MICELLIZATION IN MODEL SURFACTANT SYSTEMS

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ABSTRACT

Formation of micelles in model lattice surfactant systems was studied by a novel methodology based on grand-canonical Monte Carlo simulations. The methodology involves combining free-energy information from a series of simulations in small systems by histogram reweighting. The solution osmotic pressure as a function of overall volume fraction of surfactant shows a sharp break at the critical micelle concentration (cmc) at sufficiently low temperatures. Studies in larger systems at appropriate values of the surfactant chemical potential are used to investigate the size distribution of micellar aggregates. The methodology allows for a clear distinction between micellization and macroscopic phase separation. Two symmetric diblock surfactants have been considered in the present work. The cmc was found to increase with increasing temperature. The enthalpy change on micellization was determined to be proportional to the chain length of the surfactant. The mean micelle aggregation numbers were found to decrease at higher temperatures and increase with overall surfactant volume fraction for temperatures near the upper limit for micellar aggregation. These observations indicate that simple geometric packing concepts for micelle formation do not adequately describe temperature and composition effects in non-ionic surfactant solutions.
1. INTRODUCTION

Many surfactants form micellar aggregates in liquid solutions when their concentration exceeds a certain threshold that depends primarily on surfactant architecture, the solvent, presence of added components (such as co-surfactants or salts) and temperature. Micellar solutions are important for a number of technological applications, including detergency, catalysis, pharmaceutical, food and cosmetics formulations and tertiary oil recovery. The “self-organizing” principles behind micelle formation are relevant for understanding biomembranes and can be utilized for synthesis of novel materials. From a thermodynamic point of view, the formation of micelles is not a true phase transition, as it does not involve creation of a new macroscopic phase. While there are no sharp discontinuities in thermodynamic properties, the existence of micelles in solution can be detected by a variety of macroscopic measurements, one of which is the presence of a relatively sharp change of slope in a curve of the osmotic pressure plotted against total surfactant concentration. The surfactant concentration at which this break occurs is defined as the “critical micelle concentration” (cmc).2

There is significant interest in developing theoretical5-9 and simulation10-24 models of the micellization process. Computer simulations are increasingly being used to study the structure and thermodynamics of micelles. Such simulations can be classified into two broad categories. In the first, micelles of a certain size and shape are assumed to exist and the simulations probe their structure and short-time dynamics. Detailed atomistic models of the surfactant molecules can be studied by this method.10,11 The other simulation approach is to study the process of spontaneous micelle formation. Because actual time scales for micelle formation are much longer than the times that can be probed by simulations of atomistically detailed models4, spontaneous micelle formation is typically studied in simplified models. Large system sizes are usually required to ensure that a sufficient number of micelles are present in the simulations.

The first objective of the present paper is to describe a novel simulation methodology for determining critical micelle concentrations (cmc’s) and aggregation behavior in micellar solutions. The methodology is based on grand-canonical Monte Carlo (GCMC) simulations combined with histogram reweighting and has several advantages over previously available
approaches. The technique provides rapid estimates of cmc’s from simulations in relatively small systems and is less susceptible to hysteresis and metastability effects. It also allows a clear distinction between micellization and macroscopic phase separation. We apply this methodology to determination of cmc’s and distributions of micelle sizes above the cmc, for two different symmetric model surfactants over a range of temperatures. The results are compared to available simulation data and to qualitative trends observed experimentally in non-ionic surfactant solutions. Although the model systems studied do not represent accurately any specific real system, physical insights into general characteristics of aggregation in micellar solutions can be gained from the simulations.

2. METHODOLOGY

2.1 Histogram-Reweighting Grand-Canonical Monte Carlo

The simulation methodology used in this work is grand-canonical Monte Carlo (GCMC). A GCMC simulation is performed in a simulation cell of size $V$, under periodic boundary conditions. The inverse temperature, $\beta=1/k_BT$, where $k_B$ is Boltzmann’s constant and the chemical potential, $\mu$, are specified as input parameters to the simulation. The surfactant solutions are modeled on a lattice with a monomeric solvent filling positions not occupied by the surfactant, so that the system can be considered as a one-component system. Particles are created and destroyed in the simulation cell with acceptance probabilities, $P_{acc}$:

$$P_{acc}(N \rightarrow N+1) = \min \left[ 1, \frac{V}{N+1} \exp (-\beta \Delta U + \beta \mu) \right]$$
$$P_{acc}(N \rightarrow N-1) = \min \left[ 1, \frac{N}{V} \exp (-\beta \Delta U - \beta \mu) \right]$$ (1)

where $N$ is the number of particles in the simulation cell for a certain configuration and $\Delta U$ is the configurational energy change on addition or removal of a particle. There are several advantages of the GCMC approach over canonical-ensemble simulations in which temperature, volume, and number of particles in the system are held fixed. In surfactant solutions, micellar aggregates form at relatively low concentrations and, therefore, a large system size needs to be used in a canonical simulation to ensure that there are sufficient surfactant molecules to form
aggregates. In a GCMC simulation, the number of surfactant molecules in the system fluctuates, depending on the presence and aggregation number of micelles that form. Much smaller system sizes, which equilibrate significantly faster, can be used. In addition, GCMC simulations provide direct information on the free energy of the system, a quantity of fundamental interest.

