

Computer simulations of surfactant structures

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Computer simulations are continuing to enable significant progress to be made in research concerning the structure, dynamics and rheology of surfactant structures and how these parameters relate to the topics of surfactant self-assembly, micelles, amphiphilic monolayers, bilayers and oil solubilization. The best insight into self-assembly and oil solubilization has come from idealized models. For monolayers, quantitative agreement with experimental data has been achieved in predicting tilt transition, tilt angle and direction. A level of sophistication of simulations has been attained whereby perfect agreement with experiments is pursued on complex issues such as the ordering of the chain backbones in various monolayer phases. For bilayers, most relevant time scales may still be just outside the reach of standard molecular dynamics simulations; nevertheless, ingenious computational techniques that go beyond standard molecular dynamics and Monte Carlo simulations have enabled much faster progress than previously estimated.

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Abbreviations

CMC	critical micelle concentration
LB	Langmuir–Blodgett
MC	Monte Carlo
MD	molecular dynamics
SAM	self-assembled monolayers
SCF	self-consistent field

Introduction

In 1953, 40 years ago, the first molecular computer simulation was carried out at the Los Alamos National Laboratories in the USA. Molecular computer simulations provide a direct route from the microscopic to the macroscopic world, and can thus provide information that may be difficult to obtain from real experiments. One can divide molecular simulations into two categories: those on realistic systems, and those on model systems. The two types of simulation usually serve different purposes. If the objective is to obtain data of 'experimental nature' then simulations become especially important if these data are not accessible by experimentation. On the other hand, if the objective is to test a concept or theory, one tries to simplify the model as much as possible such that it retains only the essential aspects of the system, and the theory can be tested directly. This article covers both types of simulations.

In addition, computer simulations can be further classified according to whether or not quantum effects are taken into account. The scope of this article is limited to classical simulations. The two simulation techniques that have been used for investigating surfactant structures are molecular dynamics (MD) and the Monte Carlo (MC) technique. The MD method is based on the numerical solution of Newton's equations of motion for a set of atoms or molecules, that is, the sampling of equilibrium averages is tied to the natural time evolution of the interacting atoms. In the MC approach, configurations are generated using random numbers obeying rules that ensure that mean values taken over the sample correspond to the correct ensemble averages. In both methods, the input is an intermolecular potential and the results of a simulation consist of structural or thermodynamics properties (and also dynamic properties in the case of MD).

Self-assembly in solutions

It has been known for quite some time that surfactant molecules, which contain a hydrophobic chain and a hydrophilic headgroup, can form a variety of aggregates with properties different from those of the unassembled molecules. Indeed, spherical micelles, rod-like micelles, bilayers, reverse micelles and vesicles have all been observed in the laboratory. A detailed understanding of surfactant self-assembly is of importance for applications ranging from the transport of molecules through a cell membrane to the removal of stains in a washing machine.

Ideally, one would like to use a realistic description of surfactant and water molecules in order to get quantitative agreement with experimental data. Such simulations have rarely been attempted, however, because a realistic model simulation is limited to a few nanoseconds, whereas important phenomena of micellar solutions, such as surfactant exchange, micellar formation and break-up, can occur on a millisecond time scale. For n-octanol–water systems, this does not appear to be the case [1]. Using the united-atom approach for alcohol chains and the simple point charge model for water molecules, deBolt and Kollman [1] clearly witnessed the formation of n-octanol aggregates within a 2 ns simulation. The aggregates formed resemble reverse micelles in which the hydroxyl bonds of the alcohols are stabilized by a hydrogen bonded network formed by water molecules in the core. Cluster sizes in this system tend to vary from two to 80 molecules, and clusters of five octanols appear to be the most frequently encountered aggregates.

In the absence of experimental verification, it remains to be seen how useful these types of molecular simulations are at the present time, given the constraints on the

length of molecular simulations. It is not clear, considering the projected speed-up of computers (approximately three times faster each year), that MD simulations can lead to thermodynamically equilibrated systems for realistic surfactant molecules in water. Hopefully, 'smarter' MC techniques can be used to circumvent this limitation. Although it has not yet been attempted, the configurational-bias MC technique may be capable theoretically of predicting the size distribution of micelles given sufficiently large systems [2].

