Articles

Microcalorimetric Study of the Influence of Alcohols on the Critical Micelle Concentration and Thermodynamic Functions of Nonaqueous Micelle Solutions at 298.15 K

Hong-Lin Zhang,*,[†] Zhe Kong,[†] Yong-Mei Yan,[†] Gan-Zuo Li,[‡] and Li Yu[‡]

College of Chemical Science, Qufu Normal University, Qufu Shandong, 273165, PRC, and Key Lab for Colloid and Interface Chemistry of Shandong University, Jinan, 250100, PRC

The power−time curves of the micellization process were determined for two kinds of anionic surfactants [sodium laurate (SLA) and sodium dodecyl sulfate (SDS)] and a kind of nonaqueous solvent [*N*,*N*-dimethyl formamide (DMF)] with mixed alcohols by titration microcalorimetry. From the data of the lowest point and the area of the power−time curves, the critical micelle concentration (CMC) and ΔH_m^0 were obtained. ΔG_m^0 and ΔS_m^0 were also calculated according to the thermodynamic theory. For different surfactants, cosurfactants, and solvents, the relationships between the alcohol's carbon number, concentration, and CMC and the thermodynamic functions are discussed. For an identical alcohol concentration at the same temperature, the values of CMC, ΔH_m^0, ΔG_m^0, and ΔS_m^0 decrease with an increase in the carbon number of the alcohol. For each alcohol at the same temperature, the CMC and ΔG_m^0 increase, while ΔH_m^0 and ΔS_m^0 decrease with an increase in the alcohol concentration.

1. Introduction

A lot of effort has been put into research on the effect of organic additives (especially alcohols) on the micellization process in aqueous solutions. However, such research in nonaqueous solvents has received only limited attention over the last ten years.[1–7] Besides the theoretical significance of studies of the properties of surfactants under different conditions, research on alcohol influence on critical micelle concentration (CMC) and thermodynamic functions of surfactants in nonaqueous solutions also has some industrial applications.[8–11] For example, some new highly effective pesticides, such as netenpyrem and thiamethoxam cannot be dissolved in water or apolar solvents. They have to be made as dusting or wettable powders which lowers the killing efficiency and also harms the environment. To avoid these problems, it is better to dissolve these materials in polar solvents, which requires a better understanding of the relationships among surfactant, cosurfactant, and polar solvent.

The CMC is an important character of the surfactant solution. Physicochemical properties change negligibly around the CMC. Thus, the CMC is difficult to determine using common methods, such as density, interfacial tension, electrical conductance, or viscosity measurements. However, thermal effects change considerably around the CMC. The power−time curve of the micellization process can be determined by microcalorimetry, and the thermodynamic functions (ΔH_m^0, ΔG_m^0, ΔS_m^0) can be calculated.

The purpose of this work was to study the effects of some long-chain alcohols on the micellization process of sodium dodecyl sulfate (SDS) and sodium laurate (SLA) in *N*,*N*-dimethyl formamide (DMF) solution. These surfactants have been chosen because they are widely used and commercially available. Our work essentially involves the determination of the CMC and the thermodynamic functions such as ΔH_m^0, ΔG_m^0, and ΔS_m^0 by microcalorimetry. In the presence of various long-chain alcohols, the relationships among the CMC, thermodynamic functions, and the alcohol's carbon number and concentration in DMF during the micellization process are discussed. The microcalorimetric study of this aspect has not been previously reported.

2. Experimental

2.1. Instrument. The 2277 thermal activity monitor (Sweden) involves an isothermal thermostat containing 23 L of water that holds up to four independent calorimetric units. A 4 mL stainless steel titration ampule unit is inserted in the thermostats. The titration ampule unit is equipped with a stirrer and a stirrer motor. To rotate the stirrer shaft at the desired speed [(0 to 120) rpm], a kelf turbine is used as the 4 mL ampule is filled with 2 to 3 mL of solution.

2.2. Materials. Solvent: *N*,*N*-dimethyl formamide (DMF) (AR grade, from Tianjin Kermel Chemical Reagents Development Center).

Surfactants: sodium laurate [$CH_3(CH_2)_{10}COONa$ (SLA)]; sodium dodecyl sulfate [$CH_3(CH_2)_{11}SO_4Na$ (SDS)] (AR grade, from Shanghai Chemical Reagents Plant).

Cosurfactants: *n*-heptanol; *n*-octanol; *n*-nonanol; *n*-decanol (AR grade, from Shanghai Chemical Reagents Plant).

