Sphere-to-rod transitions of micelles in model nonionic surfactant solutions

Zaid A. Al-Anber\textsuperscript{a,b}, and Josep Bonet i Avalos\textsuperscript{a}

Departament d’Enginyeria Química, Etsaq, Universitat Rovira i Virgili, Edifici E, Campus de Sescelades, Avinguda dels Països Catalans, 26 43007 Tarragona, Spain

M. Antonio Floriano\textsuperscript{c}

Dipartimento di Chimica Fisica, Università di Palermo, Viale delle Scienze, Parco d’Orléans, 90128 Palermo, Italy

Allan D. Mackie

Departament d’Enginyeria Química, Etsaq, Universitat Rovira i Virgili, Edifici E, Campus de Sescelades, Avinguda dels Països Catalans, 26 43007 Tarragona, Spain

(Received 8 August 2002; accepted 26 November 2002)

The transition of spherical to rod-like micelles is studied in a lattice model for amphiphiles using the single chain mean-field (SCMF) theory and grand-canonical Monte Carlo (GCMC) simulations. A linear combination of the free energy of spherical and infinite cylindrical geometries is assumed in the SCMF theory to estimate the free energy of rod-like micelles. The SCMF theory finds that the symmetric \( H_4T_4 \) amphiphile at a dimensionless temperature scale, \( T^* \), of \( T^* = 6.5 \) favors the formation of spherical micelles at all investigated overall amphiphile concentrations. On the other hand, the asymmetric \( H_1T_6 \) amphiphile at \( T^* \) between 8.5 and 12.5 starts by forming spherical micelles (first \( \text{cmc} \)) at low overall amphiphile concentrations and then forms rod-like micelles (second \( \text{cmc} \)) as the overall amphiphile concentration increases. The GCMC simulations also find that the symmetric \( H_4T_4 \) amphiphile forms spherical micelles while the asymmetric \( H_1T_6 \) amphiphile tends to form rod-like micelles. The second \( \text{cmc} \) is found to increase with increasing \( T^* \) whereas it decreases with increasing tail length. Our results are in good qualitative agreement with experimental observations. © 2003 American Institute of Physics. [DOI: 10.1063/1.1539048]

I. INTRODUCTION

Amphiphilic molecules derive their name due to their dual nature: a hydrophilic head that likes to be in water, and a hydrophobic tail that prefers not to be. Amphiphiles are also known as surfactants because they are able to strongly modify the surface properties of the solution. In order to minimize water–hydrocarbon contacts while maximizing head–water interactions, above a certain concentration known as the critical micellar concentration (\( \text{cmc} \)), amphiphile molecules tend to self-assemble into aggregates known as micelles. The shape that a micelle takes is controlled by many parameters such as temperature, concentration, additives, structural groups, and ionic strength. Changes in these parameters may induce several changes in micellar structure including more or less sharp geometrical transitions. Experimentally it has been found that micellar aggregates can be approximated by spheres, disks, ellipsoids, and rods. At low concentrations of nonionic surfactants, micelles are always nearly spherical. However, it has been observed\textsuperscript{1–5} that an increase in concentration may cause either an increase in the number of spherical aggregates with little change in size or it may lead to a second critical micelle concentration where a transition to rod-like aggregates can be observed.

Although the aggregation of amphiphiles plays an important role in several natural phenomena and in many industrial applications (food digestion, pharmaceutical, biochemical, drug delivery, environmental, medical research, and in tertiary oil recovery), the theoretical understanding and modeling of their behavior are still fairly primitive. In recent years, many studies have been undertaken with the objective of elucidating the different equilibrium structures that micellar systems are able to form.\textsuperscript{6–10} However, most of this work deals mainly with the simple spherical geometrical structures whereas the parameters governing the transition between different geometries are not well known.

Previous theoretical investigations can be classified into several categories. In molecular simulations, for example, a microscopic model is exactly solved by means of numerical calculations. A second effort is based on the application of phase field theories, which use one or more order parameters to define a phenomenological free energy. Finally, the surfactant free energy can be calculated in the mean-field of the other chains in the aggregate. The single chain mean field (SCMF) theory\textsuperscript{11} and self-consistent field (SCF) theory,\textsuperscript{12,13} for instance, adopt this approach. These theories use a molecular model of the surfactant from which the free energy is constructed, to be then solved numerically.
It is convenient to classify the molecular simulation studies into two categories: molecular dynamics (MD),10,14–22 and Monte Carlo (MC) simulation methods.11,23,34 In MD simulations, the equations of motion are solved numerically for each amphiphile. The advantage of this method is that time dependent phenomenon become accessible, however, only relatively short times can be simulated because of the fairly demanding and calculation intensive nature of these studies. Thus, if the time scale of interest is longer than that practically accessible, the simulation is unable to capture the phenomenon of interest. Rector et al.10 in their MD simulations, adopted a simple two-particle surfactant model. In their treatment, they use the Widom14 test-particle method to determine the cmc for a surfactant model consisting of one hydrophilic and another hydrophobic particle joined by nonharmonic springs. Karaborni et al.15 studied the effect of chain length and head group properties on the internal micelle structure, micellar shape, and chain conformation inside the micelle. They found that the average aggregate shape is somewhat nonspherical, regardless of head group size and surfactant chain length. The molecular dynamics simulations of Palmer and Liu16 incorporated an additional bending energy term using a quasi-realistic model. Hatton et al.17 Smit et al.18–20 and recently Fodi et al.21 used coarse-grained models to study the self assembly of a nonionic surfactant systems. These models give access to much longer time scales than those accessible with realistic potentials and, as a consequence, the surfactants can self-assemble into their preferred structures. With realistic potentials, it is usually necessary to pre-assemble the micelle prior to the simulation.

