Micellization of a Series of Dissymmetric Gemini Surfactants in Aqueous Solution

Xiaoyong Wang,[†] Jinben Wang,[†] Yilin Wang,*,[†] Jianping Ye,[‡] and Haike Yan[†]

Key Laboratory of Colloid and Interface Science and Key Laboratory of Photochemistry, Center of Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

Robert K. Thomas

Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom

A series of dissymmetric gemini surfactants, $[C_mH_{2m+1}(CH_3)_2N(CH_2)_6N(CH_3)_2C_nH_{2n+1}]Br_2$ (designated as $C_mC_6C_nBr_2$, with constant $m + n = 24$ and $m = 12, 13, 14, 16, 18$), have been investigated by electrical conductivity measurement, steady-state fluorescence measurement, and time-resolved fluorescence quenching. The critical micelle concentration (CMC) and the micelle aggregation number (N) were determined and the micropolarity of micelle was characterized. The micelle ionization degree (α) was obtained using a combination of electrical conductivity data and N. Furthermore, the Gibbs free energy of micellization (ΔG_{mic}) and the entropy of micellization (ΔS_{mic}) were studied. The results have shown that the degree of dissymmetry (m/n) has an important effect on the micellization in aqueous solution. As the m/n ratio increases, the CMC value decreases linearly, the N value at the CMC increases slightly (from 22 to 30), and α decreases slightly down the series. The value of ΔG_{mic} becomes more negative for greater m/n ratios, which supports the belief that the micellization will be more spontaneous and the contribution, per CH_2 unit, to micellization increases as the m/n ratio increases. The calculated thermodynamic parameter $|T\Delta S_{mic}|$ is much larger than $|\Delta H_{mic}|$, which indicates that the micellization of the $C_mC_6C_nBr_2$ series is entropy-driven. However, the micropolarity of the micelle that is sensed by pyrene varies little, irrespective of the m/n ratio.

Introduction

The possibilities of using gemini amphiphiles to create new types of surfactants have already been attracting increased attention.[1−5] These novel surfactants have many unique properties that are superior to those of their single-chain counterparts, such as remarkably low critical micelle concentrations (CMCs); much higher efficiency, in regard to reducing surface tensions; unusual aggregation morphologies; and better wetting, solubilizing, and foaming properties,[6,7] which make them potentially useful in many applications, for example, in soil remediation, enhanced oil recovery, drug entrapment and release, and the construction of high-porosity materials. Considerable effort has been exercised to design and synthesize an enormous variety of gemini surfactants with the required properties[8−11] and to understand the relationship between the architectures of gemini surfactants and their various properties in aqueous solution.[12−15]

Dicationic quaternary ammonium compounds are a type of gemini surfactant, with the general structure $[C_mH_{2m+1}(CH_3)_2N-(CH_2)_sN(CH_3)_2C_nH_{2n+1}]Br_2$, designated as $C_mC_sC_nBr_2$, where m and n indicate the numbers of C atoms in the two side alkyl chains, and s indicates the number of C atoms in the spacer, respectively. So far, the most investigated gemini surfactants are symmetrical, i.e., $m = n$. The properties of these surfactants, such as CMC value, micelle ionization degree (α), aggregate

morphology, phase behavior, rheological properties, area per molecule adsorbed at the air/water interface, and enthalpy of micellization (ΔH_{mic}), have been studied by a range of experimental methods, including electrical conductivity,[16] surface tension,[17,18] cryo-transmission electron microscopy,[19] ultrasonic absorption relaxation,[20] X-ray diffraction,[21] small-angle neutron scattering (SANS),[22] and microcalorimetric measurements.[14,23] Recently, dissymmetric gemini surfactants $C_mC_sC_nBr_2$ with $m \neq n$ have appeared in a few reports.[24−29] These dissymmetric gemini surfactants consist of two hydrophobic hydrocarbon chains with different lengths and two identical headgroups. Oda and co-workers[24,25] studied the $C_mC_2C_nBr_2$ series for n and m values of 8−18, and their results indicated that the hydrophobic chain length and dissymmetry of the surfactants have a strong influence on the micellization process. Sikirić et al.[28] reported that the dissymmetric gemini surfactant $C_{12}C_2C_{14}Br_2$ exhibits peculiar properties in aqueous solution, i.e., high polydispersity and the coexistence of three populations of differently sized aggregates. In our previous paper,[29] we used microcalorimetry to measure the CMC and ΔH_{mic} values of a series of dissymmetric gemini surfactants with the composition $C_mC_6C_nBr_2$, where $m + n = 24$ and $m = 12, 13, 14, 16$, and 18. There is a small decrease in the CMC while a very large decrease in the ΔH_{mic} value is observed as the m/n ratio increases. This observation is consistent with a large increase in the hydrophobic contribution to micellization with increasing m/n ratios. However, because the value of α is unavailable, the Gibbs free energy of micellization (ΔG_{mic}) and the entropy of micellization (ΔS_{mic}) of the $C_mC_6C_nBr_2$ series cannot be obtained. Presently, less

