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1987

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William MacKnight, *University of Massachusetts Amherst*

Anna C. Balazs

F. E. Karasz



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The Aggregation of Reverse Micelles

A Computer Simulation

ANNA C. BALAZS,[†] FRANK E. KARASZ,*
AND WILLIAM J. MACKNIGHT

*Polymer Science and Engineering, University of Massachusetts,
Amherst, MA 01003*

Received January 15, 1987; Accepted June 1, 1987

ABSTRACT

We have developed a computer simulation to model the formation of reverse micelles in two dimensions. Several of the qualitative results obtained from these calculations agree with experimental observations. Specifically, we have shown that the chain length has a large influence in determining the size and shape of the aggregate. We predict the existence of a critical tail length: Chains below this value will form an extended lamella-like structure, whereas chains longer than this value will form clusters that appear ellipsoid or circular in cross-section. Finally, we obtained a scaling law that relates the aggregation number (N) to the length of the tail (L): $N \sim L^{-1.14}$. A physical model to account for the observed exponent will be developed in a future paper.

Index Entries: Reverse micelles; inverse micelles; micellization; surfactant aggregation; self-associating systems.

INTRODUCTION

In recent years, there has been an increasing interest in the aggregation of self-assembling systems (1,2). The formation of micelles is an example of such a process. Though there exists a voluminous amount of

*Author to whom all correspondence and reprint requests should be addressed.

[†]Present Address: Department of Materials Science and Engineering, 848 Benedum Hall, University of Pittsburgh, Pittsburgh, PA 15261

information on micelles (3), relatively less is known about reverse or inverse micelles. Because of their commercial viability as solubilizing agents (4) and catalysts (5), as well as the fact that they provide another model system that undergoes self-association, these clusters are now undergoing extensive investigation. Reverse micelles are formed from surfactant molecules in nonpolar solutions. They are so named for their structure, which is the "reverse" of micelles in aqueous solutions: The polar head groups of the surfactant molecule comprise the core of the aggregates, and the hydrophobic tails face the nonpolar solvent (6). A remarkable feature of these systems is the small size of the aggregates they form (7,8), which contrasts with the large micellar aggregates observed in aqueous solutions. Moreover, it is generally agreed that the concept of a critical micelle concentration is inappropriate when describing reverse micelles (9). Another feature of this system is its ability to take up water in the polar core or interior of the cluster (8).

Aside from these observations, few attempts have been made to explain the formation, stability, or association patterns of reverse micelles (8). One of the driving forces for micelle formation in nonaqueous systems is the attraction between the polar groups (10), either through a dipole-dipole interaction (9,11) or hydrogen bonding (8). In addition, there are dispersion forces present between the apolar hydrocarbon tails (6). Though the fundamental thermodynamic equations of self-association were developed by Hill in 1963 (12), they have as yet not been applied to aggregation of reverse micelles. However, there is experimental evidence to support a sequential self-association model for this process (6,8,11). In this scheme, the cluster grows from a monomer (a single chain) to an n -mer by adding one monomer at a time ($n - 1$) times. This growth process is limited by the diffusion of the reactive monomer to the surface of the growing cluster (6,8), and the system may be considered as an example of diffusion-limited aggregation. However, steric hindrance between the hydrocarbon tails limits the size of these aggregates (10). Thus, as the clusters get larger, further acceptance of monomers becomes too difficult, and the growth process stops (6,8). Recent experimental work finds a surprising monodispersity in aggregate size (13).

In order to clarify the role of the hydrocarbon moiety, we use a computer simulation to examine the influence of the length of the tail on the size and shape of reverse micelles. Although models and experimental evidence exist to correlate the role of chain length on micelle structure in aqueous solutions (14), few such systematic studies exist for reverse micelles (8,10). The advantage afforded by this computer simulation is that it yields both a qualitative and quantitative means of understanding the factors that influence the morphology of the cluster. First, the figures generated via this method allow us to actually visualize the growth and changes in the aggregate. Second, various features of the cluster are easily computed, such as the radius of gyration or the average motility of a hydrocarbon tail in the micelle. Third, "experiments" to systematically

alter the tail length are easily carried out, and, hence, we can examine how this variation affects the aggregation process. Finally, the procedure used here is similar to that traditionally used to study diffusion-limited aggregation (15). As is common in these types of calculations, we will search for scaling laws that characterize the reverse micelle.

