Thermodynamics of Hydrophobic Interaction of Dissymmetric Gemini Surfactants in Aqueous Solutions

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We have used microcalorimetry to measure the critical micelle concentrations (CMC) and enthalpies of micellization (ΔH_{mic}) of the series of dissymmetric cationic 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 $n + m = 24$ and $n = 6, 8, 10, 11, 12$. There is a small decrease in CMC as the ratio m/n increases but this decrease is not much larger than the error. On the other hand there is a very large decrease in the enthalpy of micellization with m/n. This is consistent with a large increase in the hydrophobic contribution to micellization with m/n. To explain the relative invariance of the CMC, there must be a corresponding large increase in the entropy of micellization with m/n. The change in the hydrophobic contribution is explained in terms of the relative strengths of internal and external hydrophobic contacts down the series.

Introduction

Since 1993 many reports have shown that modifying the molecular structure of gemini surfactant can control the self-assembling process.[1−7] For cationic gemini compounds with the general structure $[C_mH_{2m+1}(CH_3)_2N(CH_2)_sN(CH_3)_2C_nH_{2n+1}]Br_2$, designated as $C_mC_sC_nBr_2$, micellization is strongly dependent on the length of both free alkyl chains and spacer and on the dissymmetry in the hydrophobic chain.[8−22] Thermodynamic measurements can play an important role in understanding the micellization process. In particular, values of the enthalpy (ΔH_{mic}) and entropy (ΔS_{mic}) of micellization give more insight into the process of micellization than the simple determination of Gibbs free energy (ΔG_{mic}) from the critical micelle concentration (CMC). This may prove helpful in relating the molecular structure of surfactant to the physicochemical properties of micellization, especially in the comparison of the pattern observed for the geminis with those of their monomeric counterparts.[23−26]

Until now, there have been few reports on the thermodynamic properties of micellization for gemini surfactants in aqueous solutions.[27−33] Recently we have systematically determined the thermodynamic parameters of the $C_mC_sC_mBr_2$ series with $S = 3, 4, 6, 8, 10, 12$ by microcalorimetry.[23,24] The enthalpy and entropy of micellization of the series showed a striking pattern that is completely concealed by the behavior of the free energy of micellization, which is the most widely used method of comparison because it is more accessible. In the present work, we extend our studies to the dissymmetric gemini surfactants, i.e., $C_{13}C_6C_{11}Br_2$, $C_{14}C_6C_{10}Br_2$, $C_{16}C_6C_8Br_2$, and $C_{18}C_6C_6Br_2$ with $m + n = 24$. For these systems the only reported work is on the phase behavior of the $C_mC_2C_nBr_2$ series with n and m

from 8 to 18. As shown by Oda et al.,[18,21] the hydrophobic chain length and dissymmetry of the surfactants has a strong influence on the micellization process. Here we report the CMCs and enthalpies of micellization of the $C_mC_6C_nBr_2$ series with $n + m = 24$ and $n = 6-18$.

Materials and Methods

The $C_mC_6C_nBr_2$ series with $m + n = 24$ were synthesized and purified as follows. The *N,N*-dimethylalkylamines $[C_mH_{2m+1}N(CH_3)_2$, in which $m = 6, 8, 10, 11, 12]$ were reacted with a large excess (more than 6-fold) of dibromohexane in dry acetone at 303 K for several days in order to form the required intermediates of $C_mH_{2m+1}N(CH_3)_2C_6H_{12}Br_2$. After removal of the solvent the mixture was shaken with water and the excess dibromide removed by continuous liquid extraction with heptane. The aqueous residue was freeze-dried to give the salt $C_mH_{2m+1}N(CH_3)_2C_6H_{12}Br_2$. The *N,N*-dimethylalkylamines $[C_nH_{2n+1}N(CH_3)_2$, in which $n = 12, 13, 14, 16, 18]$ were reacted with the appropriate precursor $C_mH_{2m+1}N(CH_3)_2C_6H_{12}Br_2$ in dry acetone with stirring at 303 K for 72 h. The products were recrystallized in various solvent or solvent mixtures (acetone for tridecyl and tetradecyl compounds, ethanol−acetone for hexadecyl product and ethanol for octadecyl series). The recrystallization was repeated at least three times.

All the products gave similar ^{1}NMR spectra and the expected elemental analysis results. Taking the asymmetric gemini with $m = 18$, $n = 6$ for example, δ 0.7 (t, 6H), 0.95−1.40 (m, 40H), 1.60 (m, 8H), 2.89 (m, 12H), 3.20 (m, 8H), and the C, H, N anal. found (calcd) %, C 60.12 (60.11), H 11.04 (10.90), N 4.15 (4.12).

