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ORIGINAL ARTICLE

Study on the Synthesis and Surface Active Properties of a Novel Surfactant with Triple Quaternary Ammonium Groups and Triple Dodecyl Chains Derived from Glycerin

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Abstract The new triple chain surfactant was firstly prepared by ring-opening and a quaternization reaction with 2-(chloromethyl)-oxirane, tertiary amine and propane-1,2,3-triol as starting materials. The surfactant was characterized by MS and elementary analysis. Air–Liquid surface tension was measured by using a tensiometer at temperatures from 298 to 318 K respectively and in various salt solutions (NaX). The results show that with the increase of temperature, the values of critical micelle concentration (cmc) can achieve a minimum at 308 K. The maximum surface adsorption capacity Γ decreases, while the minimum molecule $A_{\min}$ area increases. With the increase in temperature and the decrease in counterionic diameter, the values of cmc decrease from 8.09×10^{-5} to 5.52×10^{-5} mol/L, and the adsorption capacity Γ increase from 1.80×10^{-10} to 2.74×10^{-10} mol/m^2, while there are almost no influences to surface tension (γ_{cmc}). The free energy of micelle formation is negative (−85.2 to −92.0 kJ/mol).

Keywords Triple-chain surfactant · Synthesis · Surface active properties · Thermodynamic properties

Introduction

In the past decade, new types of surfactants consisting of two hydrophobic and two hydrophilic groups connected by a flexible or rigid spacer chain in a molecule, called dimeric or gemini surfactants, have attracted considerable interests [1–16], because of their unique physicochemical properties such as lower critical micelle concentration (cmc), higher efficiency in reducing surface tension and better wetting ability than conventional monomeric surfactants [1, 17–19]. It has been shown that the cmc values of the gemini surfactants decrease unexpectedly when the number of carbon atoms in the hydrophobic chain exceeds a certain number, and this behavior is caused by the formation of small non-surface-active premicellar soluble aggregates [2, 3, 8–13]. Similarly it is chemically possible to combine conventional monomeric surfactant molecules to form trimeric surfactants, which may have some special properties different from the monomeric and gemini surfactants. However, studies on trimeric surfactants are just at the beginning [19–24] and only a few trimeric surfactants have been reported [25–28]. In this paper we report the synthesis and the adsorption and micellization properties of a so-called III-12-4 trimeric surfactant, and how the properties were affected by temperature and electrolytes. Saturated adsorption, critical micelle concentration, minimum surface tension achievable, as well as some thermodynamic parameters such as standard free energy, enthalpy and entropy of micellization were obtained.

Experimental Procedures

Materials

N,*N*-dimethyldodecan-1-amine of industrial grade (98% purity) from FeiXiang Chemicals China, and 2-(chloromethyl)oxirane and propane-1,2,3-triol of analytical grade from Sinopharm Chemical Reagent China were used as received. Sodium fluoride, sodium chloride and sodium

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bromide of analytical grade from Sinopharm Chemical Reagent China were heated at 773 K for 5 h before use. Other chemicals used were all analytical grade. Double distilled water was used throughout the experiments.

Synthetic Procedure

The synthesis of the III-12-4 surfactant is a two-step process as shown in Scheme 1. In the first step an intermediate (**1a**) was formed by the reaction of propane-1,2,3-triol with 2-(chloromethyl)oxirane, and in the second step the intermediate was converted to target compound (**1b**) by quaternization with *N*,*N*-dimethyldodecan-1-amine.

To form the intermediate 2-(chloromethyl)oxirane was added dropwise into a mixture of propane-1,2,3-triol with 19.2% NaOH aqueous solutions at 50–60 °C and reacted for 8 h, with the molar ratio of the reactants kept at *n*(propane-1,2,3-triol):*n*(2-(chloromethyl)oxirane):*n*(NaOH) = 1:3:3 and the NaCl produced was eliminated by extraction with 1-butanol. Then the intermediate, together with the hydrogen chloride, was dropped into *N*,*N*-dimethyldodecan-1-amine at 80 °C and reacted for 45 h to form the target compound (**2a**). The mole ratio of the reactants was controlled at *n*(**1a**):*n*(*N*,*N*-dimethyldodecan-1-amine):*n*(HCl) = 1:3:3 and it was crucial that the dropping velocity of the hydrogen chloride should be controlled at approximately 1/6 of that of the intermediate. The target product as white powders was obtained after the final product was washed with petroleum ether and 1-butanol and recrystallized three times from 2-propanone followed by drying in a vacuum.

