

Synthesis and Properties of Novel Alkyl Sulfonate Gemini Surfactants

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Abstract A series of novel dialkyl disulfonate gemini surfactants ($2C_n$ -SCT where n is the carbon number of the hydrophobic chain) were synthesized from cyanuric chloride, aliphatic amine and taurine. The chemical structures of the prepared compounds were confirmed by 1H NMR, ^{13}C NMR, IR spectra, and ESI-MS. Their critical micelle concentrations (CMC) in the aqueous solutions at 25 °C were determined by surface tension and electrical conductivity methods. With the increasing length of the carbon chain, the values of their CMC initially decreased, and then increased with an alkyl chain length of 14. The surface tension measurements of $2C_n$ -SCT (except for $n = 14$) determined that there is a low CMC, a great efficiency in lowering the surface tension, and a strong adsorption at the air–water interface. In addition, adsorption and micellization behavior of $2C_n$ -SCT were estimated from pC_{20} , the minimum average area per surfactant molecule (A_{min}), and standard free energy micellization and adsorption (ΔG_{mic}° and ΔG_{ads}°). These properties are significantly influenced by the chain length n , and the adsorption is promoted more than the micellization.

Keywords Gemini surfactants · Synthesis · Surface tension · Electrical conductivity

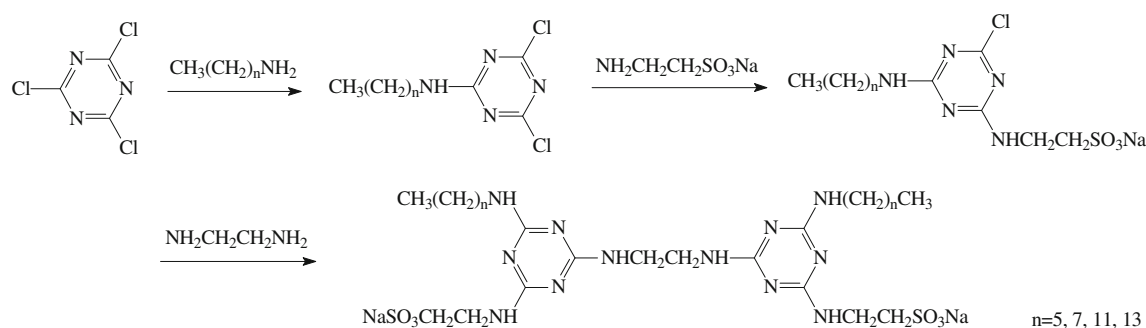
Introduction

Gemini surfactants represent a class of surfactants made up of two amphiphilic moieties connected at the level of, or very close to, the head groups by a spacer group [1]. The current interest in such surfactants arises from three essential properties [1, 2]. First, their CMC values are generally one to two orders of magnitude lower than for the corresponding conventional (monomeric) surfactants. Secondly, they are more efficient than the corresponding conventional surfactants in decreasing the surface tension of water. Thirdly, aqueous solutions of some gemini surfactants with short spacers can have a very high viscosity even at a relatively low surfactant concentration, whereas the viscosity of the corresponding monomeric surfactant solution is always low.

Most reports on cationic gemini surfactants focus on quaternary ammonium gemini surfactants. There are relatively few reports concerning anionic gemini surfactants [3–6]. There is not enough data to establish the relationship between the structures of anionic gemini surfactants and their properties [6]. Thus, it is also important to synthesize novel anionic gemini surfactants with different structures and study their properties.

In this paper, we synthesized novel dialkyl disulfonate gemini surfactants $2C_n$ -SCT by three-step reactions, and investigated their surface properties by measuring the surface tension (γ_{cmc}), critical micelle concentrations (CMC), the minimum average area per surfactant molecule (A_{min}), and then calculated the standard free energy of micellization and adsorption (ΔG_{mic}° , ΔG_{ads}°). In addition, we discussed the effect of the chain length on the properties. The gemini surfactants possess a novel structure, as shown in Scheme 1. The design makes use of a well-established idea, that is, triazine works as a linkage which

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Scheme 1 Synthesis of the C_n -SCT and $2C_n$ -SCT

links the hydrophilic head group, the hydrophobic tail and a spacer group. The three chlorines of the cyanuric chloride react with $-NH_2$ step by step at high yield, so the reaction is quite simple [7, 8].