In our simulations, we take advantage of the histogram-reweighting approach described previously. In this approach, data from a single simulation are used to obtain the thermodynamic properties of a system over a range of temperatures and densities. Several simulations at appropriate values of the chemical potential and temperature are combined to obtain the thermodynamic properties for any desired set of conditions. Histogram reweighting requires collection of data for the probability of occurrence, \( f(N,U) \), of \( N \) particles with total configurational energy in the vicinity of \( U \) in the simulation cell. This probability distribution function follows the relationship

\[
f(N,U) = \Omega(N,V,U)\exp(\beta \mu N - \beta U) / \Xi(\mu,V,\beta),
\]

where \( \Omega(N,V,U) \) is the microcanonical partition function (density of states) and \( \Xi(\mu,V,\beta) \) is the grand partition function. \( \Omega \) depends on the occupancy, while \( \Xi \) is fixed during a given simulation run. An estimate for the entropy, \( S(N,V,U) \), within an additive constant, \( C \), for the range of densities and energies covered in a simulation can be obtained by a simple transformation of equation (2):

\[
S(N,V,U)/k_B = \ln \Omega(N,V,U) = \ln[f(N,U)] - \beta \mu N + \beta U + C.
\]

Different simulation runs at chemical potentials and temperatures covering the range of interest can be combined using the method of Ferrenberg and Swedsen to produce a global estimate for the entropy function, again within an additive constant. From this function, properties can be calculated at any chemical potential and temperature, provided that the original simulation data covered energies and densities relevant for the new conditions. An estimate for the grand partition function, \( \Xi(\mu,V,\beta) \), within an unknown multiplicative constant, \( C' \), can be obtained from

\[
\Xi(\mu,V,\beta) = C' \sum_{U,N} \exp[S(N,V,U) - \beta U + \beta \mu N].
\]
The logarithm of the grand partition function is equal to the product of pressure and volume for a system, so pressure can be obtained from

$$\beta PV = \ln \Xi(\mu, V, \beta) = \ln C' + \ln \left[ \sum_{\nu, N} \exp \left( S(N, V, U) - \beta U + \beta \mu N \right) \right]. \quad (5)$$

The unknown constant in equation 5 can be obtained from matching low-density results to the ideal gas equation of state, $\beta PV = N$.

### 2.2 Model and Simulation Details

In the model studied here, originally proposed by Larson$^{28}$, space is discretized into a cubic lattice of sites in three dimensions. Solvent molecules occupy single sites whereas amphiphile molecules occupy chains of connected sites. An entity on a given lattice site interacts equally with sites located along vectors $(0,0,1), (0,1,1), (1,1,1)$ and the vectors resulting from symmetry operations with respect to the three spatial directions, resulting in a coordination number of 26. No interactions at greater distances are present. Connected sites along the amphiphile backbone are restricted to be along the same 26 vectors of interaction. The abbreviation $H_xT_y$ is used to denote an amphiphile which has $x$ head sites and $y$ tail sites.

All systems studied were binary mixtures of amphiphile and H-monomers. The lattice was fully occupied. The resulting two-component, fixed density system is equivalent to a one-component, variable density system of amphiphile. The two descriptions are completely equivalent; we have adopted the simpler one-component description for the simulations, but describe the results in the language of the two-component system. The pressure calculated from the simulations is equivalent to the osmotic pressure of the amphiphile in the two-component system.

Interactions of strength $\varepsilon_{HH}$ occur between two head groups, a head group and solvent monomers and two solvent monomers. Interactions of strength $\varepsilon_{HT}$ occur between head or solvent groups and tail groups and of strength $\varepsilon_{TT}$ between tail groups. Temperature was normalized by the energy scale $\varepsilon$, defined by...
\[ \varepsilon = \varepsilon_{\text{HT}} - \frac{1}{2}\varepsilon_{\text{HH}} - \frac{1}{2}\varepsilon_{\text{TT}}. \]  

The \( \varepsilon_{\text{TT}} \) interaction was set to -2 (resulting in attractive interactions for nearest-neighbor tail-tail contacts) and the \( \varepsilon_{\text{HH}} \) and \( \varepsilon_{\text{HT}} \) interactions were set to zero. Pressure calculated from equation 5 was normalized so that for an ideal-gas state,

\[
\lim_{\rho \to 0} \left( \frac{P}{T} \right) = \rho
\]

where \( \rho \) is the reduced density of the surfactant, in molecules per lattice unit cell. For a surfactant molecule with \( J \) beads, the density \( \rho \) and volume fraction \( \varphi \) are simply related by the expression \( \varphi = J\rho \).

Simulations were performed in cubic boxes under periodic boundary conditions. A typical mix of moves was 50% particle creation/annihilation steps and 50% reptation steps. As in the previous study of surfactant aggregation by our group,\(^{20}\) cluster moves in a ratio of 0.1% were used in the larger system sizes to achieve significant displacements of micellar aggregates. The reason for the low proportion of cluster moves was their high computational cost. Configurational-bias sampling methods\(^{29,30}\) were used to facilitate insertions and removals of surfactant molecules. The first monomer of a chain was placed in a random unoccupied position. Subsequent monomers were placed on unoccupied positions on the lattice, provided such positions existed along the directions of growth permitted by lattice connectivity. The “Rosenbluth weight” for each growth step was calculated as the ratio of the number of unoccupied sites divided by the total number of sites, \( z=26 \). The Rosenbluth weight of the chain when it had fully grown, \( W_{\text{new}} \), was calculated as the product of the weights calculated during each growth step. The reverse occurred during particle removal: a chain selected at random was “unzipped” from one randomly selected end to the other, and the Rosenbluth weight of the existing configuration was calculated as segment by segment was eliminated.