Measurements of Surface Tension

The surface tension of the surfactant solutions with various electrolytes was measured using a DCA tensiometer (Thermo Cahn, America) at 298.0 ± 0.1, 303.0 ± 0.1, 308.0 ± 0.1, and 313.0 ± 0.1 K respectively. The surface tension of pure water was measured to be 72.0 mN/m at 298.0 K.

Results and Discussion

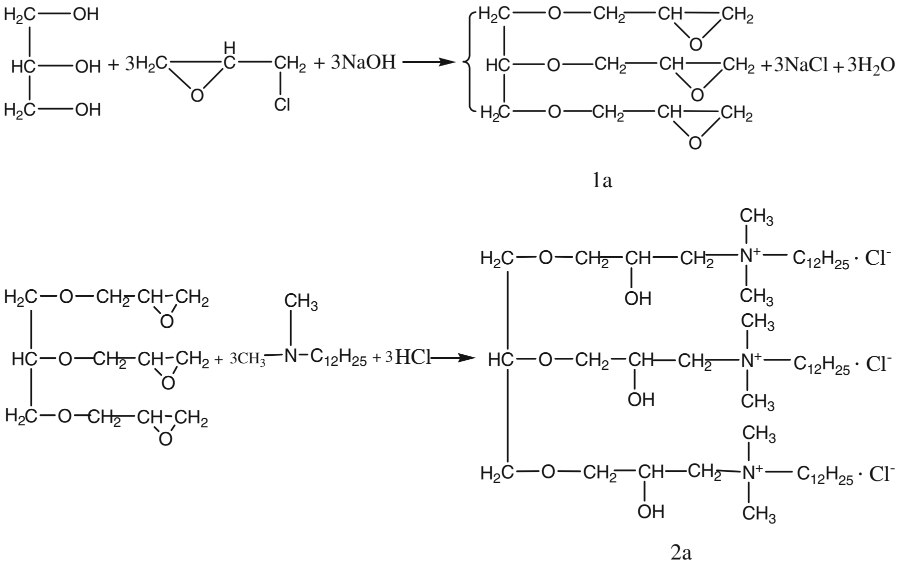
Structural Assessment of the Target Compound

To confirm the structure of the synthesized target compound, elemental analysis was carried out using MS and the mass spectrum was measured using elementary analysis. The contents of C, H, and N in the target compound are found to be 64.65, 11.22 and 4.08%, respectively, which are very close to the theoretical contents of the three elements, or 64.26, 11.50 and 4.16%. The mass spectrum of the target compound is shown in Fig. 1a, which indicates that there is no whole molecular ion peak, but three main fragment ion peaks, i.e., $m/z = 214$, 242 and 463.5. The probable structures of the fragments are shown in Fig. 1b [29].

Surface Chemical Properties of III-12-4 in the Presence of Different Counterions

In general the critical micelle concentration (cmc) and the surface tension at cmc (γ_{cmc}), which is usually taken as the minimum surface tension achievable by a surfactant, are the most important parameters to characterize the surface activity of a surfactant [30]. For conventional ionic surfactants, surface activity is usually enhanced, i.e. both cmc and γ_{cmc} decreased, with the addition of electrolytes containing the counterion of the surfactants. The reason is that the electrostatic repulsion between surfactant ions in a