An alternative approach is to use a model oil-water-surfactant system. If such a model is sufficiently simple, micelle formation may be observed in a simulation. Such a simple model can be used to investigate systematically the effect of molecular structure on micellar shape, critical micelle concentration (CMC) and size distribution. The main features of this model are the preferred interactions of the hydrophilic surfactant headgroups with the solvent, and the preferred interactions of the hydrophobic chain groups with each other. The self-assembly of single chain surfactants with different headgroups into variously shaped micelles was a prominent outcome of earlier simulation studies that used this model [3]. The shapes of the micelles found in the simulations closely resembled those found both experimentally and predicted by geometrical principles.

More recently, MD simulations have been used to investigate the morphology and dynamics of a new class of surfactants that are of potential importance in several industrial applications. Simulation results show that new dimeric surfactants, which have been termed gemini, form structures and have dynamic properties that are drastically different from those of single chain surfactants [4]. At the same weight fraction, single chain surfactants form spherical micelles whereas gemini surfactants whose two headgroups are coupled by a short hydrophobic spacer form thread-like micelles. When the surfactant concentration is increased, the micellar shapes change from linear thread-like aggregates to branched tree-like micelles. This shape transition provides an explanation of the unexpected viscosity behavior of gemini surfactants. More importantly, branched micelles have recently been seen for the first time in cryo-transmission electron microscopy experiments [5*].

One can simplify the system even further by considering surfactant molecules to be lattice chains [6]. The lattice models are inspired by the work of Widom and co-workers (reviewed in [7]). The main focus of most of these studies has been the general properties of the oil-water-surfactant phase diagram, rather than the effects of changes in the molecular structures (for an excellent review of lattice models, see [7]). Simulations such as these are ideal for testing theories. For example, in a recent publication, Wijmans and Linse [8] attempted to compare MC results with self-consistent field (SCF) theory. CMCs,

aggregation numbers and micellar shapes were reported for a model of a non-ionic surfactant composed of a linear chain of 'A' particles connected with a linear chain of 'B' particles. Surprisingly, the SCF data deviated quite significantly from MC calculations. The authors attributed, the variation in results to the poor prediction of the chemical potential of monomeric surfactants in the bulk phase; this implies that SCF theory predicts a lower CMC than do MC simulations. The difference in aggregation number and micellar shape is attributable to the lack of micellar shape fluctuations in the SCF theory.

Micelles

Over the past 15 years, considerable experimental work, structural models, and computer simulations have examined micellar structure and dynamics in detail. Areas of investigations have included aggregate shape and fluctuations, chain conformations, penetration of water into the core, extent of counterion coupling with headgroups, and the behavior of solutes. Somewhat unexpectedly, simulations of micelles have not progressed as much as one would expect. Intuitively, one would assume that micelles are much easier to model than amphiphilic monolayers or bilayers; in reality, this is not the case. For example, because it is not possible to simulate the self-assembly of micelles in realistic models, one must specify the aggregate size of the simulated micelle *a priori*. In real systems, micelles have a wide distribution of sizes for which average measured properties can be different from the properties of one single micelle with a size equal to the most probable aggregate size. Therefore, the quantitative agreement with experimental data has not been realized, as hoped, even using the most refined interatomic models.

Two general approaches have been used to model micelles: full micelles, in which surfactant, counterions and water molecules are simulated; and constrained micelles, in which water and counterions are not modeled explicitly but instead an external spherical potential is introduced. This potential limits the movement of surfactants within a sphere. Both approaches suggest a structure that differs significantly from the original 'pincushion' image attributed to Hartley. The simulations have demonstrated micelles that are much more disordered and which undergo large shape fluctuations. Full and constrained micelle simulations yield very similar results with regard to the ordering of the C-C bonds, the average conformation of the alkyl tails, and the average locations of the various atoms in the alkyl chains.