THE MODEL

The simulation is started by placing a seed chain, of specified length but random configuration, at the center of a two-dimensional lattice. The chain is composed of N beads, the first of which is designated as the "head" and is represented as a dark circle in the following figures. The remainder of the chain forms the "tail." No lattice site is permitted to be doubly occupied, so all chains in the simulation can be said to obey the excluded volume criteria. The location of the first chain remains fixed. Another chain of equal length is introduced and allowed to execute a self-avoiding random walk. A new chain starts its random walk from a point on a large circumference, whose radius is equal to the sum of the radius of gyration of the present cluster plus the value of the chain length under consideration.

The random walk executed by the mobile chain is composed of two parts: translation and a "wiggling" motion. First, the entire chain is translated in one-of-four directions to be picked at random: up, down, to the left, or to the right. Second, a bead in this chain is randomly selected. The chain motion now attempted depends on the local conformation surrounding this bead: The allowed moves are different for an end bead, a bead colinear with its two nearest neighbors, or a bead forming a "crank-shaft" configuration. Detailed discussions of this point can be found elsewhere (16–18). The appropriate motion is attempted and is accepted if it meets the excluded volume criteria. We refer to this motion as "wiggling" the chain.

The walk continues until the head of the second chain occupies a site that is one lattice site or one diagonal site away from the head on the seed chain, i.e., the first or second nearest neighbor lattice site. Then, the head on chain number two is stopped and remains stuck at this lattice position. The remaining portion of the chain (the tail) is free to "wobble" about so long as it remains attached to the stationary head. When two heads have become paired in this manner, a third is introduced onto the lattice. At this point, a chain is picked at random (in this case, either chain 2 or 3). A check is made to determine whether the chain's head is stationary. If it is not (chain 3), the chain is first translated and then "wiggled." If chain 2 were to be picked, it is only "wiggled": A bead on the chain is selected at random, and an appropriate chain motion is attempted. A check is now made to see if the moves just executed have resulted in any two heads being located one lattice unit or one lattice di-

agonal apart. If not, a chain is again picked at random and the procedure above is repeated. If, on the other hand, a new head-head pairing is found, another chain is added to the lattice and, again, the procedure above is repeated. The simulation comes to a halt when a specified number of chains are incorporated into the cluster or the specified number of steps have been executed.

The simulation models the case in which the attraction between the polar head groups is sufficiently strong and the binding constant is significantly large that the degree of dissociation from the cluster is negligible. Moreover, it is assumed that there is no rearrangement of the head groups after they have come into contact with each other. The dispersive or repulsive force between the tails is included in this model by requiring that all chains obey the excluded volume criteria (evc). However, this force is taken to be sufficiently weak that the tails are allowed to "wiggle" about (subject to the evc) even after they are incorporated into the micelle. Finally, the simulation models the formation of reverse micelles in the absence of water molecules in the interior core.

RESULTS AND DISCUSSION

In order to investigate the influence of chain length on aggregation number and the morphology of the cluster, the length of the tail was systematically varied from 5 to 25 lattice spacings. The tremendous effect of chain length on the size and shape of the aggregate is clearly evident in Fig. 1. The clusters in each frame represent the state of growth after 15,000,000 time steps. For a chain length of five lattice units (frame a) a spatially extended structure emerges that locally resembles a bilayer or lamellar phase. For this case, other chains are not sterically hindered from joining the cluster, and running the simulation for a longer time would result in a more extensive network. On the other hand, chains of length ten and greater form small, tight clusters that have reached their maximum size: No further growth of these clusters took place when the program was run for an additional 1,000,000 time steps. Here, the tails sterically hinder a new chain from attaching to the aggregate. Clearly, there is a critical tail length: Below this value extended networks are formed, whereas above this value, small clusters are created.

