

# Thermodynamics of Molecular Self-Assembly of Cationic Gemini and Related Double Chain Surfactants in Aqueous Solution

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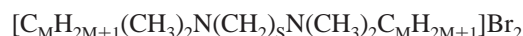
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Microcalorimetric measurements have been made on the series of gemini surfactants  $[\text{C}_M\text{H}_{2M+1}(\text{CH}_3)_2\text{N}(\text{CH}_2)_S\text{N}(\text{CH}_3)_2\text{C}_M\text{H}_{2M+1}]\text{Br}_2$ , designated  $\text{C}_M\text{C}_S\text{C}_M\text{Br}_2$ , where M and S indicate the numbers of carbons in the side chains and spacer respectively, for M = 12 and S = 3, 4, 6, 8, 10, 12. For comparison, parallel measurements have been made on the series of double-chain, singly charged surfactants dodecyltrimethylammonium bromides, designated as  $\text{C}_{12}\text{C}_N\text{Br}$  with N = 1, 2, 4, 6, 8, 10, 12, where N is the number of carbons in the secondary alkyl chain. The choice of this second series was to compare each  $\text{C}_M\text{C}_S\text{C}_M\text{Br}_2$  with its nearest equivalent monomer  $\text{C}_{12}\text{C}_{S/2}\text{Br}$ . The values of the critical micelle concentrations (cmc) were found to be in good agreement with other measurements, showing a maximum at S = 4–6 for the geminis and a nonlinear variation with chain length for the  $\text{C}_{12}\text{C}_N\text{Br}$  series. For both series of surfactants, the enthalpies of micellization,  $\Delta H_{\text{mic}}$ , are all exothermic and show a marked minimum in magnitude at S = 4–6 or N = 4–6. The variation of  $\Delta H_{\text{mic}}$  and  $\Delta S_{\text{mic}}$  across both series shows that the balance between enthalpic and entropic contributions to the process of micellization changes substantially with S or N.

## Introduction

The possibilities of using gemini amphiphiles to create new types of surfactants have recently been attracting increasing attention.<sup>1–11</sup> Their unusual physicochemical properties in comparison with those of conventional surfactants, such as much lower critical micelle concentrations (cmc), better wetting, greater surface tension lowering, and unusual morphologies, could make them potentially useful in many fields of application, for example, in soil remediation, enhanced oil recovery, drug entrapment and release, etc. Considerable effort has been made to design and synthesize new forms of geminis with the required properties,<sup>12–18</sup> to elucidate the relationship between the molecular structure of geminis and their aggregate morphology in aqueous solution<sup>4,5,19–22</sup> and to understand the factors underlying the variation of their thermodynamic properties with the length of the side chains and the spacers.<sup>23–27</sup>

So far, the most widely studied geminis are dicationic quaternary ammonium compounds having the following structure:



referred to as  $\text{C}_M\text{C}_S\text{C}_M\text{Br}_2$  where M and S indicate the numbers of carbons in the side alkyl chain and the spacer, respectively. The properties of these compounds, such as cmc values, degree of ionization of the micelle, aggregate morphology, phase behavior, rheological properties, and area per molecule adsorbed at the air/water interface, have been studied by a range of experimental methods, for example, electrical conductivity,

