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Enthalpies of Transfer of Amino Acids from Water to Aqueous Cationic Surfactants Solutions at 298.15 K

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Enthalpies of solution of five amino acids, glycine, *l*-alanine, *l*-valine, *l*-serine, and *l*-threonine in aqueous solutions of three quaternary ammonium surfactants, $[C_nH_{2n+1}(CH_3)_2NCH_2CH_2OH]Br$ ($n = 12, 14, 16$), have been measured at 298.15 K with a microcalorimeter. Enthalpies of transfer of amino acids from water to aqueous surfactant solutions have been derived. It has been observed that, at relatively low concentrations of the surfactant solutions, amino acids are still in the water phase and mainly interact with the hydrophilic head groups of the surfactant molecules. With an increase of the concentration of the surfactant solutions, the microenvironment of amino acids changes, and the molecules might insert into the micelles and interact with the hydrophobic tail groups of the surfactant molecules. The results are discussed in terms of a delicate balance of hydrophobic and hydrophilic interactions and differences in the molecular structure of amino acids.

Introduction

Surfactants are recently attracting increasing interest due to their extensive employment in pharmaceutical and biotechnological processes, as well as their large range of applications including purification, reconstitution, and crystallization of membrane proteins.[1,2] Much attention has been focused on surfactant−protein interactions because they modulate the functional properties of proteins.[3] The interaction of protein with surfactant is not easy to answer owing to the complicated structure of the biological macromolecules.[4] Therefore, amino acids, as model compounds of proteins, are usually investigated for understanding the thermodynamic behavior of proteins, especially in determining functional group contributions to the biopolymer conformational stability.[5,6] Some systems involved different surfactants and amino acids are discussed by using various experimental methods.[1,3,4,7–11]

Enthalpy of transfer of amino acids into different solutions can provide useful information regarding the solute–solvent interaction.[5,12–14] In the present work, we report the enthalpies of transfer of glycine, *l*-alanine, *l*-valine, *l*-serine, and *l*-threonine, from water to aqueous quaternary ammonium surfactant solutions at 298.15 K. The investigated concentrations of these cationic surfactants, $[C_nH_{2n+1}(CH_3)_2NCH_2CH_2OH]Br$ ($n = 12, 14, 16$), are higher than their critical micelle concentrations (CMC). The results derived from this study are mainly to present information about the delicate balance of hydrophobic and hydrophilic interactions in the aqueous surfactant solutions.

Experimental Section

Materials. Five amino acids ($RCH(NH_2)COOH$), glycine ($R = H$), *l*-alanine ($R = CH_3$), *l*-valine ($R = CH(CH_3)_2$), *l*-serine ($R = CH_2OH$), and *l*-threonine($R = CH_2(OH)CH_3$), were biological reagents with mass fraction >99.0 % obtained from Shanghai Chemical Co., China. They were twice recrystallized from aqueous ethanol solution and dried under a vacuum at 348 K for 6 h before use. A homologous series of three quaternary ammonium surfactants, *N*-dodecyl-hydroxyethyl-dimethyl ammonium bromide, *N*-tetradecyl-hydroxyethyl-dimethyl ammonium bromide, and *N*-cetyl-hydroxyethyl-dimethyl ammonium bromide ($[C_nH_{2n+1}(CH_3)_2NCH_2CH_2OH]Br$ ($n = 12, 14, 16$)), were synthesized from the reactions of 1-bromododecane, 1-bromotetradecane, and 1-bromohexadecane with dimethylethanolamine, respectively, in acetone at about 60 °C for 6 h. The crude products were purified by recristallization from the mixed solvents of acetone and methanol. The structures for these surfactants were normally confirmed by elemental analysis, nuclear magnetic resonance spectroscopy, and infrared spectroscopy. NMR spectra were recorded on a Bruker Avance DMX 500 instrument. IR spectra were obtained with a NEXES 470 FT-IR spectrometer. Elemental analysis was obtained by a Calabo EA 1110 elemental analysis instrument. *N*-Dodecyl-hydroxyethyl-dimethyl ammonium bromide: ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 0.84 (t, 3H), 1.22 (m, 18H), 1.51 (m, 2H), 3.43 (t, 2H), 3.46 (s, 6H), 5.07 (s, 1H), 3.47 (t, 2H), 4.12 (m, 2H); IR (KBr) ν 3346, 2916, 2850, 1483, 1418, 1370, 1073, 880, 719 cm^{-1}. Anal. Calcd for $C_{16}H_{36}NOBr$: N, 4.14; C, 56.79; H, 10.72. Found: N, 4.15; C, 56.70; H, 10.75. *N*-Tetradecyl-hydroxyethyl-dimethyl ammonium bromide: ^1H NMR (500 MHz, $CDCl_3$, 298 K) δ 0.88 (t, 3H), 1.26 (m, 22H), 1.56 (m, 2H), 3.47 (t, 2H), 3.48 (s, 6H), 5.07 (s, 1H), 3.49 (t, 2H), 4.13 (m, 2H); IR (KBr) ν 3346, 2916, 2851, 1484, 1419, 1394, 1072, 880, 718 cm^{-1}. Anal. Calcd for $C_{18}H_{40}NOBr$: N, 3.82; C, 59.00; H, 11.00. Found: N, 3.86; C, 59.32; H, 11.22. *N*-Cetyl-

