

Effect of Long-Range and Steric Hydrophilic Interactions on Micellization of Surfactant Solutions: A Monte Carlo Study in 2-D

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Monte Carlo simulations of aqueous surfactant solutions have been performed on a two-dimensional lattice in a canonical ensemble. The simulations are based on four different models of surfactants with chainlike geometry and several types of interactions between the surfactant headgroups. The effect of number of headgroups (N_{HG}) and the types of interactions between them (short-range versus long-range) has been examined on the surfactant aggregation. The simulations show that the aqueous solutions of surfactant chains with $N_{\text{HG}} > 1$ and a short-range head-head interactions behave in a manner similar to that of the solutions of surfactant chains with $N_{\text{HG}} = 1$ and long-range electrostatic interactions between the headgroups. The similarity of the results in the two models is discussed on the basis of free energy of micellization and is shown to be an effect of similar excluded volume of headgroups in the two models.

1. Introduction

Recent years have seen a surge in the applications involving use of surfactant self-assembly phenomena. The fact that surfactant molecules, composed of hydrophobic tail groups and hydrophilic headgroups, can aggregate or self-assemble in an aqueous environment has been exploited in many diverse areas of engineering and medical science in a variety of applications, such as environmental, pharmaceutical, biological, and surface engineering.^{1–4} Depending upon their concentration and their geometry, surfactant molecules assemble in a spectrum of structures, e.g., spherical, cylindrical, bilayers, etc. This very nature of surfactant solutions has been driving research efforts in developing adequate theories to explain the self-assembly phenomena and to predict the phase behavior of the surfactant solutions. Two major approaches are seen in the literature explaining the aggregation behavior of surfactant molecules, namely, phenomenological models and computer simulations.

The phenomenological studies usually hinge on the ability to calculate the chemical potential of free and associated surfactant molecules.^{2,5–6} Therefore, a geometry of the aggregate, e.g. sphere, cylindrical, etc., is often assumed and the free energy of these structures is calculated. The structure with the lowest energy for the conditions of interest is then chosen as the equilibrium structure. By calculation of the difference between the standard chemical potential of an amphiphilic molecule in the aggregated state and one in the free state, the size distribution of the aggregates can be determined. However,

such an approach precludes the identification of unexpected novel aggregate structures and is unable to probe the dynamics of micellar systems.

Recently, there has been an enhanced interest in the computer simulation studies of the micellization behavior in the aqueous surfactant solutions due to the ever-increasing computational power of today's computers.^{7–30} These studies can conveniently be divided in two broad categories: molecular dynamics simulations; Monte Carlo simulations.

The molecular dynamics simulations of surfactant solutions have been performed both with and without the

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explicit presence of the solvent molecules.^{7–18} In some cases the chemical groups in the surfactant chains have been modeled as spheres interacting with each other via Lennard-Jones potentials. Newton's equations of motion are solved for each sphere interacting with other spheres in the simulation cell. Some of these MD simulations are very expensive computationally and, therefore, sometimes require a preassembly of structures and a limit on the number of molecules that can be simulated in a reasonable amount of time.

The Monte Carlo simulation studies of surfactant solutions have been performed widely in the past 15 years. These techniques are generally based on lattice models in which a surfactant molecule is represented as a chain of chemical groups occupying certain grid sites on a two or three-dimensional lattice. Extensive work has been done by Larson,^{19–23} showing that surfactant self-assembly can be achieved by Monte Carlo simulations without having to resort to any preassembled micellar structure or shape. Most of Larson's work has focused on three-component amphiphile–oil–water systems, and quantitative predictions of the phase behavior have been made by using a temperature integration method. By performing his simulations at different conditions of temperatures and concentrations, Larson has shown the ability of these models to predict self-assembly into lamellar, packed cylindrical, and spherical phases as well as bicontinuous structures.

Several Monte Carlo studies have been carried out for the measurement of the micellar properties, such as critical micelle concentration (cmc), micellar size, micellar shape, aggregation number, polydispersity, etc. Care^{24–26} has studied both two-dimensional and three-dimensional lattice models of binary mixtures of water–surfactant systems in a canonical ensemble. The cluster size distribution has been determined as a function of temperature and concentration. The cluster size distributions show a significant polydispersity, and a peak in these distributions is taken as indicative of micelle formation.

More recently, lattice surfactant systems were studied by grand-canonical Monte Carlo (together with histogram-reweighting) techniques.²⁷ Both amphiphilic molecules of symmetric and asymmetric architectures have been investigated. The osmotic pressure and chemical potential/volume relationships are determined as a function of temperature. The cmc is then determined as a function of temperature from the osmotic pressure curve.

Monte Carlo simulations of a three-dimensional lattice model of an amphiphile–solvent system are presented and examined by Talsania et al.²⁸ for their effectiveness in predicting the thermodynamics of self-association of amphiphiles in solution. Monte Carlo simulations have also been used by this group for studying the solubilization of solute molecules in surfactant aggregates.²⁹ The effect of the ratio of headgroup size to tail group size on micellar properties has also been investigated.

Several reviews on the simulation studies of surfactant solutions have appeared in the literature recently.^{30,31} These reviews contain information about the surfactant simulation modeling in general and provide a critical overview of the current state of research in this area. Simulation studies of copolymers done by Mattice et al.^{32,33} provide additional insight into the appropriateness of using the lattice-based MC models for surfactant solutions.

The Monte Carlo work to date has used short surfactant chains having a structure H_xT_x , where H and T represent the head and tail groups of the surfactant chains. The main driving force for surfactant aggregation in these prior studies originates from an unfavorable interaction between the hydrophobic tail groups of the surfactant chains and the solvent (water) and a favorable interaction between the hydrophilic headgroups and the solvent (water). Some studies also model the interaction between the headgroups as short-range nearest-neighbor repulsion. The repulsive interaction between the headgroups of the surfactant chains is responsible for limiting the size of the micelle. There is, however, a controversy in the modeling of head–head interactions, and relatively scant attention has been paid to resolve the issue.

