Slow Orientational Dynamics of Water Molecules at a Micellar Surface

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The dynamics of water molecules near an aqueous micellar interface is studied in an atomistic molecular dynamics simulation of cesium pentadecafluorooctanoate (CsPFO) in water. The dipolar orientational time correlation function (tcf) and the translational diffusion of the water molecules are investigated. Results show that both the reorientational and the translational motion of water molecules near the micelle are restricted. In particular, the orientational tcf exhibits a very slow component in the long time which is slower than its bulk value by 2 orders of magnitude. This slow decay seems to be related to the slow decay often observed in experiments. The origin of the slow decay is analyzed.

1. Introduction

In natural systems, water molecules are often confined within or at the surface of self-organized molecular assemblies.[1–6] Recently, several groups have studied the dynamics of such water molecules by using many different techniques, including dielectric relaxation,[3,4] solvation dynamics,[6,7] NMR relaxation dispersion (NMRD),[4] and intermolecular water–solute NOE studies.[5] These studies have led to the surprising discovery of the existence of a second, *very slow*, component in the dynamics of water in such restricted environments.[6] This second component decays in the hundreds to thousands of picoseconds. The first component remains ultrafast, similar to that in bulk water. The slow second component appears to be unique to water in complex systems and may play an important role in many chemical reactions such as electron transfer. The origin of this slow component is not clearly understood. It has been suggested that an equilibrium between bound and free water at the surface of the biomolecule or the self-organized assembly can give rise to this slow decay.[2–7]

To understand the origin of the slow decay, we have performed atomistic molecular dynamics (MD) simulations of a micelle in water. The simulations reveal that while the dipolar correlation function of the water molecules which are far from the surface decay on their usual fast time scale, the ones near the micelle show a *very slow decay*. It is further found that this slowing down can be attributed at least partly to an interesting transient hydrogen bonding arrangement where two neighboring, hydrogen-bonded water molecules are hydrogen bonded to oxygen atoms of two neighboring polar headgroups of the micelle. The lifetime of such an arrangement depends not only on the dynamics of surrounding water molecules (and hence the temperature), but also on the vibrational dynamics of the micellar atoms. We found a very slow decay at the very long time which can indeed be attributed to the existence of quasi-bound water molecules on the surface of the micelle.

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In the next section, we discuss the simulation details. In Section 3, we present the results and discuss their significance. Section 4 contains the concluding remarks.

2. Simulation Details

In this simulation, the surfactant is pentadecafluorooctanoate, with cesium being the counterion, commonly referred to as CsPFO. The CsPFO–H_2O system has been well studied experimentally[8,9] and is regarded as a typical binary system to exhibit micellization.[10] The amphiphiles are believed to form disk-shaped (oblate ellipsoid) micelles, stable over an extensive range of concentration and temperature.[8,9] As a function of concentration, the system exhibits isotropic, nematic, and lamellar phases. In the nematic phase, the mesogenic units are the individual micelles. The critical micelle concentration is around 0.02 weight fraction of CsPFO in water. At 350 K, the isotropic phase is stable up to a weight fraction of 0.62 and the average aggregation number is around 60.

The molecular dynamics simulation was carried out in the NVT ensemble for an aggregate of 62 CsPFO molecules in 10 562 water molecules, i.e., at a weight fraction of 0.15. The initial configuration of the micelle was built to mimic experimental data pertaining to its size and shape.[9] This configuration for the micelle with linear dimensions of 45, 45, 25 Å along its principal axes, was placed in a box of water with linear dimensions of 84, 84, 55 Å. Water molecules in hard contact with the micelle were removed by observation. The counterions were placed at random positions among the water molecules with the constraint that they were at least 7 Å away from the micellar headgroups. The potential for water molecules is the extended simple point charge (SPC/E) model,[11] the counterions carry a unit positive charge, which is compensated by a $+0.4e$ charge on the carbon of the octanoate headgroup and a $-0.7e$ charge on each of the oxygens of the headgroup.[12] The surfactant is modeled with explicit fluorine atoms and interactions between the fluorocarbon tails were obtained from the work of Sprik et al. on poly(tetrafluoroethylene).[13] Other details of the potential parameters along with results on the structure and dynamics of the micelle will be provided in a subsequent paper. The equations of motion were integrated with the reversible reference

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system propagator algorithm (RESPA) scheme[14] using the PINY-MD package[15] with an outer time step of 4 fs. Coulombic interactions were treated using the particle mesh Ewald method. The system was initially equilibrated under constant pressure conditions, to arrive at a "natural" simulation box size of linear dimensions 81.4, 81.4, and 52.6 Å. The system was further equilibrated for around 0.5 ns under constant volume conditions, and the micelle was found to be stable, with a total average pressure of around 100 atm. The analyses reported here were carried out from different sections of a subsequent 2.5 ns trajectory.

