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A comparison of self-assembly in lattice and off-lattice model amphiphile solutions

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Lattice Monte Carlo and off-lattice molecular dynamics simulations of h_1t_4 and h_4t_1 (head/tail) amphiphile solutions have been performed as a function of surfactant concentration and temperature. The lattice and off-lattice systems exhibit quite different self-assembly behavior at equivalent thermodynamic conditions. We found that in the weakly aggregating regime (no preferred-size micelles), all models yield similar micelle size distributions at the same average aggregation number, albeit at different thermodynamic conditions (temperatures). In the strongly aggregating regime, this mapping between models (through temperature adjustment) fails, and the models exhibit qualitatively different micellization behavior. *© 2002 American Institute of Physics.* [DOI: 10.1063/1.1461355]

INTRODUCTION AND MOTIVATION

Due to the tremendous importance of micellar solutions in various industrial and biological applications,[1,2] many theoretical and modeling studies of the self-assembly of amphiphilic molecules in solution have addressed questions of micellar structure, shape, size distribution, kinetics of formation, and solution phase properties. However, nanoscale structural heterogeneity and complications with obtaining equilibrium configurations largely prohibit brute-force atomistic simulations of amphiphile self-assembly. The few reported atomistic simulations are limited to systems with a single micelle of predefined size and are unable to discern whether the resulting structures correspond to equilibrium conditions.[3–5]

More progress has been made in coarse-grained simulations of micelle forming amphiphile solutions. Lattice Monte Carlo (MC)[6–10] and bead-spring molecular dynamics (MD)[11–14] and MC[15] simulations of model surfactant systems have investigated phase behavior, micelle shape and size distribution, free energy of amphiphiles in solution, dynamics of self-assembly, and other properties of micellar solutions. In these coarse-grained simulations, the surfactant molecules are composed of head (*h*) and tail (*t*) segments consisting of one bead (off-lattice MD and MC) or occupying one lattice site (lattice MC) each. Solvent molecules (*s*) are likewise considered to occupy single lattice sites. While both techniques are more efficient than atomistic MD simulations, lattice MC methods are computationally more expedient than the coarse-grained off-lattice MD or MC simulations. Furthermore, taking the lattice system as incompressible allows treating the solvent implicitly, i.e., as empty sites. For a lattice system with ternary (*h*-*t*-*s*) interactions, the excess solution energy may be expressed in terms of three exchange energy parameters, given as $\Delta w_{ij}=z(E_{ij}-\frac{1}{2}[E_{ii}+E_{jj}])$, where z is the lattice coordination number, $i, j=h, t, s$, and E_{ij} is the interaction energy between segments of type i and j on nearest neighbor lattice sites. Since all combinations of intermolecular energies that yield the same Δw are equivalent on the incompressible lattice, we can arbitrarily set $E_{ss}=E_{hs}=E_{ts}=0$, allowing us to ignore interactions involving surfactant molecules with the predominant solvent molecules.

Although incompressible lattice MC simulations are computationally expedient, their wide use raises the important question of how the assumed incompressibility affects the thermodynamics of self-assembly. In other words, does compressibility significantly influence the self-assembly of the h_xt_y surfactants, or are the effects of compressibility negligible, making the incompressible lattice MC method an attractive alternative to the more realistic but much more expensive off-lattice methods? A hint of the importance of compressibility effects emerges from studies of polymer blends, where the asymmetry in intermolecular interactions is typically much weaker than in micelle forming amphiphile solutions. The importance of compressibility for polymer blend thermodynamics has been demonstrated by extensive lattice cluster theory (LCT) computations of blend properties,[16] especially LCT predictions of a significant pressure dependence to the phase behavior of polymer blends,[17] a prediction subsequently confirmed experimentally.[18] Furthermore, it is computationally expedient to ignore the solvent degrees of freedom, both in incompressible lattice and in off-lattice simulations, as recently done in a MC study of self-assembly of diblock amphiphiles.[15] A recent combined liquid state theory and MD simulation study of polymer solutions with and without explicit solvent[19] shows that the solvent strongly influences the polymer structure and phase behavior. Simulations of amphiphile solutions are compared