---

* Author to whom the correspondence should be addressed. E-mail: yilinwang@iccas.ac.cn.

† Key Laboratory of Colloid and Interface Science.

‡ Key Laboratory of Photochemistry.

Dissymmetric Gemini Surfactants in Aqueous Solution

J. Phys. Chem. B, Vol. 107, No. 41, 2003 **11429**

works about dissymmetric gemini surfactants are available. To obtain a further understanding of the physicochemical properties of the $C_mC_6C_nBr_2$ series, much more work should be done.

In the present paper, the micellization of the dissymmetric gemini surfactants $C_mC_6C_nBr_2$, with $m + n = 24$ and $m = 12$, 13, 14, 16, and 18, has been investigated. The CMC is obtained by electrical conductivity measurement and steady-state fluorescence measurement. The value of N is determined by time-resolved fluorescence quenching (TRFQ). The α values are then calculated from electrical conductivity curves and N, using the method of Evans.[30] The α and ΔH_{mic} values from the past microcalorimetric work[29] permit the determination of the ΔG_{mic} and ΔS_{mic} values in the $C_mC_6C_nBr_2$ series. The micropolarity of these dissymmetric gemini surfactants is characterized by steady-state fluorescence measurement. All the present studies are intended to further the understanding of the dissymmetry effect on the micellization of the gemini surfactants.

Experimental Section

Materials. The $C_mC_6C_nBr_2$ series, with $m + n = 24$ and $m = 12$, 13, 14, 16, and 18, were synthesized and purified as described previously.[29] Pyrene was purchased from Aldrich and recrystallized from ethanol. Benzophenone was purchased from Fluka and recrystallized from ethanol. Triply distilled water was used in all experiments.

Electrical Conductivity Measurement. The electrical conductivity was used to determine the CMC and the α value of the $C_mC_6C_nBr_2$ series.[31] The conductivity of the surfactant solutions was measured as a function of concentration, using a JENWAY model 4320 conductivity meter. The measurements were performed in a temperature-controlled, double-walled glass container with a circulation of water. A fraction of a solution that was ~10 times more concentrated than the estimated CMC of the surfactant was successively added to 8 mL of water. Sufficient time was alloted between successive additions to allow the system to equilibrate. During the conductivity run, the temperature of the solution was maintained at 25.0 ± 0.1 °C.

Steady-State Fluorescence Measurement. Fluorescence techniques were used to study the micropolarity and the CMC of the $C_mC_6C_nBr_2$ series, from measurement of the pyrene polarity index (I_1/I_3) at a concentration far above the CMC or as a function of the surfactant concentration (C), respectively.[32] I_1/I_3 is the ratio of the intensities of the first and third vibronic peaks in the fluorescence emission spectrum due to pyrene. The fluorescence intensities were measured using a Hitachi model F-4500 spectrofluorometer that was equipped with a thermo-stated water-circulating bath. Pyrene was excited at a wavelength of 335 nm, and the emission spectra was scanned over the spectral range of 350−500 nm. All the measurements were conducted at 25.0 ± 0.1°C.