While dealing with discrete molecules or ions, it is often impossible to objectively define different interfacial layers precisely. This is because of the constant exchange of molecules between such layers. Our interest is to observe the slow dynamics of water near the interface. This is obviously the strongest for those water molecules whose residence times within any defined layer are the longest. Simulations prior to ours have also looked at the dynamics of water, but they chose to include all water molecules that were in an interfacial layer at an arbitrary reference time to be "part" of that layer. Thus, such analyses could have contributions from water molecules which got exchanged to neighboring layers. In our study, the distance-dependent orientational correlation function of water molecules was calculated by following only those molecules which stayed within a given distance from the micellar surface throughout that particular run. This seriously curtails the number of qualifying water molecules, particularly since our operating temperature of 350 K is above ambient conditions, when water is quite mobile. For example, on average, for a time period of 72 ps, only 18 water molecules are always present within 6 Å from any headgroup.

Thus, both the distance from the headgroup and the residence time define the location of a water molecule among the different layers. This effectively filters out molecules or ions which relax rapidly, so that we could focus on only those species with a slow component in their dipolar relaxation. We found that water molecules more than 20 Å away behave identically as those in the bulk.

The dipolar orientational time correlation function is defined as usual by the following relation:

$$C_\mu(t) = \frac{\langle \mu_i(t) \cdot \mu_i(0) \rangle}{\langle \mu_i(0) \cdot \mu_i(0) \rangle} \qquad (1)$$

where $\mu_i(t)$ is the dipole moment vector of ith water molecule at time t, and the angular brackets denote averaging over water molecules, as well as over initial configurations, (0).

The cutoff distances for classifying molecules and ions as *near* or *far* were chosen after studying their pair correlation functions with the headgroup carbon. Another consideration was to obtain a fair number of molecules or ions that can satisfy the rigorous criterion of residence within a layer throughout a particular run (lengths defined in captions to the figures). The first neighbor shell of a headgroup consists of cesium ions and water molecules. Since the counterions and water molecules are in constant exchange between different coordination shells of the headgroup, a distance cutoff based only on the position of the minimum in the first peak of the pair correlation function might yield only a few (or none) ions or molecules, because of the strict condition of allowing only those molecules which stay in that region throughout a particular time period. Thus, a definition of different interfacial layers based on positions of coordination shells, is not quite useful for water molecules which
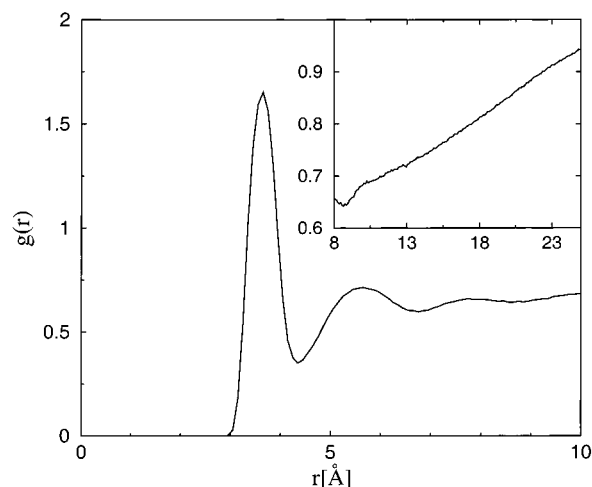

Figure 1. Pair correlation function $g(r)$ for headgroup carbon–water oxygen pair, where r is the radial distance. The normalization is over spherical shells, assuming a uniform and homogeneous water distribution, similar to work on homogeneous, bulk liquids. Since water cannot be present within the micelle, the pair correlation function will not be equal to 1, at distances typically considered to be long, say, 10 Å. Inset shows the long-range approach of $g(r)$ to the value of 1, as expected.

have considerable mobility in the direction perpendicular to the local micellar surface. Wherever possible, we have employed realistic cutoffs for interfacial layers based on the first coordination shell around the headgroup.