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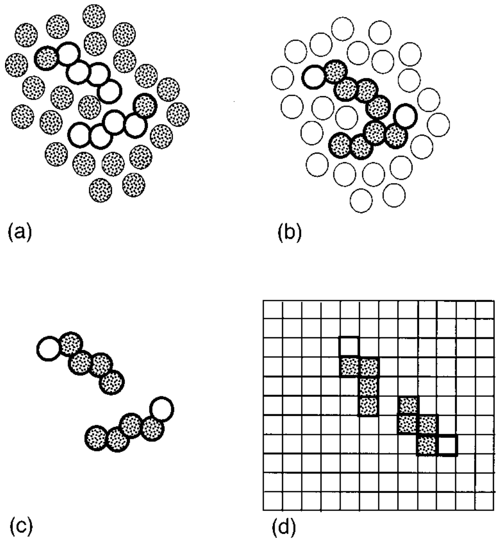

FIG. 1. Schematic representation of h_1t_4 surfactants in the (a) solvophobic and explicit solvent, (b) tail attraction and explicit solvent, (c) tail attraction and implicit solvent, and (d) incompressible lattice models.

here using several different lattice and off-lattice models (with and without solvent) to determine the influence of model details and solvent representation on the self-assembly behavior of these systems.

SIMULATIONS OF AMPHIPHILE SOLUTIONS

Systems studied

We have performed MD simulations and lattice MC simulations of *h-t-s* systems consisting of h_1t_4 or h_4t_1 surfactant molecules and monomeric solvent. In the MD simulations, surfactant molecules are represented as bead-necklace chains, and solvent molecules are taken as single beads. All beads have the same diameter ($\sigma=1.0$) and interact via potentials based on the Lennard-Jones (LJ) interaction $U_{LJ}(r)=4[r^{-12}-r^{-6}]$, where the well-depth is chosen as unity. Attractive interactions are modeled by a truncated and shifted LJ potential of the form $E^{\mathrm{att}}(r)=U_{LJ}(r)-U_{LJ}(r_c)-(r-r_c)[dU_{LJ}(r)/dr]|_{r=r_c}$ with $r_c=2.5$, insuring that both the energy and force vanish at the cutoff radius r_c and that $E^{\mathrm{att}}=-1.0$ at $r=2^{1/6}$. Excluded volume (purely repulsive) interactions are modeled by the Weeks–Chandler–Anderson (WCA) potential[20] $E^{\mathrm{rep}}(r)=U_{LJ}(r)-U_{LJ}(r_c)$, with $r_c=2^{1/6}$ and $E^{\mathrm{rep}}(r)=0$ for $r\geqslant r_c$. The lattice simulations assign the interaction energy between nearest neighbor segments as $E=-1.0$ or 0.0.

Three off-lattice and two lattice ($z=6$ and $z=26$) systems, illustrated in Fig. 1, are investigated. The interaction parameters for these cases are summarized in Table I. In the solvophobic case [Fig. 1(a)], aggregation of surfactants is due to the ‘‘solvophobic’’ effect, i.e., interactions of the surfactant tail with the solvent are relatively unfavorable compared to solvent–solvent and head–solvent interactions. In the tail attraction case [Fig. 1(b)], self-assembly of surfactants is driven by specific attraction between surfactant tails. The tail attraction model has also been simulated without solvent molecules [Fig. 1(c)], referred to hereafter as the implicit solvent system. Each of these systems is also represented using the incompressible lattice model [Fig. 1(d)] with the Δw values given in Table I.

TABLE I. Summary of surfactant–solvent interactions for the amphiphile solutions simulated.

Interaction	Tail attraction	Solvophobic	Implicit solvent	Lattice $z=26$	Lattice $z=6$
E_{hh}	WCA	LJ	WCA	0	0
E_{ss}	WCA	LJ	N/A[a]	0	0
E_{tt}	LJ	WCA	LJ	−1	−1
E_{hs}	WCA	LJ	N/A[a]	0	0
E_{ht}	WCA	WCA	WCA	0	0
E_{ts}	WCA	WCA	N/A[a]	0	0
Δw_{hs}	0[b]	0[b]	0[b]	0	0
Δw_{ht}	4.2[b]	4.2[b]	4.2[b]	13	3
Δw_{ts}	4.2[b]	4.2[b]	4.2[b]	13	3

[a] There were no solvent molecules in this simulation.

[b] Calculated assuming $\Delta w=\int_0^{r_c=2.5}(E^{\mathrm{att}}(r)-E^{\mathrm{rep}}(r))g(r)r^2dr$, where $g(r)$ is radial distribution function of an athermal (WCA) monomeric fluid at $\rho=0.7$.