surface tension, cryotransmission electron microscopy, ultrasonic absorption relaxation, X-ray diffraction, small-angle neutron-scattering (SANS), etc.<sup>28–37</sup> The most striking results are the unusual aggregation behaviour and that for a constant value of M the value of the cmc passes through a maximum at S = 5 while the surface excess at the air/water interface passes through a minimum at S = 10–12. Most attention has therefore been devoted to these results. Diamant and Andelman,<sup>38</sup> for example, on the basis of a theoretical model suggested that the dominant factor in determining the last two properties above is the balance of the repulsive interaction between the head groups, the attractive interaction between the hydrophobic tails and the conformational entropy of the spacer. Zana<sup>23,24</sup> also proposed a relationship between the free energy of transferring a mole of alkyl chains from water to the hydrophobic core ( $\Delta G_{\text{mic}(\text{chain})}$ ) and the cmc and used it to explain the greater decrease of the cmc values of geminis with chain length compared with the corresponding monomeric surfactants. Most of the published data is based on only the values of the free energy of micellization, as determined from the cmc. However, it is probable that a more detailed examination of the constituent parts of the free energy, i.e., the enthalpy and entropy of micellization, could lead to a deeper understanding of the molecular detail and the driving forces involved in the self-assembly process of these surfactants. There are surprisingly few reports of calorimetric measurements on gemini and the related monomeric cationic surfactants.<sup>14,26,39,40</sup> In this paper, we report the results of calorimetric studies for the alkanediyl- $\alpha,\omega$ -bis (dodecyltrimethylammonium bromides), designated as  $\text{C}_{12}\text{C}_S\text{C}_{12}\text{Br}_2$  with S = 3, 4, 6, 8, 10, 12. For comparison, we have chosen to make parallel measurements on the series of double chained monomeric surfactants, the dodecyltrimethylammonium bromides, designated as  $\text{C}_{12}\text{C}_N\text{Br}$  with N = 1, 2, 4, 6, 8, 10, 12, where N is the number of carbons of the

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secondary alkyl chain. We have used a precision microcalorimeter to determine the cmc values and the enthalpies of micelle formation ( $\Delta H_{\text{mic}}$ ). From these two quantities we have determined the free energy of micelle formation ( $\Delta G_{\text{mic}}$ ) and the entropy of micelle formation ( $\Delta S_{\text{mic}}$ ).

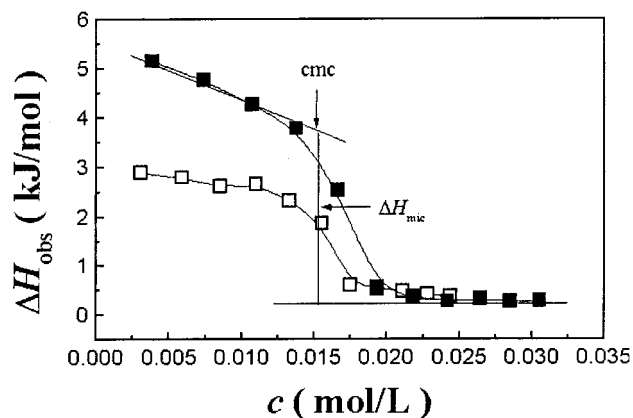
### Experimental Section

**Materials.** The  $\text{C}_{12}\text{C}_s\text{C}_{12}\text{Br}_2$  ( $S = 3, 4, 6, 8, 10, 12$ ) series was synthesized and purified according to the method of Menger.<sup>3</sup> The  $\text{C}_{12}\text{C}_N\text{Br}$  ( $N = 2, 4, 6, 8, 10, 12$ ) series was obtained by reacting dimethyldodecylamine with an excess of the corresponding alkylbromide in methanol at 40 °C for two weeks. Following evaporation of the methanol and washing with diethyl ether to remove excess alkyl bromide, the products obtained were recrystallized at least three times from acetone, ethanol, petroleum ether, or a methanol– $\text{H}_2\text{O}$ –petroleum ether mixture, depending upon the alkyl chain length. The final products were dried under vacuum. Dodecyltrimethyl ammonium bromide (DTAB) (99%) was obtained from Aldrich Chemical Company, Inc. and used as received. All of the surfactant solutions (concentration > cmc) were prepared using doubly distilled water.

