ESR Studies on the Micellization Behaviors of a Series of Novel Asymmetric Gemini Surfactants

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The synthesis of a new series of asymmetric cationic gemini surfactant and the investigation of their micellization behaviors by electronic spin resonance (ESR) as well as the surface tension measurements were reported. 4-Oxo-2,2,6,6-tetramethylpiperidine-*N*-oxyl (4-oxo-TEMPO) is used as the spin probe. The surfactants studied have the general formula $[C_nH_{2n+1}N^+(CH_3)_2C_6H_{12}N^+(CH_3)_2C_mH_{2m+1}]Br_2^-$, referred to as dimeric *n*-6-*m* surfactants, in which *n* and *m* are the numbers of carbon atoms in the asymmetric side alkyl chains. From the experimental data, rotational correlation time τ_c, surface tension and critical micelle concentration (cmc) values, the physical properties of these new surfactants have preliminarily been evaluated. It is shown that this new series of asymmetric gemini surfactants has interesting micellization behaviors, and they are very different in aggregating tendency from their asymmetric analogues.

Keywords gemini surfactants, ESR, micellization

Introduction

In recent years, bis(quaternary ammonium) surfactants or gemini surfactants, in which two cationic surfactant moieties are connected with the ammonium head group by a ploymethylene chain, namely, a spacer have become of interest due to their exceptional surface activity and remarkably promising utility in skin care, construction of high-porosity materials, analytical separations, solubilization processes, *etc*.. Hence, the studies for this type of gemini surfactants on the aggregating behavior in aqueous solution, microstructure of the aggregates and behavior at the air-water interface, have been taken out extensively.[1-6] Especially, some new classes of amphiphilic gemini surfactants as vehicles for gene delivery have been reported[7] and the possibility as a ideal vector of DNA has been explored.

However, most of the studies for this kind of cationic gemini compounds focus on the surfactants with symmetrical structures which are referred to as *m*-*s*-*m*, in which *m* and *s* denote the number of the carbon atoms in the symmetrical alkyl chains and the spacer alkyl chain, respectively. The general chemical formulas of symmetrical and unsymmetrical gemini surfactant were investigated in this work (Fig. 1). Studies on the preparation and properties of quaternary ammonium gemini surfactants with unsymmetrical hydrocarbon substitution have also been reported, but are uncommon. Oda and co-workers[8,9] have reported the synthesis of a series of unsymmetrical surfactants and the effect of the dissymmetric extent of the surfactant molecules on their self-assembled behaviors in aqueous solutions. Their synthesis proceeded with *N*,*N*,*N*′,*N*′-tetramethylethylenediamine and proper alkyl bromides as starting reactants. Thus the spacer alkyl chain of the prepared gemini surfactants was of two carbon atoms.

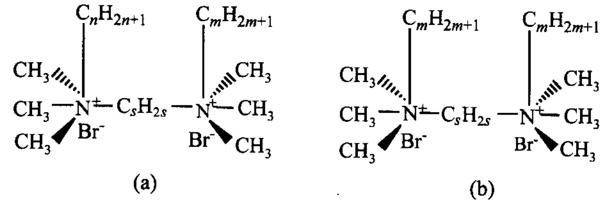

Fig. 1 General chemical formulas of symmetric and asymmetric gemini surfactants: (a) C_m-C_6-C_n, (b) C_m-C_6-C_m.

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A new series of dissymmetric gemini compounds with spacer length longer than two carbon atoms has been synthesized using much different synthetic methods. The physical properties of the newly prepared surfactants were preliminarily evaluated by ESR and surface tension measurements.

Experiment

Materials

All reagents used were purchased from Aldrich with the exception of some amines (dimethylamine, *N*, *N*-dimethylhexylamine, *N*, *N*-dimethyloctylamine and dimethyldecylamine were from Fluka Ltd.) and the spin probe, 4-oxo-TEMPO (4-oxo-2,2,6,6-tetramethylpiperidine-*N*-oxyl) were purchased from Sigma. All the solvents were of commercially available reagents. UHQ water was used for all experiments.

Synthesis of asymmetric gemini surfactants

The asymmetric gemini surfactants, C_{18}-C_6-C_6, C_{16}-C_6-C_8 and C_{14}-C_6-C_{10} were prepared in two-step shown as the following schemes:

$$C_mH_{2m+1}N(CH_3)_2 + BrC_6H_{12}Br \longrightarrow [C_mH_{2m+1}N(CH_3)_2C_6H_{12}Br]^+Br^-$$

$$C_nH_{2n+1}N(CH_3)_2 + [C_mH_{2m+1}N(CH_3)_2C_6H_{12}Br]^+Br^- \longrightarrow C_n\text{-}C_6\text{-}C_m$$