Monte Carlo simulations of amphiphilic solutions in lattices have been used extensively in the last 20 years. Larson23–25 has studied the structure of aggregates for different types of amphiphiles in solution. Mattice et al.26–28 calculated segment distribution profiles of the micelles and the dependence of the cmc on the surfactant composition. Desplat and Care29 performed lattice Monte Carlo simulation where the surfactants consisted of s particles with one of them serving as a head and the remaining s-1 forming the tail of the surfactant. Their calculation captured the micellar size distribution as a function of temperature. Equilibrium properties of nonionic micelles were also studied by Linse et al.30 and Mackie et al.11 using lattice Monte Carlo simulations. Equilibrium size and shape distributions of self-assembled micelles were investigated by Hatton et al.31 They found that the equilibration of simulated micellar systems is better monitored using the average aggregate size rather than the configuration energy of the system. Rajagopalan et al.32 simulated the effects of the amphiphile tail length on the first cmc. Their simulations are consistent with experimental results for several non-ionic surfactants in water. The thermal behavior of aggregates of amphiphilic molecules in water for a three-dimensional lattice model was studied by Figueiredo and Girardi.33 Their model consists of amphiphilic molecules with a single polar head and a hydrophobic tail formed of monomers in a solution of water where the water molecules are modeled as occupying one lattice site. Florian et al.34 studied the formation of micelles by a novel methodology based on grand-canonical Monte Carlo (GCMC) simulations. Their methodology is based on the combination of free-energy information from a series of simulations in small systems by histogram reweighting.

Methods based on phase field theories1,35,36 do not rely as much, if at all, on the computer capacity as in the case of MD and MC techniques. These theories have been applied to the study of micellization and phase behavior for nonionic surfactant solutions. A major drawback with these treatments is that they contain parameters that cannot be directly related to a microscopic model. Finally, a mean-field approximation based on the use of ideal Gaussian chains can be used. For instance, the SCF theory was originally developed by Scheutjens and Fleer37,38 to treat polymer adsorption. Later it has been generalized by Leermakers12,13 to treat surfactant aggregates. Bohmer et al.39,40 showed that this theory closely follows many experimental observations. Linse41 demonstrated how the SCF theory can be used to model solutions of poly(ethylene oxide)-poly(propylene oxide) copolymers and lastly Wijmans and Linse30 used the SCF to study the aggregation of short nonionic linear surfactant chains in spherical micelles and compared their findings with their MC simulations on the same system. These results showed that the SCF theory fails in predicting the right micellar size distribution and cmc, giving larger aggregation numbers and a cmc much lower (by several orders of magnitude) than the results obtained by simulation. A slightly different approach is offered by the SCMF theory, originally developed by Szleifer for dry core micelles,42,43 and generalized for polymer solvent systems.44 Mackie et al.11 applied the SCMF theory to treat micellar systems without the assumption of a sharp interface and a dry core for lattice amphiphiles. The predictions of the theory were compared with MC simulations and excellent quantitative agreement was found for the first cmc. Furthermore, the predictions for the molecular organization in the aggregates were in very good agreement with the simulation results. However, the micelle aggregation numbers were under-predicted. Recently Szleifer et al.45 applied the SCMF theory to a continuous space model. They found that the micellar size distribution was in very good agreement with MD calculations. In general, the main advantage of mean-field calculations is the ability to estimate the micelle properties with relatively little computational effort as compared to molecular simulations. In contrast, the simulations are useful for providing detailed quantitative information in numerical form but do not give the overall qualitative view. In general, mean-field theories, which are easier to solve, provide a good initial overview of the system with simulation providing more detailed information where required. In summary, the combination of simulation and mean-field theory can contribute, in a complementary fashion, to a better understanding of the behavior of the system.

In the present work we are mainly concerned with micellar shape. As mentioned before, many experimental studies have reported that a transition of spherical micelles into elongated ones may occur above a certain value of the bulk surfactant concentration, referred to as the second cmc.46–48 Recently, Bernheim-Grosswasser et al. concluded that micellar populations of both the dimeric (geminis)49 and nonionic
surfactant C_{12}E_5 \textsuperscript{50} are characterized by two distinct stages and two distinct micelle sizes when the amphiphile concentration and temperature increase. Also, their studies show that the diameter of the endcaps of the elongated micelles is larger than that of the cylindrical body. Nonionic surfactants C_{12}E_5 was also studied experimentally at 3 \degree C by Otto Glatter et al.\textsuperscript{51} They found that two peaks are formed in the cluster distribution indicating that cylindrical structures are formed.