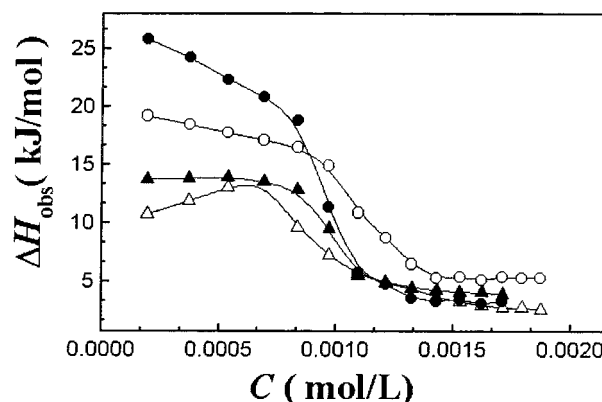
**Method.** An improved LKB-2107 isothermal titration microcalorimeter with a 1 mL sample cell was used for measuring directly the cmc and the enthalpy of micelle formation of surfactant solution. The precision of electrical calibration is better than  $\pm 1\%$ . The accuracy was tested by measuring the dilution enthalpy of a concentrated sucrose solution (0.985 mol/L). The resulting value ( $-0.643 \pm 0.015$  kJ/mol) agreed well with the literature value ( $-0.653$  kJ/mol).<sup>41</sup> The sample cell and the reference cell of calorimeter were initially loaded with 0.5 mL and 0.7 mL pure water, respectively. Concentrated surfactant solution was injected in small aliquots to the stirred sample cell using a 500  $\mu\text{L}$  Hamilton syringe controlled by a Braun 871182 pump. Each aliquot was 10–20  $\mu\text{L}$ , and addition of concentrated solution continued until the desired range of concentration had been covered. All experiments were performed at  $303.15 \pm 0.02$  K.

### Results

The titration processes were found to be endothermic for all of the surfactants under consideration, indicating that the enthalpies of micelle formation are all negative. Moreover, each experiment gave a break corresponding to the critical micelle concentration (cmc). The typical calorimetric curves of the variation of the observed enthalpies of dilution ( $\Delta H_{\text{obs}}$ ) with concentration ( $C$ ) for the two series of surfactants,  $\text{C}_{12}\text{C}_s\text{C}_{12}\text{Br}_2$  and  $\text{C}_{12}\text{C}_N\text{Br}$ , are shown in Figures 1 and 2, respectively. As has been discussed previously for conventional surfactants,<sup>42,43</sup> 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.  $\Delta H_{\text{mic}}$  can therefore be obtained from the difference between the observed enthalpies of the two linear segments of the plots as shown in Figure 1. The term  $\Delta G_{\text{mic}}$  is calculated from the cmc and the degree of dissociation,  $\beta$ , of the micelle, following procedures in the literature,<sup>24</sup> and  $\Delta S_{\text{mic}}$  is derived from  $\Delta H_{\text{mic}}$  and  $\Delta G_{\text{mic}}$ . Using values of  $\beta$  from the literature,<sup>29,47</sup> we derive the set of results given in Table 1. Our cmc values and their variation with  $S$  for the  $\text{C}_{12}\text{C}_s\text{C}_{12}\text{Br}_2$  series of surfactants agree well with those obtained by noncalorimetric methods.<sup>29,31</sup> The values of  $\Delta H_{\text{mic}}$  are also in approximate agreement with those measured for three of the geminis by Grosmaire et al.,<sup>39</sup> but it must be



**Figure 1.** Typical calorimetric curves of the variation of  $\Delta H_{\text{obs}}$  with  $C$  for the  $\text{C}_{12}\text{C}_N\text{Br}$  series at 303.15 K. The initial concentrations of surfactants: (■)  $\text{C}_{12}\text{C}_1\text{Br}$  100 mM; (□)  $\text{C}_{12}\text{C}_2\text{Br}$  80 mM.



**Figure 2.** Typical calorimetric curves of the variation of  $\Delta H_{\text{obs}}$  with  $C$  for the  $\text{C}_{12}\text{C}_s\text{C}_{12}\text{Br}_2$  series at 303.15 K. The initial concentration of the surfactant is all 5 mM: (●)  $\text{C}_{12}\text{C}_3\text{C}_{12}\text{Br}_2$ ; (○)  $\text{C}_{12}\text{C}_4\text{C}_{12}\text{Br}_2$ ; (▲)  $\text{C}_{12}\text{C}_6\text{C}_{12}\text{Br}_2$ ; (△)  $\text{C}_{12}\text{C}_8\text{C}_{12}\text{Br}_2$ .

noted that their measurements were made at 35 °C, whereas ours are at 30 °C. The discrepancies could be explained by variation of  $\Delta H_{\text{mic}}$  with temperature. The enthalpies of micellization of this series are all exothermic, and there is a strong negative minimum around  $S = 4-6$ , corresponding to the maximum in the cmc values.