The overall small aggregation numbers observed in these calculations agree favorably with experimentally observed values and are, in fact, characteristic of reverse micelles (7,8). Moreover, the decrease in micellar size with increasing chain length has also been experimentally observed (10,19). It has been postulated that a lamella structure might occur if the tail and head groups were of comparable size (8). The diagram in Fig. 1(a) would appear to agree with this prediction. For longer tail lengths, micelles that appear ellipsoidal in cross-section have also been reported (8). This shape coincides with that seen in frame 1(b). The

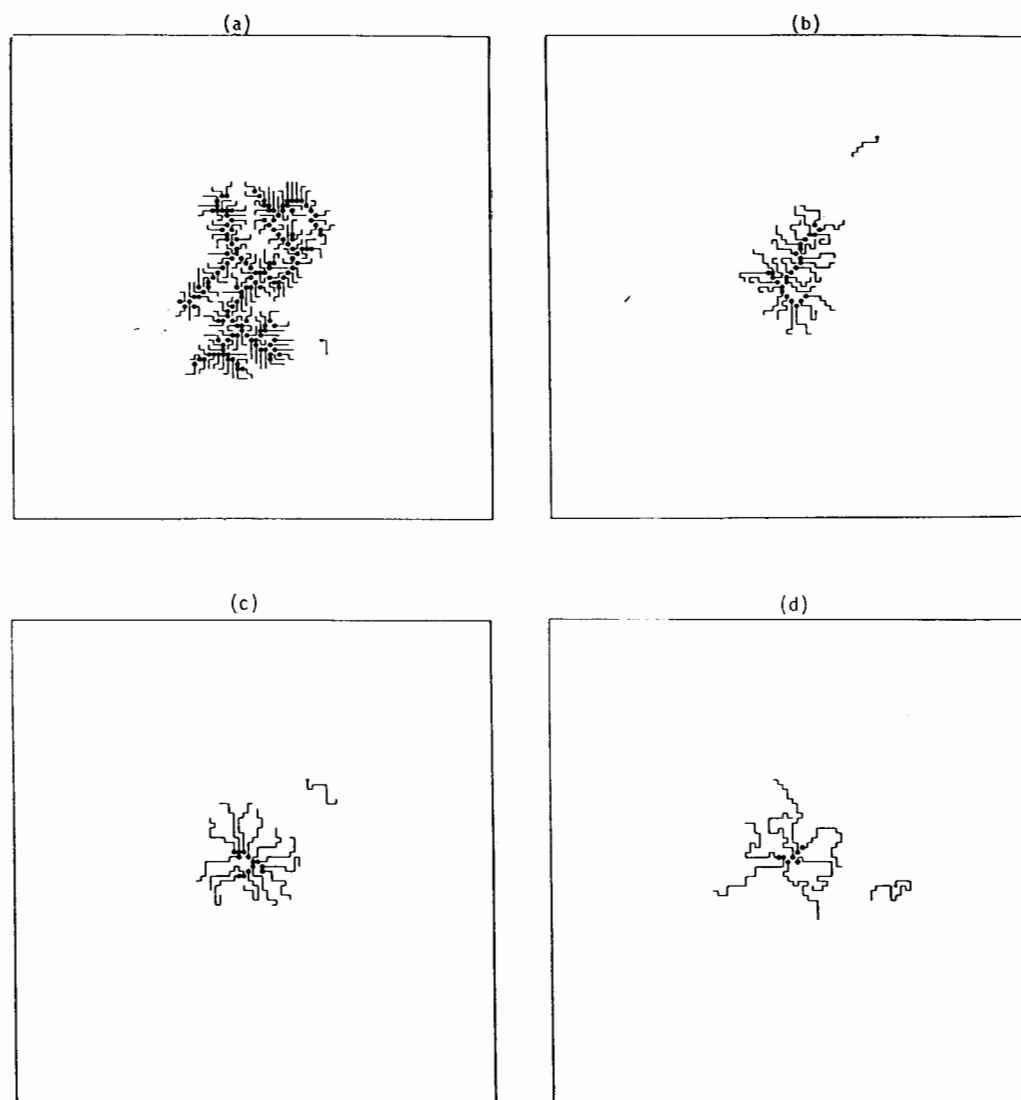


Fig. 1. The clusters in each frame represent the state of growth after 15,000,000 time steps. However, frame (a) represents a chain 5 lattice spaces in length, (b) 10 lattice spaces, (c) 15 spaces, and (d) corresponds to chains 20 lattice spaces long. The filled circle represents the head group, and the long, flexible chain represents the tail. The head groups that are incorporated into the cluster are drawn larger than those on free chains. In (a), there are 147 chains in the cluster, the cluster in (b) contains 25 chains, in (c), there are 13 chains in the aggregate, and in (d), there are only 7 chains forming the cluster.

figures in 1(c)–(d), would indicate that for tails significantly longer than the head group, micelles that appear more circular in cross-section are formed.