Owenson and Pratt³⁴ have shown that to achieve a surfactant aggregation yielding finite size micelles one needs to include long-range repulsive interaction between the headgroups. The views of Owenson were refuted by Smit et al.¹⁶ in their molecular dynamics studies of surfactant systems in which they showed the self-assembly of surfactant chains without any long-range interactions between the headgroups. The views of Smit et al. have been well supported by numerous other simulation studies that have reported surfactant self-assembly with only short-range repulsive interactions between the headgroups. However, there is a notable difference between the structure of surfactant chains used by Owenson and Pratt and the ones used by other investigators. Owenson and Pratt modeled the surfactant chains with only one headgroup, whereas, in the model of Smit et al., the structure of surfactant chains is H_xT_y , with $x, y \geq 2$.

The objective of this paper is to understand the effect of interactions between the headgroups on the aggregation behavior of surfactant molecules. The paper is organized as follows. First, we present in section 2 the details of the 2-D models used in studying the effect of the number of headgroups and the nature of the interactions between these groups on the aggregation behavior. Simulation results are reported in section 3.1. The different models studied in this work are compared on the basis of the cmc values obtained from our simulation results. We use several definitions of cmc that exist in the literature. Since different definitions lead to different cmc values (in any given model), the comparison between models is done only within a given cmc definition. This is followed by a discussion of our two-dimensional simulation results in section 3.2, based on the free energy of micellization and excluded volume theory. Finally, we conclude the paper with a brief summary of the findings of the work and a discussion of dimensionality effects and temperature effects on the simulations of our models in section 4.

2. Models and Method

2.1. Models. In this work, the surfactant chains have been modeled as chains of connected grid sites on a two-dimensional square lattice. With representation of the headgroups by H and tail groups by T, surfactant chains having two different structures H_xT_y have been modeled with $x = 1, y = 12$ and $x = 7, y = 12$. The empty grid sites are considered as occupied by the water molecules, which are represented by a W. To bring out the effect of long-range and steric hydrophilic interactions on the micellization behavior of surfactant molecules in the aqueous solution, four different models of surfactant types and headgroup interactions have been considered, namely, strong long-range (SLR), short-range (SR), long-range (LR), and long headgroup (LHG). In the LR, SR, and SLR models surfactant chains of H_1T_{12} type were used. In the LHG model, we have used surfactant chains

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(H_7T_{12}) with 7 headgroups and 12 tail groups. In SR and LHG models, the headgroups of surfactants H_1T_{12} , and H_7T_{12} interact via a short-range nearest-neighbor type interaction. In the LR and SLR models, the headgroups of H_1T_{12} type surfactants have a long-range Coulombic interaction with a cutoff distance of 30 grid units. As indicated below, a stronger interaction value was used for headgroup repulsion in the SLR model than in the other models.

Surfactant aggregation in the aqueous solutions is widely understood to be an entropic effect.⁵ The surfactant chains in water aggregate to avoid the decrease in water entropy due to structuring of water around the free surfactant molecules. However, numerous successful simulations of models have been performed that ignore the water structure.^{18–29} These models use an unfavorable energetic interaction between the tail and water groups that is often interpreted as an effective result of the interplay between energy and entropy gain that drives aggregation. We follow the generally accepted scheme in which these energy and entropy effects are buried into an effective positive interaction energy term ϵ_{WT} . Also, a negative interaction energy term ϵ_{WH} has been used in all the models for the solvophilic headwater interactions. The interaction between a headgroup of one chain and a tailgroup of another chain, ϵ_{TH} , is assumed to be unfavorable and that it increases the energy. The headgroups of the surfactants have a positive repulsive interaction ϵ_{HH} . The total energy of the water/surfactant system is calculated by the following expression:

$$U = (\epsilon_{WW}n_{WW} + \epsilon_{WT}n_{WT} + \epsilon_{WH}n_{WH} + \epsilon_{TH}n_{TH} + \epsilon_{TT}n_{TT} + \epsilon_{HH}n_{HH}) \quad (1)$$

Here n_{WW} , n_{WT} , n_{WH} , n_{TH} , n_{TT} , and n_{HH} are the total numbers of water–water (WW), water–tail (WT), water–head (WH), tail–head (TH), tail–tail (TT), and head–head (HH) nearest-neighbor contacts in the solution and $\epsilon_{WW} = 0$, $\epsilon_{WT} = 0.77 k_B T$, $\epsilon_{WH} = -4.44 k_B T$, $\epsilon_{TH} = 0.77 k_B T$, $\epsilon_{TT} = 0$, and $\epsilon_{HH} = 4.44 k_B T$ ($44.4 k_B T$ in the SLR model) are the interaction energies of the respective contacts. We choose interaction energies empirically that give a micelle-like behavior. The interaction energy used for a water–tail contact appears to be consistent with the free energy change in transferring a surfactant chain from an aqueous environment to an oil-like environment. According to Stokes and Evans,³⁵ the free energy change in transferring a surfactant chain from an aqueous solution to an oil-like interior is 3.0 kJ/mol per CH_2 group. Assuming two water molecules per CH_2 group, as in our 2-D square grid model, this translates to 0.015 eV that agrees well with the water–tail interaction strength of 0.019 eV (at room temperature). The interaction between the headgroups compares well with the interaction strength between two point charges separated by a distance of 3 Å in an aqueous medium. In the LR and SLR models, another term is added to the eq 1 to account for the long-range Coulombic interaction between the headgroups and is given by

$$U_{\text{long-range}} = \sum_{\text{pairs}} \phi/d_{HH} \quad (2)$$

where $\Phi = \epsilon_{HH}$ and d_{HH} = distance between the headgroups for $1 < d_{HH} <$ cutoff distance (30 grid units).

Evidently, the models have been simplified by considering no interaction between the water molecules and no interaction between the tailgroups of the surfactant molecules. Also, the headgroups have been assumed to interact similarly as the water molecules with the hydrophobic tail groups of the surfactant chains.