The growth of spherical micelles into elongated ones has been investigated using simple packing arguments by assuming a spherocylindrical geometry.\textsuperscript{1} These arguments assume that the spherocylindrical micelles consist of cylinders terminated by hemispherical endcaps of the same diameter as the cylinder. It is also assumed that the surfactants have a standard chemical potential that is lower in the cylindrical body than in the endcaps. These two assumptions are sufficient to explain the micellar growth. Porte et al.\textsuperscript{48} accounted for the existence of a second \textit{cmc} using a phenomenological structure model of linear micelles. Recently, Ben-Shaul et al.\textsuperscript{52} have also used a molecular-level theory to study amphiphile packing in linear micelles. They found that the early stages of growth involve an energetic barrier, resulting in a gap in the micellar size distribution. Small micelles appeared in solution when they studied at low amphiphile concentration. They demonstrated the concept of the second critical micelle concentration, which represents in this case a transition from spherical to cylindrical micelles, by way of calculations of micellar size distributions and average aggregation numbers as a function of the total amphiphile concentration.

The major objective of this work is to apply SCMF theory and the GCMC simulation method to study dilute micellar solutions of single tail nonionic surfactants and, in particular, to investigate the transition between spherical and cylindrical micelles and hence to calculate the second critical micelle concentrations. Another objective is to study the effect of tail length of amphiphile molecules and the temperature on the second critical micelle concentration, \textit{cmc}.

The rest of this work is organized as follows: the theoretical modeling and methodology are presented in Secs. II and III, respectively, Sec. IV contains our results and discussion, and finally the main conclusions of this work are given in Sec. V.

II. THEORETICAL MODELING

A. Lattice model

In the model studied here, originally proposed by Larson,\textsuperscript{21} space is divided up into a cubic lattice of sites in three dimensions with a coordination number, $z$ (the number of nearest neighbor sites), equal to 26. We model the amphiphile molecules as linear chains of freely jointed segments (beads) each occupying one lattice site whereas the solvent occupies single sites. We refer to the amphiphile molecules as $H_yT_x$, where $x$ and $y$ represent the number of segments in the head-group $H$ and tail $T$, respectively. A water-like solvent particle is denoted by $H$ and an oil-like particle by $T$.

This model is suitable for describing the behavior of nonionic surfactants such as poly(oxyethylene) referred to as C$_mEO_n$, where the oxyethylene units (–C–C–O–) make up the head part and the alkyl chain forms the tail. Given that a head group $H$ in our model is approximately equivalent to one oxyethylene unit and one tail $T$ represents about 3 CH$_2$ groups,\textsuperscript{21} then the $H_4T_4$ and $H_7T_6$ surfactants studied in this work are roughly equivalent to the real surfactants of C$_{12}$EO$_4$ and C$_{18}$EO$_5$, respectively.

All systems studied are binary mixtures of amphiphile and solvent. The lattice is fully occupied. If an H-type site belonging to a water monomer or the head of a surfactant interacts with another H-type site the resulting energy is $e_{HH}$. An interaction occurs when two sites are in contact. The $T$–$T$ and $H$–$T$ interaction energies are denoted by $e_{TT}$, and $e_{HT}$, respectively. There is only one relevant energy parameter due to the lattice conservation equations: $e = e_{HT} + 1/2 e_{HH} - 2 e_{TT}$. The $e_{TT}$ interaction was set to $-2$ (resulting in attractive interactions for nearest-neighbor tail–tail contacts) and the $e_{HH}$ and $e_{HT}$ were set to zero. A dimensionless temperature scale, $T^*$, was defined as $T^* = k_B T / e$ where $k_B$ is Boltzmann’s constant and $T$ is the temperature. It should be stressed that a different choice of energy parameters would have no real physical significance with regards to the behavior of the model and would merely modify the dimensionless temperature scale.

B. Mass action model

Let us consider the equilibrium condition for a micellar system. This is given by the requirement that the chemical potential of the amphiphile should be the same in all environments, i.e., as an isolated amphiphile in solution, in small globular micelles, or in any type of aggregate of arbitrary geometry and size. For an ideal solution,

$$\mu_N = \mu_N^0 + \frac{k_B T}{N} \ln \frac{X_N}{N} = \text{const} = \mu_1,$$  \hspace{1cm} (1)

where $X_N$ is the concentration of aggregates containing $N$ amphiphiles in the solution, $\mu_N$ and $\mu_1$ are the chemical potentials of an aggregate of size $N$ and an isolated amphiphile in solution, respectively; $\mu_N^0$ is the standard chemical potential per amphiphile molecule in an aggregate of size $N$. The preferred packing geometry of the micelle is that corresponding to $\mu_N^0 = \text{min}^1$ for an aggregate of fixed size $N$. Rewriting the above equation to obtain the cluster distribution in terms of the mole fraction of the molecules in aggregates of size $N$ gives

$$X_N = N \left[ X_1 \exp \left( \frac{\mu_1^0 - \mu_N^0}{k_B T} \right) \right]^N,$$ \hspace{1cm} (2)

where $\mu_1^0$ is the standard chemical potential of an isolated amphiphile. The cluster size distribution is determined by the difference in the standard chemical potentials between an isolated amphiphile and an amphiphile in the aggregate ($\mu_1^0 - \mu_N^0$). The SCMF theory described below is designed to determine this difference of standard chemical potential for micelles of arbitrary size $N$ and a specified geometry.
C. Spherocylindrical case