Solution (1): 0.005 mol·L^{-1} of surfactant (SLA or SDS) in DMF solution containing cosurfactant, 0.1 mol·L^{-1}, 0.5 mol·L^{-1}, 1.0 mol·L^{-1}, 1.5 mol·L^{-1}, and alcohol (*n*-heptanol, *n*-octanol, *n*-nonanol, or *n*-decanol).

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* Corresponding author. E-mail: zhanghl1946@163.com.

[†] Qufu Normal University.

[‡] Key Lab for Colloid and Interface Chemistry of Shandong University.

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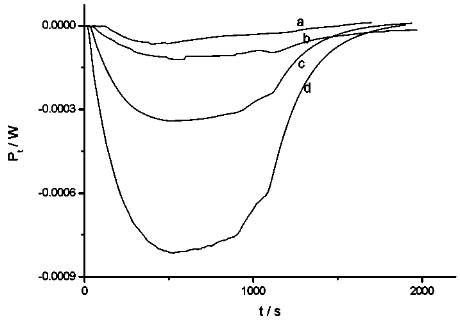

Figure 1. Power−time curves of the micelle formation process for 0.005 mol·L^{-1} of SLA in DMF containing different concentrations of *n*-octanol at 298.15 K. (a) 0.1 mol·L^{-1}; (b) 0.5 mol·L^{-1}; (c) 1.0 mol·L^{-1}; (d) 1.5 mol·L^{-1}.

Table 1. Critical Micelle Concentration (CMC) of SLA and SDS in DMF in the Presence of Different Concentrations of Alcohols at 298.15 K

		10^4 CMC mol·L^{-1}			
surfactant	alcohol	0.1 mol·L^{-1}	0.5 mol·L^{-1}	1.0 mol·L^{-1}	1.5 mol·L^{-1}
SLA	*n*-heptanol	4.22 ± 0.05	5.66 ± 0.05	6.22 ± 0.06	6.44 ± 0.06
	n-octanol	4.00 ± 0.04	5.33 ± 0.06	5.88 ± 0.04	6.11 ± 0.05
	n-nonanol	3.77 ± 0.03	5.00 ± 0.05	5.55 ± 0.05	5.82 ± 0.06
	n-decanol	3.54 ± 0.05	4.66 ± 0.04	5.26 ± 0.06	5.55 ± 0.05
SDS	*n*-heptanol	4.77 ± 0.05	5.66 ± 0.05	6.11 ± 0.06	6.44 ± 0.06
	n-octanol	4.44 ± 0.04	5.22 ± 0.04	5.77 ± 0.05	6.22 ± 0.06
	n-nonanol	3.89 ± 0.06	4.77 ± 0.06	5.55 ± 0.05	5.99 ± 0.05
	n-decanol	3.55 ± 0.05	4.44 ± 0.06	5.22 ± 0.04	5.77 ± 0.06

2.3. Method. In this experiment, the 4 mL stainless steel titration ampule with 2 mL of organic solvent was put into the microcalorimeter. After preheating, a titration tube was used to titrate 0.5 mL of solution (1) into the organic solvent in the ampule. The operator rotated the stirrer shaft at the desired speed of 120 rpm. Meanwhile, the power−time curves were recorded using a data acquisition system. All measurements were carried out three times, and the average values of the power−time curves were obtained at 298.15 K with a deviation of less than ± 1.5 %.

The rate of titration was controlled at 0.02 mL·min^{-1}, and the volume of titrant solution and solvent in the ampule was fixed. Thus, according to response time, the concentration of the system at certain times can be obtained.

3. Results and Discussion

3.1. Determination of Critical Micelle Concentration (CMC). The power−time curves of the micellization process were determined for different systems at 298.15 K. Partial curves are shown in Figure 1.

The CMC can be obtained according to the corresponding concentration at the lowest point of the power−time curves.[12] The CMCs of SLA and SDS in the DMF system containing different concentrations of alcohols at 298.15 K are shown in Table 1.

3.1.1. Relationship between the CMC and the Concentration of Alcohol. The plots of the CMC of SLA or SDS against the concentration of alcohol in DMF at 298.15 K are given in Figure 2. The CMC increases with an increasing concentration of alcohol.

3.1.2. Relationship between the CMC and the Carbon Number of the Alcohol. The CMC values of curves vs the carbon number of the alcohol (n_c) in DMF/long-chain alcohol systems are presented in Figure 3. It can be seen that the CMC of surfactants decreases with an increase in the carbon number of the alcohol.