An improved LKB-2107 isothermal titration microcalorimeter with a 1 mL sample cell was used for direct measuring of the CMCs and enthalpies of micellization following the instrumental and experimental procedures described in our previous papers.[34]

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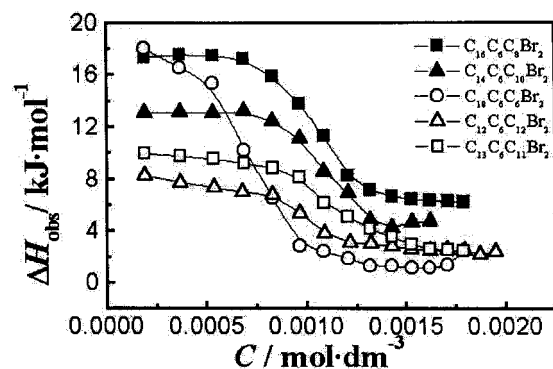
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Figure 1. Variation of the observed enthalpies (ΔH_{obs}) with concentration (C) of $C_mC_6C_nBr_2$ series with $n + m = 24$ at 298.15 K. Initial concentrations of surfactants: 5mM.

It has a precision of electrical calibration better than ±1% and its accuracy was tested by measuring the dilution enthalpy of a concentrated sucrose solution, giving results in good agreement with the literature values.[35] For the experiments on the surfactants, the sample cell and the reference cell of the calorimeter were initially respectively loaded with 0.5 and 0.7 mL of pure water. A concentrated solution of surfactant was injected into the stirred sample cell via a 500 μL Hamilton syringe controlled by a Braun 871182 pump. A series of injections, each 10−20 μL, was made until the desired range of dilution had been covered. The interval between two injections was 15−20 min, which was sufficiently long for the signal to return to the baseline. All errors are quoted as the standard deviation of the mean estimated from three to five experiments. The experiments were performed at 298.15 ± 0.02 K.

Results and Discussion

Calorimetric curves for the $C_mC_6C_nBr_2$ series in pure water at 298.15 K are shown in Figure 1, where the observed enthalpies of dilution (ΔH_{obs}) are plotted against the final concentrations (C) of the surfactants. All the titration processes were found to be endothermic and showed an abrupt decrease at a threshold concentration, indicating that the enthalpies of micellization are all negative. Following our observations on other surfactants,[23−26] when the final concentration is in the premicellar region, the added micelles dissociate into monomers and the monomers are then diluted; when the final concentration is above the CMC, the added micelles are only diluted. Hence we can distinguish the CMC and the enthalpy change (ΔH_{mic}) associated with micellization according to literature methods.[36−38] On each plot a clear break corresponding to micelle formation was observed, allowing identification of the CMC by using an extrapolation;[36,38] meanwhile the enthalpy of micellization, ΔH_{mic}, is obtained from the difference between the observed enthalpies of the two linear segments of the plot,[37] as shown in Figure 2.

The dissymmetric gemini series has the same headgroups, the same spacer, and the same number of hydrophobic units. As shown by Zana,[15] the distance between the two headgroups in a molecule with spacer $S = 6$ is comparable with that which would be obtained by electrostatic repulsion between two similar monomer units, which would be expected to be invariant with m/n. Dissymmetry should therefore be the principal factor determining the CMC and micellization enthalpy. The dilution enthalpies (Figure 1) at all concentrations increased from $m = 12$ to 16 at constant $m + n = 24$, indicating an increase in the hydrophobic interaction between the hydrophobic chains of the molecules, just as observed for cationic surfactants with
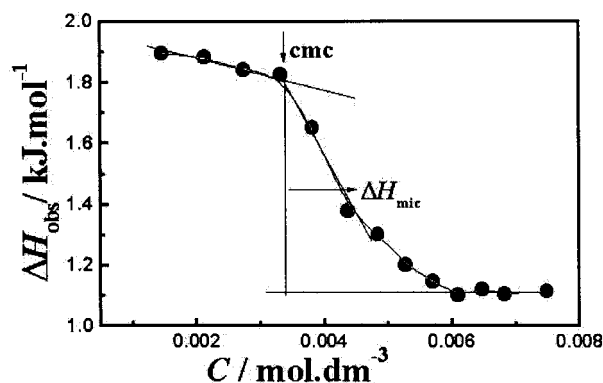

Figure 2. Example of determining the CMC and ΔH_{mic} from the microcalorimetric curve.