Scheme 1



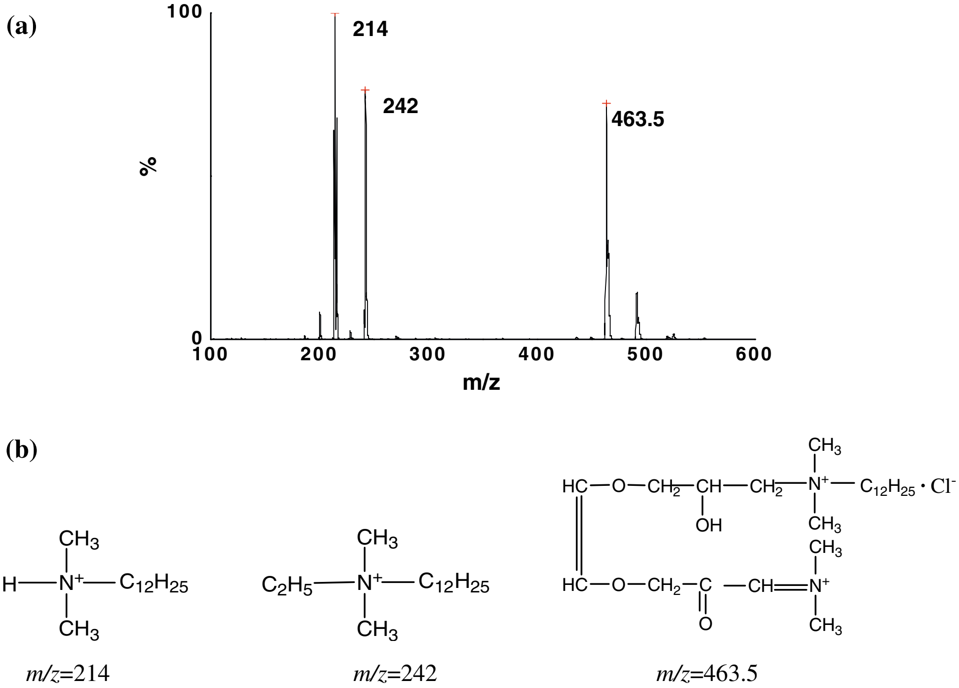


Fig. 1 **a** Mass spectrum of III-12-4. **b** Structures of the main fragments formed in mass spectrum measurement

monolayer or a micelle is weakened due to the presence of large amount of counterions, which greatly compressed the electrical double layer, and as a result monolayers can be arranged more compact and micelles are easier to form [30].

The γ-log c curves of III-12-4 solutions in the presence of 0.10 mol/L different electrolytes at various temperatures were shown in Fig. 2. The data show that for III12-4, similar electrolyte effects were observed, i.e. in the presence of 0.1 mol/L NaF, NaCl or NaBr, both the cmc and γ_{cmc} of the III-12-4 greatly decreased. However, there exist second-order differences between the electrolytes, that is the smaller the radius of the counterions, the stronger the effect, probably because the counterions of smaller radius have larger charge density and thus have stronger bonding tendency to oppositely charged monolayers or micelles. The less counterionic radius, the more the radius of hydrated canon are, and the less the shielding effect on polar groups of III-12-4 is [30].

Surface Chemical Properties of III-12-4 at Different Temperatures [30, 31]

According to the Gibbs adsorption equation

$$- \mathrm{d}\gamma = nRT\Gamma d \ln C \tag{1}$$

the maximum or saturated adsorption $\Gamma_{\max}$ of a surfactant in the presence of excess counterions ($n = 1$) is given by

$$\Gamma_{\max} = \frac{-1}{2.303RT}\left(\frac{\partial \gamma}{\partial \lg C}\right)_{T,\max} \tag{2}$$

and the minimum molecular area $A_{\min}$ in monolayer can be calculated by following equation

$$A_{\min} = \frac{1}{N_{\mathrm{A}}\,\Gamma_{\max}} \times 10^{14}\left(\mathrm{nm}^2\right) \tag{3}$$

where N_{A} is the Avogadro constant. The calculated $\Gamma_{\max}$ and $A_{\min}$ from Fig. 2, together with the cmc, γ_{cmc}, and pC_{20} values obtained from Fig. 2 are listed in Table 1, where C_{20} is the concentration required to reduce the surface tension of pure water by 20 mN/m and pC_{20} is the negative logarithm of C_{20}. As shown in Table 1, the cmc value of III-12-4 changes with temperature and a minimum cmc is achieved at 308 K, no matter whether excess electrolyte is added or not. It is known that with the increase of temperature, the hydration of hydrophilic groups weakens, which is propitious to the formation of micelles. On the other hand, the increase of temperature also causes destruction of the structure formed by the water molecules around hydrophobic groups of surfactant molecules, which goes against formation of micelles. Thus a minimum cmc can be achieved, usually at 303–308 K. Obviously in micelle formation III-12-4 behaves similar to the conventional ionic surfactants. However, the effect of temperature on γ_{cmc} is very small, which may relate to the special structure of III-12-4 or the molecular chains that are hard to bend due to the huge dimension of molecules.