3. Results and Discussion

3.1. Microscopic Structure of Water at the Surface. As in any micellar system, water does penetrate up to a couple of CF_2 groups from the headgroup. The pair correlation function of water molecules around the headgroups is shown in Figure 1. The water molecules are preferentially found at 3.65 Å away from the headgroup carbon, with an average coordination number of 6.3. The water molecules are quite structured with respect to the surfactant headgroups, which would play a direct role in determining their dynamics.

The very fast dynamics in bulk water is due to the extended hydrogen bond (H-bond) network. For water molecules at the surface of an organized assembly, this network gets seriously disrupted. Water molecules near the interface, instead, can form hydrogen bonds with the oxygens of the headgroups. Steric considerations might determine the nature of such hydrogen bonds, i.e., whether a water molecule forms two hydrogen bonds with the same headgroup or only one.

Classical molecular dynamics simulations using empirical potentials reproduce the effect of hydrogen bonding primarily from ionic interactions, and from the fact that ions have a finite size. In the following discussion, we define a hydrogen bond purely from this perspective, i.e., using only a distance criterion. With this caveat, we present a snapshot of a part of the micellar configuration in Figure 2. We find that the two oxygens of each headgroup are connected to independent water molecules, i.e., a water molecule is hydrogen bonded to a surfactant molecule only by one hydrogen bond. Such a configuration will necessarily curtail the rotational motion of the water molecule. Its reorientation will then be determined by the configurational fluctuations involving two independent amphiphiles. Thus the dynamics of water molecules will be closely interlinked with that of the macromolecular assembly. It is also important to note that, on average, there are *three* hydrogen bonds per oxygen
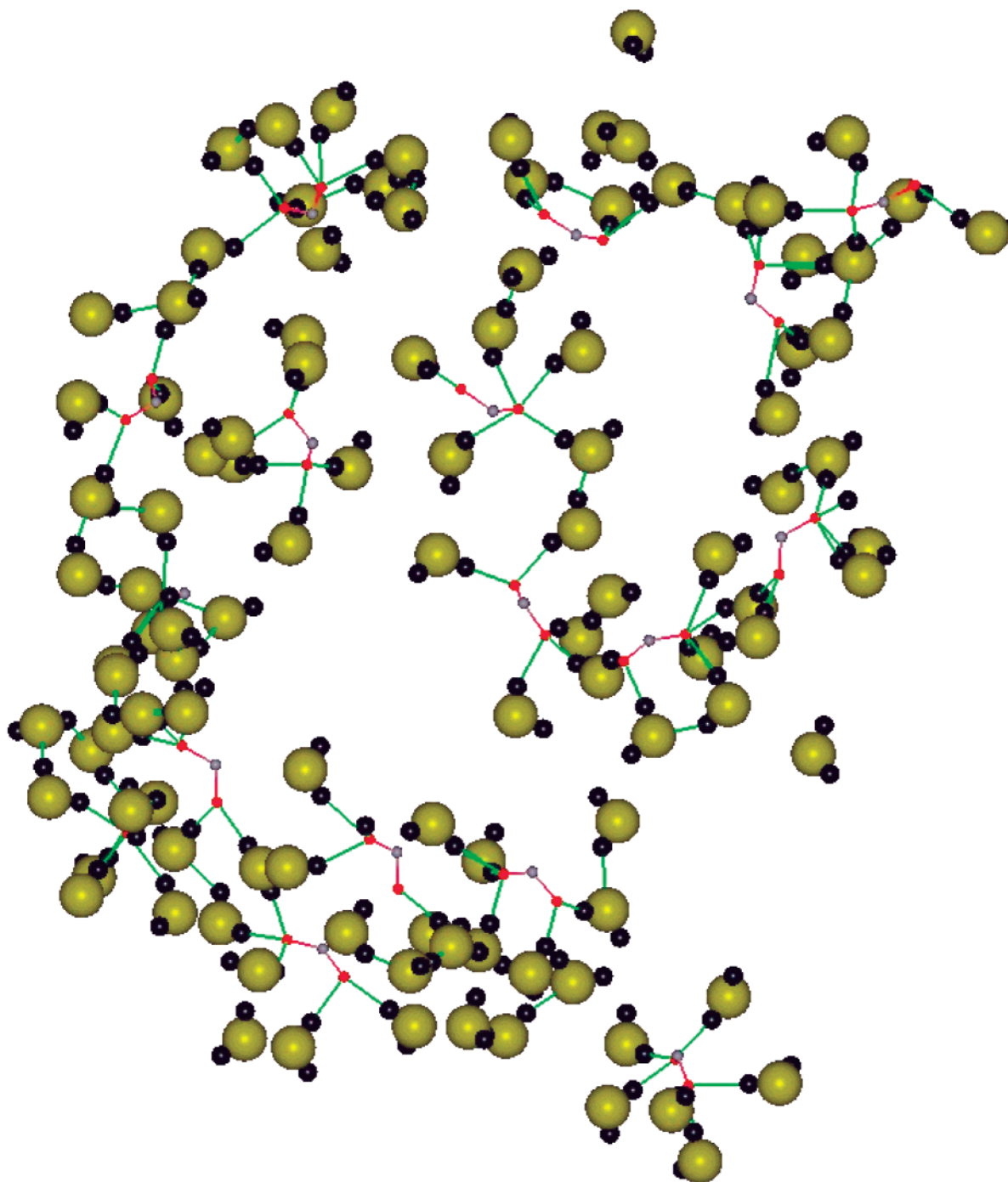
Figure 2. Snapshot of a part of the micelle configuration along with water. Water molecules in the first coordination shell of the headgroup oxygens are shown, i.e., these water molecules are within a distance of 4.3 Å away from the headgroup carbon. Greenish yellow: water's oxygen; black: water's hydrogen; grey: headgroup carbon; red: headgroup oxygen. The green colored bonds denote hydrogen bonding between the headgroup oxygen and water's hydrogen and are obtained using a distance criterion.