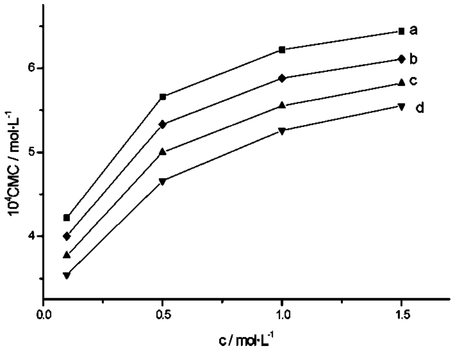

Figure 2. CMC−*c* curves for SLA in DMF in the presence of different alcohols of different concentrations: ■, *n*-heptanol; ◆, *n*-octanol; ▲, *n*-nonanol; ▼, *n*-decanol.

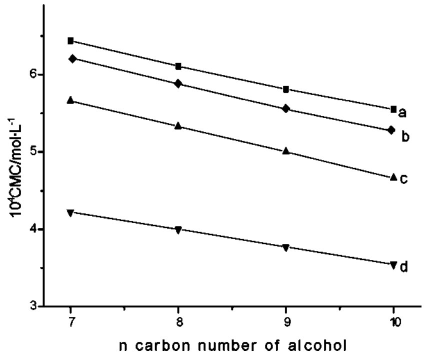

Figure 3. CMC−*n* curves for SLA in DMF in the presence of different concentrations of alcohols. (a) 1.5 mol·L^{-1} of alcohol; (b) 1.0 mol·L^{-1} of alcohol; (c) 0.5 mol·L^{-1} of alcohol; (d) 0.1 mol·L^{-1} of alcohol.

In general, the CMC values increase with an increase in solvent polarity and decrease with an increase in dielectric constant.

For ionic surfactants, the CMC can be deduced from the following equation[13]

$$\log \mathrm{CMC} = Z(1-\alpha)\left[\log \frac{2000\pi\sigma^2}{\epsilon_r RT} - \log c_i\right] + \left[\frac{\Delta G_{(-\mathrm{CH_2}-)}}{2.3RT}\right]n + \text{constant} \quad (1)$$

where Z is the charge of the surfactant ion; α is the fraction of the counterions bound by the micelle in the case of ionic surfactants; σ is the surfactant's charge density on the micelle; ϵ_r is the dielectric constant of the solvent; c_i is the concentration of counterions in the polar solution; $\Delta G_{(-\mathrm{CH_2}-)}$ is the contribution of the hydrophobic group to the free energy change of the micellization process; and n is the carbon number of the surfactant.

Equation 1 predicts the effect of electrolyte and organic additives on the CMC of the ionic surfactants. In these solutions, because the polarity of DMF is stronger than that of alcohols, the increasing concentration of alcohol can decrease the dielectric constant ϵ_r of the solvent. Thus, the CMC of ionic surfactants will increase. Equation 1 also indicates that the CMC will increase with a decrease in the extent of binding of the counterion to the micelle.

The CMC of ionic surfactants will decrease with the length of the alcohol chain in the same concentration. Shirahama and Kashiwabara[10] have attempted to explain the observed CMC decrease in terms of a reduction of the free-energy of the micelle due to a diluted surface charge density on the micelle.

Table 2. $\Delta H_{\mathrm{m}}^{0}$ of the Micellization Process of Ionic Surfactants (SLA and SDS) in DMF in the Presence of Different Concentrations of Alcohols at 298.15 K

		$\Delta H_{\mathrm{m}}^{0}$ (kJ·mol^{-1})			
surfactant	alcohol	0.1 mol·L^{-1}	0.5 mol·L^{-1}	1.0 mol·L^{-1}	1.5 mol·L^{-1}
SLA	*n*-heptanol	−7.11 ± 0.10	−13.07 ± 0.19	−22.83 ± 0.38	−37.27 ± 0.52
	n-octanol	−10.0 ± 0.11	−16.89 ± 0.21	−34.69 ± 0.44	−60.23 ± 0.81
	n-nonanol	−14.59 ± 0.14	−21.20 ± 0.24	−50.45 ± 0.61	−88.44 ± 1.05
	n-decanol	−18.62 ± 0.16	−25.75 ± 0.27	−67.54 ± 0.83	−126.13 ± 1.78
SDS	*n*-heptanol	−7.13 ± 0.11	−13.78 ± 0.13	−31.59 ± 0.32	−65.47 ± 0.86
	n-octanol	−10.36 ± 0.11	−19.16 ± 0.17	−47.14 ± 0.41	−88.42 ± 1.25
	n-nonanol	−14.91 ± 0.15	−27.25 ± 0.32	−63.06 ± 0.89	−116.86 ± 1.51
	n-decanol	−19.72 ± 0.19	−38.96 ± 0.37	−82.38 ± 1.07	−152.51 ± 1.56