Determination of cluster distributions was performed following the convention used in our previous work.\(^{20}\) According to this convention, 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. Cluster size distributions are insensitive to this choice and similar distributions would result if the definition of the clusters were to be based on both head and tail segments.

The surfactant $\text{H}_3\text{T}_3$ was studied on cubic lattices of linear size $L=15$ and 30, while $\text{H}_4\text{T}_4$ was studied on lattices of length $L=15$ and 40. CPU time requirements on a DEC Alpha 500 MHz processor for a typical run for $\text{H}_3\text{T}_3$ on the $L=30$ lattice were 3 hr / $10^6$ Monte Carlo steps per particle. Run lengths ranged from $10^5$ - $10^7$ Monte Carlo steps per particle, depending on density and system size. A long-period ($> 2 \times 10^{18}$) random number generator was used.

Statistical uncertainties for selected conditions were obtained by performing independent sets of runs (usually four) at identical thermodynamic conditions, but using different random number sequences. The statistical uncertainties were obtained as the standard deviation of results from the independent simulations.

3. RESULTS AND DISCUSSION

3.1 Determination of Critical Micelle Concentrations

A number of grand-canonical Monte Carlo simulations at both increasing and decreasing values of the chemical potential was performed for each surfactant and temperature studied at overlapping ranges of surfactant volume fractions. The results were combined through histogram reweighting. The runs extended to chemical potentials sufficiently low to cover the density region in which surfactant molecules are dispersed as monomers. By increasing the chemical potential, nearly spherical micelles with a well-defined core of tail groups formed readily in simulations of smaller system sizes ($L=15$). For the larger systems ($L=30$ or 40), some hysteresis was observed, especially at lower temperatures, as will be discussed in section 3.4. An important benefit that resulted from using small system sizes is that the range of volume fractions sampled was broader, since the relative density fluctuations scale as $L^{-3/2}$ with box size. Thus, a small number of simulation runs was sufficient to cover the volume fraction range from the ideal state of singly dispersed surfactant molecules to the cmc. In addition, simulation time
and computer memory requirements, that scale as $L^3$ for a fixed number of Monte Carlo steps per particle, were significantly lower for the smaller systems.

We define the reduced osmotic pressure of the solution as $JP/T$, where $J$ is the total number of beads in the amphiphile. Our results for this quantity are plotted in Figure 1 against the overall volume fraction of surfactant for the $\text{H}_4\text{T}_4$ system, at two temperatures, $T=6.5$ and $T=8$. At the lower temperature (triangles in Figure 1) and at low surfactant concentrations, the reduced osmotic pressure follows closely a line with unit slope, thus corresponding to singly dispersed surfactant molecules that behave in a nearly ideal fashion. At a volume fraction of approximately $\phi\approx0.0045$ there is a sharp break in the curve. Points at greater volume fraction follow a nearly straight line with a much lower slope, approximately equal to 1.7%. In thermodynamic terms, this indicates that the independent “particles” in the system are now aggregates of surfactant molecules rather than monomers. For the higher temperature, (circles and crosses in Figure 1), there are gradually increasing deviations from the ideal line at moderate surfactant volume fractions, around $\phi=0.02$. One can still observe a relatively well-defined second straight segment above $\phi=0.04$, with slope approximately equal to 8%.

We define the critical micelle concentration, $\phi_{\text{cmc}}$, as the overall volume fraction of surfactant at which the ideal line of unit slope and the second straight segment in the osmotic pressure plot intersect. The physical significance of this definition is that it corresponds to the volume fraction at which surfactant micelles start appearing in the system. Above this point, added surfactant molecules form micellar aggregates and the concentration of “free” surfactant in solution remains constant and (at least approximately) equal to $\phi_{\text{cmc}}$. The equivalence of $\phi_{\text{cmc}}$ defined from the osmotic pressure curve of small systems and the concentration of free surfactant in solution at equilibrium with micelles is demonstrated in section 3.2.

There is some ambiguity in the definition of the cmc at higher temperatures, since the change in slope in the osmotic pressure curve is gradual. Different choices as to the section of data to be fitted to the second straight line, however, have only a minor effect on the calculated values of $\phi_{\text{cmc}}$. This situation is entirely analogous to the one encountered experimentally. A gradual change in slope of a measurable quantity associated with formation of micelles is often observed. Using our proposed definition, we calculated the cmc’s at $T=6.5$ and $T=8$,
respectively, as $\phi_{\text{cmc}}=0.0045\pm0.0001$ and $\phi_{\text{cmc}}=0.0270\pm0.0002$. Mackie et al.\textsuperscript{20} have estimated that the volume fraction of surfactant at which the micelle peak disappears for H$_4$T$_4$ at $T=6.5$ is 0.005, in good agreement with the present calculation. The earlier study was performed in the canonical ensemble using much larger systems of $L=80$ to 120 at low overall surfactant volume fractions. The present calculations require a small fraction of the computer time required for the earlier constant-volume calculations.