A simple model was used to estimate the standard chemical potential of spherocylinders, $\mu^{0}_{N}(\text{sph/cyl})$ for an aggregate of size $N$ by assuming a linear combination of the free energy of spherical and infinite cylindrical geometries.

$$\mu^{0}_{N}(\text{sph/cyl}) = \frac{1}{N} \left[ N_{\text{sph}}^{*} \mu_{\text{sph}}^{0} + (N - N_{\text{sph}}^{*}) \mu_{\text{cyl}}^{0} \right],$$

where $N=N_{\text{sph}}^{*}+N_{\text{cyl}}$ is the total number of amphiphiles in the spherocylinder, $N_{\text{cyl}}$ is the number of amphiphiles in the cylindrical section, $N_{\text{sph}}^{*}$ is the number of amphiphiles in the spherical section. The standard chemical potential, $\mu_{\text{sph}}^{0}$, is chosen as the minimum as a function of number of chains in the aggregate and $\mu_{\text{cyl}}^{0}$ is the minimum value of standard chemical potential in the infinite cylindrical geometry. The micellar size distribution of spherocylindrical micelles is calculated by introducing Eq. (3) into the mass action model, Eq. (2).

It should be noted that we use here a combination of cylindrical and spherical sections corresponding to the respective minimum free energy for each case even though the diameters of the two sections may be different.

D. SCMF theory

The basic idea of SCMF theory is to consider a central chain with all of its intramolecular interactions exactly taken into account while the intermolecular interactions are considered within a mean-field approximation. Since a micellar aggregate is clearly inhomogeneous, the intermolecular mean-field interaction is also inhomogeneous. The theory is derived by determining the probability distribution function, $pdf$, which is the probability that for a given geometry the amphiphile will be found in a particular conformation. From this distribution any property of the chain can be computed as an ensemble average. To use this theory, it is necessary to specify the geometry of interest. In order to find the $pdf$, a mean-field approximation is invoked and the simpler problem of any arbitrary chain under the average interaction with its neighbors is solved. Specifically, the $pdf$ that minimizes the free energy per chain is sought subject to the lattice single occupancy constraints corresponding to the given aggregation geometry.

In this work we consider the aggregate in concentric layers. For a dilute solution of micelles we can write the Helmholtz free energy, $F$, of a micelle fixed in space with $N$ amphiphiles as

$$\beta F = \beta N E - \frac{S}{k_{B}} - \beta \sum_{r} n_{s} \mu_{s},$$

where $E$ is the total energy of the amphiphiles in the micelle, $S$ is the entropy of the micelle, $\beta = 1/k_{B}T$, $n_{s}$ is the number of solvent molecules, $T$ is the temperature, and $\mu_{s}$ is the standard chemical potential of the solvent. The probability distribution function, $P(\alpha)$, is found by minimizing the free energy (4) subject to the packing constraint equation $[\phi_{1}(r) + \phi_{2}(r) = 1]$ by introducing a set of Lagrange multipliers, $\pi(\alpha)$, to give

$$P(\alpha) = \left\{ \begin{array}{l}
q_{s}^{*} \left( \frac{q_{s}^{*}}{\alpha} \right)^{n_{s}} \exp \left( \int \pi(r) \right) n_{s}(r) \right\} \frac{\alpha}{n_{s}}$$

$$q^{*} = \exp \left( -\int \pi(r) \right) n_{s}(r) \left( \frac{\alpha}{n_{s}} \right),$$

where $\langle \rangle$ denotes an ensemble average, $\alpha$ is the set of nonoverlapping independent chain configurations, $r$ is the radial distance from the center of the spherical and infinite cylindrical micelles, $\phi_{s}(r)$ is the fraction volume of solvent and, $\phi_{c}(r)$ is the chain volume fraction, $V(r)$ is the total volume of the system in layer $r$, $n_{s}/T$ is the number of head (tail) groups, $n_{s,T}(r)$ is the number of nonoccupied nearest-neighbor contacts in shell $r$ per chain, $n_{s,TT}$ is the number of intramolecular tail–tail contacts per chain, and $\chi_{TT} = \beta e_{TT}$ is the dimensionless interaction parameter. The solvent density profile, $\phi_{s}(r)$, is given by

$$\phi_{s}(r) = \exp \left( -\int \pi(r) + \beta \mu_{s} \right),$$

where the thermodynamic equilibrium condition that the chemical potential of the solvent, $\mu_{s}$, must be constant at all $r$ has been introduced. $\pi(r)$ is the osmotic pressure necessary to keep the $\mu_{s}$ constant at all $r$. The $cmc$ and micellar size distribution is obtained by Eq. (1) which requires the standard chemical potential of formation,

$$\beta \mu_{0}^{s} = \frac{\partial (\beta F)}{\partial N} = -\ln q - n,$$

where $n$ is the number of sites occupied by an amphiphile and is constant. The derivation of Eqs. (6) and (7) has previously been presented.11