Simulations were run in the canonical ensemble following the Metropolis method. First, we introduce N_{ch} number of surfactant chains (H_xT_y) randomly in a square grid lattice of size $L \times L$. These surfactant chains occupy $N_{ch}(x+y)$ grid sites, and the rest of $((L \times L) - N_{ch}(x+y))$ grid sites are occupied by the water molecules. The energy of a random configuration is then calculated by eq 1. The surfactant chains are then allowed to make Monte Carlo moves on the lattice as explained in the next

section. The move is always selected if it reduces the overall energy of the system. If an MC move results in an increase in the overall energy, then the move is either accepted or discarded depending upon a transition probability. Several millions (about 8–12 million) of Monte Carlo moves were used in all the cases to obtain reliable statistical averages once thermal equilibration is achieved. To eliminate any finite grid-size effects, simulations were run in four different grid-sizes (64×64 , 128×128 , 192×192 , 256×256). The energy/chain for each grid size was plotted as a function of the grid size at a given surfactant concentration. We have used the following definition of surfactant concentration:

$$X_{ch} = \frac{N_{ch}}{((L \times L) - (N_{ch}(x+y))) + N_{ch}} \quad (3)$$

Here X_{ch} is the concentration of surfactant chains, N_{ch} is the number of surfactant chains, L is the grid size, and x and y are the numbers of headgroups and tailgroups, respectively, in a surfactant chain. It must be noted that the simulations were performed in a two-dimensional grid and hence the concentrations may differ from the experimental concentration values. A plateau was obtained in all the energy versus grid size plots for a grid size of 192×192 . This simply indicated that a grid size of 192×192 meets the requirement of thermodynamic limit and, therefore, most of the results presented in this paper have been taken from a simulation cell of size 192×192 .

2.2. Brief Review of MC Method. The simulations, in all the models, consisted of four types of Monte Carlo (MC) moves—forward and backward reptation, global chain translation, flip, and global cluster moves. In the reptation moves, an end group (headgroup for forward reptation and tailgroup for backward reptation) of the surfactant chain is randomly selected. This is followed by a random selection of a nearest-neighbor site. The selected end group of the chain is then moved to this new site if it is vacant, and the rest of the groups in the chain move in the same direction by one grid site or else the move is discarded. In the flip move, a tailgroup in a kink position is moved to an empty, diagonally opposite site on the square lattice. The random global translation of chain involves random selection of a group of a randomly selected chain and a random selection of a new grid site. The selected group is then moved to the new grid site while maintaining the original structure of the chain, provided all the new sites to be occupied by all the groups in the chain are empty. Finally, a global cluster translation move was included, in which first a group is randomly selected in a randomly selected chain. This is followed by a random selection of a new grid site. The selected group is then moved to the new grid site along with the cluster to which this chain is associated. For the purpose of our simulations, we define a cluster as a group of surfactant chains sharing nearest-neighbor sites. A cluster updating method was used similar to those published in the literature.²⁷ The cluster translations are important in the sense that after the formation of clusters the sampling of phase space can become extremely slow with the other moves, and the system might get trapped in a metastable state. The cluster translations eliminate such possibilities and allow efficient sampling of the phase space.

3. Results and Discussion

3.1. Simulation Results. The results obtained from the simulations in SLR, SR, LR, and LHG models have been plotted for (a) the concentration of monomers (nonaggregated surfactant chains) in a simulation cell vs overall concentration of surfactant chains (Figure 1), (b) energy/chain in a simulation cell as a function of overall concentration of surfactant chains (Figure 2), and (c) cluster size distributions (Figure 3). Each of these plots provides important insights into the physics and chemistry of the aggregation behavior in the aqueous surfactant solution. Prior studies have shown that cluster size distributions and plots of concentration of single chains as a function of overall surfactant concentration could be used for the determination of micellar properties, such as

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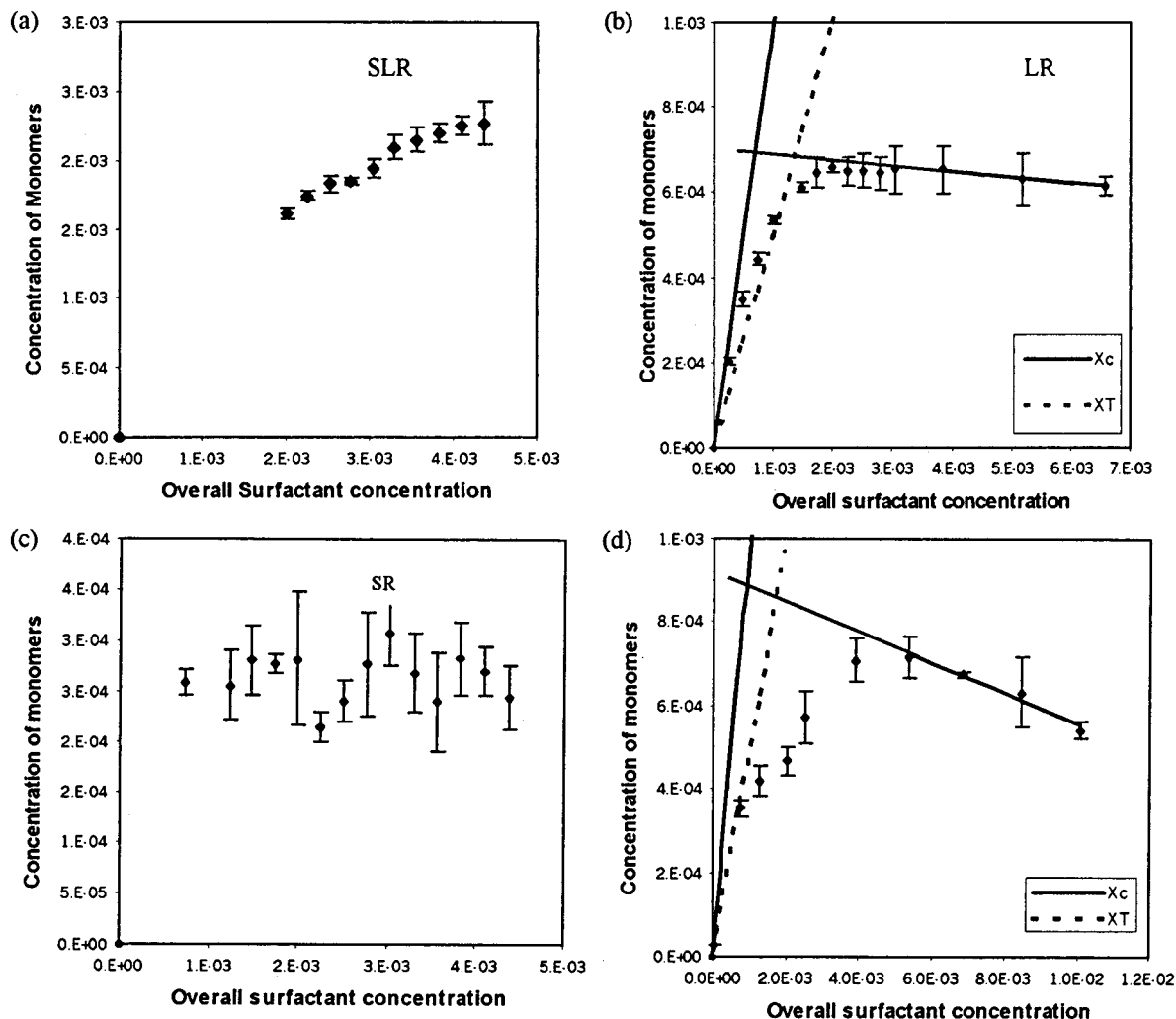