At higher temperatures the slope of the second straight segment increases. Physically, this implies that the independent kinetic entities in solution involve fewer surfactant molecules. In addition, the range of volume fractions over which a second approximately straight segment can be drawn becomes narrower. It seems reasonable to define an upper limit to the slope of the second straight line, above which it is no longer appropriate to interpret the osmotic pressure curves as resulting from the formation of well-defined aggregates. The cmc concept is much less useful at still higher temperatures. We propose the term “critical micelle temperature” ($T_{cm}$) to describe this point, by analogy to the cmc. It should be recognized that this temperature is not a true critical point, and that, just as for the cmc, there is some arbitrariness in its definition. We have used an upper cutoff of 10% for the slope of the second straight segment. The upper temperatures for micelle formation from the osmotic pressure curves in $L=15$ boxes were found to be $T_{cm}=8.25\pm0.1$ for H$_4$T$_4$ and $T_{cm}=7.0\pm0.1$ for H$_3$T$_3$.

Cmc’s as a function of temperature for H$_4$T$_4$ and H$_3$T$_3$ in $L=15$ boxes are listed in Table 1 and plotted in Figure 2. The two surfactants studied have comparable cmc’s at their respective $T_{cm}$. Table 1 also lists the estimated value of the chemical potential at the cmc, $\mu_{\text{cmc}}$. The reference point for all chemical potentials in this work is the reversing random walk with no interactions. The cmc’s increase with temperature and decrease with increasing chain length of the hydrophobic tail. Experimentally, the system that more closely matches our model solutions is one of non-ionic surfactants in a slightly polar medium. In a study\textsuperscript{32} of n-dodecyl and n-tetradecyl hexaoyxyethylene (C$_{12}$E$_6$ and C$_{14}$E$_6$) in formamide it was found that the cmc (mol/l) increased, on raising the temperature from 25 to 40 °C, from 0.0391 to 0.0455 and from 0.0131 to 0.0144 for the two surfactants respectively. Our simulations are in qualitative agreement with these observations.
The lines shown in Figure 2 were fitted to the points using an equation of the form

$$\ln(\varphi_{\text{cmc}}) = A + B/T$$

where $A$ and $B$ are parameters. For a first-order phase transition, parameter $B$ would be proportional to the enthalpy of the transition, if solution non-idealities at the cmc can be neglected for the oligomers. Formation of micelles is not a first-order transition, but the data still follow equation 8 quite well, as shown in Figure 2. Parameters $A$ were obtained as $3.49 \pm 0.06$ for $H_3T_3$ and $4.26 \pm 0.07$ for $H_4T_4$. Parameters $B$ were determined to be $-47.3 \pm 0.4$ for $H_3T_3$ and $-63.0 \pm 0.5$ for $H_4T_4$, in reduced units. The ratio of the $B$ parameters between the two systems is almost exactly 3:4, the same ratio as for the chain lengths of the two surfactants. Additional calculations for different surfactant architectures will be required to confirm that the same trend holds for other surfactant chain lengths of the same “homologous series.” It would also be of interest to study asymmetric surfactant systems with respect to this quantity. Such studies are currently under way and will be the topic of a subsequent publication.

### 3.2 Equivalence of Small and Large Systems

Small systems have significant computational advantages for the calculation of cmc’s, as they permit determination of osmotic pressure curves with low statistical uncertainties over a broad range of temperatures. However, one may question whether the cmc’s calculated in such systems are relevant in the thermodynamic limit of infinite system size. In the $L=15$ system, a single micelle of $H_4T_4$ molecules with aggregation number $N=100$ results in a volume fraction of surfactant of $\varphi=0.24$, much greater than the cmc’s at any temperature. Clearly, larger systems are required in order to observe formation of micelles at relatively low overall volume fractions. Therefore, we need to establish the equivalence of the small and large systems with respect to their thermodynamic behavior. Establishing this equivalence is complicated by the fact that the presence of stable micellar aggregates results in significant hysteresis and equilibration problems for the large systems at lower temperatures.

The first test of equivalence of the small and large systems is to determine whether the equation-of-state determined in the small systems is still valid for the larger systems, in which
micellar aggregates are present at much smaller volume fractions. In Figure 1, two sets of points for the osmotic pressure as a function of surfactant volume fraction in $L=15$ and $L=40$ systems are shown at the higher temperature, $T=8$. The two sets agree within statistical uncertainties. In Figure 3, the volume fraction of $H_4T_4$ at $T=8$ is plotted against the chemical potential of the surfactant. Results from histogram-rewriting calculations in the small ($L=15$) systems and single-run results for the large ($L=40$) systems are shown. From these two figures, it is clear that the small and large systems result in identical equations-of-state at this relatively high temperature, not far from $T_{cm}$. This is remarkable, given that the two system sizes present significantly different microscopic pictures with respect to micelle formation. From Table 1, at this temperature $\phi_{cmc}=0.0270$ and $\mu_{cmc}=-46.8$. A dashed vertical line in Figure 3 marks the critical chemical potential. In the large system, for the run at $\mu=-45.5$ (second point from the right), the mean volume fraction was $<\phi>=0.0464$, corresponding to $<N>=370$ surfactant molecules. The corresponding quantities for the small system were $<\phi>=0.043$ and $<N>=18.4$ molecules. The mean volume fractions are equal within statistical uncertainties. Figure 4 shows the volume fraction of clusters for this run as a function of cluster aggregation number, $M$, as circles. Aggregates of mean size $\overline{M}=48$ are present in the large system. The small system does not contain a sufficient number of particles to form micelles, but follows the same equation-of-state.