III. METHODOLOGY

A. SCMF theory

To solve the packing constraint equations, space was discretized into finite concentric layers and the number of segments per layer of each generated chain was counted. To find the lateral pressure, $\pi(r)$, we substituted the form of the $pdf$ [Eq. (5)] and that of the solvent density profile, $\phi_{s}(r)$, [Eq. (6)] into the packing constraint equations. The result is a set of nonlinear self-consistent equations that can be solved by standard numerical methods. The necessary input data that is needed to solve the equations (the set of nonlinear self-consistent equations) are the chain conformations, the number of chains in the aggregate, shell volumes, and the temperature. The outputs are the set of lateral pressures, $\pi(r)$. With these quantities and the $pdf$ [Eq. (5)], any desired average conformational and thermodynamic property of the micellar aggregate can be obtained.

The chain conformations were generated using the Rosenbluth and Rosenbluth chain growth algorithm.53 Intramolecular tail–tail interactions, $n_{s,TT}(\alpha)$, were calculated.
exactly for all the configurations. Once a set of configurations is obtained, they can be placed on the lattice, and the chain distributions (tail, head and nearest neighbor contacts) can be counted as a function of the distance from the aggregate center.

In this work, 50,000 chain configurations were randomly generated and placed on a lattice divided into spherical and infinite cylindrical shells. The first tail segments of the configurations were placed at four different radii on the diagonal and straight as well as their symmetrically inverted configurations for a total of 16 different positions for each configuration. This means that we use a set of $8 \times 10^3$ chain configurations for each system model. The same results were obtained when $10^7$ configurations were used.

Once all of the chain configurations were generated, the packing constraint equations were solved by using the appropriate nonlinear equation solving routines from the IMSL library. The standard chemical potential of a micelle containing $N$ amphiphiles was calculated using Eq. (7) by summing over the set of chain configurations and the different positions. The cluster size distribution, $X_{N}$, was calculated by introducing the values of the standard chemical potential of an isolated amphiphile and $N$-micelles that were calculated by the SCMF theory within the mass action model.

We define the first critical micelle concentration as the isolated amphiphile concentration at which a line of unit slope passing through the origin intersects a straight line through the free isolated amphiphile concentration beyond the onset of micellization in a plot of free isolated amphiphile concentration versus total amphiphile mole fraction. The physical meaning of this definition is that it corresponds to the mole fraction at which spherical micelles start appearing in the system.\(^1\)

To estimate the standard chemical potential of a spherocylinder (rod-like) for an aggregate of size $N$, the minimum value of the standard chemical potential in the spherical and infinite cylindrical geometries was found. The result of substituting these values into Eq. (3) gives the standard chemical potential of a spherocylinder. The cluster size distribution of spherocylinders and hence the second critical micelle concentration were calculated by introducing values of the standard chemical potential of isolated amphiphiles and $N$-spherocylinders micelles into the mass action model. We define the second critical micelle concentration as the point at which a straight line passing through the saturated spherical concentration intersects a line passing through spherical concentration before it saturates in a plot of spherical micelles mole fraction versus total amphiphile mole fraction as shown in Fig. 1.

\section*{B. GCMC}

The GCMC method with multihistogram reweighting was used as in previous work.\(^3^4\) This approach is based on performing a number of simulations for a given amphiphile architecture at selected temperatures and different values of imposed chemical potentials in order to collect histograms of the probability of observation of a certain energy and number of particles. The histograms are then combined using the technique of Ferrenberg and Swendsen\(^3^5\) to obtain the free energy of the system over the range of temperatures and chemical potentials covered in the simulations.

Simulations were performed in cubic boxes under periodic boundary conditions. The determination of cluster distributions was performed following the convention used in previous work.\(^1^1\) Two amphiphile molecules are considered to be in the same cluster if any tail segments of the first molecule are within the interaction range of a tail segment of the second molecule. A typical mix of attempted moves was 70% particle creation/annihilation, 0.5% cluster moves, and the balance reptations. Cluster moves consist of displacing an aggregate as a whole in a random direction. In order to satisfy a detailed balance, attempted cluster moves fail if the move results in the creation of new clusters. The cluster moves are necessary to achieve significant displacements of micellar aggregates but have a relatively high computational cost. Configurational-bias sampling methods\(^5^5\) were used to facilitate insertions and removals of amphiphilic molecules. A long period ($> 2 \times 10^{18}$) random number generator\(^5^6\) was used.