Figure 1. Monomer concentration as a function of overall surfactant concentration in the (a) SLR model, (b) LR model, (c) SR model, and (d) LHG model.

critical micelle concentration, aggregation number, etc. In this study, we have also used the energy/chain in the simulation cell as a function of concentration for the determination of micellar properties.

A. Monomer Concentration as a Function of Overall Surfactant Concentration. Several definitions of critical micelle concentration (cmc), based on the plots of monomer concentration versus overall surfactant concentration, have been proposed in the literature. Care et al.²⁴ have defined cmc (X_C) as the concentration at which a line of unit slope passing through the origin intersects a straight line through the monomer concentration beyond the onset of micellization. Israelachvili³⁶ has defined the cmc as the overall surfactant concentration at which the concentration of surfactant chains in the aggregates is equal to the concentration of monomers. Talsania et al.²⁸ have used Israelachvili's definition of cmc to define cmc (X_T) as the concentration at which the curve representing single chain concentration as a function of overall surfactant concentration intersects a straight line through the origin with a slope of 0.5.

It can be seen from Figure 1b,d that the single chain concentration in the LR and LHG models first rises with the overall surfactant concentration and then decreases slightly. Similar results have been reported in the

literature for surfactant chains with more than one headgroup in relatively shorter chains.^{24–26} The observed decrease in the monomer concentration at higher overall concentrations is also in agreement with the simulation results and experimental observations reported in the literature.^{24,26} Care et al have been successful in predicting a decrease in monomer concentration beyond the cmc by applying a correction for nonideality in the chemical potentials of the surfactants in the solution and the micelles in the mass-action model of Moroi.³⁷ We have obtained the critical micelle concentrations in the two models (LR and LHG) on the basis of above two definitions (X_C and X_T) and these values are reported in the Table 1.

We observe in Figure 1a that, in the SLR model, in which the headgroups of the surfactant chains interact by a very strong long-range Coulombic interaction, the concentration of monomers keeps on increasing with the overall concentration of surfactant chains. This indicates that the solution remains largely a dispersion of single chains with the strong repulsion between the headgroups not allowing the surfactant chains to come together despite the nonfavorable hydrophobic tail–water interactions. In the case of only nearest-neighbor short-range interactions (SR) between the headgroups of surfactant chains H_1T_{12} ,

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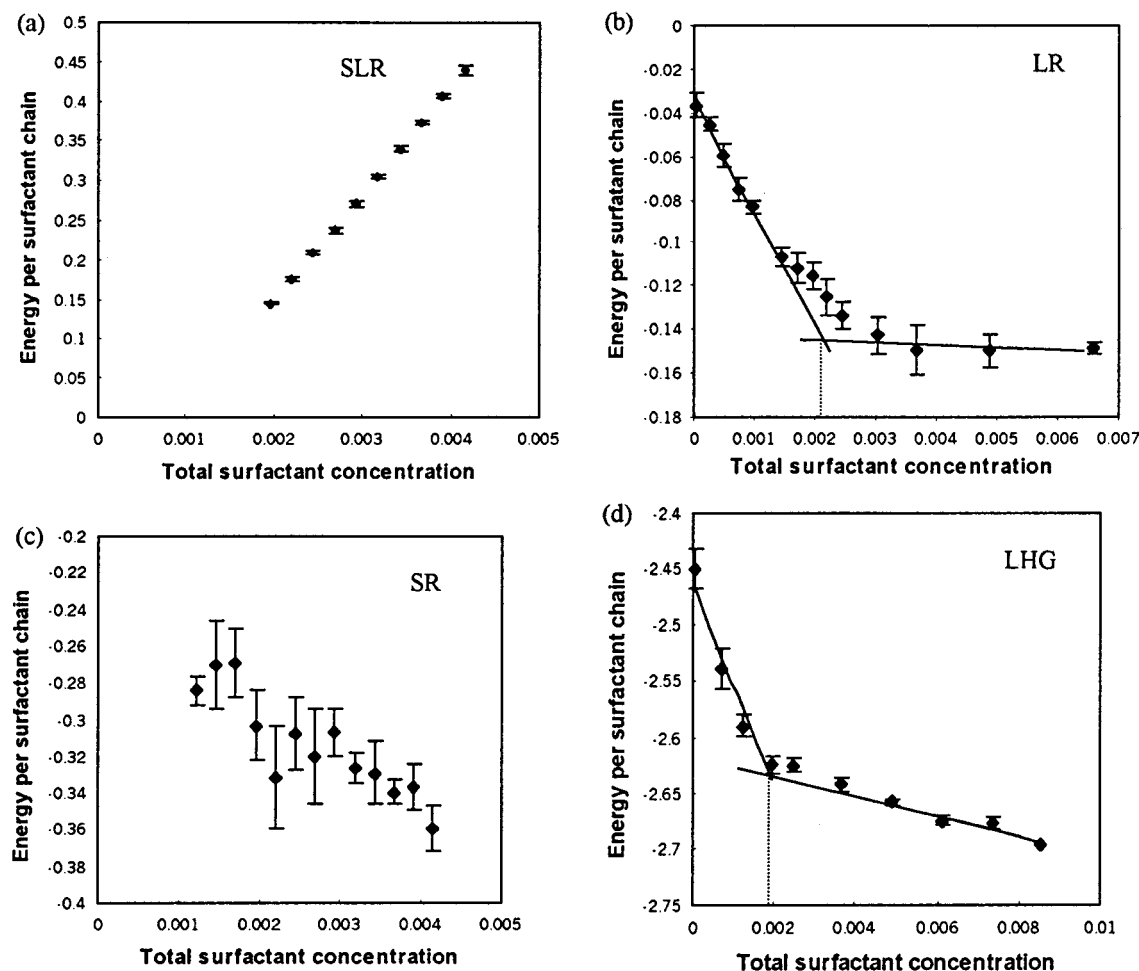