Time-Resolved Fluorescence Quenching (TRFQ). This method was used to determine the micelle aggregation number (N) of the $C_mC_6C_nBr_2$ surfactants. Pyrene was used as a fluorescence probe, and benzophenone was used as a quencher of the fluorescence probe. Pyrene fluorescence decay curves were monitored using a Horiba model NAES-1100 single-photon-counting spectrophotometer (excitation at 325 nm, emission at 375 nm). All the measurements were made at 25.0 ± 0.1 °C. For each sample, the decay of the fluorescence probe was recorded in the absence and presence of quencher, separately. Corresponding to these two situations, the time dependence of the fluorescence intensity can be respectively

fitted to the following equations:[33−36]

$$I(t) = I(0) \exp\left(-\frac{t}{\tau}\right) \tag{1}$$

$$I(t) = I(0) \exp\{-A_2 t - A_3[1 - \exp(-A_4 t)]\} \tag{2}$$

where $I(t)$ and $I(0)$ are the fluorescence intensities at time t and time zero, respectively; τ is the fluorescence lifetime; and A_2, A_3, and A_4 are three time-independent fitting parameters. The value of τ is estimated by fitting eq 1. When the probe and quencher remain in micelles and their residence time in the micelles is much longer than the probe fluorescence lifetime, the fitting parameters are given by

$$A_2 = \frac{1}{\tau}$$

$$A_3 = \frac{[\text{quencher}]}{[\text{micelle}]}$$

$$A_4 = k_q \tag{3}$$

where k_q is the rate constant for intramicellar quenching. The molar micelle concentration (denoted as [micelle]) can be expressed as $(C − CMC)/N$; thus, the micelle aggregation number N can be calculated from

$$N = \frac{A_3(C − CMC)}{[\text{quencher}]} \tag{4}$$

where C is the surfactant molar concentration.

Results and Discussion

Critical Micelle Concentration. Figure 1 shows the electrical conductivity measurements of the $C_mC_6C_nBr_2$ series, where the electrical conductivity (K) is plotted against the surfactant concentration (C). For all surfactants and the range of surfactant concentration studied, K increases as C increases; however, the rate of increase in K, relative to C, is different below and above the CMC. At low concentrations, surfactant molecules are completely ionized. Above the CMC, portions of the counterions are bound to micelles, which causes a reduction in the effective charge of the micelle. Thus, the slope of K vs C above the CMC is smaller than that below the CMC, as shown in Figure 2. Each curve of K vs C furnishes two straight lines, which intersect at the concentration that corresponds to the micelle formation, which allows identification of the CMC.

Figure 3 presents the variations of the pyrene polarity ratio I_1/I_3 with the surfactant concentration C. These plots have the
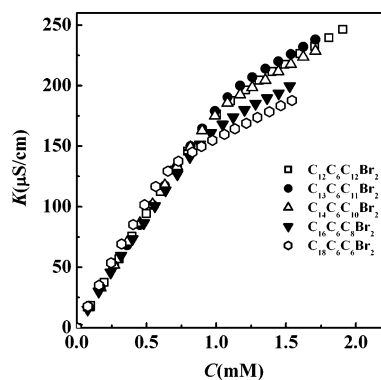

Figure 1. Variation of the electrical conductivity (K) with the surfactant concentration (C) of the $C_mC_6C_nBr_2$ series at 25.0 ± 0.1 °C.
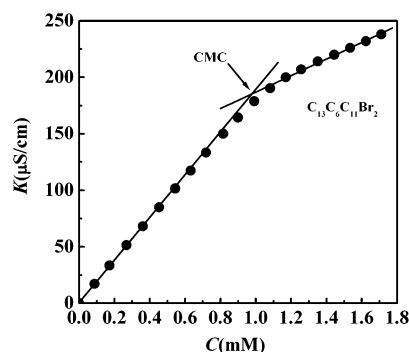
Figure 2. Graphic example of how the CMC is determined from the electrical conductivity curve.
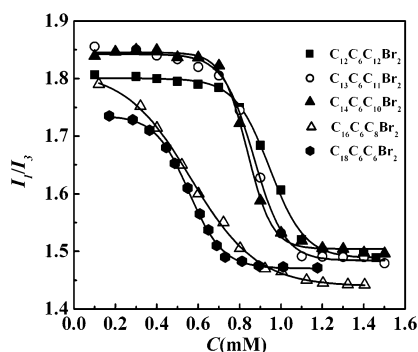