\section*{IV. RESULTS AND DISCUSSION}

In the present work, we limit our investigation to the linear symmetric model amphiphile $H_4T_4$ at $T^\circ = 6.5$ and the linear asymmetric model amphiphile $H_3T_6$ at $T^\circ = 8.5, 9.5, 10.5, 11.5,$ and 12.5.

We have divided the results into two major sections: system $H_4T_4$ (symmetric) and $H_3T_6$ (asymmetric). For the symmetric amphiphile, we study the effect of the total amphiphile concentration on the transition between spherical and spherocylinder (rod-like) shapes. For the asymmetric amphiphile, we also study the effect of the total concentration of amphiphile on the transition between spherical and spherocylinder shapes as well as the effect of the temperature and the amphiphile tail length on the cluster size distribution and second $cmc$.

\subsection*{A. $H_4T_4$ system}

The equilibrium size and shape distributions of $H_4T_4$ micelles have been previously studied by Monte Carlo
simulations. In addition, it has been shown that, for the same system, the SCMF results for the cmc and for the cluster size distribution are in close agreement with those derived by simulation. In this section we use SCMF theory to study the micellar shape at $T^* = 6.5$. Two micellar geometries (sphere and infinite cylinder) were used to calculate the standard chemical potential, $\mu^0_N$, as a function of the aggregate size $N$ as reported in Fig. 2. It should be stressed here that the $x$ axis in Fig. 2 corresponds to the total number of amphiphiles in the aggregate for the spherical and spherocylindrical geometries whereas it refers to a 10 lattice site section in the case of the infinite cylinder (a cylinder of infinite length always has an infinite number of amphiphiles; hence it is necessary to specify the number of amphiphiles belonging to a finite section of the infinite cylinder). For both geometries, it can be seen that $\mu^0_N$ decreases as $N$ increases indicating that the aggregation process is energetically favored. A minimum in the above quantity is reached for $N \approx 55$ in the case of spherical micelles and, therefore, this value has to be considered as the most probable aggregation number. The spherocylindrical case, as shown by the solid line, is estimated as a linear combination of the two geometries [see Eq. (3)] and, hence, it interpolates between the two minima. As $N$ increases, the spherocylindrical chemical potential approaches asymptotically that of the minimum $\mu^0_N$ of the infinite cylinder. Comparing between the $\mu^0_N$ of spherical and infinite cylindrical micelles, we observe that the minimum of $\mu^0_N$ in the spherical geometry (at $N \approx 55$) is lower than that for the infinite cylindrical case. Simple packing arguments suggest that the micelles tend to form the shape that has a lower standard chemical potential and, therefore we deduce that the $\text{H}_4\text{T}_4$ system aggregates only into spherical micelles.

In Fig. 3 the cluster size distributions, $X_N$, is given for spherocylindrical micelles at different values of the overall amphiphile mole fraction, $X_t$ ($X_t = 0.24$ and 1.2 mol%). We can compare qualitatively our result with the experimental observations which suggest that elongated micelles appear when two distinct micellar populations form in the cluster size distribution as $X_t$ increases. It can be noted from Fig. 3 that as $X_t$ increases, only one peak is present in the cluster size distribution at $N \approx 55$, which is the same as for the spherical case. This implies that the spherical micelles are always favored due to their lower free energy. On comparing with our GCMC simulations as shown in Fig. 4, we observe that spherical micelles are formed in the system. In addition, our observation is in good qualitative agreement with that found by the MC simulations, which find that the $\text{H}_4\text{T}_4$ micelles are always spherical, although with a peak in the cluster size distribution at $N = 80$.

![Fig. 2. Standard chemical potential of $\text{H}_4\text{T}_4$, $\mu^0_N/k_BT$, as a function of aggregate size $N$ at $T^* = 6.5$. Circles, squares, and solid lines represent spherical, infinite cylindrical, and spherocylindrical geometries, respectively. In the case of the infinite cylindrical geometry, the $x$ axis gives the number of surfactants for a 10 lattice site section of the infinite cylinder.](image1)

![Fig. 3. Aggregate mole fraction $X_N$ of $\text{H}_4\text{T}_4$ in spherocylindrical micelles vs aggregate size $N$ at different values of the overall amphiphile mole fraction $X_t$ and $T^* = 6.5$. The short-dashed line corresponds to 1.2 mol % and the solid line corresponds to 0.24 mol %.

![Fig. 4. Configuration for $\text{H}_4\text{T}_4$ system, 40×40×40 lattice, $\mu = -48.6$, and $T^* = 6.5$. The mole fraction of the amphiphile for this configuration is 2.25 vol %. Tail groups are light colored and head groups are dark colored.](image2)
Figure 5 represents the density profiles of head and tail segments as a function of the radial distance for spherical and infinite cylindrical geometries corresponding to the minimum of the standard chemical potential for the formation of the respective geometries. From these results it can be observed that the hydrophobic core radius for the minimum cylindrical free energy is about 80% that of the spherical micelles. Qualitatively, this difference arises from the fact that in spherical micelles only a small number of chains are stretched to the limit because the available volume in a sphere decreases quadratically with the distance from the interface, whereas most chains are relaxed and enjoy nearly maximal conformational freedom. In contrast, in a cylindrical micelle, the available volume decreases only linearly with the distance from the interface, implying that a larger fraction of the chains must be fully stretched when the radius of the hydrophobic core is equal to the chain length. Our results are in good agreement with experimental observations as well as with simple empirical arguments.