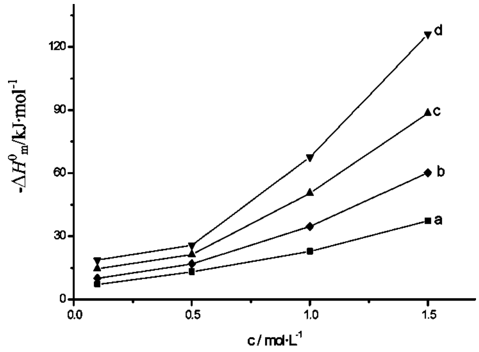

Figure 4. $-\Delta H_{\mathrm{m}}^{0}\sim c$ curves for SDS in DMF and in the presence of different alcohols of different concentrations: ■, *n*-heptanol; ◆, *n*-octanol; ▲, *n*-nonanol; ▼, *n*-decanol.

They were able to present the relationship given by eq 2 that

$$\ln\left[-2.303\cdot\frac{d\log(\mathrm{CMC})}{d\Phi_{\mathrm{a}}}\right]=\Delta G_{\mathrm{tr}}^{0}/RT+1.5 \qquad (2)$$

where Φ_{a} is the mole fraction of the added alcohol at infinite dilution. $\Delta G_{\mathrm{tr}}^{0}$ is defined as

$$\Delta G_{\mathrm{tr}}^{0}=\mu_{\mathrm{a}}^{0}-G_{\mathrm{a}}^{0}=RT\ln\gamma_{\mathrm{a}}^{0} \qquad (3)$$

where μ_{a}^{0} is the standard free energy of the alcohol in the alcohol−water binary mixture; G_{a}^{0} is the standard free energy of the pure alcohol; and γ_{a}^{0} is the activity coefficient of the alcohol in the binary mixture.

The γ_{a}^{0} will increase with an increasing total number of carbon atoms in the alcohol, so that the CMC decreases.

From our results, the overall effect is the decrease of the CMC with the increment of the carbon number of alcohol, because α of the system increases with the increment of carbon number of alcohol, which indicates that the CMC of the anionic surfactant will decrease. With an increase of the concentration of the long-chain alcohol, for the counterions, the extent of binding to the micelle will increase and the CMC will decrease. The above discussions are consistent with the experimental results.

3.2. Measurement of ΔH_{m}^{0}. The power−time curve of the micellization process was determined by titration microcalorimetry. The area of the curve which represents the thermal effect was obtained. The standard enthalpy changes ($\Delta H_{\mathrm{m}}^{0}$) of the micellization process of SLA and SDS in DMF containing different concentrations of alcohols were calculated. The $\Delta H_{\mathrm{m}}^{0}$ data are given in Table 2.

3.2.1. Relationship between ΔH_{m}^{0} and the Concentration of Alcohol. The curves of the enthalpy changes ($\Delta H_{\mathrm{m}}^{0}$) of SLA and SDS in DMF containing alcohol vs the concentrations of alcohol can also be obtained. The curves are shown in Figure 4. As shown in the figure, the $\Delta H_{\mathrm{m}}^{0}$ decreases with an increase in the concentration of alcohol.

3.2.2. Relationship between ΔH_{m}^{0} and the Carbon Number of Alcohol. The plot of the enthalpy change ($\Delta H_{\mathrm{m}}^{0}$) of SLA and SDS in DMF containing different long-chain alcohols against the carbon number of the alcohol can be obtained similar to that described above. The curves are shown in Figure 5. As shown in the figure, the $\Delta H_{\mathrm{m}}^{0}$ of the anionic surfactant decreases with an increase in the carbon number of the alcohol.

3.2.3. Characteristic Rule and Discussion of ΔH_{m}^{0} in the Micellization Process. The micellization process is mainly determined by the hydrophobic action of the surfactant in DMF. Under the condition of identical temperature, an increase in alcohol concentration can cause the hydrophobic action to increase, because the hydrophobic action of a long-chain alcohol is bigger than that of DMF. With an increase in alcohol concentration, the increment of the absolute value of $\Delta H_{\mathrm{m}}^{0}$ is similar to the data given in Table 2.