Figure 2. Energy/surfactant chain as a function of overall surfactant concentration in the (a) SLR model, (b) LR model, (c) SR model, and (d) LHG model.

the single chain concentration is seen to be changing very slowly and staying very low relative to the overall surfactant concentration. Even at overall concentrations as low as $\sim 1 \times 10^{-3}$, the single chain concentration is less than 3×10^{-4} . This indicates the readiness with which surfactant chains form aggregates when only the short-range interactions are present between the headgroups of surfactant chains H_1T_{12} . These results also provide an indication that the critical micelle concentrations for SR model lies below and that for the SLR model lies above the concentrations studied in this work. Stated otherwise, in the SR model $X_{cmc} < 1 \times 10^{-3}$ and in the SLR model $X_{cmc} > 4 \times 10^{-3}$.

B. Energy/Surfactant Chain as a Function of Overall Surfactant Concentration. In Figure 2, we have plotted the energy/chain as a function of overall surfactant concentrations in the different models. It can be seen that the energy/chain curve in the case of LR and LHG models shows a change in slope. This result is similar to the experimental observations in which a solution property shows a change in the slope with respect to the overall concentration around cmc. The cmc is then taken as the intersection of two linearly extrapolated lines. We have, therefore, used the plots in the Figure 2 to determine cmc on the basis of energy (X_{en}) in the LR and LHG models. The cmc's in two cases were obtained by the intersection points of the linear regression lines on the initial and final portions of the data points. The cmc values thus obtained were $\sim 2 \times 10^{-3}$ in both LR and LHG models. The energy/chain in the SLR model keeps on increasing

with the overall concentration. This result is due to the overwhelming repulsive interaction between the headgroups of the surfactant chains that increases with the increasing concentration. As the strong repulsive forces inhibit chains from coming closer, the increased tail-water contacts also increases the overall energy. In the SR model, the energy/chain, in the concentration range studied, shows a slow monotonic decrease with increasing concentration. This is similar to the high concentration behavior of LR and LHG models, suggesting that the cmc is lower than the concentrations studied.

C. Cmc from Cluster Size Distributions. Figure 3a,b displays the cluster size distributions for each of the cases studied (SLR, SR, LR, LHG) for a high concentration and a low concentration, respectively. In the low concentration regime, the cluster size distributions are seen to be monotonically decreasing in all the models, except for the SR model. In the SR model we can see a shoulder already forming at small aggregation numbers, indicating the tendency of surfactant chains to form aggregates even at low concentrations. This indicates that the lowest concentration studied in the SR model is greater than cmc. At higher concentrations, as shown in Figure 3b, the cluster size distribution is again a monotonically decreasing function in the case of SLR model, indicating a dispersion of surfactant chains in the aqueous solution. The inset in Figure 3b shows the cluster size distributions for SR model at high aggregation numbers. It is seen that it has peaks at very high aggregation numbers close to

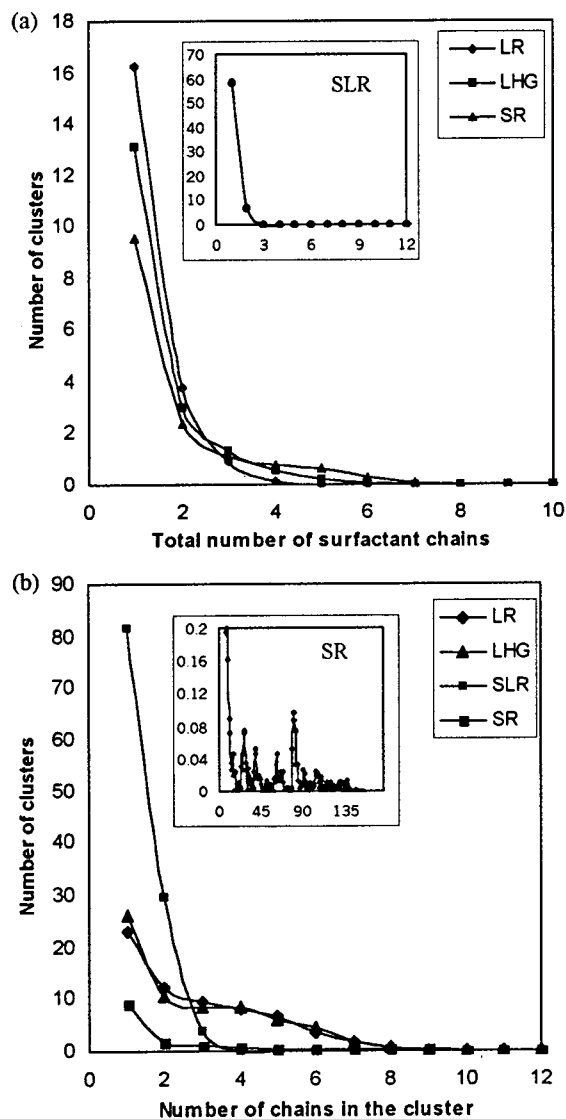


Figure 3. Representative cluster size distributions (a) at a low concentration of 7.39×10^{-4} in LR, SR, and LHG models and a concentration of 2.02×10^{-3} in SLR (inset) and (b) at a high concentration of 5.18×10^{-3} in LR and LHG models and a concentration of 4.36×10^{-3} in SR and SLR models. The inset in (b) shows cluster size distribution in the SR model at high cluster sizes.