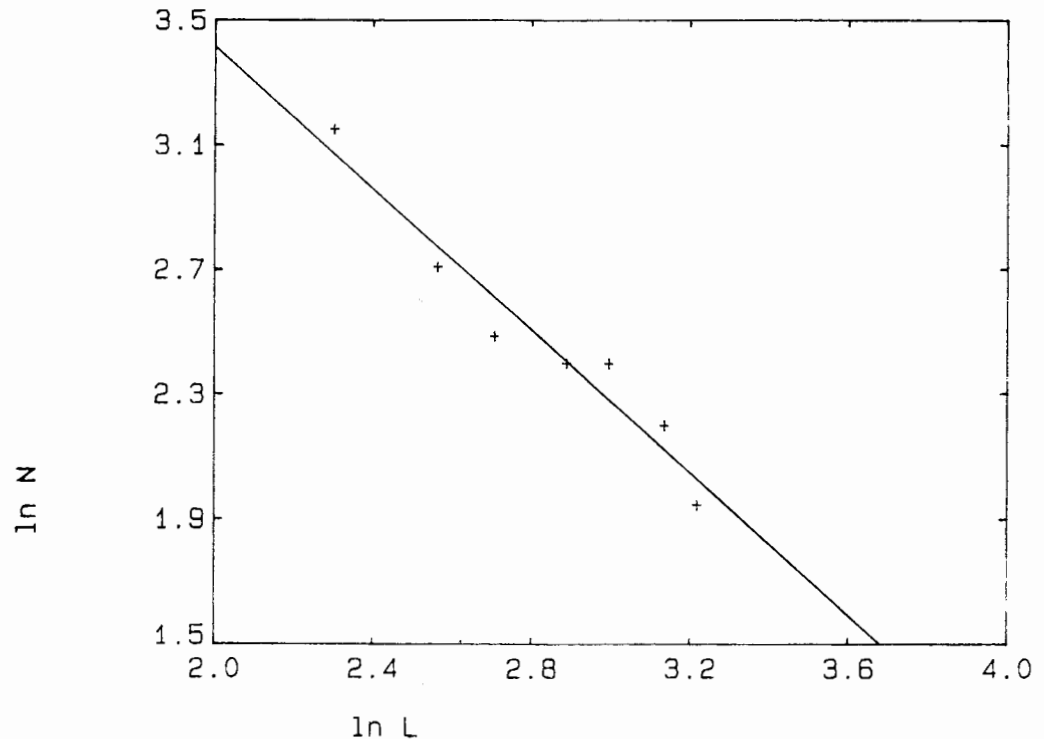


Fig. 2. The natural logarithm of N (the aggregation number) is plotted against \ln of L , where L is the length of the chain. The value of the slope is -1.137 ± 0.142 .

We attempted to quantify our results concerning the steric hindrance produced by long tails. Moreover, as noted in the introduction, the growth of these clusters is diffusion-limited. Thus, in analogy with the small particle diffusion-limited aggregates, we aimed at obtaining a scaling law that characterizes the evolution of the cluster. In this case, a scaling law that relates the aggregation number to the chain length is required. Figure 2 shows a plot of the natural logarithm of the aggregation number, N , (for $N > 10$) versus $\ln L$, where L is the chain length. The value of the slope is -1.137 ± 0.142 . Thus, we in fact find that N varies as $L^{-1.14}$. In a later paper, we will attempt to develop a physical model to account for this exponent.

ACKNOWLEDGMENTS

We are pleased to acknowledge support from AFOSR 86-0100. A.C.B. gratefully acknowledges assistance from Brian Pinette.

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