ion of the headgroup, unlike in, for example, liquid water, where they form only two hydrogen bonds. This is primarily because the headgroup oxygens are covalently coordinated only to the headgroup carbon. Such a 3-fold coordination has been reported in simulations of other macromolecular systems.[12] Another interesting observation is that while a water molecule is bonded to one headgroup by one hydrogen bond, the same water molecule is hydrogen-bonded to another water molecule which is hydrogen-bonded to a neigboring headgroup. This implies the existence of an orientational order on the surface water molecules imposed by the micellar assembly. This extended hydrogen bonding with micellar headgroups is probably one of

the reasons for the slowdown of orientational relaxation of surface water molecules (see later). It is still an open question whether the breaking of these hydrogen bonds gives rise to the observed time scale, as predicted in theoretical studies.

3.2. Translational Diffusion. We have calculated the mean square displacement of water molecules at different distances away from the micellar surface. These are shown in Figure 3. The translational diffusion of water molecules is definitely restricted, but the extent of immobility is not dramatic, even at distances as close as 6 Å from the surface. It might well be that only a certain fraction of the water molecules are "bound" to the micellar headgroups. At this temperature of 350 K, we have
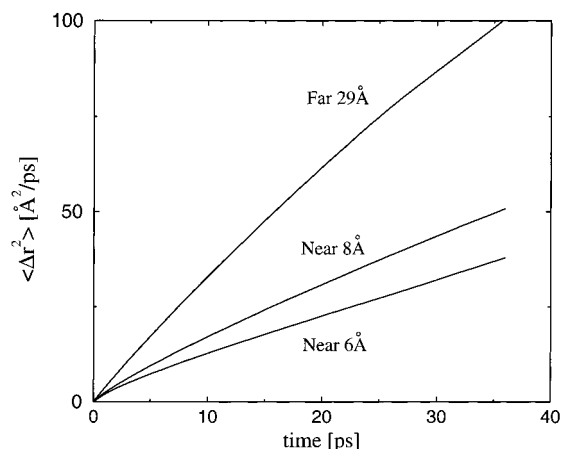
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Figure 3. Mean square displacement for water molecules near to and far away from the micellar headgroups. *Near* molecules are those which stay within the specified distance from the headgroups for a time period of 72 ps, and *far* are those which stay beyond the specified distance for the same time period.
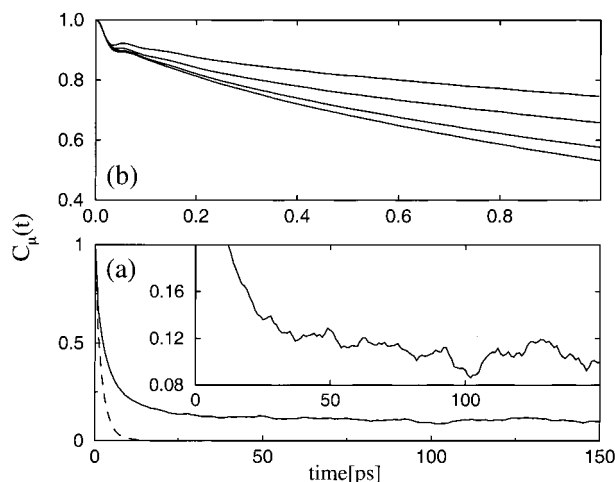