Figure 3. Variation of the pyrene polarity ratio (I_1/I_3) with the surfactant concentration (C) of the $C_mC_6C_nBr_2$ series at $25.0 \pm 0.1°$ C.
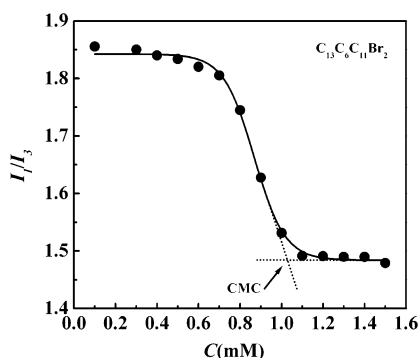

Figure 4. Graphic example of how the CMC is determined from the pyrene polarity ratio (I_1/I_3) curve.

usual sigmoidal shape, with a rapid decrease of I_1/I_3 at C values slightly below the CMC and a stabilization at high C values, which indicates the formation of the micelle. Thus, the CMC can be taken as the concentration that corresponds to the intercept between the linear extrapolations of the rapidly varying portion of the curve and of the almost-horizontal portion at high concentration, as shown in Figure 4. The CMCs obtained by electrical conductivity and steady-state fluorescence measurements are in good agreement, which are summarized in Table
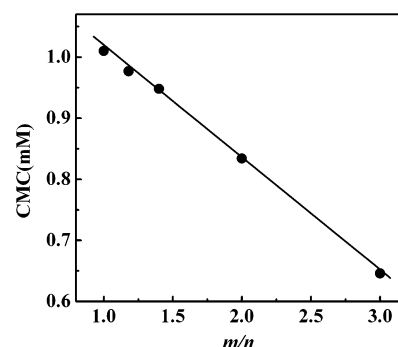

Figure 5. Variation of the CMC with the degree of dissymmetry (m/n), at 25.0 ± 0.1 °C, for the $C_mC_6C_nBr_2$ series with $m + n = 24$ and $m = 12, 13, 14, 16,$ and 18.

1. The dissymmetric gemini $C_mC_6C_nBr_2$ series have the same headgroups, the same spacer, and the same total number of the hydrophobic units, except for two hydrocarbon chains with different lengths. As indicated by Zana et al.,[19] the distance between the two headgroups in a molecule with a spacer value of $s = 6$ is comparable to that which would be obtained by electrostatic repulsion between two similar monomer units, which would be expected to be invariant with the degree of dissymmetry (m/n). Therefore, the m/n ratio should be the principal factor that determines the CMC and other thermodynamic properties for the $C_mC_6C_nBr_2$ series. Here, m is 12, 13, 14, 16, and 18; correspondingly, n is 12, 11, 10, 8, and 6, respectively. Interestingly, the CMCs of the $C_mC_6C_nBr_2$ series decrease linearly as the m/n ratio increases, as presented in Figure 5. This is different from the empirical tendency in the conventional single-chain cationic surfactant analogues, where the log(CMC) value decreases linearly as the carbon number of hydrophobic moieties increases. For the dissymmetric gemini series, the addition of a methylene to the short alkyl chain is less effective to micellization than the addition of methylene to the long alkyl chain. This observation indicates that the hydrophobic interaction of the dissymmetric geminis is different from that of the symmetric geminis.[29] For the symmetric geminis, the number of hydrophobic units that are interacting will be the same for intermolecular and intramolecular interactions, and, therefore, the hydrophobic interaction will be minimized. However, for the dissymmetric series, as the m/n ratio increases, the ratio of the number of hydrophobic units that are interacting intermolecularly to those that are interacting intramolecularly will increase. Hence, the hydrophobic interaction is gradually optimized with increasing m/n values.

Micelle Aggregation Number. The micelle aggregation number (N) has been obtained using TRFQ. Figure 6 shows the variation of N, expressed as the number of surfactant molecules per micelle, relative to the $C_mC_6C_nBr_2$ concentration C. N increases as C increases for the five geminis. This increase is more marked for the dissymmetric gemini surfactant with a

TABLE 1: Critical Micelle Concentration (CMC), Micelle Aggregation Number (N), and Micelle Ionization Degree (α) for the $C_mC_6C_nBr_2$ Series at 25.0 ± 0.1 °C