Table 1. Critical Micelle Concentration (CMC) of Surfactants Determined at 298.15 K

surfactant $[C_nH_{2n+1}(CH_3)_2NCH_2CH_2OH]Br$	CMC 10^3 mol·L^{-1}
$n = 12$	13.43
$n = 14$	3.36
$n = 16$	0.84

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Table 2. Enthalpies of Solution ($\Delta_{sol}H_m$) of Amino Acids in Aqueous Solutions of Surfactants, $[C_nH_{2n+1}(CH_3)_2NCH_2CH_2OH]Br$, at 298.15 K

	m_{sur}	$\Delta_{sol}H_m$/kJ·mol^{-1}				
surfactant	10^3 mol·kg^{-1}	glycine	*l*-alanine	*l*-valine	*l*-serine	*l*-threonine
	0	$14.17^a \pm 0.02$	$7.60^a \pm 0.01$	$3.15^a \pm 0.01$	$11.30^a \pm 0.03$	$10.35^a \pm 0.01$
	0	14.20^b	7.67^b	3.12^b	11.49^c	10.33^c
$n = 12$	20.10	13.90 ± 0.01	7.88 ± 0.03	3.53 ± 0.03	11.80 ± 0.05	11.22 ± 0.05
	29.60	13.86 ± 0.01	7.84 ± 0.03	3.20 ± 0.01	11.47 ± 0.02	11.01 ± 0.04
	40.20	13.67 ± 0.04	7.79 ± 0.01	2.75 ± 0.04	11.45 ± 0.02	10.69 ± 0.03
	49.90	14.08 ± 0.01	7.94 ± 0.02	2.69 ± 0.04	11.69 ± 0.04	9.78 ± 0.04
	59.70	14.54 ± 0.03	8.06 ± 0.03	3.48 ± 0.03	11.93 ± 0.05	10.40 ± 0.01
	69.90	14.43 ± 0.03	7.97 ± 0.02	3.97 ± 0.05	11.73 ± 0.04	10.97 ± 0.05
	79.60	14.35 ± 0.01	7.87 ± 0.02	3.87 ± 0.05	11.61 ± 0.03	10.90 ± 0.02
	89.80	14.30 ± 0.04	7.79 ± 0.02	3.75 ± 0.04	11.56 ± 0.01	10.83 ± 0.02
$n = 14$	3.953	13.99 ± 0.02	7.74 ± 0.02	3.38 ± 0.02	11.68 ± 0.03	10.88 ± 0.04
	7.988	13.89 ± 0.03	7.70 ± 0.02	3.13 ± 0.01	11.41 ± 0.01	10.76 ± 0.04
	9.988	13.86 ± 0.03	7.68 ± 0.01	2.80 ± 0.03	11.32 ± 0.01	10.24 ± 0.01
	14.97	14.06 ± 0.01	7.84 ± 0.02	3.51 ± 0.03	11.34 ± 0.01	10.90 ± 0.03
	19.92	14.29 ± 0.01	7.93 ± 0.03	2.59 ± 0.04	11.58 ± 0.02	11.21 ± 0.05
	24.95	14.27 ± 0.03	8.01 ± 0.04	3.78 ± 0.05	11.85 ± 0.04	11.08 ± 0.04
	29.93	14.19 ± 0.01	7.96 ± 0.04	2.58 ± 0.04	11.57 ± 0.03	11.06 ± 0.04
	34.95	13.92 ± 0.01	7.64 ± 0.01	2.67 ± 0.04	11.48 ± 0.01	10.88 ± 0.03
$n = 16$	0.9817	14.02 ± 0.02	7.76 ± 0.02	3.34 ± 0.02	11.57 ± 0.02	10.76 ± 0.03
	1.968	13.93 ± 0.03	7.75 ± 0.01	3.13 ± 0.01	11.51 ± 0.01	10.73 ± 0.02
	2.984	13.85 ± 0.01	7.72 ± 0.01	2.92 ± 0.02	11.39 ± 0.01	10.18 ± 0.01
	3.964	14.17 ± 0.01	7.94 ± 0.03	3.04 ± 0.01	11.52 ± 0.02	10.83 ± 0.03
	4.973	14.38 ± 0.02	7.97 ± 0.03	3.62 ± 0.04	11.54 ± 0.02	10.98 ± 0.03
	5.986	14.33 ± 0.01	7.89 ± 0.03	3.57 ± 0.03	11.62 ± 0.03	10.85 ± 0.04
	6.987	14.31 ± 0.03	7.82 ± 0.02	3.54 ± 0.03	11.61 ± 0.03	10.79 ± 0.02
	7.988	14.24 ± 0.01	7.75 ± 0.01	3.42 ± 0.02	11.52 ± 0.02	10.74 ± 0.01