Experimental

Materials and Equipment

2-Aliphatic amino-4,6-dichloro-1,3,5-triazine (CT) was prepared as in previous work [9]. Taurine (ex Johnson Matthey Corporation), ethylenediamine, acetone, heptane, ethanol, sodium carbonate, hydrochloric acid (all from the third reagent plant, Tianjin) were of analytical grade. Doubly distilled water was used to prepare the solutions in all experiments.

The solution surface tensions were measured by using a K12 automatic tensiometer (Krüss Corporation, Germany) using the du Nouy ring method. The conductivity of the surfactant solutions was measured by using a low-frequency conductivity analyzer (Model DDS-307, Shanghai Precision & Scientific Instrument Corporation). Bruker ARX400 NMR Spectrometer (Bruker BioSpin Corporation, Switzerland), FTIR-8400S Spectrometer (Shimadzu Corporation, Japan), Vario EL Spectrometer (Elementer Corporation, Germany), and Bruker Apex IV FTMS (Bruker BioSpin Corporation, Switzerland) were used to identify the structures and purities of the compounds.

Synthesis

The four surfactants were synthesized in just three steps following Scheme 1.

Synthesis of 2-Aliphaticamino-4,6-Dichloro-1,3,5-Triazine (CT)

2-Aliphaticamino-4,6-dichloro-1,3,5-triazine (CT) was prepared in our lab by a reaction of cyanuric chloride with

aliphatic amine, and recrystallized twice from heptane for purification.

Synthesis of Sodium 2-(4-Chloro-6-(Alkylamino)-1,3,5-Triazine-2-ylamino) Ethane Sulfonate (C_n -SCT)

According to the literature [10], this class of monomeric surfactants C_n -SCT was synthesized by mixing an aqueous solution of 0.1 mol of taurine and 150 mL acetone solution of 0.11 mol of CT. The temperature was maintained at 45 °C and pH = 8, by adding 10% Na_2CO_3 . The process was monitored by TLC on silica gel plates and eluent system acetone: toluene: water = 6:1:0.5 (by volume). When the reaction was completed, the mixture was concentrated in vacuo, refrigerated and precipitated, then filtered. The filter cake was washed three times with acetone. The white solid was collected.

The structures and purities of prepared surfactants were confirmed by 1H -NMR, IR spectrum and Elementary Analysis. Table 1 shows the results. When the carbon number of hydrocarbon chains are 6, 8, 12 and 14, the monomeric surfactants are represented by C_6 -SCT, C_8 -SCT, C_{12} -SCT and C_{14} -SCT, respectively.

Synthesis of Sodium 2,2'-(6,6'-(Ethane-1,2-Diylbis(azanediyl) bis (4-(Alkylamino) -1,3,5-Triazine -6,2-diyl)) bis (azanediyl))diethane Sulfonate ($2C_n$ -SCT)

An aqueous solution of 0.055 mol of ethylenediamine was added to 100 mL of an aqueous solution of 0.1 mol of C_n -SCT. The temperature was maintained at 90 °C and pH = 8, by adding 10% Na_2CO_3 . The process was monitored by TLC on silica gel plates and eluent system methanol: toluene = 6:1 (by vol). When the reaction was completed, the mixture was cooled to room temperature and acidified to pH = 2 by addition of concentrated HCl. The resulting precipitate was filtered, washed with water (to remove unreacted ethylenediamine and inorganic salts), and neutralized with sodium hydroxide solution. A clear aqueous solution was obtained, and this was concentrated

Table 1 The assignment of ^1H -NMR, IR spectra and the element analysis results of $\text{C}_n\text{-SCT}$