In comparison with the geminis, the singly charged surfactants,  $\text{C}_{12}\text{C}_N\text{Br}$ , have much higher cmc values, and their enthalpies of micellization are lower. Once again the variation of  $\Delta H_{\text{mic}}$  with the secondary alkyl chain length goes through a less marked negative minimum for a value of  $N = 4-6$ , i.e., similar to the minimum in the geminis at  $S = 4-6$ . The effects of the length of the spacer and of the length of the second alkyl chain on the thermodynamics of micellization are shown in Figures 3 and 4.

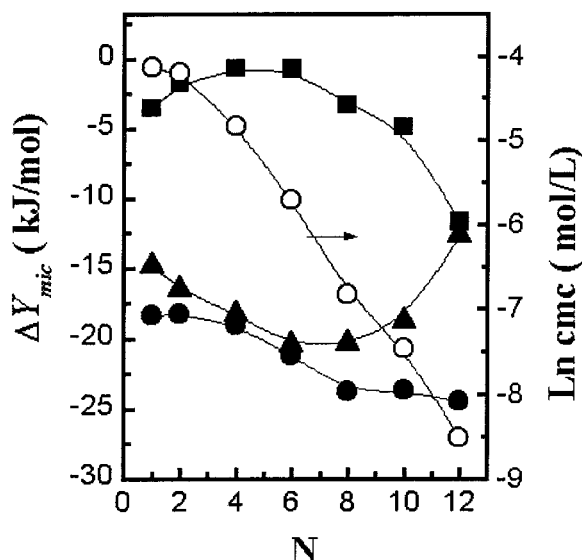
### Discussion

Woolley et al.,<sup>44</sup> and Mosquera et al.<sup>45</sup> have reported the cmc values and the enthalpies of micelle formation for alkyltrimethylammonium bromides ( $\text{C}_X\text{TAB}$ ) at 298.15 K. Their cmc values decrease dramatically with increasing chain length, and the enthalpies of micelle formation change linearly from a small positive value to negative values. The corresponding entropies of micellization are all positive and increase with chain length. The enthalpies of micellization are positive when  $X \leq 10$  and the process of micellization must then be driven by the entropy, but the enthalpies of micellization become negative when  $X >$