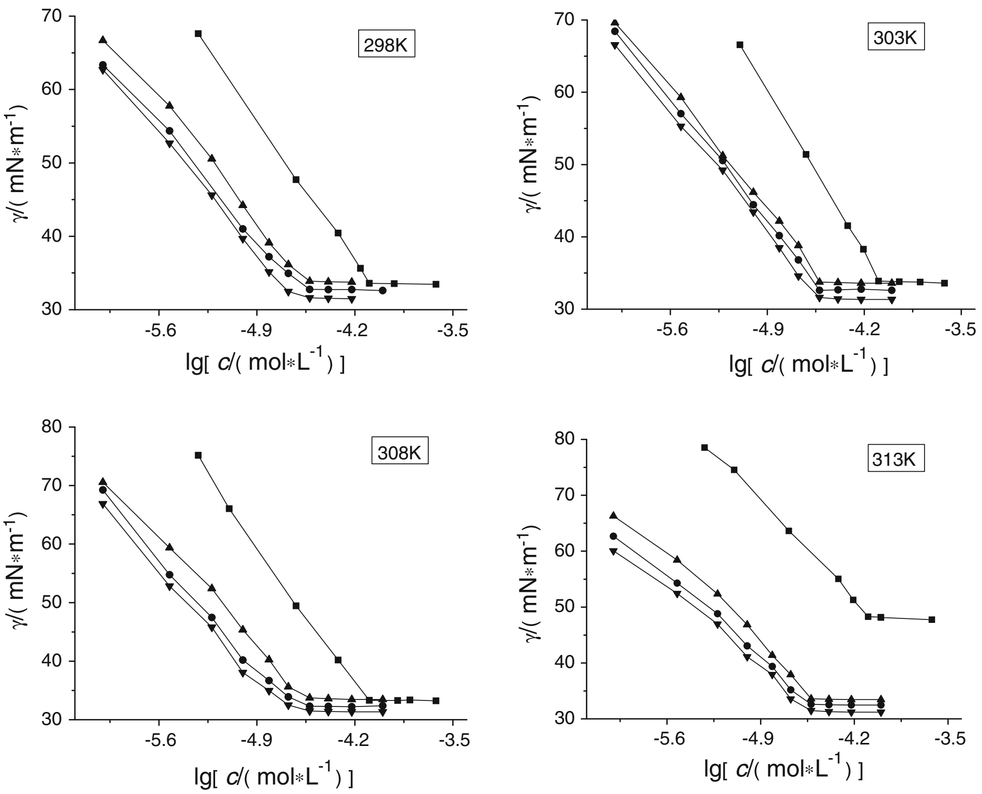


Fig. 2 The γ-log c curves of III-12-4 aqueous solutions at various temperatures in the presence of 0.10 mol/L electrolytes: *inverted filled triangles* NaF, *filled circles* NaCl, *filled triangles* NaBr, *filled squares* nothing

Table 1 Surface chemical properties of III-12-4 in 0.10 mol/L NaX

NaX	T (K)	10^5 cmc (mol/L)	γ_{cmc} (mN/m)	10^{10} Γ_{max} (mol/m^2)	A_{min} (nm^2)	pC_{20} (mol/L)	cmc/C_{20}
–	298	15.01	34.89	1.84	0.90	4.630	6.403
	303	13.87	34.20	1.53	1.09	4.637	6.013
	308	12.70	33.92	1.45	1.15	4.651	5.686
	313	14.99	33.68	1.37	1.91	4.762	8.666
NaF	298	7.94	34.87	2.74	0.61	5.016	8.238
	303	6.78	34.73	2.03	0.82	5.069	7.947
	308	5.52	33.72	1.95	0.86	5.166	8.090
	313	7.92	33.59	1.87	0.89	5.204	12.67
NaCl	298	8.01	34.85	2.72	0.61	5.015	8.291
	303	6.81	34.55	2.02	0.82	5.063	7.873
	308	5.55	33.74	1.94	0.86	5.163	8.078
	313	8.01	33.58	1.83	0.91	5.203	12.78
NaBr	298	8.09	34.81	2.69	0.62	5.014	8.355
	303	6.93	34.23	1.96	0.85	5.059	7.938
	308	5.56	33.46	1.93	0.86	5.161	8.055
	313	8.03	33.24	1.80	0.92	5.201	12.76

Table 1 also indicates that with or without excess electrolyte, the maximum adsorption of III-12-4 decreases with increasing temperature. The main reason is that the adsorption of surfactant molecules is affected by not only the electric exclusion between the polar groups, but also the thermal motion of the molecules in the monolayer. Increasing temperature boosts up thermal motion of molecules, and the distance between molecules in monolayer therefore increases and the adsorption decreases [32].