		CMC (mM)				α	
$C_mC_6C_nBr_2$	m/n	conductivity measurement	fluorescence measurement	microcalorimetric measurement[a]	N^b	using Evans[30]	using Figure 1[c]
$C_{12}C_6C_{12}Br_2$	1	1.01	1.09	0.89	22	0.21	0.40
$C_{13}C_6C_{11}Br_2$	1.18	0.98	1.04	0.86	24	0.20	0.39
$C_{14}C_6C_{10}Br_2$	1.4	0.95	0.99	0.82	26	0.19	0.37
$C_{16}C_6C_8Br_2$	2	0.83	0.88	0.73	28	0.18	0.36
$C_{18}C_6C_6Br_2$	3	0.65	0.71	0.58	30	0.16	0.29

^{a} From ref 29. ^{b} Values at the CMC. ^{c} Determined from the slopes of the two straight lines above and below the CMC in Figure 1.

Dissymmetric Gemini Surfactants in Aqueous Solution

J. Phys. Chem. B, Vol. 107, No. 41, 2003 **11431**
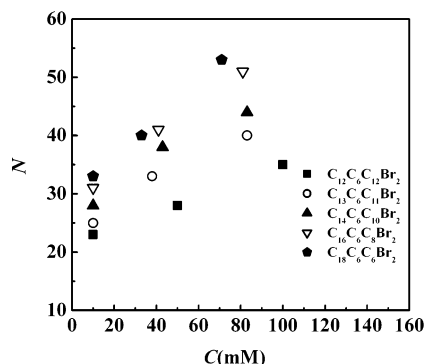

Figure 6. Variation of the micelle aggregation number (N), relative to the surfactant concentration (C) of the $C_mC_6C_nBr_2$ series at 25.0 ± 0.1 °C.

higher m/n ratio. Thus, the tendency toward micellar growth is much stronger for the gemini surfactant with the higher degree of dissymmetry. From the results, the approximate values of N for the $C_mC_6C_nBr_2$ series at the CMC can be derived, which are 22, 24, 26, 28, and 30 for m = 12, 13, 14, 16, and 18, respectively, as listed in Table 1. Obviously, at the CMC, N is only slightly dependent on m/n, increasing from 22 to 30 as m/n increases from 1 to 3. Such N values correspond to 44−60 hydrocarbon chains per micelle and are similar to the aggregation numbers calculated from Tanford's equations for spherical micelles with a hydrophobic core with a radius equal to the length of a dodecyl group in the fully stretched conformation (56).[37] Therefore, at the CMC, the micelles of the $C_mC_6C_nBr_2$ series should be almost spherical. Furthermore, the geminis with higher m/n values have slightly larger N values, which indicate a slightly more compact globular structure.

Micelle Ionization Degree. The micelle ionization degree (α), which is a fundamental feature of the ionic surfactant micelles, is certain to have an important role in its micellization. A better understanding of α may provide insight into the unique properties of ionic surfactants and also aid in the future design of new ionic gemini surfactants. The electrical conductivity method is often used to determine the CMC as well as the value of α. Normally, α can be taken as the ratio of the slopes of the two straight lines above and below the CMC from the plot of the conductivity against the surfactant concentration.[31] However, it has been recently shown that the value of α so obtained is overestimated, because the conductivity of the micelles is underestimated.[38] A method that was demonstrated by Evans[30] yields more-realistic values.[38,39] As early as 1956, Evans had demonstrated that the value of α could be estimated from the electrical conductivity data. Following Evans' idea, the electrical conductivity data of the $C_mC_6C_nBr_2$ series may be fitted to the equation

$$S_2 = \frac{(A-B)^2}{A^{4/3}}(S_1 - \Lambda_{Br^-}) + \frac{A-B}{A}\Lambda_{Br^-} \quad (5)$$

where S_1 and S_2 are the slopes of the conductivity plot below and above the CMC, respectively; A is the aggregation number of alkyl chains of the $C_mC_6C_nBr_2$ series in one micelle, which is double the micelle aggregation number N at the CMC (A = $2N$); B is the number of Br⁻ counterions that are bound to the micelle; and Λ_{Br^-} is the equivalent conductivity of the Br⁻ counterion, which may be taken as the value at infinite dilution (78.4×10^{-4} S·m²/mol at 25.0 °C). Thus, α can be calculated