A second important aspect of the equivalence of large and small systems is the question whether it is appropriate to identify the cmc with the point at which there is a break in the slope of the osmotic pressure curve in the small systems. Table 2 summarizes our calculations for the large systems studied. The oligomer volume fractions shown in the table, $\phi_{oligo}$, were obtained by summing the volume fractions of clusters of aggregation numbers $M<M_{\text{min}}$, where $M_{\text{min}}$ is the aggregation number at which the distribution of cluster sizes has a minimum. For example, for the data shown in Figure 4, $M_{\text{min}}$ is near 20. Micellar volume fractions $\phi_{\text{mic}}$ were obtained by summing the contributions of clusters with $M\geq M_{\text{min}}$. It is clear by comparing tables 1 and 2 that the volume fractions of oligomers observed in the large systems are very near the $\phi_{cmc}$ values obtained in the small systems. The effect of overall volume fraction of surfactant on oligomer volume fractions is discussed in detail in section 3.4.
3.3 Micellization or Macroscopic Phase Separation?

For an infinite system, first order transitions are manifested by sharp discontinuities in the thermodynamic properties, for example in pressure versus density curves of a one-component system. In small systems studied by simulation methods, discontinuities are rounded and it is often difficult to determine whether a first-order transition is taking place. In the present work, we suggest using osmotic pressure versus concentration curves to determine the cmc. It should be pointed out, however, that a system undergoing a phase transition, rather than micellization will also exhibit behavior analogous to that shown in Figure 1 for small system sizes.

To illustrate this point, we have considered the chain molecule \( H_8 \). The phase behavior of this model has been studied previously.\(^ {26,33} \) At temperatures lower than the critical point at \( T_c = 11.87 \), there are first-order transitions between a low-density gas and a high-density liquid. The pressure versus volume fraction curves for the \( H_8 \) system, at \( T = 11.5 \) and \( T = 9 \) are shown in Figure 5. The behavior is quite similar to that of the \( H_4 T_4 \) system shown in Figure 1 for the small system size. The volume fraction of the saturated gas, \( \phi_{\text{gas}} \), has been calculated in \(^ {26} \) as \( \phi_{\text{gas}} = 0.122 \) for \( T = 11.5 \) and \( \phi_{\text{gas}} = 0.011 \) for \( T = 9 \). These volume fractions are at the beginning of the second straight segments in Figure 5. Our proposed construction gives \( \phi_{\text{cmc}} = 0.0598 \) for \( T = 11.5 \) and \( \phi_{\text{cmc}} = 0.012 \) for \( T = 9 \). However, this behavior does not correspond to formation of micelles. This is shown in Figure 6, which shows cluster size distributions for this system at \( T = 11.5, \ L = 40 \), at a chemical potential that leads to an average volume fraction of \( \langle \phi \rangle = 0.1104 \pm 0.0002 \). This volume fraction is twice the “cmc” and comparable to the volume fraction of the saturated gas at equilibrium with a dense liquid. There is no peak at high aggregation numbers. Data collected (not shown in Figure 6 for clarity) extend to \( M = 907 \) and decay slowly with \( M \).

An interesting observation is that the two sets of points in Figure 1 fall on the same line at high surfactant concentrations at \( T = 8 \). This is due to the fact that the transition is between singly dispersed surfactants and an aggregate of finite size. For a first-order transition, the second straight line would have a slope that depends on system size, becoming parallel to the x axis for an infinite system. This is illustrated when the data for \( T = 11.5, \ L = 15 \) (circles) are compared to \( L = 40 \) (crosses) in Figure 5. For the large system size, the data follow the same curve only up to
the location of the phase transition. Above that concentration, the data fall on a straight line of nearly zero slope.

In conclusion of this section, behavior similar to that shown in Figures 1 and 5 is a necessary, but not sufficient condition for establishing that a system forms stable micellar aggregates. Cluster size distributions in simulation boxes large enough to contain aggregates at low overall volume fractions are needed in order to confirm the existence of micelles. In addition, the osmotic pressure versus surfactant loading curves need to be independent of simulation system size in order to confirm that the system is not undergoing a macroscopic phase separation.

3.4 Aggregation Behavior above the CMC

In order to study the effect of temperature and surfactant loading on the free surfactant concentration and size of micellar aggregates, we performed a series of simulation in larger boxes, \( L=40 \) and \( L=30 \), respectively for \( \text{H}_4\text{T}_4 \) and \( \text{H}_3\text{T}_3 \). For the lower temperatures, for which the cmc occurs at a low overall volume fraction of surfactant, very large systems would be required in order to observe formation of micelles near the cmc\(^4\). For example, for the \( \text{H}_4\text{T}_4 \) system at \( T=6 \), we obtained \( \phi_{\text{cmc}}=0.0019 \). At twice this volume fraction, we expect roughly equal number of surfactant particles appearing as monomers and as micellar aggregates. At these conditions, Table 2 indicates that the mean micellar aggregation number is \( M \approx 100 \). A system with 200 particles at twice the cmc has \( L=75 \). However, a fundamental difficulty exists for such large systems at relatively low temperatures. Aggregates of intermediate aggregation numbers between the oligomers and the fully formed micelles have higher free energies than either oligomers or micelles. In a simulation of finite length, hysteresis effects are expected to be quite severe. This was confirmed by our observations. For any but the smallest systems studied, simulations at chemical potentials above the critical micellar chemical potential listed in table 1 exhibited significant hysteresis. This hysteresis manifested itself in multiple ways. In particular, chemical potential values significantly above the \( \mu_{\text{cmc}} \) values listed in table 1 were required to induce a system to form micelles when no aggregates were present in the initial configuration. Conversely, chemical potentials significantly below the values of \( \mu_{\text{cmc}} \) in table 1 were required to destroy micellar aggregates in a system in which they were initially present. Over a broad
range of chemical potentials above $\mu_{\text{cmc}}$, simulations remained in the same aggregation state, with the number of micellar aggregates remained over the course of the run. These observations are only slightly sensitive to details of the simulation runs such as the length and particular mix of Monte Carlo moves. This is not surprising, given that a nucleation event, formation of an aggregate of a minimum size or a fluctuation that reduces the size of an existing micelle below a critical size, needs to occur in a system to change the number of micelles present.