Table 1. Summary of 2-D Critical Micelle Concentration Values ($\times 10^{-3}$) in the LR and LHG Models Obtained from Various Definitions

cmc	LR model	LHG model	cmc	LR model	LHG model
X_T	1.2	0.85	X_{en}	~ 2	~ 1.9
X_C	0.8	0.9	X_{RN}	2	2.0

the number of chains in the solution and a peak at monomers. This provides further confirmation that the surfactant chains are more likely to form increasingly larger aggregates in the absence of any size limiting interactions between the headgroups. For LR and LHG, the cluster distributions show a shoulder. This is indicative of the presence of a micellar phase in the solution.

A theoretical definition of cmc (X_{RN}) based on cluster size distributions was proposed by Nagarajan and Ruckenstein.⁶ According to this definition, cmc is the concentration at which a transition in the shape of the micelle size distribution occurs from a monotonically decreasing function to one possessing a minimum and a maximum. A critical concentration was defined at which the size

distribution has a horizontal inflection point. The critical point is the close lower bound of the cmc. Following the definition of Nagarajan and the evolution of cluster size distributions in our data, we predict cmc values in the LR model and the LHG model that exceed the cmc values obtained with the other definitions discussed above. Nagarajan's definition does not appear to be adapted to our systems. Although a horizontal inflection point appears at very high concentration, a change in slope with micelle size distribution occurs at much lower concentration, in agreement with the cmc values obtained from energy and monomer concentration. We, therefore, propose a less restrictive definition of cmc based on micelle size distribution; i.e., cmc is the concentration at which an inflection point (horizontal or nonhorizontal) is first seen in the cluster size distributions. This definition may be well suited for the solutions with smaller aggregation numbers, such as in our 2-D system. Using this definition we find $X_{RN} = 0.002$ in the LR model and $X_{RN} = 0.002$ in the LHG model. Therefore, it can be noted from Table 1 that despite the different definitions of cmc lead to different cmc values in a given model, within each cmc definition the LR and LHG models appear to have similar properties.

Finally, we observe a good qualitative agreement between the critical micelle concentration trends obtained from our 2-D simulations and the cmc's obtained from experiments. For example, experiments have shown that the cmc of nonionic surfactants increases with increasing number of headgroups.³⁵ Also, higher cmc values are observed in the ionic surfactants than in nonionic surfactants.³⁵ In our simulations also, a higher cmc is predicted for the nonionic surfactant in the LHG model ($N_{HG} = 7$) than for the nonionic surfactant in the SR model ($N_{HG} = 1$). Similarly, the critical micelle concentrations for ionic surfactants predicted by LR and SLR models are significantly larger than the critical micelle concentration predicted by the SR model. The agreement between the 2-D cmc values predicted by nonionic LHG model and ionic LR model may seem to be surprising at this point, but our analysis shows this to be a dimensionality effect. The dimensionality effect is discussed more completely in the Conclusions on the basis of the arguments developed in the next section.

3.2. Discussion. In the simulation of all the models (LR, SR, LHG, and SLR) in this work we have chosen surfactant chains with 12 hydrophobic tailgroups. Therefore, the hydrophobic effect driving the surfactant tails to aggregate in aqueous environment is expected to be the same in all the models. The difference in aggregation behavior in the four models would then appear to be the result of the different repulsive interactions between the headgroups in our models. In the LR and SLR models they are long-range Coulombic in nature, and in the SR and LHG models, purely steric. The effect of long-range and steric repulsions between the headgroups on the aggregation behavior is discussed below.

It has been well-known that the aggregation of surfactant chains in the aqueous solutions results from a hydrophobic effect, i.e., an effective unfavorable interaction between the hydrophobic tail-groups of surfactant chains and the solvent (water).⁵ Also, the existence of an opposing force is necessary to prevent the growth of micelles to infinitely large sizes. This repulsive force in micelles primarily comes from the headgroups. In the case of ionic surfactant the electrostatic charge on the headgroups is considered to be a major factor in providing the necessary repulsive force. For nonionic surfactants, however, the

repulsion is presumed to be steric in origin.⁵ The free energy of micellization can, therefore, be expressed as

$$\Delta F_{\text{mic}} = \Delta F_{\text{rep}} - T\Delta S \quad (4)$$

where ΔF_{rep} results from the repulsion between the headgroups of the surfactants and $-T\Delta S$ is the entropic contribution resulting from the ordering of water molecules around the hydrophobic tailgroups. In our models, the entropic contribution, $T\Delta S$, has been modeled as an unfavorable interaction (ϵ_{TW}) between the surfactant tailgroups and water molecules. The change in free energy due to repulsion between the headgroups, ΔF_{rep} , is composed of an energetic contribution and a steric contribution and is given by

$$\Delta F_{\text{rep}} = \Delta E - T\Delta S_{\text{conf}} \quad (5)$$

The energetic term ΔE arises from an electrostatic repulsion between the headgroups, and the steric contribution ($-T\Delta S_{\text{conf}}$) is a result of the change in configurational entropy of the hydrophilic headgroups of surfactants in the micellar state versus the surfactants in the isolated state.

