Micellar Aggregates of Gemini Surfactants: Monte Carlo Simulation of a Microscopic Model

Prabal K. Maiti[1] **and Debashish Chowdhury**[1,2,*]

[1]Department of Physics, Indian Institute of Technology,

Kanpur 208016, U.P., India[†]

[2]Institute for Theoretical Physics, University of Cologne

D-50937 Köln, Germany[‡]

Abstract

We propose a "microscopic" model of *gemini* surfactants in aqueous solution. Carrying out extensive Monte Carlo simulations, we study the variation of the critical micellar concentration (CMC) of these model gemini surfactants with the variation of the (a) length of the spacer connecting the two hydrophilic heads, (b) length of the hydrophobic tail and (c) the bending rigidity of the hydrocarbon chains forming the spacer and the tail; some of the trends of variation are counter-intuitive but are in excellent agreement with the available experimental results. Our simulations also elucidate the dependence of the shapes of the micellar aggregates and the magnitude of the CMC on the geometrical shape and size of the surfactant molecules and the electrical charge on the hydrophilic heads.

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* To whom all correspondence should be addressed;

E-mail: debch@thp.Uni-Koeln.de (till 30th June, 1997).

† (Permanent Address); E-mail: debch@iitk.ernet.in

‡ (Address till 30th June, 1997)

Soap molecules are common examples of surfactant molecules; these not only find wide ranging applications in detergent and pharmaceutical industries, food technology, petroleum recovery etc. but are also one of the most important constituents of cells in living systems. Therefore, physics, chemistry, biology and technology meet at the frontier area of interdisciplinary research on association colloids formed by surfactants [1]. The "head" part of surfactant molecules consist of a polar or ionic group. The "tail" of many surfactants consist of a single hydrocarbon chain whereas that of some other surfactants, e.g., phospholipids, are made of two hydrocarbon chains both of which are connected to the same head [2]. In contrast, *gemini* surfactants [3, 4, 5, 6], consist of two single-chain surfactants whose heads are connected by a "spacer" chain and, hence, these "double-headed" surfactants are sometimes also referred to as "dimeric surfactants" [7, 8]. The gemini surfactants have several unusual properties. Some of these properties, which make these very attractive for potential industrial use, are crucially influenced by the aggregation of the surfactants and the morphologies of these supramolecular aggregates. Therefore, in order to gain insight into the physical origin of some of the unusual properies of gemini surfactants, in this letter we propose a simple microscopic model and study the formation and morphologies of the supramolecular aggregates of these model gemini surfactants by Monte Carlo (MC) computer simulations.

When put into an aqueous medium, the "heads" of the surfactants like to get immersed in water and, hence, called "hydrophilic" while the tails tend to minimize contact with water and, hence, called "hydrophobic" [2]. The spacer in gemini surfactants is usually hydrophobic but gemini surfactants

with hydrophilic spacers have also been synthesized[9]. A multi-component fluid mixture containing water and surfactants minimizes the free energy by forming "*self-assemblies*" (i.e., supra-molecular aggregates) of surfactants, such as monolayer and bilayer membranes, micelles, inverted-micelles, vesicles, etc. [10]. Micelles are formed when the concentration of the surfactants in water exceeds what is known as the critical micellar concentration (CMC) [2].

On the basis of intuitive physical arguments, it is usually expected that a longer hydrocarbon chain should lower the CMC. On the contrary, two unusual features of the CMC of gemini surfactants with ionic heads are: (i) for a given fixed length of each of the two tails, the CMC *increases* with the length of the spacer till it reaches a maximum beyond which CMC *decreases* with further increase of the spacer length [7, 11, 12, 13]; (ii) for a given length of the spacer, the CMC *increases* with increasing tail length [4, 5]. Moreover, the micellar aggregates formed by the gemini surfactants with short spacers even at low concentrations just above the CMC are "long, thread-like and entangled" [8, 14], in contrast to the spherical shapes of the micelles formed by single-chain surfactants at such low concentrations. Our aim is to understand the physical origin of these unusual properties of gemini surfactants.

A microscopic lattice model of double-chain surfactants (with a single head) in aqueous solution was developed by Bernardes[15] by modifying the Larson model of single-chain surfactants [16, 17, 18]. In this letter we propose a microscopic lattice model of gemini surfactants by extending Bernardes' model so as to incorporate two hydrophilic heads connected by a *hydrophobic*

spacer.