**TABLE 1: The cmcs and Thermodynamic Parameters of  $C_{12}C_8C_{12}Br_2$  and  $C_{12}C_NBr$  at 303.15 K**

| type                     | cmc (mM)         | $\Delta H_{mic}(kJ/mol)$ | $\Delta G_{mic}(kJ/mol)^a$ | $-T\Delta S_{mic}(kJ/mol)^b$ |
|--------------------------|------------------|--------------------------|----------------------------|------------------------------|
| $C_{12}C_3C_{12}Br_2$    | $0.84 \pm 0.03$  | $-15.69 \pm 0.47$        | $-31.75 (-21.47)^c$        | -16.06                       |
| $C_{12}C_4C_{12}Br_2$    | $1.01 \pm 0.01$  | $-9.38 \pm 0.28$         | $-30.24 (-20.26)^c$        | -20.86                       |
| $C_{12}C_6C_{12}Br_2$    | $0.83 \pm 0.02$  | $-8.85 \pm 0.25$         | $-29.84 (-19.74)^c$        | -20.99                       |
| $C_{12}C_8C_{12}Br_2$    | $0.68 \pm 0.02$  | $-9.53 \pm 0.33$         | $-28.49 (-18.34)^c$        | -18.96                       |
| $C_{12}C_{10}C_{12}Br_2$ | $0.28 \pm 0.03$  | $-13.95 \pm 0.55$        | $-30.14 (-19.02)^c$        | -16.19                       |
| $C_{12}C_{12}C_{12}Br_2$ | $0.21 \pm 0.03$  | $-18.03 \pm 0.64$        | $-29.45 (-18.12)^c$        | -11.42                       |
| $C_{12}C_1Br$            | $15.90 \pm 0.40$ | $-3.54 \pm 0.05$         | -18.37                     | -14.83                       |
| $C_{12}C_2Br$            | $14.96 \pm 0.29$ | $-1.72 \pm 0.03$         | -18.22                     | -16.50                       |
| $C_{12}C_4Br$            | $7.96 \pm 0.22$  | $-0.70 \pm 0.02$         | -19.00                     | -18.30                       |
| $C_{12}C_6Br$            | $3.29 \pm 0.09$  | $-0.72 \pm 0.02$         | -21.20                     | -20.48                       |
| $C_{12}C_8Br$            | $1.08 \pm 0.03$  | $-3.35 \pm 0.10$         | -23.76                     | -20.41                       |
| $C_{12}C_{10}Br$         | $0.58 \pm 0.02$  | $-4.91 \pm 0.17$         | -23.69                     | -18.78                       |
| $C_{12}C_{12}Br$         | $0.20 \pm 0.02$  | $-11.74 \pm 0.29$        | -24.49                     | -12.75                       |

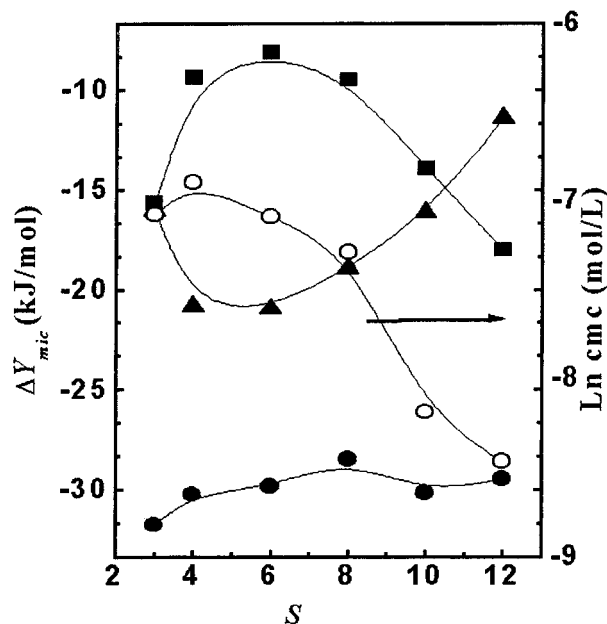
<sup>a</sup> Calculated from ref 24 using the equation,  $\Delta G_{mic} = (1 + \beta)RT \ln(CMC)$ ; where CMC is expressed in the molarity of surfactant;  $\beta$  can be taken from refs 29 and 47. <sup>b</sup> Calculated from the equation  $\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic}$ . <sup>c</sup> The value given in parentheses was calculated from ref 24 using the equation  $\Delta G_{mic} = (0.5 + \beta)RT \ln(cmc) - RT/2 \ln 2$ , where the cmc is expressed in the molarity of each chain of surfactant.



**Figure 3.** Variation of the thermodynamic parameters of micellization ( $\Delta Y_{mic}$ ) for  $C_{12}C_NBr$  with the secondary alkyl chain length ( $N = S/2$ ) at 303.15 K. (■)  $\Delta H_{mic}$  vs  $N$ , (▲)  $\Delta S_{mic}$  vs  $N$ , (●)  $\Delta G_{mic}$  vs  $N$ , and (○) cmc vs  $N$ .

10, and the micellization process is then driven jointly by the enthalpy and entropy.