Compound (yield)	^1H NMR (400 MHz, DMSO) δ/ppm	IR (KBr) ν/cm^{-1}	Elementary analysis (found/calculated)/%		
			C	H	N
$\text{C}_6\text{-SCT}$ (85%)	0.83 ~ 0.86(t,3H), 1.25(s,6H), 1.46(s,2H), 2.63 ~ 2.67(m,2H), 3.15 ~ 3.25(s,2H), 3.45 ~ 3.49(m,2H), 6.10(s,1H), 6.50(s,1H)	3,386, 3,261, 2,930, 2,857, 1,635, 1,573, 1,438, 1,199, 1,049, 798, 725	36.47/ 36.72	5.28/ 5.33	19.05/ 19.47
$\text{C}_8\text{-SCT}$ (82%)	0.82 ~ 0.84(t,3H), 1.23(s,10H), 1.44(s,2H), 2.62 ~ 2.66(m,2H), 3.15 ~ 3.26(s,2H) 3.45 ~ 3.49(m,2H), 6.10(s,1H), 6.50(s,1H)	3,386, 3,259, 2,923, 2,854, 1,635, 1,573, 1,438, 1,199, 1,049, 798, 725	39.87/ 40.26	5.91/ 5.98	17.69/ 18.06
$\text{C}_{12}\text{-SCT}$ (81%)	0.82 ~ 0.86(t,3H), 1.22(s,18H), 1.44(s,2H), 2.62 ~ 2.64(m,2H), 3.15 ~ 3.24(s,2H), 3.45 ~ 3.49(m,2H), 6.10(s,1H), 6.50(s,1H)	3,249, 3,386, 2,920, 2,850, 1,620, 1,573, 1,435, 1,199, 1,049, 798, 725	45.64/ 45.99	6.99/ 7.04	15.52/ 15.77
$\text{C}_{14}\text{-SCT}$ (78%)	0.82 ~ 0.84(t,3H), 1.22(s,22H), 1.44(s,2H), 2.62 ~ 2.64(m,2H), 3.15 ~ 3.24(s,2H), 3.45 ~ 3.47(m,2H), 6.10(s,1H), 6.60(s,1H)	3,249, 3,386, 2,920, 2,851, 1,632, 1,573, 1,438, 1,199, 1,049, 798, 725	48.01/ 48.35	7.42/ 7.47	14.61/ 14.84

in vacuo and refrigerated to obtain the solid products. The products were recrystallized twice from ethanol and kept for use.

The structures and purities of prepared surfactants were confirmed by ^1H NMR, ^{13}C NMR, IR spectra and ESI-MS. Table 2 shows the results. When the carbon number of hydrocarbon chains are 6, 8, 12 and 14, the surfactants are referred to as $2\text{C}_6\text{-SCT}$, $2\text{C}_8\text{-SCT}$, $2\text{C}_{12}\text{-SCT}$ and $2\text{C}_{14}\text{-SCT}$, respectively.

Surface Tension Measurements

CMC values were determined by the surface-tension method. Measurements were taken until constant surface tension values indicated that equilibrium with an experimental error within 0.2 mN/m had been reached. For the four gemini surfactants, the surface tensions of their aqueous

solutions were measured at 25 °C. The curves of surface tension versus log of surfactant concentrations ($\gamma \sim \log C$) were plotted and their CMC values were determined from the break points. At the same time the surface tensions corresponding to CMC, γ_{cmc} , were also obtained on the curves of $\gamma \sim \log C$.

Conductivity Measurement

CMC values were also determined using the electrical conductivity method. Conductivity of the surfactant solutions was measured as a function of concentration with by using a low-frequency conductivity analyzer at 25 °C, and the measurement was repeated twice. The error of electrical conductivity value is $\pm 0.2 \mu\text{S}/\text{cm}$. The CMC was determined as the concentration at the intersection of the liner portions of the plots.

Table 2 The assignment of ^1H NMR, ^{13}C NMR, IR spectra and ESI-MS results of $2\text{C}_n\text{-SCT}$