The Larson model was originally developed for ternary microemulsions which consist of water, oil and surfactants. In the spirit of lattice gas models, the fluid under investigation is modelled as a simple cubic lattice of size $L_x \times L_y \times L_z$. Each of the molecules of water (and oil) can occupy a single lattice site. A surfactant occupies several lattice sites each successive pairs of which are connected by rigid nearest-neighbour bond. A single-chain surfactant can be described by the symbol [18] $\mathcal{T}_m\mathcal{N}_p\mathcal{H}_q$ where $\mathcal{T}$ denotes *tail*, $\mathcal{H}$ denotes *head* and $\mathcal{N}$ denotes the 'liaison' or neutral part of the surfactants. m, p and q are integers denoting the lengths of the tail, neutral region and head, respectively, in the units of lattice sites. Thus, each surfactant is a self-avoiding chain of length $\ell = (m + p + q)$. The "water-loving" head group is assumed to be "water-like" and, similarly, the "oil-loving" tail group is assumed to be "oil-like". Bernardes' lattice model of double-chain surfactants with a single hydrophilic head can be described by the symbol $\mathcal{T}_m\mathcal{N}_p\mathcal{H}_q\mathcal{N}_p\mathcal{T}_m$. In terms of the same symbols, the microscopic lattice model of a gemini surfactant, which we propose here, can be represented by the symbol $\mathcal{T}_m\mathcal{N}_p\mathcal{H}_q\mathcal{S}_n\mathcal{H}_q\mathcal{N}_p\mathcal{T}_m$ where n is the number of lattice sites constituting the spacer represented by the symbol $\mathcal{S}$. We shall refer to each site on the surfactants as a *monomer*.

Jan, Stauffer and collaborators [17] reformulated the Larson model in terms of Ising-like variables, in the same spirit in which a large number of simpler lattice models had been formulated earlier [19] for the convenience of calculations. In this reformulation, a classical Ising spin variable S is assigned to each lattice site; $S_i = 1$ (-1) if the i-th lattice site is occupied by

a water (oil) molecule. If the j-th site is occupied by a monomer belonging to a surfactant then $S_j = 1, -1, 0$ depending on whether the monomer at the jth site belongs to head, tail or neutral part. The monomer-monomer interactions are taken into account through the interaction between the corresponding pair of Ising spins which is assumed to be non-zero provided the spins are located on the nearest-neighbour sites on the lattice. Thus, the Hamiltonian for the system is given by the standard form

$$H = -J \sum_{<ij>} S_i S_j. \tag{1}$$

where attractive interaction (analogue of the ferromagnetic interaction in Ising magnets) corresponds to $J > 0$ and repulsive interaction (analogue of antiferromagnetic interaction) corresponds to $J < 0$ [17]. Temperature T of the system is measured in the units of J (the Boltzmann constant $k_B = 1.0$).

We have considered three possible Larson-type microscopic lattice models of *ionic* gemini surfactants. In the simplest model, which we call model A, the monomers belonging to heads have Ising spin $+2$ to mimic the presence of charge. The repulsive interaction between a pair of ionic heads is taken into account through an antiferromagnetic interaction $J = -1$ between pairs of nearest neighbour sites both of which carry spins $+2$; however, the interaction between all other pairs of nearest-neighbour spins is assumed to be $J = 1$. The short-range of the repulsive (antiferromagnetic) interaction between the "charged" heads corresponds to very strong screening of the Coulomb repulsion between ionic heads by the counterions. Molecular dynamics (MD) simulations of a similar molecular model of gemini surfactants has been carried out by Karaborni et al. [20]. In this letter we summarize

only the most important results on the model A with *hydrophobic* spacer; the results for the models B and C will be reported, together with the results for the model A with hydrophilic spacer, in a longer paper elsewhere [21].

In order to investigate the influence of the ionic heads on the results, we have also considered a model of gemini surfactants with non-ionic polar heads which is obtained from the model A by replacing all the $+2$ Ising spin variables by Ising spin $+1$ (and, accordingly, the interactions -1 between the heads on nearest-neighbour sites are replaced by $+1$). Moreover, in order to investigate the role of the chain stiffness we have introduced a chain bending energy; every bend of a tail or a spacer, by a right angle at a lattice site, is assumed to cost an extra amount of energy $K(> 0)$.