The equivalence of the results in the LR and LHG models can be explained by comparing the free energy of micellization in the two systems. As the surfactant chains in both the models have equal number of tailgroups ($N_{\text{tail}} = 12$), the entropic contribution ($-T\Delta S$) to the free energy of micellization (ΔF_{mic}) in the two models is expected to be of the same order. The free energy of micellization in the LR and LHG models can, therefore, be compared on the basis of ΔF_{rep} only. Furthermore, since the surfactant chains in the LR model consist of only one headgroup, the entropic contribution to the repulsion between the headgroups $-T\Delta S_{\text{conf}}$ is zero. The quantity ΔF_{rep} in the LR model can, therefore, be represented as

$$(\Delta F_{\text{rep}})^{\text{LR}} = \Delta E^{\text{LR}} = \sum_{\text{ipair}} \frac{\phi}{d_{\text{ipair}}} \quad (6)$$

where the summation index ipair is the count of headgroup pairs in a micelle. In the LHG model, the energetic term ΔE in eq 5 is due to a short-range interaction between the headgroups that ceases for headgroup separated by grid spacing greater than 1 grid unit. The energetic contribution to the headgroup repulsions in LHG model is, therefore, negligible compared to the entropic contribution. We can now express the change in free energy due to headgroup repulsion in the LHG model as

$$(\Delta F_{\text{rep}})^{\text{LHG}} = -T\Delta S_{\text{conf}} \quad (7)$$

To gain a quantitative understanding of eqs 6 and 7, we simply consider the case of a pair of two surfactant chains. From eq 6, the $(\Delta F_{\text{rep}})^{\text{LR}}$ in this simple case will be given by

$$(\Delta F_{\text{rep}})^{\text{LR}} = \frac{\phi}{d} \quad (8)$$

For determining $(\Delta F_{\text{rep}})^{\text{LHG}}$, in the LHG model it is necessary to know the change in configurational entropy of the headgroups as a function of distance between these

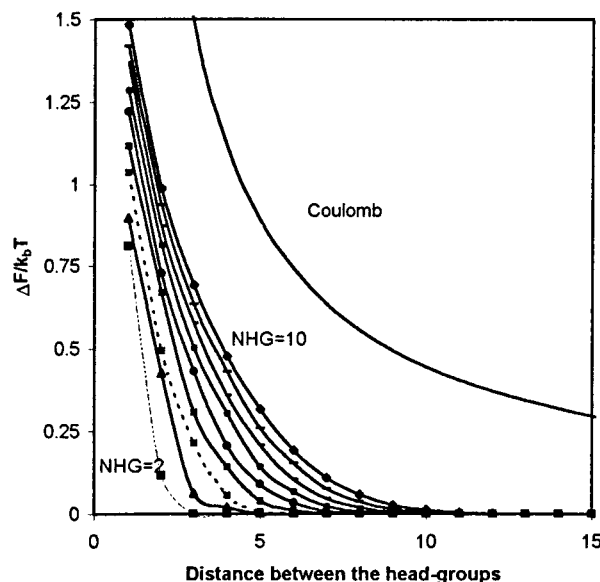


Figure 4. Illustration of steric repulsive interaction between the surfactant headgroups as a function of distance between the constrained first headgroups of the pair of surfactant chains. The curves have been plotted for a number of surfactants with varying number of hydrophilic headgroups. Each plot between $N_{\text{HG}} = 2$ and $N_{\text{HG}} = 10$ corresponds to an increment by 1 in the N_{HG} value. The steric interaction has been compared with the Coulombic repulsive interaction shown.

groups. Following Flory,³⁸ we can calculate ΔS_{conf} by constraining the first headgroup of the surfactant chains at a distance d , allowing the rest of the headgroups to explore all the possible configurations. For each distance d , the change in entropy, ΔS_{conf} , can be obtained from the following expression:

$$\Delta S_{\text{conf}} = k_B \ln \frac{W_d}{W_0} \quad (9)$$

Here W_d is the number of possible configurations of the headgroups when the first headgroups of the interacting surfactants are separated by a distance d and W_0 is the number of configurations when they are separated by infinitely large distances. Therefore, the change in free energy due to headgroup repulsion in LHG model is given by

$$(\Delta F_{\text{rep}})^{\text{LHG}} = -k_B T \ln \frac{W_d}{W_0} \quad (10)$$

On the basis of the above analysis, the steric interactions between the headgroups of a pair of surfactant chains of type $H_x T_{12}$, for $x \in [2, 10]$, have been calculated on a 2-D lattice and compared with $(\Delta F_{\text{rep}})^{\text{LR}}$ for a single pair of ionic surfactants $H_1 T_{12}$ in the Figure 4. It can be seen in Figure 4 that as the number of headgroups (N_{HG}) in the LHG model increases, $(\Delta F_{\text{rep}})^{\text{LHG}}/k_B T$ becomes increasingly long-range. Also, for a given distance d between the constrained first headgroups of the two chains, $(\Delta F_{\text{rep}})^{\text{LHG}}/k_B T$ increases with N_{HG} . It can be noted that the steric interaction between the headgroups of surfactant chains in the LHG model is not negligible compared to $(\Delta F_{\text{rep}})^{\text{LR}}$. For instance, when the constrained headgroups are separated by a distance $d = 4$ grid units, $(\Delta F_{\text{rep}})^{\text{LHG}} \sim 1/3 (\Delta F_{\text{rep}})^{\text{LR}}$.

(38) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1975.