Compound (yield)	^1H NMR (400 MHz, DMSO) δ/ppm	^{13}C NMR (400 MHz, DMSO) δ/ppm	IR (KBr) ν/cm^{-1}	ESI-MS (positive) m/z
$2\text{C}_6\text{-SCT}$ (64%)	0.84 ~ 0.86(t,6H), 1.25(s,12H), 1.44(s,4H), 2.63(m,4H), 3.14(s,4H) 3.18 ~ 3.37(m,4H), 3.47(m,4H), 6.27 ~ 6.52 (s,6H)	14.08(q), 22.25(t), 26.29(t), 29.46(t), 31.24(t), 36.86(t), 50.78(t), 165.48(s), 165.73(s)	3,399, 2,927, 2,856, 1,576, 1,522, 1,448, 1,184, 1,050, 752	707.28229 [M + H] ⁺
$2\text{C}_8\text{-SCT}$ (67%)	0.83 ~ 0.85(t,6H), 1.24(s,20H), 1.44(s,4H), 2.63(m,4H), 3.13(s,4H), 3.18 ~ 3.35(m,4H), 3.46(m,4H), 6.26 ~ 6.51 (s,6H)	14.09(q), 22.23(t), 26.63(t), 28.87(t), 29.48(t), 31.39(t), 36.86(t), 50.75(t), 165.48(s), 165.77(s)	3,412, 2,925, 2,853, 1,576, 1,517, 1,448, 1,192, 1,051, 752	763.34352 [M + H] ⁺
$2\text{C}_{12}\text{-SCT}$ (73%)	0.83 ~ 0.86(t,6H), 1.23(s,36H), 1.43(s,4H), 2.61(m,4H), 3.12(s,4H), 3.19 ~ 3.36(s,4H) 3.46(m,4H), 6.26 ~ 6.50(s,6H)	14.08(q), 22.23(t), 26.64(t), 28.87(t), 29.05(t), 29.49(t), 31.44(t), 36.85(t), 50.77(t), 165.47(s), 165.70(s)	3,408, 2,919, 2,851, 1,582, 1,521, 1,452, 1,186, 1,051, 755	875.46772 [M + H] ⁺
$2\text{C}_{14}\text{-SCT}$ (90%)	0.83 ~ 0.86(t,6H), 1.23(s,44H), 1.42(s,4H), 2.60(m,4H), 3.12(s,4H), 3.20 ~ 3.35(s,4H) 3.45(m,4H), 6.26 ~ 6.50(s,6H)	14.05(q), 22.24(t), 26.67(t), 28.88(t), 29.08(t), 29.51(t), 31.46(t), 36.83(t), 50.78(t), 165.48(s), 165.69(s)	3,400, 2,917, 2,850, 1,577, 1,513, 1,468, 1,185, 1,050, 753	931.53022 [M + H] ⁺

Result and Discussion

Critical Micellar Concentration (CMC) and Surface Tension (γ_{cmc})

The surface tensions of aqueous solutions of gemini surfactants $2C_n$ -SCT were measured at 25 °C. The results of surface tension measurements are shown in Fig. 1. The surface tensions decrease with increasing concentrations and then reach clear break points, which are taken as CMC.

The maximum surface excess, Γ_{max} , at the air–water interface was calculated by applying the Gibbs adsorption isotherm equation [11],

$$\Gamma_{\text{max}} = -\frac{1}{2.303nRT} \left(\frac{d\gamma}{d \log C} \right)_T \quad (1)$$

where γ is the equilibrium surface tension in mN m^{-1} , Γ_{max} is the saturation adsorbed amount in $\text{mol}/1,000 \text{ m}^2$, R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the absolute temperature, C is the surfactant concentration, and $(d\gamma/d \log C)$ is the slope in the surface tension isotherm when the concentration is near the CMC. The value of n is taken as three for a dimeric surfactant made up of a divalent surfactant ion and two univalent counterions in the absence of a swamping electrolyte. In order to extract the minimum surface area occupied by a surfactant molecule, A_{min} (nm^2), at the air–water interface when the surface adsorption was saturated, Eq. 2 was used,

$$A_{\text{min}} = \frac{10^{14}}{N_A \Gamma_{\text{max}}} \quad (2)$$

where N_A is Avogadro's number. When Γ_{max} is in mol cm^{-2} , A_{min} is in nm^2 .

