucine has a large hydrophobic volume. The similar conclusion has been also obtained for ionic surfactants in different size alkyl chain tetraalkylammonium salt and alcohol solutions.[46,47]

According to the mass action model of micellization, the thermodynamic parameters of micellization for ionic surfactants in aqueous solution can be obtained by using the following relationship:[48]

$$\Delta G_m^o = (2 - \beta)RT \ln X_{cmc} \quad (6)$$

$$\Delta H_m^o = -(2 - \beta)RT^2(\mathrm{d} \ln X_{cmc}/\mathrm{d}T) \quad (7)$$

$$\Delta S_m^o = (\Delta H_m^o - \Delta G_m^o)/T \quad (8)$$

where ΔG_m^o, ΔH_m^o, and ΔS_m^o are the free energy, the enthalpy, and the entropy of micellization and X_{cmc} is the value of cmc expressed in mole fraction.

The values of $\mathrm{d} \ln X_{cmc}/\mathrm{d}T$ were determined by fitting $\ln X_{cmc} \sim T$ with the polynomial function

$$\ln X_{cmc} = a + b(T/\mathrm{K}) + c(T/\mathrm{K})^2 \quad (9)$$

where a, b, and c are respective polynomial constants. Then

$$\mathrm{d} \ln X_{cmc}/\mathrm{d}T = b + 2c(T/\mathrm{K}) \quad (10)$$

The obtained thermodynamic parameters of micellization for SDS in aqueous dipeptide solution are listed in Tables S7 to S9 in the Supporting Information.

From the values of ΔG_m^o in Table S7 (Supporting Information), it can be seen that, in the presence of dipeptides, the free energy of micellization is negative, which indicates that micelle formation is a thermodynamically favorable process. The ΔG_m^o values decrease with the increase of temperature. This suggests that the dehydration of SDS molecules at high temperature is a predominant factor in the formation of a micelle.

The ΔH_m^o values given in Table S8 (Supporting Information) are positive at low temperature and become negative at higher temperatures. A similar change in the sign of ΔH_m^o was observed for a number of ionic surfactants as it usually occurs between (20 and 40) °C.[42] Positive values of ΔH_m^o such as those noted at the lower temperature are generally attributed to the release of structural water from the hydration layers around hydrophobic parts of the micelle. The hydration degree of the alkyl chain should decrease with increasing temperature, so the increase in temperature should lead to a decrease in the endothermic contribution to the values of ΔH_m^o. The negative ΔH_m^o values suggest that the London dispersion interaction is an alternative force contribution for micellization.[49] The values of entropy of micellization ΔS_m^o (Table S9, Supporting Information) are positive and decrease with rising temperature at a constant dipeptide concentration. The positive values of ΔS_m^o indicate overall randomness in the systems due to the release of structured water molecules around hydrocarbon chains. The decrease of the degree of hydration around the alkyl chain of the surfactant due to rising temperature leads to a decrease in the value of ΔS_m^o observed at higher temperatures.

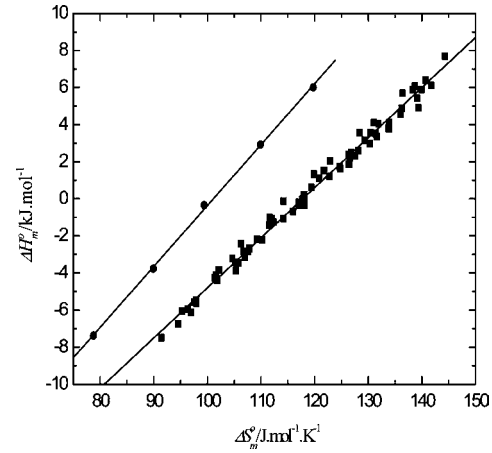

Figure 2. Enthalpy−entropy plot for surfactant SDS: ●, in water; ■, in aqueous dipeptide solution.