Figure 4. Dipolar time correlation function for water molecules. Only those molecules which are located within (called *Near*) or beyond (called *Far*) the specified distance for the period of time mentioned have been considered for this calculation. (a) Continuous line: molecules within 10 Å; dashed line: molecules beyond 25 Å. These were obtained by averaging over five independent trajectories each of length 330 ps. Inset shows, in expanded scale, the near-constancy of the time correlation function for water molecules within 10 Å from the micellar surface. (b) Short time decay of the same function for water molecules in various regions for trajectories of length 2.4 ps (from top to bottom: near 4.5 Å, near 6 Å, near 10 Å, far 28 Å).

found water molecules to stay within a 10 Å shell from the headgroup up to about 350 ps, and not any longer. This gives us an idea of the lifetime of bound water molecules.

3.3. Orientational Dynamics. Unlike translational diffusion, the reorientational motion of water molecules is severely affected near the micellar interface. Within linear response theory, the dipolar correlation function which is a measure of reorientational motion, is related to dielectric relaxation experiments. In this heterogeneous system, the total dielectric response will have contributions from the micelle, the solvent, and from cross correlations. In this article, we focus our attention on the contribution of the water molecules in specific regions around the micelle. In Figure 4a, we show the dipolar orientational correlation function ($C_\mu(t)$) against time for individual water molecules located both close to and far from the micellar surface. The decay of the dipolar correlation in the bulk shows the expected behavior—after a transient period, its decay is nearly exponential with a

time constant close to 3 ps (note that the temperature is 350 K). The situation for *near* water is completely different. Here a very slow decay emerges after about 20 ps. This decay has a time constant larger than 100 ps. The data for near water is for those molecules which stayed within 10 Å from the headgroup. Even with such a liberal cutoff distance, we could clearly see the presence of slow orientational dynamics. In the inset, we show the slow decay in an expanded scale. The orientational time correlation function nearly stays at a constant value of 0.04 for over 100 ps, indicating that these water molecules exhibit a restricted reorientational motion. This feature is accentuated as one approaches the interface. In Figure 4b, we show the decay of $C_\mu(t)$, on shorter time, at different distances from the surface of the micelle. The graphs show the dramatic slowing down of the decay as the micelle surface is approached.

What is the origin of the slow decay observed here? On the basis of our analysis of the simulation results, we believe that two mechanisms could be operative. First is the existence of extended hydrogen bonding of water with the headgroups of the micellar assembly. As the micelle is essentially immobile in the time scale of the motion of water molecules, the extensive hydrogen bonding with polar headgroups certainly slows down the dynamics. The second reason, operative in the very long time, is the presence of quasi-bound water molecules. The mechanism is similar to Lipari and Szabo's[16] explanation of NMR relaxation of a spin confined in a cone, except that in this case, the water molecules eventually escape. We found the decay of the last 4−5% is really slow and probably occurs with a time scale of several hundred picoseconds. Our analysis shows that only a few water molecules stay at the surface for such a long time.

4. Conclusions

The most important result of the present study is undoubtedly the appearance of the slow component in the dipolar orientational correlation function, with a relaxation time 2 orders of magnitude slower than that in the corresponding bulk solvent. This aspect seems to be in agreement with the experimental results on reverse micelles, even though our simulations have been performed on regular micelles. This indicates that the slowing down of the reorientational motion of water need not necessarily arise from its confinement within a spherical region, but could be a much general property of water present at interfaces.

The reorientational motion and diffusion of water molecules in different hydration shells was earlier examined in micelles of sodium octanoate using the molecular dynamics method by Watanabe and Klein.[12] In the time scales of a few picoseconds, they also observed slow reorientational and translational dynamics of water near the micelle.

Our calculations also show that the mean square displacement of the water molecules near the surface is much slower than those in the bulk. This indicates a transient, partial localization of the water molecules, which is also reflected in their orientational time correlation function (Figure 1). Our simulations point to the dominant role of the micelle as the reason for the slow dynamics. This feature merits further attention, and might require simulations of other micellar systems. Our simulations have been performed at 350 K, a temperature not quite relevant to biological systems. Micellar dynamics will get seriously restrained at ambient conditions, which will lead to a further slowing down of water reorientation.

Note Added in Proof. Details of our potential model can be found in refs 17 and 18.

References and Notes

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