Methodology

Simulations are performed for solutions with surfactant mole fractions ranging from 2×10^{-3} to 1.7×10^{-2}. In MD simulations, the *h-t* and *t-t* bonds within a given surfactant molecule are constrained to length 1.0 using the SHAKE algorithm.[21] The systems contain between 30 and 250 surfactant molecules and 15000 solvent molecules and have a constant segment number density $\rho=0.7$. The implicit solvent simulations employ a Brownian dynamics algorithm described previously[22] with a friction coefficient of 13.3, along with the same simulation box size and number of surfactants as for the MD simulations with explicit solvent. The lattice MC simulations are performed on a $25\times25\times25$ simple cubic lattice using the configurational-bias MC method described elsewhere.[23] The lattice size is chosen to yield the same surfactant density and number of molecules as in the off-lattice simulations.[24]

RESULTS AND DISCUSSION

Micellization

We define two surfactant molecules as belonging to the same micelle when any of their tail segments are within a distance of 2.0. Figure 2 shows the mole fraction of free surfactant X_1 as a function of the total surfactant mole fraction X_{surf} for all models at equivalent thermodynamic conditions, corresponding to the same reduced temperature $T^*=kT/\Delta w$. Saturation in the curves for $X_1(X_{\mathrm{surf}})$ is usually associated with micelle formation. We observe phase separation at the highest surfactant concentration studied only for the tail attraction h_1t_4 system. Clearly, the four different models exhibit disparate self-assembly behavior. Note that while the $X_1(X_{\mathrm{surf}})$ curves are qualitatively similar for the h_4t_1 and h_1t_4 systems, there is a significant difference in nature of self-assembly between these systems. The micelle size distribution for all h_1t_4 systems is monotonically de-

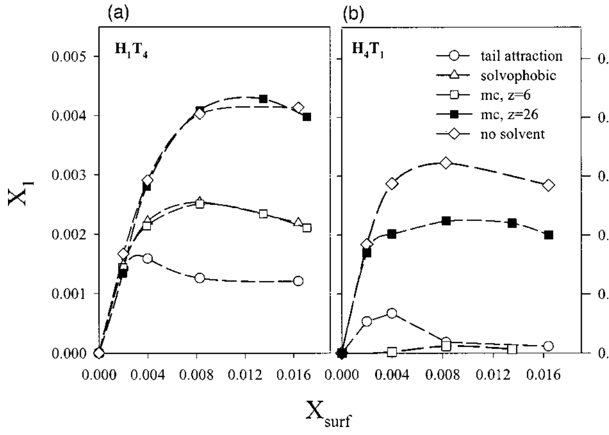

FIG. 2. Mole fraction of free surfactant molecules (X_1) as a function of the total surfactant mole fraction (X_{surf}) (a) h_1t_4 at $T^*=0.357$, (b) h_4t_1 at $T^*=0.06$.

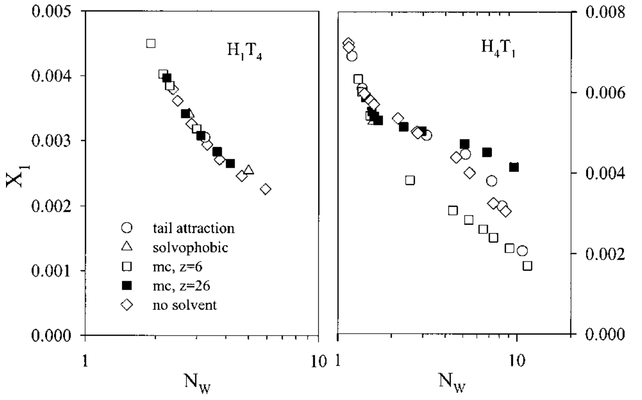

FIG. 3. The mole fraction of free surfactant (X_1) as a function of the weight-average micelle size (N_W) for composition $X_{\mathrm{surf}}=8\times10^{-3}$ at various T^*.

creasing for all T down to the phase separation temperature. The same trend is displayed by the h_4t_1 systems at high T, but upon cooling, the distribution becomes bimodal, indicating the formation of preferred-size micelles before the system phase separates at even lower T. We define the temperature range in which the micelle size distribution is monotonically decaying (or has a peak) as the weakly (strongly) aggregating regime. Systems with h_1t_4 surfactants do not exhibit a strongly aggregating regime, which is consistent with recent phase equilibrium calculations from lattice MC simulations for this system.[25] In the h_4t_1 solvophobic system with explicit solvent, the solvent undergoes a glass transition before the system reaches the strongly aggregating regime, precluding simulations for that regime.