One possibility for overcoming the free energy barriers associated with formation of new micelles and destruction of existing ones is to utilize umbrella sampling methods in order to force a system to sample states it would not otherwise visit. However, based on the observed equivalence between small and large systems, it was felt that such methods were not necessary. While the overall number of micelles did not change for simulations at low temperatures over a broad range of chemical potentials above $\mu_{\text{cmc}}$, the volume fraction of oligomers and the distribution of aggregate sizes were not sensitive to the initial conditions or the imposed value of the chemical potential. Our simulations in larger systems were performed at combinations of chemical potentials and surfactant volume fractions that were suggested to be thermodynamically stable by the small-system calculations. In Table 2, the volume fraction of micelles for simulations for which the final number of micellar aggregates is determined by the initial state of the system are shown in italics. At higher temperatures, hysteresis effects disappear and new micellar aggregates form readily in the course of the simulations.

Typical configurations of the H$_4$T$_4$ system in the larger system ($L=40$) are shown in Figures 7 and 8. Due to the periodic boundary conditions, micelles often appear dissected by the boundaries, thus affording views of the densely packed hydrophobic core. In Figure 7, a single micelle is present in the system, along with some surfactant molecules not attached to the aggregate. In Figure 8, several micelles are present in the system, but the system is still dilute enough so that the mean distance between micelles is sufficiently large for minimal interference among different aggregates.

A key quantity of interest in Table 2 is the oligomer volume fraction in the presence of micelles, $\phi_{\text{oligo}}$. In all cases, $\phi_{\text{oligo}}$ at low overall volume fractions of surfactant is equal to or slightly higher than $\phi_{\text{cmc}}$. The differences between $\phi_{\text{oligo}}$ and $\phi_{\text{cmc}}$ are only a few percent at low
temperatures, while at high temperatures near $T_{cm}$ the difference is more pronounced, reaching 25\% for H$_3$T$_3$ at $T=7$. This implies that, in agreement with experimental observations\textsuperscript{1}, the volume fraction of free surfactant is constant or increases slightly as the cmc is crossed.

At overall volume fractions of surfactant significantly higher than $\phi_{cmc}$, the volume fraction of oligomers decreases. Some of this decrease is due to an excluded volume effect, as proposed previously.\textsuperscript{21,24} As the volume fraction of micelles increases there is less available solution volume to accommodate free surfactant. This effect has been incorporated in theories for formation of micelles in non-ionic surfactants\textsuperscript{9} and has been seen in other simulation studies.\textsuperscript{19-21,24}

Another quantity of interest is the distribution of aggregate sizes as a function of temperature and overall surfactant volume fraction. Cluster size distributions for H$_4$T$_4$, $T=8$ have already been shown in Figure 4. Figure 9 shows the distribution of volume fractions of clusters for H$_4$T$_4$ at $T=6.5$, a temperature which is significantly below $T_{cm}$, the upper temperature limit for micelle formation, for this surfactant. Figure 10 shows the distribution of volume fractions of clusters for H$_3$T$_3$ at $T=7$, a temperature identified as $T_{cm}$ for this surfactant. For each temperature, three different curves corresponding to different overall volume fractions of surfactant are shown.

From the data in Table 2 and Figures 4, 9 and 10, several patterns emerge. In all cases, at low aggregation numbers, the volume fraction of aggregates decreases rapidly with aggregation number. For temperatures much lower than $T_{cm}$, no clusters of intermediate sizes between oligomers and fully formed micelles were observed in the simulations, implying that the free energy of surfactant in such clusters is significantly higher than either in free solution or in a fully formed micelle. At low temperatures (Figure 9) surfactant molecules added to the solution do not change the average aggregation number of existing micelles, but form additional aggregates of approximately the same type. By contrast, at high temperatures (Figures 4 and 10) the micellar peak is not fully separated from the oligomeric peak. These observations are consistent with the gradual loss of definition for the break in the osmotic pressure curves seen in section 3.1 and confirm that $T_{cm}$ is a reasonable upper limit for “true” micelle formation.
The distribution of aggregate sizes, \( \phi(M) \), approximately follows a Gaussian form at low to moderate overall surfactant volume fractions:

\[
\phi(M) \propto \exp\left[ -\frac{(M - \overline{M})^2}{W} \right].
\]

where \( W \) is a parameter determining the width of the distribution. At high overall surfactant volume fractions, slow-decaying “tails” appear at high aggregation numbers and deviations from the Gaussian distribution are present. This is seen most clearly in Figure 10. Gaussian curves fitted to the micellar peaks are shown as continuous lines in Figures 4, 9 and 10. Parameters \( \overline{M} \) and \( W \) of the fitted curves are reported in Table 2.

The effect of overall surfactant concentration on \( \overline{M} \) is small at low temperatures. However, the mean micelle aggregation number becomes an increasing function of overall surfactant concentration at high temperatures. For example, for the shorter surfactant, H3T3 at \( T_{cm} \), \( (T=7, \text{Figure 10}) \), \( \overline{M} \) shifts from 40 just above the cmc to 55 at an overall volume fraction of surfactant equal to three times the cmc.