Acetone was an optimal medium for the quaternization reactions and the dialkylated product precipitated from solution, while the monoalkylated compounds and the reactants remained insolution. Furthermore, it was impossible for the possible side product, the symmetric dialkylated salts, to occur in the final product. Because all starting materials used to synthesize the asymmetric gemini surfactants were very easily dissolved in acetone at room temperature, the repeated recrystalizations were enough to guarantee the purity of the final products. It is especially noticeable that trace remnants of dibromohexane in the mono-ammonium salts could result in the significant impurities in the final asymmetric gemini products. Ethyl ether was used as the solvent to extract the dibromohexane remnants from the mono-ammonium salt aqueous solution, as mentioned above, and it was found that at least 7 times of extracting were needed, for the most cases, to remove the dibromohexane from the systems completely. The structures of the synthesized compounds were confirmed by the spectral and elemental analysis data. Proton NMR spectra were obtained using a Bruker AC-200F NMR spectrometer, and $CDCl_3$ as the solvent. All the products gave the very similar ^1H NMR spectra and expected elemental analysis results. Take example for the asymmetric gemini surfactant of $n = 18$, $m = 6$, δ: 0.7 (t, 6H), 0.95—1.40 (m, 40H), 1.45—1.65 (m, 8H), 2.83—3.00 (m, 12H), 3.03—3.20 (m, 8H), anal. calcd (found) %, C 60.12 (60.11), H 11.04 (10.90), N 4.15 (4.12).

Methods

All surface tension measurements in this work were carried out on the Krüss K10T digital tensiometer, with a Pt du Noüy ring attachment. The measurements were made at 298 K.

The ESR spectra were recorded with a Bruker Esp300E spectrometer operating at X-band with 100 KHz magnetic field modulation at 1 K and 1.28 mW microwave power at room temperature. The spin probe was kept at a constant concentration of 5×10^{-5} mol/L in each measurement. The labeled samples were stirred and shaken for 12 h at (20 ± 2) ℃. All spectra run using a glass capillary. The values of the rotational correlation time τ_c can be determined from ESR spectra and calculated according to the following equation[10]:

$$\tau_c = D\Delta W(m = 1)[(I(m = 0)/I(m = 1))^{1/2} + (I(m = 0)/I(m = -1))^{1/2} - 2]$$

where $D = 6.6 \times 10^{-10}\ s^{-1}G^{-1}$, ΔW is the peak-to-valley line width at the $m = 1$ peak; $I(m = 1)$, $I(m = 0)$ and $I(m = -1)$ are the peak-to-valley heights at m.

Results and discussion

The critical micelle concentration (cmc) and the surface tension at the cmc (γ_{cmc}) were determined from the break point of each surface tension vs. log(concentration) plots in Fig. 2 and were listed in table 1. It is found that the cmc values are only slightly different with the change of asymmetric extent (n—m) for this series of gemini surfactants and, interestingly, these cmc values are in the order of: C_{12}-C_6-C_{12} > C_{14}-C_6-C_{10} > C_{16}-C_6-C_8 > C_{18}-C_6-C_6. For the above systems, the nearly linear decrease of cmc (absolute value) upon the increasing asymmetrical extent to 0 to 12 is surprisingly noted. It is different to the empirical tendency in the conventional single chain cationic surfactant analogues, where log (cmc) decrease linearly with the increase of carbon number of hydrophobic moiety.

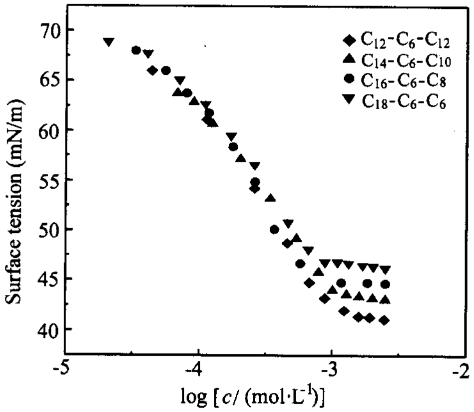

Fig. 2 Variation of surface tension with the concentration for C_n-C_6-C_m.

Table 1 Values of cmc for C_n-C_6-C_m series

Surfactant	cmc (mmol/L)[a]	cmc (mmol/L)[b]
C_{12}-C_6-C_{12}	1.12	1.06
C_{14}-C_6-C_{10}	0.96	0.93
C_{16}-C_6-C_8	0.85	0.82
C_{18}-C_6-C_6	0.74	0.73

[a] represents the data from surface tension measurement.

[b] represents the data from ESR method.

The variations of ESR spectra of 4-oxo-TEMPO in C_{12}-C_6-C_{12} surfactant solution at several concentrations were presented in Fig. 3. It shows that both the line width ratio and the height ratio are related to the surfactant concentrations. In low-viscosity medium, such as in water and gemini surfactant solutions below cmc, the ESR spectra of the spin probe exhibit a narrow three-line pattern. The width of high-field line gradually broadens with the increase of the surfactant concentration above cmc, which is attribute to the anisotropic microenvironment where the spin probe stays.