The effects of varying the secondary alkyl chain length ( $N$ ) in the  $C_{12}C_NBr$  series on the cmc values and the thermodynamic properties of micellization are quite different from those for the  $C_XTABs$ . The cmc values decrease much less with increasing number of methylene groups than those of the  $C_XTAB$  series. For example,  $C_{12}C_6Br$  has one more methylene than  $C_{16}TAB$ , but its CMC is about five times larger than that of  $C_{16}TAB$ . This indicates that the effective hydrophobicity of each added methylene of the secondary alkyl chain in the double chain surfactant is less than that of each methylene in the single chain surfactant. Wang et al.<sup>46</sup> observed a comparable phenomenon in an investigation of the adsorption of single- and double-chain surfactants on a clay surface. The difference may result from the added methylenes in the  $C_{12}C_NBr$  compounds being much closer to the head group than in  $C_XTAB$  series. For example, when  $N < 6$ , the secondary alkyl chain might not be long enough to insert into the hydrophobic micelle core and can therefore lie only at the interface between the hydrophobic core and water.<sup>47</sup> This would lead to a reduction in the effective hydrophobicity of the secondary alkyl chain. This, in turn, would cause the cmc values of the double chain surfactants to change



**Figure 4.** Variation of the thermodynamic parameters of micellization ( $\Delta Y_{mic}$ ) for  $C_{12}C_8C_{12}Br_2$  with the spacer length ( $S$ ) at 303.15 K. (■)  $\Delta H_{mic}$  vs  $S$ , (▲)  $\Delta S_{mic}$  vs  $S$ , (●)  $\Delta G_{mic}$  vs  $S$ , and (○) cmc vs  $S$ .

much less than those of the single chain surfactants as the number of methylenes increases. The negative enthalpy of micelle formation results mainly from van der Waals interactions and hydrophobic interactions. In the double chain surfactants, if the effective hydrophobicity of the second alkyl chain is lowered, the hydrophobic interaction will be weakened, making  $\Delta H_{mic}$  less negative. Compared with the single chain surfactants, the larger area per head group and hence larger degree of ionization of the micelle, will lead to larger steric repulsion, which would also contribute positively to the negative  $\Delta H_{mic}$ . When  $N > 6$ , the secondary alkyl chain is long enough to penetrate into the micelle core and the hydrophobic interaction is enhanced. Hence, the values of  $\Delta H_{mic}$  become much more negative.

The geminis  $C_{12}C_8C_{12}Br_2$  have been considered as the dimers of the corresponding single-chain surfactants  $C_XTAB$  with a spacer, but better representations are either as a combination of one single-chain surfactant  $C_XTAB$  with one double-chain surfactant  $C_{12}C_NBr$ , where  $N = S$ , or a combination of two double-chain surfactants, where  $2N = S$ . Either of the latter two combinations is preferable to the first because they make an allowance for the spacer. However, the data for the double-

chain series of compounds has hitherto not been available. The cmc values and thermodynamic properties of the geminis are quite different from their corresponding monomeric equivalents,  $C_{12}C_8S_2Br$ . As can be seen from Table 1, the cmc values of the  $C_{12}C_8S_2C_{12}Br_2$  are generally an order of magnitude less than those of the  $C_{12}C_8S_2Br$ , indicating a strong influence of the chemical structure on the cmc. This can be seen from Table 1 to result mainly from the more negative values of their enthalpies of micelle formation.

The entropies of micellization are all positive for both series and go through a maximum for both series, corresponding to the enthalpy minima. We will discuss this in more detail in a later paper where we examine the temperature dependence of the enthalpies of micellization. For the moment, we just note the following interesting comparison between  $C_{12}C_8C_{12}Br_2$  and its corresponding "monomer",  $C_{12}C_4Br$ . Enthalpy and entropy both make important contributions to the micellization of  $C_{12}C_8C_{12}Br_2$ , whereas the micellization process for  $C_{12}C_4Br$  is driven mainly by entropy. The two entropies are almost the same. Hence, the large difference in the cmc stems entirely from the negative enthalpy of micellization of the gemini. This makes it clear that it is dangerous to draw conclusions about the factors determining micellization from cmc values ( $\Delta G_{mic}$ ) alone.

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