There is a strong effect of temperature on the mean micelle aggregation number. For both surfactants, \( \overline{M} \) decreases with increasing temperature. The values of \( \overline{M} \) near \( T_{cm} \) are almost half the values observed at the lowest temperatures studied for each surfactant. The effect of surfactant architecture on \( \overline{M} \) is less clear. At the same reduced distance from \( T_{cm} \), both surfactants form aggregates of comparable aggregation number. The effects of temperature and surfactant concentration on \( W \), the width of the distributions, are relatively weak. There is a general trend towards broader distributions at higher temperatures, especially for the shorter surfactant. The shorter surfactant also has higher values of \( W \) at the same reduced distance from \( T_{cm} \) than the longer surfactant.

The aggregate size distributions shown in Figure 9 are comparable to the distributions obtained in our earlier single-temperature study of the same surfactant, but the new results have significantly smaller statistical uncertainties. In the previous study, a surprising observation was that counter to expectations, at overall volume fractions of surfactant lower than 2%, the
mean micelle size shifted to higher values. This is not confirmed by our present study. In light of our new results, we conclude that the likely reason for the shift seen in the earlier study was lack of equilibrium with respect to the total number of micelles in the system. The micellization behavior for H₄T₄ and H₃T₃ at T=6.5 has also been studied by Larson¹². In that study, an increase in mean micelle size from M=68 to M=84 was observed on changing the overall surfactant concentration from 8% to 20%. While mean micelle sizes from our work and from¹² are comparable, there are quantitative disagreements that may, once again, be due to hysteresis effects in the earlier canonical-ensemble study. For the H₃T₄ system studied in¹², it was observed that the mean micelle size decreased with increasing temperature, in agreement to our observations.

In the present work, we have not studied in detail the shape of the micelles that form or their internal structure. For the H₄T₄ surfactant at T=6.5, our earlier work²⁰ indicated that aggregates of size M<100 are nearly spherical in shape, and contain a densely packed hydrophobic core. An investigation of the effects of surfactant architecture and temperature on the shape of micellar aggregates is currently under way and will be the subject of a forthcoming publication.

4. CONCLUSIONS

The present work establishes a new approach for the determination of critical micelle concentrations by simulation in model surfactant systems. The approach is based on grand-canonical Monte Carlo calculations combined with histogram-rewriting techniques. The approach is not restricted to the model lattice surfactants studied, but should be generally applicable to lattice and continuous-space systems. Our proposed strategy for the determination of cmc’s and the structure of micelles by simulation consists of the following steps:

(a) The first step is to perform calculations in simulation boxes of the smallest possible realistic size. Small simulation boxes are advantageous for the determination of critical micelle concentrations because calculations require modest computational resources and result in sampling of broad ranges of surfactant concentrations, thus facilitating histogram reweighting. In addition, the use of small systems eliminates hysteresis effects present for
larger systems at lower temperatures. The lower limit to the size that can be studied is imposed by the presence of long-range forces and by geometric considerations on the size of the surfactant molecules and aggregates.

(b) Results from a number of simulations in small systems are combined to obtain the osmotic pressure and chemical potential / volume fraction relationships as a function of temperature. The cmc as a function of temperature and $T_{cm}$, the upper critical temperature for micelle formation, can be obtained from the osmotic pressure curves.

(c) From the chemical potential versus volume fraction curves one can then determine appropriate combinations of chemical potential and temperature for study of larger systems at conditions for which micellar aggregates at a certain overall volume fraction are thermodynamically stable. Larger systems allow for formation of non-interacting aggregates at overall volume fractions not much higher than the cmc’s obtained in step (b). The size distribution of micelles and other geometric characteristics can be determined in these larger systems.

Simulation studies of surfactant formation in diblock copolymer systems yield new insights into the physics of the micellization process for non-ionic surfactant solutions. In particular, the present work and other recent studies $^{21,24}$ have identified an upper temperature limit for formation of well-defined micelles. In the present study we have proposed a computational method for the rapid determination of this upper critical micelle formation temperature.

The present study is the first simulation work to obtain accurate values of cmc’s for a model system over a broad temperature range. The cmc’s for two symmetric diblock surfactants were found to increase with temperature. The enthalpy change on micellization is therefore negative. The magnitude of the enthalpy change was found to be proportional to the surfactant chain length. We plan to investigate the dependence of this quantity on surfactant architecture in detail in the future.

One advantage of simulation studies over experiments is that they can be performed over broader temperature ranges. Our results for the effects of temperature and overall surfactant concentration on the mean micelle aggregation number throw into some doubt the accuracy of
simple geometric packing concepts of micelle formation. These concepts seek to explain micelle size and shape in terms of the mean shape of surfactant monomers. In our systems, the surfactant molecules do not change shape significantly as temperature is decreased, as they are fully flexible. For isolated monomers, the surfactant tails become more compact at lower temperatures in order to maximize intrachain energetic interactions. From geometric packing considerations this should have resulted in a decrease in the micelle aggregation number at lower temperatures. However, we observe that significant increases in mean micellar aggregation number take place as temperature is lowered. This suggests that a complex interplay between energetic and entropic factors determines the mean aggregate size in our model non-ionic surfactant systems.