TABLE 1: CMCs and the Enthalpies of Micellization for $C_mC_6C_nBr_2$ at 298.15 K

$C_mC_6C_nBr_2$	m/n	CMC (10^{-4} M)	ΔH_{mic} (kJ/mol)	$\Delta(\Delta H_{mic})$
$C_{12}C_6C_{12}Br_2$	1	8.9 ± 0.2	−3.67 ± 0.07	0
$C_{13}C_6C_{11}Br_2$	1.18	8.6 ± 0.2	−6.42 ± 0.12	−2.75
$C_{14}C_6C_{10}Br_2$	1.4	8.2 ± 0.2	−8.60 ± 0.17	−4.93
$C_{16}C_6C_8Br_2$	2	7.3 ± 0.2	−11.21 ± 0.22	−7.54
$C_{18}C_6C_6Br_2$	3	5.8 ± 0.1	−14.18 ± 0.28	−10.51

dissymmetric double chains.[25,26] The curve for $C_{18}C_6C_6Br_2$, however, is different with a varying premicellar region and a lower dilution enthalpy. The former suggests some premicellar aggregation. Table 1 gives the CMCs and the enthalpies of micellization obtained from Figure 1. The CMCs decrease linearly with the increasing ratio m/n with $n + m = 24$. These indicate that the effective hydrophobicity of adding a methylene group to the short alkyl chain is less than that of adding a methylene to the long alkyl chain. Zana[32,33] has postulated a relationship between the CMC and Gibbs free energy of micellization (ΔG_{mic}) for the $C_mC_SC_mBr_2$ series with $S = 3, 4, 6, 8, 10, 12$ and used it to explain the pattern of CMC values of the geminis compared with their monomeric counterparts. For the $C_mC_6C_nBr_2$ series, a discussion similar to our previous work[23−26] was put forward, although the degree of dissociation of the micelle (β) is unavailable from the present work. This will introduce some uncertainty into the value of ΔG_{mic}. The changes of CMC and β, and hence Gibbs free energy of micellization (ΔG_{mic}), are quite small, and the effect is only a little larger than the error.[23,24] In contrast, the effect of the dissymmetry ratio, m/n, on micellization enthalpy, ΔH_{mic}, is large. Thus, we can certainly conclude that there is a larger interaction energy associated with the addition of a methylene to the long alkyl chain than that of adding one methylene to the short alkyl chain. Since ΔG_{mic} is approximately constant, the increasing interaction energies must be balanced by an increasing micellization entropy.[23−26] The most direct way of showing the effect of the dissymmetry is shown in Figure 3, where we plot the difference of ΔH_{mic} between the dissymmetric and symmetric geminis with $n + m = 24$ as a function of m/n.

There are two contributions to the hydrophobic interaction on aggregation, intramolecular and intermolecular. The intramolecular interaction will be the weaker of the two because the spacer keeps the two hydrophobic chains apart. In the symmetrical gemini the number of hydrophobic units interacting will be the same for intramolecular and intermolecular interactions, and therefore the hydrophobic interaction will be minimized. However, as m/n increases, the ratio of the number of hydrophobic units interacting intermolecularly to those interacting intramolecularly will increase. Hence the hydrophobic
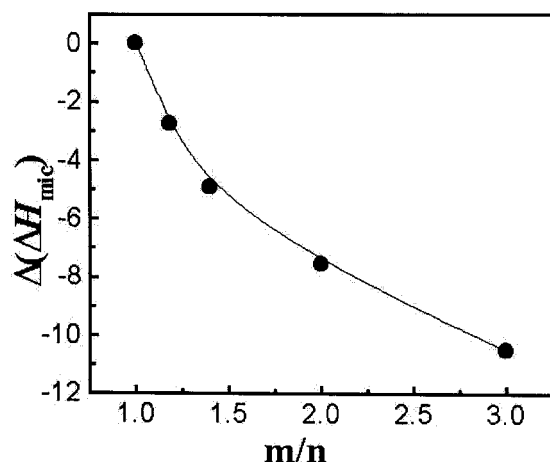
Figure 3. For $C_mC_6C_nBr_2$ series with $n + m = 24$, the variation of the difference in ΔH_{mic} between the dissymmetric and symmetric geminis with the ratio m/n.

interaction, which is known to be associated with a negative enthalpy of micellization, is gradually optimized. This is clearly seen in Figure 3. As we observed in previous papers on related surfactants, any decrease in the enthalpy of micellization tends to be compensated by an increase in the entropy contribution.[23−26] This is also approximately observed here where ΔG_{mic} remains approximately constant down the series. However, once again, the apparent invariance of the free energy conceals a more interesting underlying behavior.

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