[a] This work. [b] Ref 16. [c] Ref 17.

hydroxyethyl-dimethyl ammonium bromide: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 0.87 (t, 3H), 1.27 (m, 26H), 1.55 (m, 2H), 3.45 (t, 2H), 3.49 (s, 6H), 5.07 (s, 1H), 3.46 (t, 2H), 4.15 (m, 2H); IR (KBr) ν 3346, 2917, 2853, 1483, 1417, 1384, 1072, 881, 718 cm^{-1}. Anal. Calcd for $C_{20}H_{44}NOBr$: N, 3.55; C, 60.89; H, 11.24. Found: N, 3.52; C, 60.97; H, 11.47. No minimum was observed in the curve of surface tension versus concentration of the aqueous surfactant solution. This behavior is indicative of the absence of organic impurities.[8] The critical micelle concentration (CMC) of each surfactant was determined by the surface tension and conductance methods at (25.00 ± 0.01) °C.[15] The values of CMC for the surfactants are listed in Table 1. All the solutions investigated were prepared freshly with twice-distilled water. The samples were weighed on a Mettler AE 200 balance with a sensitivity of 0.0001 g. The molality of each amino acid solution was contained at 0.1000 mol·kg^{-1} of water.

Microcalorimetric Measurements. The measurements of enthalpies of solution were carried out with an RD496-II microcalorimeter (manufactured by the 2905 factory of the Nuclear Industry Department of China) at 298.15 K as previously described.[14] The calorimeter has a high temperature control accuracy (± 0.001 K) and a high stability (± 0.1 μV for baseline). The mixing vessel of the microcalorimeter is divided into two parts by a drop partition. The partition was first placed into the vessel with a special device. Then the solid was introduced into the lower part and the solvent into the upper part. The lower part of the reference vessel was empty, and the upper part had the same solvent as the sample vessel. The enthalpies of solution were recorded automatically. The calorimeter was calibrated by the solution enthalpy of KCl in water with the mole ratio of 1:500. Each reported enthalpy of solution is based on three replicates.

Results and Discussion

The calorimetric results of the enthalpies of solution, $\Delta_{sol}H_m$, for glycine, *l*-alanine, *l*-valine, *l*-serine, and *l*-threonine in pure water and in aqueous surfactant solutions with different concentrations are presented in Table 2.

It can be found that all of the enthalpies of solution have positive values, which indicates that the solution actions of these amino acids in the aqueous surfactant solutions are endothermic. The values of $\Delta_{sol}H_m$ in pure water are in good agreement with the literature data.[16,17] The enthalpies of transfer, $\Delta_{tr}H_m$, were derived from the difference between the enthalpy of solution of amino acids in surfactant solution, $\Delta_{sol}H_{m(s)}$, and that in pure water, $\Delta_{sol}H_{m(w)}$, respectively.[14]

$$\Delta_{tr}H_m = \Delta_{sol}H_{m(s)} - \Delta_{sol}H_{m(w)} \qquad (1)$$

The variations of $\Delta_{tr}H_m$ of amino acids with the molality of the surfactant solutions, m_{sur}, are shown in Figures 1, 2, and 3.