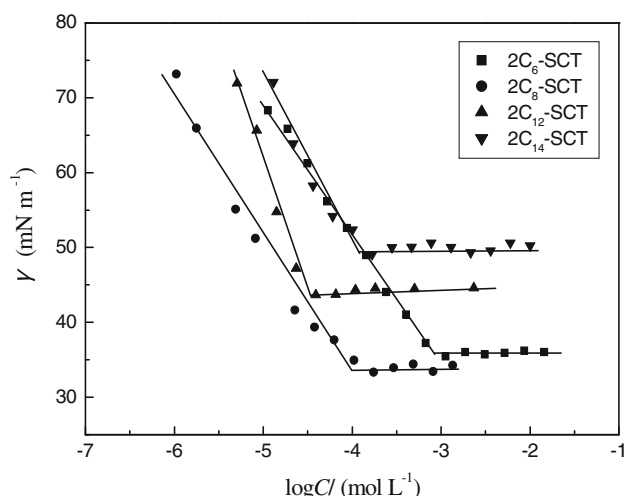


Fig. 1 Evaluation of the CMC values of $2C_n$ -SCT solutions by means of a surface-tension method

Table 3 lists the values of the CMC, γ_{cmc} , pC_{20} , Γ_{max} , A_{min} of $2C_n$ -SCT, along with the data of corresponding monomeric surfactants C_n -SCT [10] and sodium dodecyl sulfate (SDS) [11]. These results indicate that the CMC values of gemini surfactants $2C_8$ -SCT and $2C_{12}$ -SCT are about one or two orders of magnitude lower than those of the corresponding monomeric surfactants. The low CMC values of dimeric surfactants with respect to the corresponding conventional surfactants arise mainly because two alkyl chains, rather than one, are transferred at a time to the water in the micelle pseudo-phase [12], whereas the gemini surfactant $2C_{14}$ -SCT gives higher CMC and inferior efficiency in reducing the surface tension than the corresponding monomeric surfactant C_{14} -SCT.

The CMC of the conventional ionic surfactant is known to decrease with increasing number of carbon atoms in the hydrophobic groups up to about a hexadecyl group [6]. In this work, the CMC of $2C_n$ -SCT decrease from 8.92×10^{-4} to $3.34 \times 10^{-5} \text{ mol L}^{-1}$ with increasing the hydrocarbon chain from 6 to 12, which is similar to those common surfactants in a homologous series. However, when the carbon number is up to 14, the CMC increases from 3.34×10^{-5} to $1.32 \times 10^{-4} \text{ mol L}^{-1}$.

It may be resulted from the conformation of the surfactants at the interface or the curling of the two hydrophobic chain during dissolution. The formation of the micelle is the joint result of the hydrophobic effect and intermolecular force between surfactants. On the view of the conformation of $2C_n$ -SCT, two hydrophobic carbon chains are not parallel due to the presence of several nitrogen atoms in their structures. The interaction, such as curling, between the hydrophobic carbon chains of the two surfactants may hinder the formation of the micelle. This interaction appears be stronger when the carbon number is 14, thus $2C_{14}$ -SCT gives higher CMC.

The γ_{cmc} of $2C_8$ -SCT is lower than that of the corresponding monomeric surfactant C_8 -SCT. This shows that the gemini surfactant adsorbs strongly at the air–water interface, and orients itself so as to cause effective surface activity. The increase in the hydrophobic chain length from 12 to 14 renders them slight less surface active, probably due to a strong cohesion by two long hydrocarbon chains [6].

Efficiency (pC_{20}) and Minimum Surface Area (A_{min})

The efficiency can be characterized by the value of logarithm of the surfactant concentration C_{20} at which the surface tension of water is reduced by 20 mN m^{-1} . The pC_{20} ($-\log C_{20}$) value measures the efficiency of adsorption of surfactant at the air–water interface; the larger the value of pC_{20} , the greater the tendency of the surfactant to adsorb

Table 3 Surfactant data for the eight surfactants solution at 25 °C

Surfactant	CMC/(mmol L ⁻¹)	$\gamma_{\text{cmc}}/(\text{mN m}^{-1})$	pC ₂₀	$\Gamma_{\text{max}}/(10^{-10} \text{ mol cm}^{-2})$	$A_{\text{min}}/(\text{nm}^2)$	Reference
2C ₆ -SCT	0.892	35.64	3.99	1.02	1.63	This paper
2C ₈ -SCT	0.0842	33.57	5.04	1.11	1.50	This paper
2C ₁₂ -SCT	0.0334	43.87	4.72	1.97	0.84	This paper
2C ₁₄ -SCT	0.132	49.39	3.98	1.16	1.44	This paper
C ₈ -SCT	6.19	39.21	2.81	1.89	0.88	[10]
C ₁₂ -SCT	0.177	38.48	4.37	1.94	0.86	[10]
C ₁₄ -SCT	0.0358	32.53	5.01	3.07	0.54	[10]
SDS	8.2	32.5	2.5	3.16	0.53	[11]