We have carried out MC simulations of the model $\mathcal{T}_m\mathcal{N}_p\mathcal{H}_q\mathcal{S}_n\mathcal{H}_q\mathcal{N}_p\mathcal{T}_m$ of gemini surfactants for $p = q = 1$ and for three differnet values of the tail length, namely, $m = 5, 15$ and 25 in water where $L_x = L_y = L_z = 100$. The moves allowed for the surfactants in our model are same as described in ref.[18]. In reality, CMC is not a single concentration (perhaps, it is more appropriate to call it characteristic micellar concentration [17]). Following Stauffer et al.[17], we identify CMC as the amphiphile concentration where half of the surfactants are in the form of isolated chains and the other half in the form of clusters consisting of more than one neighbouring amphiphile. For a given m we have computed the CMC for spacer lengths $2 \leq n \leq 20$.

The non-monotonic variation of CMC of ionic gemini surfactants with the spacer length, shown in figs. 1 and 2, is in qualitative agreement with the experimental observations [11, 12, 13, 14]. Moreover, for a given length of the spacer, the CMC increases when the bending stiffness K of the hydrophobic

chains is switched on. Furthermore, we have observed that, for a given length of the hydrophobic spacer, the CMC of ionic gemini surfactants *increase* with the increase of the tail length [21]; this trend of variation is also consistent with the corresponding experimental observations [4, 5].

For a given tail length, the CMC of model gemini surfactants with non-ionic polar head groups decreases *monotonically* with the increase in the spacer length for both $m = 5$ and $m = 15$ (see fig.3). This is in sharp contrast to the non-monotonic variation observed for ionic gemini surfactants. However, for a given spacer length, the trend of the variation of CMC of non-ionic gemini surfactants with the tail length is similar to that observed for ionic gemini surfactants.

The snapshots of the micellar aggregates formed by the gemini surfactants with ionic heads are shown for spacer length $n = 2$ (fig. 4) and for $n = 16$ (fig.5). The morphology of the aggregates in fig.4 are similar to the "long, thread-like and entangled" micelles observed in laboratory experiments [8] and in MD simulations [20] on gemini surfactants with short spacers. Moreover, our data in fig.5 suggest that rod-like micelles are formed by gemini surfactants with $m = 15$ when the spacer length is $n = 16$. The morphologies of the aggreagtes in fig.4 and 5 are in sharp contrast with the spherical shape of the micelles (see fig.6) formed by single-chain ionic surfactants of comparable tail size even at concentrations somewhat higher than those in the figures 4 and 5.

We did not observe any significant difference in the shapes of the aggregates of ionic and non-ionic gemini surfactants for given values of m, n and comparable concentration [21], in spite of qualitatively different trends of

variation of CMC with spacer lengths.

Therefore, we conclude that (i) the shapes of aggregates are dominantly determined by the geometric shape and size of the molecules whereas (ii) the variation of CMC with spacer length is strongly influenced by the ionic charge. It would be interesting to investigate the effects of weakening of the screening (i.e., increasing the range) of the repulsive Coulomb interaction between the ionic heads on the results reported in this letter; but, such a MC study will require much larger computational resources.

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Figure Captions:

Fig.1: Variation of CMC of ionic geminis with spacer length; $m = 15$, $T = 2.2$. The symbols $\Box$ and $\times$ correspond to $K = 0$ and $K = 2$, respectively. The continuous curves are merely guides to the eye.

Fig.2: Same as fig.1, except that $m = 5$. The symbols $\triangle$ and $*$ correspond to $K = 0$ and $K = 2$, respectively.

Fig.3: Variation of CMC of non-ionic geminis with spacer length; $m = 15$ ($\Box$) and $m = 5$ ($\triangle$) both with $K = 0$ and at $T = 2.2$. The continuous curves are merely guides to the eye.

Fig.4: Snapshots of the micellar aggregates formed by ionic geminis with $m = 15$, $n = 2$ and $K = 0$ at $T = 2.2$ when the surfactant density is 0.007. The symbols black spheres, dark grey spheres and light grey spheres represent monomers belonging to head, tail and spacer, respectively.

Fig.5: Same as in fig.5, except that $n = 16$ and the density is 0.005.

Fig.6: Snapshots of micellar aggregates formed by single-chain ionic surfactants with $m = 14$ and the density 0.01. The symbols black spheres and grey spheres represent monomers belonging to head and tail, respectively.