TABLE 2: Thermodynamic Parameters of the $C_mC_6C_nBr_2$ Series at 25.0 ± 0.1 °C

$C_mC_6C_nBr_2$	m/n	ΔH_{mic} (kJ/mol)[a]	ΔG_{mic} (kJ/mol)[b]	$-T\Delta S_{mic}$ (kJ/mol)[c]
$C_{12}C_6C_{12}Br_2$	1	−3.67	−45.84	−42.17
$C_{13}C_6C_{11}Br_2$	1.18	−6.42	−46.46	−40.04
$C_{14}C_6C_{10}Br_2$	1.4	−8.60	−46.92	−38.32
$C_{16}C_6C_8Br_2$	2	−11.21	−47.96	−36.75
$C_{18}C_6C_6Br_2$	3	−14.18	−50.62	−36.44

[a] From ref 29. [b] Calculated using $\Delta G_{mic} = 2RT(1.5 - \alpha) \ln(CMC) - RT \ln 2$ from ref 41; CMC is expressed relative to the molarity of surfactant. [c] Calculated from $\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic}$.
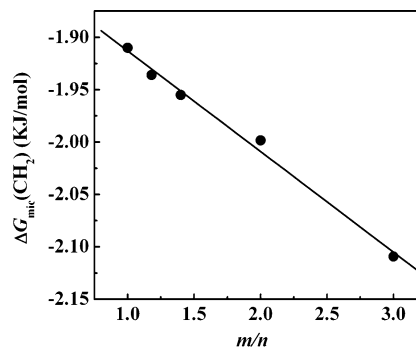

Figure 7. Variation of the $\Delta G_{mic}(CH_2)$ with the degree of dissymmetry (m/n), at 25.0 ± 0.1 °C, for the $C_mC_6C_nBr_2$ series with $m + n = 24$ and m = 12, 13, 14, 16, and 18.

according to

$$\alpha = \frac{A-B}{A} \quad (6)$$

The calculated values of α by the method of Evans are listed in Table 1. For comparison, the values of α calculated from the slopes of the two straight lines above and below the CMC are also presented. The values of α that were determined by the method of Evans are smaller. The result shows that the value of α decreases slightly as the value of m/n increases. This can be attributed to the change of micelle structure; i.e., the higher binding of counterions to the micelles arises from the closer packing of the headgroups and higher surface charge density at the micelle/solution interface.[40] Therefore, for the dissymmetric gemini with higher m/n value, because of its slightly compact structure, which was just discussed, its α value will be slightly smaller.

Thermodynamics of Micellization. For the dissymmetric $C_mC_6C_nBr_2$ series, the enthalpy of micellization (ΔH_{mic}) values were reported in the previous paper.[29] The Gibbs free energy of micellization (ΔG_{mic}) is calculated through combination with the values of the CMC and α, following procedures in the literature,[41] and the entropy of micellization (ΔS_{mic}) is derived from ΔH_{mic} and ΔG_{mic}. Table 2 presents all these thermodynamic parameters of micellization for the dissymmetric geminis. The results show that, as the m/n value increases, ΔH_{mic} and ΔG_{mic} become more negative. The changes in ΔG_{mic} reveal that the micellization process for the dissymmetric surfactants is more spontaneous for the gemini surfactant with the higher degree of dissymmetry. The Gibbs free energy, per mole of CH_2 ($\Delta G_{mic}(CH_2)$), can give a measure of the contribution of the hydrophobic interaction, per mole of CH_2, to micellization. The relationship of $\Delta G_{mic}(CH_2)$ with the degree of dissymmetry m/n is shown in Figure 7. It clearly indicates that the m/n ratio has a significant effect on the micellization of the geminis. The higher the degree of dissymmetry, the more negative the ΔG_{mic}-

11432 *J. Phys. Chem. B, Vol. 107, No. 41, 2003*

Wang et al.

(CH$_2$) values. The contribution, per mole of CH$_2$, to micellization increases as the m/n ratio increases. This observation is consistent with a large increase in the hydrophobic contribution to micellization with increasing m/n. For all the surfactants that have been investigated, it is also seen that the value of $|T\Delta S_{mic}|$ is much larger than $|\Delta H_{mic}|$, which indicates that the micellization of the C$_m$C$_6$C$_n$Br$_2$ series is entropy-driven.

