Effect of Spacers on CMCs and Micelle-forming Enthalpies of Gemini Surfactants by Titration Microcalorimetry

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Abstract: The critical micelle concentrations (CMC) and the micelle-forming enthalpies (ΔH_{mic}) of gemini surfactants were first measured by the precise titration microcalorimetry. The results showed that ΔH_{mic} values are negative, and there is an exothermal minimum between **s**=4 and **s**=6. Furthermore, the CMCs of the surfactants are in good agreement with literature values.

Keywords: Gemini surfactants, micelle-forming enthalpy, CMC, microcalorimetry.

Gemini surfactants, as a new generation of surfactants in 1990's[1], are the surfactants with two polar groups and two alkyl chains connected with a spacer. The most widely studied gemini surfactants are as follows:

$$[C_mH_{2m+1}N(CH_3)_2\text{-}(CH_2)_S\text{–}N(CH_3)_2C_mH_{2m+1}]Br_2, \text{ or } C_m\text{-}C_S\text{-}C_m \bullet 2Br^-$$

where $\mathbf{C_s}$ stands for its spacer. Studies on their interesting physico chemical properties[2,3] have made much progress, predicting that the repulsive interaction between the two head groups, hydrophobic interaction among the alkyl chains and conformational entropy in the micellization process are dominant factors. But due to the lack of their micelle-forming thermodynamic properties, the indirectly measured properties result in larger uncertainty to describe accurately the micelle-forming process. Therefore, it is very important to explain reasonably the effect of the spacers on micellization process using direct microcalorimetry, which have been triumphantly applied in conventional surfactant and their mixture systems.

In this communication, we report first the CMCs and ΔH_{mic} values of $\mathbf{C_m\text{-}C_S\text{-}C_m \bullet 2Br^-}$(**m**=12**,** **s**=2, 4, 6, 8, 10, 12) series by the precise titration microcalorimetry. The studied surfactants were synthesized and purified according to the ref.3. An improved LKB-2107 titration microcalorimeter was used for directly measuring their micelle-forming enthalpies. The sensitivity of calorimeter is about 50μJ with an error 1.4 %. The CMCs and ΔH_{mic} values at 25°C can be conveniently obtained from titration microcalorimetry curves of $\mathbf{C_m\text{-}C_S\text{-}C_m \bullet 2Br^-}$ using an on-line computer.

The CMCs and ΔH_{mic} values of $\mathbf{C_m\text{-}C_S\text{-}C_m \bullet 2Br^-}$ are listed in **Table 1**. It shows clearly that the CMCs agree quite well with literature values[2,3], and they are much lower than those of the corresponding monomeric surfactants, $\mathbf{C_m\text{-}C_{S/2}\bullet Br^-}$, which is the reason why gemini surfactants have attracted much attention in many frontier fields[4], particularly, biology, life and material sciences. All the values of ΔH_{mic} are negative and appear an exothermal minimum between s=4 and s=6 which corresponds to the maximum of CMC values. This will provide an important information for deeper understanding the effect of the spacers on the micelle-forming process.

Table 1 The CMCs and ΔH_{mic} of $\mathbf{C_m\text{-}C_S\text{-}C_m \bullet 2Br^-}$ with various spacers at 25°C

s	3	4	6	8	10	12
CMC, mol/dm^3	1.09±0.02	1.14±0.02	0.89±0.02	0.71±0.01	0.39±0.01	0.26±0.01
ΔH_{mic}, kJ/mol	-5.70±0.11	-4.15±0.08	-3.67±0.07	-4.80±0.09	-6.74±0.14	-10.10±0.15

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References

1. F. M. Menger, C. A. Littau, *J. Am. Chem. Soc.* **1993**, *115*, 10083.
2. E. Alami, G. Beinert, P. Marie, R. Zana, *Langmuir* **1993,** *9*, 1465.
3. R. Zana, M. Benrraou, R. Rueff, *Langmuir* **1991**, *7*, 1072.
4. R. Zana, *Cur. Opin. Colloid Interface Sci.*, **1996**, *1*, 566.

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