From Figures 1 to 3, we can find that the change tendency is similar for the transfer enthalpy of each amino acid from water to aqueous surfactant solutions. Moreover, there is no obvious change observed in the values of $\Delta_{tr}H_m$ with the length change of the hydrophobic group of the surfactant. This indicates that the structure of amino acid molecules has a more important effect on the interaction between the amino acid and the surfactant molecules. Since the amino acid molecules have the same charged end groups ($-NH_3^+$, $-COO^-$), the contribution of electrostatic interaction to the solution process should be approximately the same. Therefore, it is the structure interaction of the R$-$ group with the solvent that is responsible for the observed variation trends of $\Delta_{tr}H_m$.

There are three parts and two turning points in the curves of $\Delta_{tr}H_m$ versus m_{sur}. In the first part of the curves, transfer enthalpies decrease with the increase of the surfactant concentration. It is because the amino acid molecule might still be in the water phase and mainly interact with the hydrophilic headgroup of the surfactant molecule, although the concentrations of surfactants have reached the critical micelle concentration. There are a number of studies in the literature which support the idea that the glycine is a net structure breaker due to its highly polar zwitterion portion.[12–14] For this glycine/

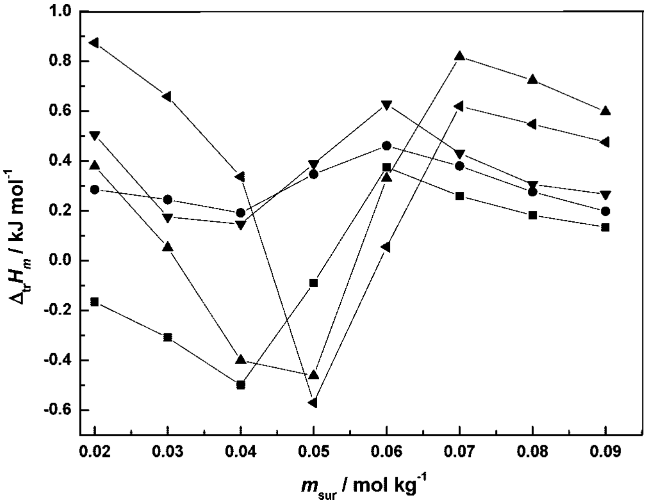

Figure 1. Enthalpies of transfer ($\Delta_{tr}H_m$) of amino acids from water to aqueous solutions of surfactant, $C_{12}H_{25}(CH_3)_2NCH_2CH_2OH]Br$, at 298.15 K: ■, glycine; •, alanine; ▲, valine; ▼, serine; solid triangle pointing left, threonine.

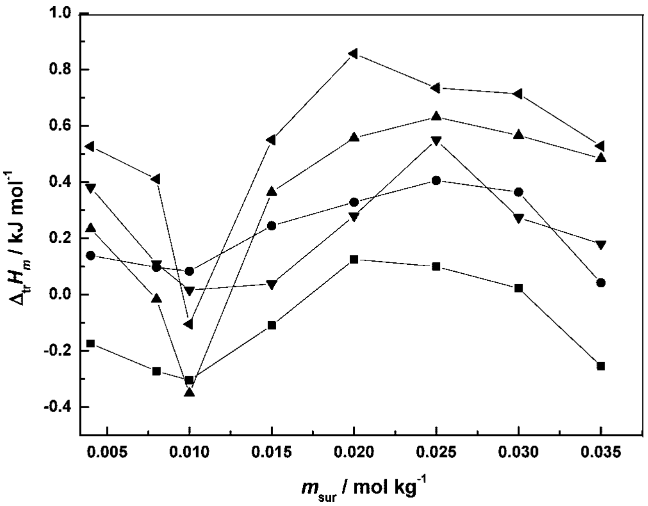

Figure 2. Enthalpies of transfer ($\Delta_{tr}H_m$) of amino acids from water to aqueous solutions of surfactant, $C_{14}H_{29}(CH_3)_2NCH_2CH_2OH]Br$, at 298.15 K: ■, glycine; •, alanine; ▲, valine; ▼, serine; solid triangle pointing left, threonine.