Micropolarity. The values of the pyrene fluorescence intensity ratio (I_1/I_3) are 1.44, 1.43, 1.44, 1.39, and 1.44 for the gemini surfactants C$_{12}$C$_6$C$_{12}$Br$_2$, C$_{13}$C$_6$C$_{11}$Br$_2$, C$_{14}$C$_6$C$_{10}$Br$_2$, C$_{16}$C$_6$C$_8$Br$_2$, and C$_{18}$C$_6$C$_6$Br$_2$, respectively. This measurement was performed at a gemini surfactant concentration of 32 mM, far above the CMC, where the probe is fully partitioned in the micelles. These values suggest that, although the m/n values are different for the C$_m$C$_6$C$_n$Br$_2$ series, there is very little effect on the micropolarity that is sensed by pyrene. Previous works have proved that the micropolarity varies little, irrespective of the nature of the spacer unit[10,42] and the degree of oligomerization.[43] This condition may be due to the fact that the micelle-solubilized pyrene is located in the micelle palisade layer.[32] This layer is essentially composed of quaternary ammonium headgroups, Br$^-$ counterions, water molecules, and α-methylene groups of surfactant alkyl chains. For the C$_m$C$_6$C$_n$Br$_2$ series, the observed constancy of micropolarity probably results from the existence of the two contrary effects that are related to the hydrophobic interaction. On one hand, as the m/n ratio increases, the hydrophobic interaction is gradually optimized. This situation is expected to result in a decrease of micropolarity, because of the tighter packing of the surfactant alkyl chains. On the other hand, this tighter packing structure may bring pyrene slightly closer to the micelle surface, on a time-averaged basis. Indeed, pyrene has been shown to interact with quaternary ammonium headgroups.[44,45] Such a change, even minor, of pyrene solubilization moving toward the micelle surface would cause an increase in micropolarity, which compensates the first effect that was just discussed. Finally, the micropolarity of these gemini surfactant micelles that is sensed by pyrene is shown to be unchanged, relative to the m/n ratio.

Conclusions

A comprehensive study has been conducted on the micellization of a series of dissymmetric gemini surfactants. The degree of dissymmetry (m/n) shows a marked effect on the micellization. As the m/n ratio increases,, the critical micelle concentration (CMC) of the C$_m$C$_6$C$_n$Br$_2$ series decreases linearly, the micelle aggregation number (N) at the CMC increases slightly (from 22 to 30), the micelle ionization degree (α) decreases slightly, and the Gibbs free energy of micellization (ΔG_{mic}) becomes more negative. The contribution, per CH$_2$ unit on hydrophobic chains, to micellization increases as the m/n ratio increases. Moreover, the finding that $|T\Delta S_{mic}| \gg |\Delta H_{mic}|$ indicates that the micellization of the C$_m$C$_6$C$_n$Br$_2$ series is entropy-driven. However, the micropolarity of the micelle that is sensed by pyrene varies little, irrespective of the m/n ratio.