Using the full micelle approach, Sprik and Shelley [9] conducted a simulation on a columnar aqueous sodium octanoate micelle in the high concentration hexagonal phase, including the electronic surfactant polarization. The emphasis of this work was placed on the significance of the induced polarization charge density and the dissociation of all counterions from the headgroups. The polarization charge density clearly showed that the micelle core was

not completely devoid of water molecules (unfortunately, this remarkable result was not discussed by the authors), in disagreement with earlier classical simulations without polarization effects (e.g. [10,11]).

Using the second approach, Karaborni and O'Connell [12] have recently simulated a constrained micelle. The variation in bond order parameters, which is indicative of the degree of preferential chain orientation normal or tangential to the aggregate radii, indicates that the bond orientations generally point in an outward direction whereas bonds closer to the center of mass are more randomly oriented. The agreement with experiment is good, showing consistency in both values and variation along the chains. Simulations showed a very fast relaxation time of the bond order of 0.5–1.0 ps, and an intermediate one of 1.8–8 ps both of which are somewhat faster than that derived from experimental NMR data (8–30 ps).

Monolayers

Monolayers are formed at the interface between two media by amphiphilic molecules. Of particular interest and experimental accessibility are monolayers of insoluble amphiphiles at the air/water interface (Langmuir monolayers), and solid/air interface [Langmuir–Blodgett (LB) and self-assembled monolayers (SAMs)] in addition to monolayers of soluble surfactants at the air/water or oil/water interface (adsorbed layers).

Langmuir monolayers

Developments in new experimental tools such as synchrotron X-ray reflection and diffraction, and Brewster angle microscopy have greatly contributed to the characterization of the different phases in Langmuir monolayers. Water-insoluble surfactants at the air/water interface form various structures, for example, long chain fatty acids form up to seven condensed phases. The phase behavior of Langmuir monolayers of long chain amphiphiles appears to be dominated by the tilting of molecules away from the normal to the interface, changes in tilt direction, and ordering of the alkyl backbone planes. Molecular simulations have been able to reproduce quantitatively most phases for fatty acids, including the magnitude of tilt angle, tilt direction and lateral pressure isotherms. The ordering of backbone planes and the role of defects in chain conformation are two issues that need to be resolved (for a review of monolayer simulations performed before 1993, see [13]).

In a recent article, Peters *et al.* [14] found a new phase in Langmuir monolayers of diglycerols. The new crystalline phase, which occurs at very high density, derives from a repositioning of the ester groups with respect to each other, and the dehydration of one ester group. As water molecules are not explicitly present in the simulations, more detailed simulation or experiments should be performed to confirm whether this new phase, which has not been seen experimentally, does exist *in vivo*.

A promising development in the characterization of phase coexistence in Langmuir monolayers is the use of Gibbs-Ensemble and configuration-bias MC [2]. This technique, which has been tested for pentadecanoic acid [15•], has the potential for predicting critical properties that may not yet be accessible experimentally.

Self-assembled monolayers

SAMs are prepared by spontaneous chemisorption of molecules from solution onto a solid substrate. From a technological viewpoint, SAMs are extremely important. Present and potential applications include adhesion, lubrication, wetting, solid surface functionalization, microelectronics and optical sensors. Mar and Klein [16•] have used MD simulations of alkanethiols on gold to calculate the effect of temperature on various properties of SAMs. Only the tilt angles are in broad agreement with experimental data, while the tilt direction, and the temperature-induced transition to a rotator phase remain areas of discussion. The ordering of the backbone planes, or alternatively the number of molecules per unit cell, appears to be in disagreement with experimental data [16•]. Whereas X-ray and He-diffraction data suggest the presence of four molecules per unit cell, simulations predict the presence of herringbone ordering, that is, two molecules per unit cell. Although for many properties the agreement with experimental data is very good, the authors conclude that further refining of the surface description is necessary to reach full agreement.