Table 3. Thermodynamic Functions ($\Delta G_{\mathrm{m}}^{0}$, $\Delta S_{\mathrm{m}}^{0}$) of Anionic Surfactants (SLA and SDS) in DMF in the Presence of Different Concentrations of Alcohols at 298.15 K

surfactant	alcohol		0.1 mol·L^{-1}	0.5 mol·L^{-1}	1.0 mol·L^{-1}	1.5 mol·L^{-1}
SLA	*n*-heptanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−25.61	−24.88	−24.65	−24.56
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	60.48	39.62	6.09	−42.64
	n-octanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−25.74	−25.03	−24.79	−24.69
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	49.46	27.32	−33.25	−119.26
	n-nonanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−25.89	−25.19	−24.93	−24.81
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	37.02	13.38	−85.64	−213.52
	n-decanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−26.04	−25.36	−25.06	−24.93
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	24.89	−1.31	−142.57	−339.59
SDS	*n*-heptanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−25.30	−24.88	−24.69	−24.56
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	60.99	37.24	−23.15	−137.27
	n-octanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−25.84	−25.08	−24.83	−24.65
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	50.74	19.88	−74.86	−214.02
	n-nonanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−25.81	−25.30	−24.93	−24.74
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	36.57	−6.55	−127.97	−309.13
	n-decanol	$\Delta G_{\mathrm{m}}^{0}$ (kJ·mol^{-1})	−26.04	−25.48	−25.08	−24.83
		$\Delta S_{\mathrm{m}}^{0}$ (J·K^{-1}·mol^{-1})	21.20	−45.25	−192.27	−428.46

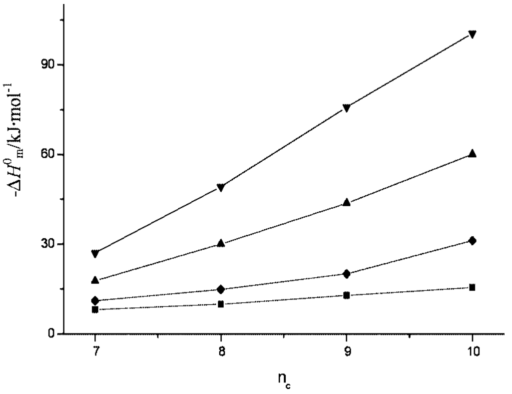

Figure 5. $-\Delta H^0_m - n_c$ curves for SLA in DMF containing alcohols of different carbon number at 298.15 K: ▼, 1.5 mol·L^{-1} of alcohol; ▲, 1.0 mol·L^{-1} of alcohol; ●, 0.5 mol·L^{-1} of alcohol; ■, 0.1 mol·L^{-1} of alcohol.

3.3. Calculation of the Free Energy and Entropy. The thermodynamic functions of the micellization process for SLA and SDS in DMF containing alcohols (*n*-heptanol, *n*-octanol, *n*-nonanol, *n*-decanol) were calculated according to eqs 4and 5.[14]

$$\Delta G^0_m = RT \ln X_{CMC} \tag{4}$$

$$\Delta G^0_m = \Delta H^0_m - T\Delta S^0_m \tag{5}$$

X_{CMC} stands for the mole fraction of surfactant in the solution at the CMC. The values of the thermodynamic functions (ΔG^0_m, ΔS^0_m) are shown in Table 3.

ΔG^0_m of the anionic surfactant decreases with an increase in the carbon number of the alcohol and increases with an increase in the concentration of the alcohol in DMF. ΔS^0_m of the anionic surfactant decreases with an increase in the concentration of the alcohol and the carbon number of the alcohol in DMF.

The variation of the CMC can also be explained according to the changes in the thermodynamic functions. For aqueous solution systems of anionic surfactants, data[15] indicate that the negative values of ΔG^0_m (about (-20 to -30) kJ·mol^{-1}) are mainly ascribed to the large positive value of ΔS^0_m ($T\Delta S^0_m$ about (29 to 49) kJ·mol^{-1}). The value of ΔH^0_m (about (2.0 to 6.0) kJ·mol^{-1}) is much smaller than that of $T\Delta S^0_m$. Therefore the micellization process in an aqueous solution is governed by the entropy. Conversely, for DMF/long-chain alcohol systems, the data (see Tables 23) indicate that the negative values of ΔG^0_m (about (-24 to -26) kJ·mol^{-1}) are minor due to the small values of ΔS^0_m (about (60 to -430) J·K^{-1}·mol^{-1}), and the value of $T\Delta S^0_m$ (about (18 to -128) kJ·mol^{-1}) is larger than the value of ΔH^0_m (about (-7 to -153) kJ·mol^{-1}). This shows that for the micellization process in the DMF/long-chain alcohol systems at the beginning the entropy is the driving force and then the enthalpy is the driving force with the increase of the concentration and the carbon number of the alcohol. There exists a tendency for the hydrophobic group of the surfactant to transfer from the solvent environment to the interior of the micelle.

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