The above discussion, based on a pair of surfactant chains, can be extended to an aggregate of surfactants by considering a micelle of aggregation number N_{ch} . Here, we try to estimate a lower bound for the number of headgroups (N_{HG}), leading to a behavioral equivalence between the LR and the LHG models. The quantity $(\Delta F_{\text{rep}})^{\text{LR}}$, given by eq 6, scales as the number of pairs of charged headgroups $N_{\text{ch}}(N_{\text{ch}} - 1)/2$ in the micelle. The major contribution to $(\Delta F_{\text{rep}})^{\text{LR}}$, however, comes from the headgroups that are separated by a minimum distance, d_{min} . Therefore, for the sake of simplicity, $(\Delta F_{\text{rep}})^{\text{LR}}$, can be expressed as

$$(\Delta F_{\text{rep}})^{\text{LR}} = N_{\text{ch}}(N_{\text{ch}} - 1) \frac{\phi}{d_{\text{min}}} \quad (11)$$

In the LHG model, the number of possible configurations W_0 scale as $(N_{\text{conf}})^{N_{\text{ch}}}$, where N_{conf} is the numbers of configurations of the headgroups while the constrained headgroups of the surfactant chains are separated by an infinitely large distance. The number of headgroup configurations at smaller distances (W_d) would be much smaller compared to W_0 . For example, in the simplest case of a compact micelle, only a very few configurations would be allowed by excluded volume. Therefore, the free energy of repulsion $(\Delta F_{\text{rep}})^{\text{LHG}}$, for an aggregate of size N_{ch} in the LHG model can be given as

$$(\Delta F_{\text{rep}})^{\text{LHG}} = k_B T N_{\text{ch}} \ln(N_{\text{conf}}) \quad (12)$$

If the aggregate size N_{ch} is known, we can find the number of headgroups needed in the surfactants of the LHG model that would yield a steric repulsion comparable to the long-range electrostatic repulsion by equating eqs 11 and 12. In our simulations of the LR and LHG models we obtain an aggregation number ~ 4 . Assuming $d_{\text{min}} = 2$ grid-spacings for the headgroups in the LR model, we get from eqs 11 and 12 $N_{\text{conf}} = 28$. From excluded volume condition we have calculated that in surfactant chains H_xT_{12} for $x \in [2, 8]$, the number of possible headgroup configurations are $N_{\text{conf}} = [3, 7, 19, 49, 131, 339, 939]$. It is seen that for $N_{\text{conf}} = 28$, there should be a minimum of 4 headgroups in the surfactant chains. It should be noted that the approach that we have used to estimate N_{ch} for equivalence between the long-range repulsion in LR and steric repulsion in LHG models will only provide a lower bound for N_{HG} . This result is in a reasonable agreement with the surfactant chains used in our simulations of LHG model.

The above analysis, therefore, helps us to understand that to achieve a finite size micelle in the computer simulations of surfactant chains it is required that an excluded volume be provided to the headgroups of the surfactants. This requirement can be met by means of either the long-range repulsive interactions between the headgroups of surfactants of H_1T_y , $y = 2$, or by a sufficiently strong steric repulsion provided by increasing the number of headgroups in the surfactants.

4. Conclusions

A two-dimensional Monte Carlo simulation study of the aqueous solutions of surfactant molecules was conducted in four different models, namely, strong long-range (SLR), short range (SR), long-range (LR), and long headgroup (LHG). Surfactant chains of type H_1T_{12} were modeled in the SR, LR, and SLR models with short-range, long-range

Coulombic, and strong long-range Coulombic interactions between the headgroups, respectively. In the LHG model, surfactant chains H_7T_{12} were modeled with a short-range repulsion between the headgroups. Simulations were carried out in a canonical ensemble with five Monte Carlo moves—reptation (forward and backward), chain translation, flip, and cluster translation. The cluster translation move was found to be extremely important in the exploration of phase space following the formation of micelles.

Our simulations indicate that with only short-range repulsion between the headgroups (SR model), the surfactants would aggregate at very low concentrations and with very high aggregation numbers. The results of SLR model show that surfactants with very strong long-range Coulombic interactions between the headgroups would largely remain a dispersion of monomers even at very high concentrations. The results of the LR and the LHG models were found to be of similar nature despite the differences in the modeling of the interactions between the headgroups.

The agreement between cmc values for a nonionic surfactant predicted by the LHG model and that of an ionic surfactant predicted by the LR models seemed surprising at first. However, on the basis of arguments presented in section 3.2, we find it to be an effect of dimensionality of our simulation models. A simple analysis of the LHG model would show that, for a given number of headgroups, the steric interaction (ΔF_{rep}) is weaker for a 3-D cubic lattice than for a two-dimensional square-lattice. For example, from eq 10, we calculate $\Delta F_{\text{rep}} = 0.8k_B T (W_d/W_0 = 16/25)$ for two surfactant chains in a 3-D cubic lattice with constrained headgroups separated by a distance of 1 grid unit, whereas ΔF_{rep} in a 2-D square lattice is estimated to be $\sim 4.4k_B T (W_d/W_0 = 4/9)$. The long-range interactions (eq 8) remain unaffected by system dimensionality. On the basis of these arguments, we expect a lower cmc for a surfactant in a 3-D LHG model than in a 3-D LR model, a result in agreement with the experimental observations.

Although, we did not carry out simulations at different temperatures, it is possible to predict the effect of temperature on the aggregation behavior of surfactants from the arguments developed in the section 3.2. In all our models (LR, LHG, SR, SLR), we describe the interactions between the various groups via energetic terms. In principle, these interactions arise from entropic effects such as those associated with structuring of water around the surfactant chains. However, these entropic effects are buried in the energy terms (ϵ_{ij} 's) in eq 1. From our models, we do not expect to see the effect of temperature on the aggregation behavior resulting from *these* entropic contributions, since the ϵ_{ij} 's in eq 1 are not made explicitly temperature dependent. However, as described in section 3.2, other headgroup configurational entropic effects come into play in the case of LHG model. As shown in eq 10, the free energy (ΔF_{rep}) of two surfactant chains in the LHG model is predominantly steric in nature (much larger than ϵ_{HH}) and is temperature dependent. A higher temperature would, therefore, result in a stronger steric repulsion between the headgroups and hence a smaller aggregation number for nonionic surfactants in the LHG model. In contrast, the long-range interaction between the headgroups of ionic-surfactants in the LR model (eq 6) is independent of temperature.

Finally, our results indicate that it is important to have an excluded volume of surface headgroups to obtain micellar type aggregates. This excluded volume can be

obtained by either having energetic repulsions (long-range Coulombic interactions) between the headgroups, e.g., in the modeling of ionic surfactants, or by steric (entropic) exclusion by increasing the number of headgroups in the surfactant chain, which could possibly be the case in modeling a nonionic surfactant.

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