Table 2 Thermodynamic parameters of micellization of III-12-4 in the presence of 0.10 mol/L NaX

NaX	T (K)	10^5 cmc (mol/L)	ΔG_{m} (kJ/mol)	ΔH_{m} (kJ/mol)	ΔS_{m} (kJ/mol K)	−T ΔS (kJ/mol)
	298	15.01	−79.11	−1.192	0.2667	−77.92
	303	13.87	−81.23	−1.212	0.2641	−80.02
	308	12.70	−83.48	−1.332	0.2615	−82.15
	313	14.99	−83.11	−1.395	0.2611	−81.71
NaF	298	7.94	−85.42	−1.455	0.2937	−83.97
	303	6.78	−88.45	−1.506	0.2869	−86.94
	308	5.52	−92.01	−1.557	0.2818	−90.46
	313	7.92	−89.75	−1.605	0.2816	−88.03
NaCl	298	8.01	−85.34	−1.452	0.2868	−83.88
	303	6.81	−88.40	−1.493	0.2835	−86.91
	308	5.55	−91.96	−1.555	0.2815	−90.40
	313	8.01	−89.63	−1.602	0.2812	−88.03
NaBr	298	8.09	−85.24	−1.450	0.2935	−83.79
	303	6.93	−88.23	−1.488	0.2863	−86.74
	308	5.56	−91.94	−1.552	0.2812	−90.39
	313	8.03	−89.61	−1.599	0.2812	−88.01

Thermodynamic Parameters of Micellization of III-12-4 in Aqueous Solutions

For trimerionic surfactants, the thermodynamic parameters of micellization, such as free energy ($\Delta G^{\mathrm{o}}_{\mathrm{m}}$), enthalpy ($\Delta H^{\mathrm{o}}_{\mathrm{m}}$), and entropy ($\Delta S^{\mathrm{o}}_{\mathrm{m}}$), in the presence of excess electrolytes can be calculated from following equations [30, 31, 33, 34]:

$$\Delta G \approx RT\{[1+(i/j)K_0]\ln \mathrm{cmc} + (i/j)K_0 \ln (i/j)\} \qquad (4)$$

for trimerionic surfactants, $i/j = 3$; in the presence of excess electrolytes, $K_0 = 1$.

$$\Delta H^0_{\mathrm{m}} = -T^2\partial \frac{\left(\Delta G^0_{\mathrm{m}}/T\right)}{\partial T} = -4RT^2 \frac{\partial \ln \mathrm{cmc}}{\partial T} \qquad (5)$$

$$\Delta S^0_{\mathrm{m}} = \frac{1}{T}\left(\Delta H^0_{\mathrm{m}} - \Delta G^0_{\mathrm{m}}\right) \qquad (6)$$

As shown in Table 2, the values of ΔG_{m} and ΔH_{m} are all negative at various temperature, indicating that the formation of micelle is spontaneous and exothermal. And the entropy of micellization (ΔS_{m}) reflects the changes of disorder due to the formation of micelle. The values of ΔS_{m} are all positive, which means that surfactant molecules are easy to join into micelles. The reason is that in aqueous solution, water molecules can form an ordered area called the "iceberg model" around surfactant molecules. With the formation of micelles, the iceberg model around surfactant molecules collapses, and disordered degree of the system enhances.

The value of ΔG_{m} increases with the counterionic radius growth. It indicates that the spontaneity in the process of micellization weakens. The important reason is that the structure of III-12-4 is huge, the negativity of counterions weakens gradually, and the interaction with surfactants weakens, which go against the formation of micelles. The value of ΔS_{m} decreases with the increase of temperature. Therefore, the micelle formation process of this system is a thermodynamically spontaneous process driven by the entropy [35].

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