The large discrepancy in the self-assembly behavior between the explicit and implicit solvent off-lattice models implies that solvent mediated interactions are important for both h_4t_1 and h_1t_4 amphiphile systems. Furthermore, differences in the extent of micellization between the two explicit solvent off-lattice models and between these models and the lattice models likely stem from compressibility effects (known to be relevant for polymer blends)[16] that lead to optimization of favorable interactions and minimization of unfavorable interactions on the subsegment length scale. For example, lattice versions of the tail attraction and solvophobic models can be shown to become inequivalent once the system is permitted to be compressible by having empty lattice sites. The importance of compressibility is further supported by our initial simulations of the pressure dependence of self-assembly in model amphiphile solutions. In particular, we find that the extent of micellization in the explicit solvent off-lattice systems depends strongly upon pressure (density); for example, a density increase of 10–15% increases the extent of micellization in the solvophobic h_1t_4 system to that found for the tail attraction system at the same temperature and composition.

Mapping of self-assembly behavior between models

Despite the difference in self-assembly behavior shown in Fig. 2 for the various models at the same thermodynamic conditions (X_{surf}, ρ and T^*), there are remarkable similarities between the models for the weakly aggregating regime. In particular, when the weight-average micelle size (N_w) is the same for a pair of systems simulated using two different models, then the micelle size distributions become identical, indicating that N_w is a good parametric variable for describing self-assembly of these model surfactant solutions in the weakly aggregating regime. Matching N_w for two models can be easily achieved by adjusting temperature. Figure 3 illustrates this correspondence between different models by showing X_1 as a function of N_w for all models at various T^* and for $X_{\mathrm{surf}}=8\times10^{-3}$. In all cases for the h_1t_4 systems and all cases for h_4t_1 systems in the weakly aggregating regime ($N_w<1.8$), plots of $X_1(N_w)$ for the different systems become universal with a single curve $X_1=X_1(N_w)$. Analogous behavior is observed for all compositions studied. This universality implies that the differences in self-assembly exhibited in Fig. 2 for the weakly aggregating regime can be removed by adjusting T^* to yield the same N_w in all models.

In contrast, in the strongly aggregating regime, this "mapping" of self-assembly behavior from one model onto another fails as clearly illustrated in Fig. 3 for the h_4t_1 system when $N_w>1.8$. Here, adjusting T^* to match N_w for the lattice and off-lattice models does not yield the same micelle size distributions. Even for the two lattice models ($z=6$ and $z=26$), the $X_1(N_w)$ curves are quite different. A direct comparison of the micelle size distributions with the same N_w for these two lattice systems reveals that the $z=26$ model tends to predict larger micelles than the model with $z=6$. On the other hand, the off-lattice explicit and implicit solvent tail attraction models yield similar $X_1(N_w)$ curves (Fig. 3) as well as similar micelle distributions at the same N_w. We conclude that (at least for this particular system) the explicit presence of the solvent molecules does not influence surfactant self-assembly except by "shifting" its location on the thermodynamic surface, even in the strongly aggregating regime. We believe that this behavior arises from the fact that the core and corona of the micelles in the h_4t_1 system are very compact due to low aggregation numbers, and therefore solvent molecules cannot penetrate inside the micelles to influence their structure. Figure 3 also illustrates that the

$X_1(N_w)$ curves from the two lattice models bound the results from off-lattice models. It may, therefore, be possible to find a lattice representation that matches the off-lattice model self-assembly behavior by adjusting the lattice coordination number, but this mapping is nontrivial and requires additional systematic studies.

CONCLUSIONS

Our comparison of incompressible lattice and off-lattice models for *h-t-s* amphiphile solutions reveals that compressibility and solvent excluded volume effects strongly influence the self-assembly behavior of the model systems, leading to widely varying degrees of self-assembly for the different models at the same thermodynamic conditions. However, in the weak aggregation regime for a given solution composition, nearly identical self-assembly behavior for the models is observed as a function of the average micelle size. For the strongly aggregating regime, this correspondence holds only for off-lattice models.

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