at the air–water interface, relative to its tendency to form micelles, and the more efficiently it reduces the surface tension [11]. The values of pC₂₀ of 2C_n-SCT are also listed in Table 3. The values of pC₂₀ of 2C_n-SCT decrease with increasing hydrocarbon chain length from 8 to 14. This result suggests that the longer the hydrocarbon chains of the anionic gemini surfactants, the weaker the adsorption at the air–water interface. Compared with the corresponding monomeric surfactants and SDS, the values of pC₂₀ of

2C_n-SCT with the n of 6–12 are much larger. This indicates that the anionic gemini surfactants are superior in their efficiency at reducing surface tension.

The minimum surface area (A_{min}) is the surface area demand per molecule on the air–water interface. Both Γ_{max} and A_{min} values are listed in Table 3. The A_{min} values of 2C_n-SCT decrease with increasing hydrocarbon chain length from 8 to 12, and then increase when the carbon number is up to 14. This result suggests that the gemini

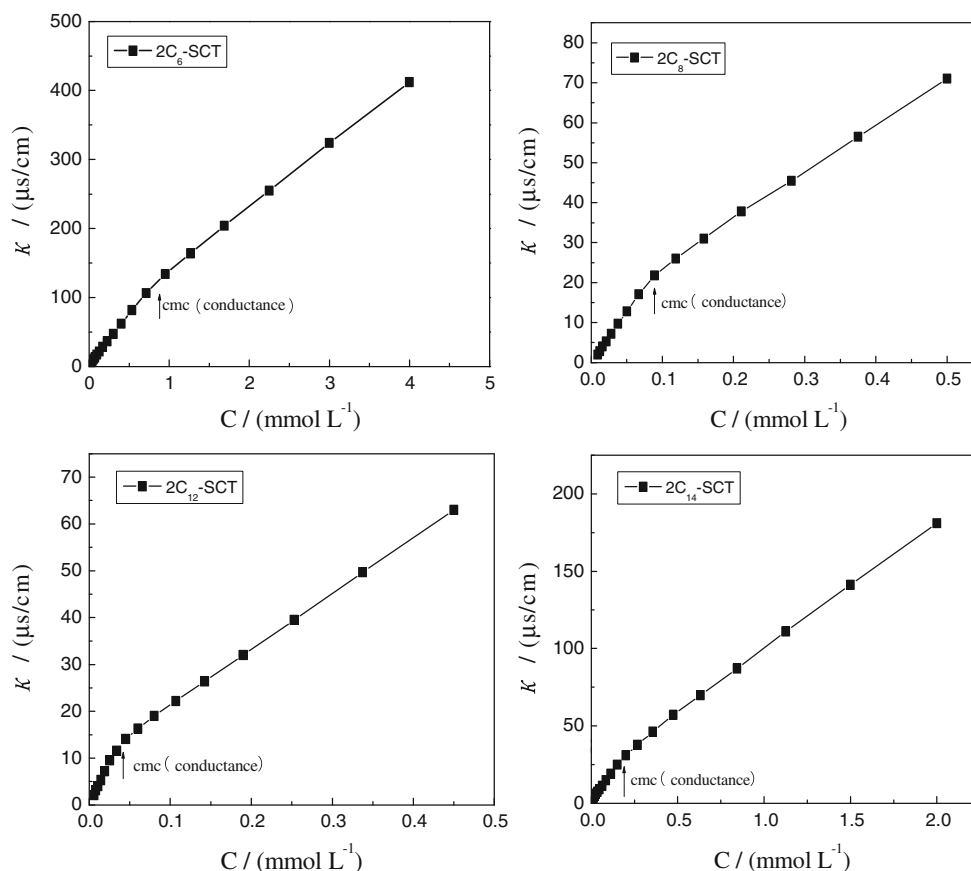
**Fig. 2** Electrical conductivity against molality of 2C_n-SCT at 25 °C