ACKNOWLEDGMENTS

Research on which this work was based was supported by a grant from the U.S. Department of Energy, Office of Basic Energy Sciences. MAF would like to acknowledge travel support by a NATO Senior Research Fellowship. AZP thanks CNR for travel support under the short-term mobility program and Prof. Sanat Kumar for helpful discussions. We also thank Prof. Binder for a copy of reference prior to publication.
REFERENCES AND NOTES


TABLE 1. Volume fraction of surfactant, ϕ_{cmc} and chemical potential, μ_{cmc}, at the cmc from histogram-rewriting calculations in the L=15 boxes. Statistical uncertainties are ±2% for ϕ_{cmc} and ±0.1 units for μ_{cmc}.

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<td>μ_{cmc}</td>
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TABLE 2. Volume fraction of oligomers, $\phi_{\text{oligo}}$, micelles, $\phi_{\text{mic}}$, mean micelle aggregation number, $\bar{M}$, and width of distributions, $W$, as a function of temperature $T$ and chemical potential $\mu$ in the larger systems studied. Entries in *italics* are sensitive to initial conditions for the corresponding simulation run, as explained in the text. Statistical uncertainties are shown in parentheses, in units of the last decimal point of the corresponding quantity.

<table>
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**FIGURE CAPTIONS**

Fig. 1. The quantity $8P/T$ versus overall volume fraction of surfactant, $\phi$, for $H_4T_4$ chains. $T=6.5$, $L=15$: ($\Delta$); $T=8$, $L=15$: ($\bigcirc$); $T=8$, $L=40$: (+). The straight line through the origin has unit slope and represents ideal behavior. Straight lines at high surfactant volume fractions are fitted as described in the text. Statistical uncertainties are smaller than the symbol size.

Fig. 2. Volume fraction of surfactant at the cmc, $\phi_{\text{cmc}}$, as a function of temperature, $L=15$. $H_3T_3$: ($\bigcirc$); $H_4T_4$: ($\Delta$). Lines are fitted to the points as described in the text.

Fig. 3. Volume fraction of $H_4T_4$ surfactant, $\phi$, *versus* the chemical potential, $\mu$, for $H_4T_4$, $T=8$. Histogram reweighting results for $L=15$: (—); single-run results for $L=40$: ($\bigcirc$). Statistical uncertainties are shown only for the $L=40$ results when larger than the symbol size. The vertical dashed line marks the critical micelle chemical potential, $\mu_{\text{cmc}}$, obtained from the $L=15$ data.

Fig. 4. Volume fraction of clusters, $\phi$, versus cluster aggregation number, $M$, for $H_4T_4$, $T=8$, $L=40$. $\mu=\,45.2$: ($\Delta$); $\mu=\,45.5$: ($\bigcirc$); $\mu=\,45.8$: ($\times$). Statistical uncertainties are comparable to the symbol size. Lines are fitted to the points for higher aggregation numbers, as discussed in the text. The volume fractions of clusters with $M=1$ to $M=5$ are off-scale for this graph. The raw data have not been smoothed, but only even values of $M$ are displayed for clarity.

Fig. 5. The quantity $8P/T$ versus volume fraction, $\phi$, for $H_8$ chains. $T=9$, $L=15$: ($\Delta$); $T=11.5$, $L=15$: ($\bigcirc$); $T=11.5$, $L=40$: (+). Lines and statistical uncertainties are as for Figure 1.
Fig. 6. Volume fraction of clusters, $\phi$, versus cluster aggregation number, $M$, for $H_8$, $T=11.5$, $L=40$, $\mu = -60.6$, $\langle \phi \rangle = 0.1104 \pm 0.0002$. Statistical uncertainties are comparable to the symbol size. The volume fraction of $M=1$ and $M=2$ are off-scale for this graph. Data for $M=141$ to $M=907$ are also off-scale. The raw data have not been smoothed, but only even values of $M$ are displayed for clarity.

Fig. 7. A configuration for $H_4T_4$ surfactant, $L=40$, $T=6$, $\mu = -50$. The volume fraction of surfactant for this configuration is $\phi = 0.0138$. Tail groups are dark-colored and head groups are light-colored.

Fig. 8. A configuration for $H_4T_4$ surfactant, $L=40$, $T=6$, $\mu = -49.95$. The volume fraction of surfactant for this configuration is $\phi = 0.0795$. Tail groups are dark-colored and head groups are light-colored.

Fig. 9. Volume fraction of clusters, $\phi$, versus cluster aggregation number, $M$, for $H_4T_4$, $T=6.5$, $L=40$. $\mu = -48.5$: (\Delta); $\mu = -48.55$: (\bigcirc); $\mu = -48.6$: (\times). Lines and statistical uncertainties are as for Figure 4. The volume fractions of monomers are off-scale for this graph. The raw data have not been smoothed, but only even values of $M$ are displayed for clarity.

Fig. 10. Volume fraction of clusters, $\phi$, versus cluster aggregation number, $M$, for $H_3T_3$, $T=7$, $L=30$. $\mu = -35.2$ (\Delta); $\mu = -35.5$ (\bigcirc); $\mu = -35.8$: (\times). Lines and statistical uncertainties are as for Figure 4. The volume fractions of clusters with $M=1$ to $M=6$ are off-scale for this graph. The raw data have not been smoothed, but only even values of $M$ are displayed for clarity.
Figure 1.

Figure 2.
Figure 3.

Figure 4.
Figure 5.

Figure 6.
Figure 7.

Figure 8.
Figure 9.

Figure 10.