B. H₃T₆ system

In this section, we study the aggregation behavior of the H₃T₆ amphiphile using both SCMF theory and GCMC simulations. Figure 6 shows the standard chemical potential calculations of SCMF theory for spherical and infinite cylindrical geometries at $T^* = 11.5$. It can be seen that, in contrast to the case for the H₄T₄ amphiphile, the minimum of the standard chemical potential, $\mu^N_0$, of the infinite cylindrical geometry is lower than that of the spherical one that forms at an aggregate size, $N$, of about 75. As a consequence, we expect that this system favors the formation of spherocylindrical micelles. In the same way as for the H₄T₄ system, the spherocylindrical case, as shown by the solid line, is estimated by considering a linear combination of the two geometries and hence interpolates between the two minima. Results of the spherocylindrical calculations at different temperatures are shown in Fig. 7. As the temperature increases, the difference between the standard chemical potential of isolated amphiphile and the minimum aggregate value, $\Delta = (\mu^0_i - \mu^0_N)/(k_BT)$, decreases ($\Delta = 5.51, 4.12, 3.87, 2.02, 1.48, 0.316$ for $T^* = 8.5, 9.5, 10.5, 11.5, 12.5, 15$, respectively), indicating that the driving force of cohesive energies to form micelles decreases. At $T^* = 15$ (not shown in the figure) the micelles do not form because the solvophobicity, which is determined by $T^*$, is not strong enough.

The calculated values of the chemical potential of the spherocylinder micelles (Fig. 7) are used in combination with the mass action model to estimate the cluster size distribution, $X_N$, as shown in Figs. 8(a) and 8(b). This figure shows the resulting $X_N$ of the micelles for $X_t$ ranging from 0.55 to 2.8 mol% at $T^* = 11.5$. At the lowest concentrations ($X_t = 0.55$ mol%) as shown in Fig. 8(a), the absence of any
peak distribution indicates that all amphiphile chains are present as isolated amphiphiles. On increasing $X_t$ to 0.6 mol %, only one relatively broad peak forms at an aggregate size of about $N = 75$, which corresponds to the minimum of the aggregate size for the spherical geometry. We suggest that this indicates a separation of the amphiphile population into spherical micelles and isolated amphiphiles. However, even at these low $X_t$ values (0.6 mol %), a tail extending towards the longer spherocylindrical micelles is clearly evident. As $X_t$ increases to 1 mol % another peak appears as shown in Fig. 8(b), indicating a transition of the spherical micelles into spherocylindrical micelles. On further increasing $X_t$ to 1.2, 1.9, and 2.8 mol %, the transition between the micelles becomes more distinct. It is clear that two micellar populations form: the first one is related to the formation of spherical micelles (first $cmc$) and the second one is due to the transition of the spherical micelles to rod-like aggregates (second $cmc$). The inset to Fig. 8(b) shows the micelle distribution for $N$ in the range from 60 to 90. The transition between spheres and rods is found to be gradual, in which the concentration of spherical micelles saturates on the appearance of the rod-like micelles in an analogous way to the first $cmc$, where the concentration of free amphiphiles saturates on the appearance of the spherical micelles. On comparing our results with experimental observations and molecular level theory, where they find that the elongated micelles appear when two distinct micellar populations form in the cluster size distribution as $X_t$ increases, we conclude that this asymmetric amphiphile forms rod-like micelles.

Another approximate idea of the shape of the aggregate can be obtained from the three average principal moments of the inertia ($I_1, I_2, I_3$, respectively) of the aggregates. These moments are the eigenvalues of the matrix of the radii of gyration. For a spherical shape, all three principal moments should be equal ($I_1 = I_2 = I_3$) whereas for a cylinder the relation $I_1 = I_2 > I_3$ will hold. Thus the ratio $I_2/I_3$ gives a rough idea of whether an aggregate, on the average, tends to assume a spherical or cylindrical geometry. Several snapshots of the aggregates were stored during MC simulations and, from these, radii of gyration and moments of inertia were calculated. We apply this criteria on our system as shown in Fig. 10 at $T^* = 11.5$. This figure shows the GCMC data of the ratios of ($I_1/I_2$) and of ($I_2/I_3$) as a function of the micellar aggregation number at a temperature of 11.5. The GCMC simulation data are consistent with the SCMF theory.
in that the peak in the size distribution centered at an aggregation number of 75 is comprised of spherical micelles. It can be observed that, for aggregates in the size range 50–75, the ratio I1/I2 is fairly constant at a value of approximately 1.1 and I2/I3 is around 1.8. This implies that, even at these low aggregation numbers, the micelles are not perfect spheres. However, for aggregation numbers greater than 75, I2/I3 increases notably while I1/I2 remains practically constant, indicating that the micelles grow in one direction to form cylindrical capped spheres (rod-like aggregates).