Table 4 Standard free energy of micellization and adsorption of 2C_n-SCT

Surfactant	CMC/ (mmol L ⁻¹)	α	$\Delta G_{\text{mic}}^{\circ}$ / (kJ·mol ⁻¹)	$\Delta G_{\text{ads}}^{\circ}$ / (kJ·mol ⁻¹)
2C ₆ -SCT	0.906	0.61	-23.64	-59.29
2C ₈ -SCT	0.0892	0.45	-33.77	-68.39
2C ₁₂ -SCT	0.0399	0.40	-37.53	-51.81
2C ₁₄ -SCT	0.148	0.52	-30.35	-49.84

surfactant 2C₁₄-SCT packs loosely at the air–water interface. A possible explanation is that the longer hydrophobic chains are more prone to bend and thus make the A_{min} value larger [14].

Degree of Counterion Binding to Micelles (β)

In order to study the aggregation behavior of 2C_n-SCT in aqueous solutions, the electrical conductivity (κ) of these solutions was measured. The changes in κ as a function of concentration are shown in Fig. 2. The CMC of 2C_n-SCT estimated from electrical conductivity plots are listed in Table 4. It can be seen that the values of CMC measured from electrical conductivity at 25 °C are in agreement with those obtained from surface tension. The degree of ionization of the micelle (α) can be obtained from the ratio of the slopes of the linear segments above and below CMC from conductivity versus molality plots. The values of α are listed in Table 4. According to α values, we can obtain β ($\beta = 1 - \alpha$) values of 0.39, 0.55, 0.60, and 0.48 for 2C₆-SCT, 2C₈-SCT, 2C₁₂-SCT and 2C₁₄-SCT, respectively.

Standard Free Energy of Micellization and Adsorption ($\Delta G_{\text{mic}}^{\circ}$ and $\Delta G_{\text{ads}}^{\circ}$)

The standard free energy of micellization, $\Delta G_{\text{mic}}^{\circ}$, for ionic Gemini surfactants can be calculated by using the equation proposed by Zana [12]

$$\Delta G_{\text{mic}}^{\circ} = RT(1/2 + \beta) \ln c_{\text{mc}} - (RT/2) \ln 2. \quad (3)$$

When the CMC is less than 10⁻² mol L⁻¹, $\Delta G_{\text{mic}}^{\circ}$ can be approximated without a significant error by Eq. 4

$$\Delta G_{\text{mic}}^{\circ} = RT(1/2 + \beta) \ln(c_{\text{mc}}/55.3) - (RT/2) \ln 2. \quad (4)$$

The standard free energy of adsorption, $\Delta G_{\text{ads}}^{\circ}$, at the air–water interface is calculated by Eq. 5 [13]

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{mic}}^{\circ} - \pi_{\text{cmc}}/\Gamma_{\text{cmc}} \quad (5)$$

where π_{cmc} represents the surface pressure at the CMC ($\pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}}$, γ_0 and γ_{cmc} represent the surface tension of water and the surfactant solution at the CMC, respectively).

The values of $\Delta G_{\text{mic}}^{\circ}$ and $\Delta G_{\text{ads}}^{\circ}$ of the anionic gemini surfactants 2C_n-SCT with n of 6–14 are listed in Table 4. The negative values of $\Delta G_{\text{mic}}^{\circ}$ and $\Delta G_{\text{ads}}^{\circ}$ mean that the anionic gemini surfactants have great ability to form micelles in solution and to adsorb at the air–water interface. The values of $\Delta G_{\text{mic}}^{\circ}$ are also smaller than the values of $\Delta G_{\text{ads}}^{\circ}$ in all the series, indicating that the adsorption is promoted more than the micellization. This result is supported by the values of large pC₂₀ as described above. In addition, the values of $\Delta G_{\text{mic}}^{\circ}$ (except for n = 14) increase with increasing hydrocarbon chain length of the gemini surfactants, suggesting that a driving force of micellization is derived from the hydrophobic moieties due to the interaction between hydrocarbon tails.

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