From Figure 2, these systems together show a very good straight line between ΔH_m^o and ΔS_m^o with a correlation coefficient of 0.995. In the absence of dipeptide, a similar linear relationship was also obtained in this study with a correlation coefficient of 0.9999. This phenomenon is known as enthalpy−entropy compensation. The relation is expressed as $\Delta H_m^o = \Delta H_m^* + T_c \Delta S_m^o$. The slope T_c is known as the compensation temperature. Our observed values in Figure 2 of (270 and 274) K in the absence and presence of peptides, respectively, are very near to the suggested value of (270 to 300) K for the water system.[50] This implies that the phenomenon of micellization in all of the systems is governed by the same structural property of water. At T_c = (270 and 274) K, the micellization process is totally independent of structural changes in the system and is dependent on enthalpic forces. Note that ΔH_m^* stands for the enthalpy effect under the condition $\Delta S_m^o = 0$. As one can seen from Figure 2, the ΔH_m^* in the presence of dipeptide is lower than that in the absence of dipeptide, which indicates that the addition of dipeptide to SDS solution makes micelles more stable.

The intensity ratio I_1/I_3 of the first (372 nm) and the third (384 nm) vibronic peaks of the pyrene fluorescence spectrum is related to the micropolarity of the microenvironment in which pyrene is solubilized. Therefore, its variation shows a change in hydrophobic environment with respect to composition. Normally, a high value of I_1/I_3 indicates a polar environment, whereas a low value indicates a nonpolar environment. The typical plot of I_1/I_3 ratios of pyrene fluorescence as a function of concentration of SDS in water and aqueous 0.04 mol·kg^{-1} dipeptide solutions are shown in Figure S2 in Supporting Information. With increasing surfactant concentration, the I_1/I_3 ratio experiences an initial flat plateau, then undergoes a sharp decrease, and maintains less change afterward. The I_1/I_3 ratio

in all of the dipeptide solutions is less than that in water. This indicates that the interactions between dipeptide and SDS make the microenvironment of SDS more hydrophobic. The I_1/I_3 ratio for the micelles of SDS in dipeptide solutions decreases in order of I_1/I_3 (glycylleucine) < I_1/I_3 (glycylvaline) < I_1/I_3 (glycylglycine). This suggests more ordering at the interface of the SDS micelles in the presence of peptide with longer alkyl chain. The ordering of the aggregate interface reduces the degree of water penetration in the hydrocarbon layer in accordance with the reduction observed in a decrease of cmc.

Conclusion

In this study, density, conductivity, and fluorescence data for the dipeptide−SDS−water systems were determined at different temperatures. The volumetric studies conclude that the dipeptides act as structure makers in SDS solutions and ion−ion interactions and ion−peptide group interactions are predominate interactions between dipeptide and SDS. The observed minimum of cmc of SDS in aqueous dipeptide solutions versus temperature is the ideal point where the dehydrations of the alkyl chain and the polar head are balanced. The addition of dipeptide in water decreases the cmc values of SDS at a given temperature. The thermodynamic parameters of micellization for SDS at different temperatures have been obtained according to the mass interaction model. The standard enthalpy of micellization is found to be positive at lower temperatures, and it becomes negative at higher temperatures. A positive entropy of micellization was observed. The weak temperature dependence of standard Gibbs free energy of micellization reflects an enthalpy−entropy compensation effect. The decrease in I_1/I_3 ratio of pyrene in SDS solution by the addition of dipeptides indicates that the micelle polarity is affected by dipeptides. The marked reduction in cmc as well as the I_1/I_3 ratio with the increase in size of the alkyl chain length of the dipeptides is probably due to the hydrophobic bonding of these dipeptides with the exposed hydrocarbon on the micelle surface. A longer alkyl chain of peptides is markedly effective in promoting the micellar formation.

Supporting Information Available:

Summary of experimental data, the data of thermodynamic parameters of micellization for SDS, the figures of specific conductivities, and I_1/I_3 ratio versus concentration of SDS. This material is available free of charge via the Internet at http://pubs.acs.org.

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