We show in Fig. 11 some typical configurations that we get from GCMC simulations at \( T^* = 11.5 \) and \( \mu = -68 \) for a system with 0.74 mol % on a 30×30×30 lattice. Only a few micelles are present in the system and these micelles appear to be roughly elongated in shape.

Due to the gradual nature of the transition, in order to locate the second \( \text{cmc} \), we have plotted the mole fraction of isolated amphiphile, \( X_1 \), and the mole fraction of spherical micelles, \( X_s = \sum_j X_j \), against the total amphiphile concentration \( X_t \), at \( T^* = 12.5 \) as shown in Fig. 12. The sum of the three quantities is equal to the total amphiphile concentration, \( X_t = X_1 + X_s + X_{rod} \). At low \( X_t \) the isolated amphiphile concentration, \( X_1 \), is approximately equal to \( X_t \), indicating that most of the amphiphile molecules in the solution are isolated amphiphiles. On increasing \( X_t \), the isolated amphiphile concentration becomes smaller than \( X_t \) and, eventually, reaches a constant value. At the same time, the concentration of spherical micelles increases (first \( \text{cmc} \)). On further increasing the amphiphile concentration, \( X_s \) also tends to reach a constant value while the spherocylindrical (rod-like) micelles start to appear (second \( \text{cmc} \)). We define the second \( \text{cmc} \) as the point at which the rod-like micelles appear in the system. Below the second \( \text{cmc} \) and above the first \( \text{cmc} \), spherical micelles can be found. Above the second \( \text{cmc} \), as more amphiphiles are added, rod-like micelles will form in addition to the already present spherical micelles. For \( T^* = 12.5 \), we find that the second \( \text{cmc} \) occurs at about 2 mol %. We consider the effect of temperature on the second \( \text{cmc} \) as shown in Fig. 13. The second \( \text{cmc} \) has a similar temperature dependence as the first \( \text{cmc} \); it increases as \( T^* \) is raised. We find that the second \( \text{cmc} \) increases exponentially with \( T^* \). In this exponential region we see that the second \( \text{cmc} \) is given by \( \text{cmc} \approx \exp[\Delta G/T^*] \) which is as generally expected.

Finally, an interesting question that arises is how the second \( \text{cmc} \) changes with the length of the hydrophobic tail group. When the tail length of \( H_3 T_6 \) is doubled one obtains...
the chain $H_3T_{12}$ and on studying the two systems at $T^* = 12.5$, we observe that the second $cmc$ decreases with increasing hydrophobic chain length (2 mol % for $H_3T_6$ and 0.016 mol % for $H_3T_{12}$) showing lower solubility. These results, namely a decrease in the second $cmc$ with an increase in the tail length, are in qualitative agreement with experimental observation.

V. CONCLUSIONS

We have applied the SCMF theory and GCMC simulations to elucidate the dilute micellar solution properties and the transition between spherical and spherocylindrical micelles of linear nonionic $H_4T_4$ and $H_3T_6$ amphiphiles. In the SCMF theory, the aggregates were assumed to be spherical and infinite cylindrical shapes. We used a simple model to estimate the standard chemical potential of spherocylinder aggregates by assuming a linear combination between the minimum of the free energy of spherical and infinite cylindrical geometries. The cluster size distributions were calculated using the standard chemical potential in combination with the mass action law for an ideal solution.

In the case of the symmetric $H_3T_4$, the SCMF theory finds that only one peak, which is around $N = 55$, forms in the cluster size distributions of spherocylinder micelles indicating that it prefers to form spherical micelles. The configurations of this system were studied using GCMC simulations and it was found that the micelle prefers to form spherical micelles. In addition, our observation is in good qualitative agreement with that found by the MC simulations. We also estimate the shape of the asymmetric $H_3T_6$ amphiphile aggregates. By using the SCMF theory, we found that two peaks are populated in the cluster size distribution; the first one refers to the transition from isolated amphiphiles to spherical micelles (first $cmc$) and the second one refers to the transition from spherical to spherocylindrical micelles (second $cmc$). We obtained good qualitative agreement with the GCMC simulations when the micelle shape was quantified using the principal moments of inertia and the configuration.

ACKNOWLEDGMENTS

This work is supported by the Universitat Rovira i Virgili, Integrated action with Italy (HI1998-0193) and financial support from the Spanish Government, DGIcyT (PB96-1025), (PPQ2001-0671, PPQ2000-2888E). We would like to thank Professor A. Z. Panagiotopoulos for making available his GCMC simulation code and also Professor A. Ben-Shaul for sending us a preprint of his work.
35 R. Nagarajan, C.-C. Wang, Langmuir 16, 5242 (2000), and Refs. 13 and 14 cited there.