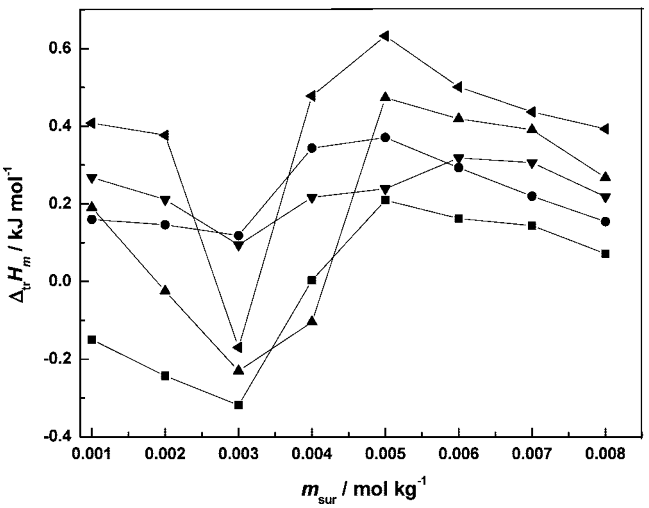

Figure 3. Enthalpies of transfer ($\Delta_{tr}H_m$) of amino acids from water to aqueous solutions of surfactant, $C_{16}H_{34}(CH_3)_2NCH_2CH_2OH]Br$, at 298.15 K: ■, glycine; •, alanine; ▲, valine; ▼, serine; solid triangle pointing left, threonine.

surfactant/H_2O system, there are two main interactions: (1) the ion–ion interactions between the zwitterions of the amino acid molecules and the ion group of the surfactant molecule and (2) the ion−hydrophilic interactions between the zwitterions of the amino acid molecules and the hydrophilic group ($HOCH_2CH_2-$) of the surfactant molecule. They give negative contributions to the transfer enthalpy. As a result, the value of the enthalpy of transfer of glycine from water to surfactant solutions is negative and decreases with the increase of the concentration of the surfactant molecule. For alanine and valine, there are typical hydrophobic groups in their molecules. The interaction between the hydrophobic group of the amino acid molecule and the headgroup of the surfactant molecule causes an endothermic effect and is dominant in the system. The transfer enthalpy, therefore, is positive at low concentrations of the surfactant solutions. In contrast, serine and threonine have hydrophilic groups. The interaction between the hydrophilic group of the amino acid molecule and the headgroup of the surfactant molecule is exothermic. However, the observed transfer of enthalpy is positive. This is because the process of dehydration of the hydrophilic group in the amino acid molecule is endothermic, which is the primary contribution in the aqueous surfactant solutions. With the increase of the concentration of surfactant solution, interactions between the ion headgroup of the surfactant molecule and the polar segment of the amino acid molecule become stronger, and the transfer enthalpies then decrease.

When the concentrations of the surfactant solutions continue to increase and exceed the first turning point, the transfer enthalpy increases. This is because amino acids may insert into the micelles and interact with the hydrophobic tails of the surfactants. According to the hydration cosphere overlap model,[18] the interactions between the hydrocarbon chain of the surfactant molecule and the ion or tail part of the amino acid molecule give a positive contribution to the enthalpy of transfer. The interactions become stronger as the length of the hydrophobic chain of the surfactant molecules increases. As a result, the concentrations corresponding to the minimum points of the curves in Figures 1 to 3 decrease as the number of the ethylene groups of the hydrophobic chain of the surfactant molecules increases. However, with the formation of more and more micelles, the hydrophobic interaction between the ethylene tails of the surfactant molecules becomes stronger. The amino acid molecules have to move to the ion head part of the micelles, and the ion–ion and ion−hydrophilic interactions become important again. The slight decrease of the values of $\Delta_{tr}H_m$ can then be observed in the third part.

Conclusions

The endothermic solution processes of five amino acids, glycine, *l*-alanine, *l*-valine, *l*-serine, and *l*-threonine in aqueous solutions of three cationic surfactants, $[C_nH_{2n+1}(CH_3)_2NCH_2\text{-}CH_2OH]Br$ ($n = 12, 14, 16$), at 298.15 K are observed. The values of the enthalpy of transfer from water to the aqueous surfactant solutions reflect the change of microenvironment of the amino acid molecule. With an increasing concentration of the surfactant molecule, the amino acid molecules first interact with the hydrophilic head groups of the surfactant molecules, then insert into hydrophobic tail groups of the micelles. The effects of the structure of amino acids on the $\Delta_{tr}H_m$ are obviously observed. With the variation of the number of $-CH_2-$ groups in surfactant molecules, the concentrations of minimum points decrease, while there are no appreciable changes observed for the values of $\Delta_{tr}H_m$. The results indicate that an overall balance between ionic−hydrophobic and ionic−hydrophilic or hydrophobic−hydrophilic and hydrophobic−hydrophobic group interactions is maintained in the amino acid−micelle system.

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