Adsorbed layers

Surfactant molecules that are soluble in water or oil form monolayers at the water/air or oil/air interface that are distinct from Langmuir monolayers. The phase behavior of soluble monolayers is less complex than that of Langmuir monolayers that exhibit a gas, a liquid phase, and sometimes a coexistence domain between the gas and liquid phases. Previous simulation attempts have concentrated on simplified models *in continuum* or on a lattice [17]. Historically, no simulations have been attempted on realistic models of soluble monolayers because of a lack of experimental data. Information on the structure of soluble monolayers has, however, recently become available through the use of neutron specular reflection. Consequently, Tarek *et al.* [18•] have performed MD simulations of tetradecyltrimethylammonium bromide monolayers at the air/water interface. In general, their simulation data show good agreement with previous simulations on monolayers of n-hexadecyltrimethylammonium chloride [19]. In addition, the relative average position of the various atoms is in good agreement with specular reflection data. The conformations and local densities of the alkyl chains are consistent with previous theories and simulations on polymeric brushes.

Bilayers

The review period encompasses a remarkable number of simulation studies of bilayers. A 1994 review of the

highlights has been presented by Pastor [20]. In general, a major concern about simulations of a bilayer in contact with water molecules is the level of sampling of the phase space. As most simulations are limited to 5ns or less, some doubt exists as to whether the bilayers are fully equilibrated. Simple checks such as the equivalence of the two sides of the bilayer are rarely performed before averaging over the entire bilayer. Despite these shortcomings, the contribution of molecular simulations to the understanding of the structure and transport of small molecules within a bilayer has grown in importance [21,22].

Marink [23•] has recently performed MD simulations on the transport of protons across a bilayer. The goal of these simulations was to check the validity of the transient hydrogen bonded chain model for the transport of protons across a bilayer. The author found that the free energy of formation of a water chain is in excess of 100 kJ/mol. In addition, the average lifetime of such a chain was less than 5 ps, which is not sufficient for a turning defect to occur, and thus only one proton can pass for every water chain. The simulation data (based on the transient hydrogen bonded chain model) differ by 12 orders of magnitude from the experimentally observed proton flux. The authors conclude that a different mechanism must be present for proton transport. It would be interesting to see the effect of amphiphile polarization [9] on the lifetime of water chains.

Oil solubilization

One of the most important properties of micelles is their capability to enhance the solubility of oily compounds which otherwise display very low solubility in water. This property is an important factor in detergency, improved oil recovery, micellar catalysis and separation. It is presently impossible for computer hardware to access phenomena that are slower than 10^{-8} s by using fully atomic models. Thus, it is imperative that simplified models are used to access phenomena such as micelle formation and oil solubilization which occur within the aforementioned time scale.

To gain a molecular insight into the solubilization mechanism, and therefore a better interpretation of the experimental data, MD simulations have been used to investigate a simple oil-water-surfactant model [24]. The simulation results indicate the presence of three oil solubilization mechanisms which operate simultaneously: collective desorption of surfactants and oil molecules from the oil droplet surface; dissolution of oil molecules in the solvent phase before being captured by micelles; and exchange of oil molecules between the oil droplet and the micelles during a soft collision. For short chain oil molecules the first mechanism is dominant whereas for longer chain oil molecules the second and third mechanisms tend to dominate.

Conclusions

It is encouraging to conclude that significant progress has been made in the area of molecular simulations of surfactant structures. Several examples exist where simulations have been a source of inspiration for experimental work. For some processes (oil solubilization or self-assembly), model systems have generated surprising results. In these systems, most of the molecular details are omitted. This loss in molecular detail is compensated for by a significant increase in time scales that can be studied in a simulation. Molecular simulations of amphiphilic monolayers have undoubtedly made the most progress towards quantitative agreement with experimentally measured properties, such as tilt angle, tilt direction and average positions of atoms. With other properties, such as chain conformation, reorientation and translational diffusion and herringbone ordering, the interpretation of data from various experimental techniques continues to attract discussion. The remaining major challenge is to extend simulations to investigate the domain morphologies of monolayers, for example, of chiral molecules.

In simulations of bilayers, the total simulation times and system sizes that one would like to use are still beyond reach of the current generation of computers. For these type of systems the development of novel simulation techniques based on MC techniques that do not suffer from the slow relaxation times in these systems is an important consideration. Molecular simulations are used in colloid and surface science in areas extending beyond the scope of this review. Within the past ten years, significant progress has been made in the areas of wetting, adhesion and friction, and thin film drainage. More importantly, a lot of exciting work remains to be done.

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