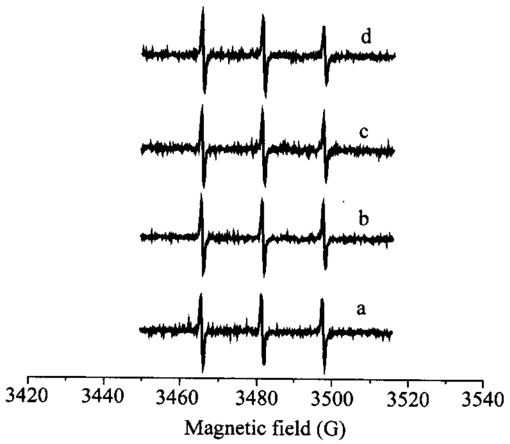

Fig. 3 Typical ESR spectra of 4-oxo-TEMPO in C_{12}-C_6-C_{12} surfactant solution with different concentration (a) 0 mmol/L, (b) 0.144 mmol/L, (c) 0.936 mmol/L, (d) 4.68 mmol/L.

The variation of the rotational correlation time τ_c of the spin probe with the surfactant concentrations is shown in Fig. 4, in which the experimental result for the symmetric gemini surfactant C_{12}-C_6-C_{12} is given for comparison. It is shown that the change of τ_c with concentration shows a similar trend for all the surfactants. At the lower concentration range, τ_c values increase gradually with the increase of the surfactant concentration, and a sharp increase occurs near the concentration where the micelles begin to form. It is also noteworthy that these breaks are not sufficiently clear-cut in comparison with some reported single chain surfactants,[11] which may be attribute to the fact that the attachment of the probe to the premicellar aggregates makes the ESR signal more sensitive to the premicellar aggregation. The effect of the premicellar aggregation on τ_c values may also be observed from the fact that the values of cmc from ESR for the surfactants are slightly lower than that obtained from surface tension data. From the figure it can been seen that the increase values of τ_c (about from 20 to 50 ps) over the whole concentration is less than the reported values of the corresponding conventional single chain surfactant.[11] This result can be explained that gemini surfactants aggregate less tightly at all concentrations. The values of τ_c are obviously different for different surfactant system over the whole concentration range, which is in the order of: C_{12}-C_6-C_{12} < C_{14}-C_6-C_{10} < C_{16}-C_6-C_8 < C_{18}-C_6-C_6. This order is consistent with that of cmc values obtained from Fig. 1 for the four surfactants. These results indicate that the microviscosity of the surfactants sensed by the probe for the different surfactants depends mainly on the asymmetrical extent or the difference between the two asymmetrical alkyl chain length ($n-m$). With the increase of asymmetrical extent ($n-m$), from 0 to 12, the microviscosity increases. From the packing consideration, this result indicates that with the alkyl chain in the surfactants increase in length, the surfactants aggregate more tightly. As shown in table 1, with the increase of asymmetric extent the value of cmc for the surfactants decreases, which is consistent with the order of τ_c values. It is to say that the more the surfactants are asymmetric the lower cmc they have and the surfactants aggregate more tightly. The above results show that the variation of the asymmetric extent of gemini surfactants with the same length of total hydrophobic chain can affect the self-aggregation behavior of these surfactants. Therefore it is appropriate to consider the asymmetric extent of gemini surfactants as an important factor for regulating the physical properties of these new surfactants.

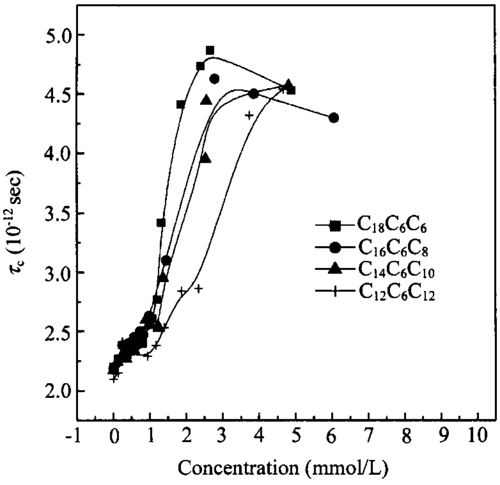

Fig. 4 Variation of rotational correlation time of the probe in the hydrophobic cores for the series of asymmetric gemini surfactants.

Conclusion

In summery, a series of new asymmetric gemini surfactants was synthesized. The preliminary evaluation for their physical properties shows that this series of new dicationic compounds synthesized is a new kind of surfactants with interesting aggregating properties. Both the surface tension and ESR methods can be used to investigate the micellization behaviors and obtain comparable results. It may be concluded from ESR data that with the increase of asymmetric of the surfactants, more compact structures are formed in the micellization process.

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