References and Notes

(1) Menger, F. M.; Littau, C. A. *J. Am. Chem. Soc.* **1991**, *113*, 1451−1452.
(2) Rosen, M. J. *CHEMTECH* **1993**, *23*, 30−33.
(3) Menger, F. M.; Littau, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 10083−10090.
(4) Zana, R. *Adv. Colloid Interface Sci.* **2002**, *97*, 205−253.
(5) Chevalier, Y. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 3−11.
(6) Menger, F. M.; Keiper, J. S. *Angew. Chem., Int. Ed.* **2000**, *39*, 1906−1920.
(7) Kim, S. S.; Zhang, W. Z.; Pinnavaia, T. J. *Science* **1998**, *282*, 1302−1305.
(8) Rosen, M. J.; Mathias, J. H.; Davenport, L. *Langmuir* **1999**, *15*, 7340−7346.
(9) De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. *J. Phys. Chem.* **1996**, *100*, 0, 11664−11671.
(10) De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. *J. Phys. Chem. B* **1998**, *102*, 6152−6160.
(11) Pinazo, A.; Wen, X.; Pérez, L.; Infante, M.-R.; Franses, E. I. *Langmuir* **1999**, *15*, 3134−3142.
(12) Danino, D.; Talmon, Y.; Levy, H.; Beinert, G.; Zana, R. *Science* **1995**, *269*, 1420−1421.
(13) In, M.; Bec, V.; Aguerre-Chariol, O.; Zana, R. *Langmuir* **2000**, *16*, 141−148.
(14) Bai, G. Y.; Yan, H. K.; Thomas, R. K. *Langmuir* **2001**, *17*, 4501−4504.
(15) Rosen, M. J.; Song, L. D. *J. Colloid Interface Sci.* **1996**, *179*, 261−268.
(16) Zana, R.; Benrraou, M.; Rueff, R. *Langmuir* **1991**, *7*, 1072−1075.
(17) Devínsky, F.; Lacko, I.; Imam, T. *J. Colloid Interface Sci.* **1991**, *143*, 336−342.
(18) Alami, E.; Beinert, G.; Marie, P.; Zana, R. *Langmuir* **1993**, *9*, 1465−1467.
(19) Danino, D.; Talmon, Y.; Zana, R. *Langmuir* **1995**, *11*, 1448−1456.
(20) Frindi, M.; Michels, B.; Levy, H.; Zana, R. *Langmuir* **1994**, *10*, 1140−1145.
(21) Alami, E.; Levy, H.; Zana, R.; Skoulios, A. *Langmuir* **1993**, *9*, 940−944.
(22) Hirata, H.; Hattori, N.; Ishida, M.; Okabayashi, H.; Frusaka, M.; Zana, R. *J. Phys. Chem.* **1995**, *99*, 17778−17784.
(23) Bai, G. Y.; Wang, J. B.; Yan, H. K.; Li, Z. X.; Thomas, R. K. *J. Phys. Chem. B* **2001**, *105*, 3105−3108.
(24) Oda, R.; Huc, I.; Candau, S. J. *Chem. Commun.* **1997**, 2105−2106.
(25) Oda, R.; Huc, I.; Homo, J.-C.; Heinrich, B.; Schmutz, M.; Candau, S. *Langmuir* **1999**, *15*, 2384−2390.
(26) Huc, I.; Oda, R. *Chem. Commun.* **1999**, 2025−2026.
(27) Oda, R.; Huc, I.; Danino, D.; Talmon, Y. *Langmuir* **2000**, *16*, 9759−9769.
(28) Sikiric, M.; Primožič, I.; Filipović-Vincekoviczcu, N. *J. Colloid Interface Sci.* **2002**, *250*, 221−229.
(29) Bai, G. Y.; Wang, J. B.; Wang, Y. J.; Yan, H. K.; Thomas, R. K. *J. Phys. Chem. B* **2002**, *106*, 6614−6616.
(30) Evans, H. C. *J. Chem. Soc.* **1956**, 579−586.
(31) Zana, R. *J. Colloid Interface Sci.* **1980**, *78*, 330−337.
(32) Zana, R. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed.; Marcel Dekker: New York, 1987; pp 241−294.
(33) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289−292.
(34) Infelta, P. *Chem. Phys. Lett.* **1979**, *61*, 88−91.
(35) Almgren, M. *Adv. Colloid Interface Sci.* **1992**, *41*, 9−32.
(36) Gehelen, M.; De Schryver, F. C. *Chem. Rev.* **1993**, *93*, 199−221.
(37) Tanford, C. *J. Phys. Chem.* **1972**, *76*, 3020−3024.
(38) Sugihara, G.; Nakamura, A. A.; Nakashima, T.-H.; Araki, Y.-I.; Okano, T.; Fujiwara, M. *Colloid Polym. Sci.* **1997**, *275*, 790−796.
(39) Zana, R. *J. Colloid Interface Sci.* **2002**, *246*, 182−190.
(40) Quirion, F.; Magid, L. J. *J. Phys. Chem.* **1986**, *90*, 5435−5441.
(41) Zana, R. *Langmuir* **1996**, *12*, 1208−1211.
(42) Zana, R.; In, M.; Lévy, H.; Duportail, G. *Langmuir* **1997**, *13*, 5552−5557.
(43) Zana, R.; Levy, H.; Papoutsi, D.; Beinert, G. *Langmuir* **1995**, *11*, 3694−3698.
(44) Lianos, P.; Viriot, M.-L.; Zana, R. *J. Phys. Chem.* **1984**, *88*, 1098−1101.
(45) Ghosh. S.; Maki, A. H.; Petrin, M. *J. Phys. Chem.* **1986**, *90*, 5210−5215.