# Dynamics of water molecules at the surface of an aqueous micelle: Atomistic molecular dynamics simulation study of a complex system

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**The dynamics of water molecules and ions near an aqueous micellar interface is a subject of intense current interest, as such a system serves as a prototype of more complex biological systems, in addition to being important in its own right. We study the dynamics by using an atomistic molecular dynamics simulation of a micelle of cesium pentadecafluorooctanoate (CsPFO) in water. This micellar system is stable over a range of temperature, allowing us to perform a detailed study of the microscopic dynamics of water at the surface of the micelle, at two different temperatures. The dipolar orientational correlation function of the water molecules and the polar solvation dynamics (SD) of cesium ions and tagged water molecules are calculated. Results show that the reorientational motion of water molecules near the micelle is restricted, and as a result exhibits a slow component which is slower than its bulk value by at least *two orders of magnitude*, in agreement with dielectric relaxation experiments. In addition, the SD of cesium ions is found to be slowed down significantly, again by more than two orders of magnitude compared to that in the bulk water. Through an analysis of partial solvation time correlation functions, we find that the cesium ions are primarily solvated by the polar headgroups, and their SD is thus intimately coupled to micellar dynamics. Both orientational dynamics and SD show strong temperature dependence.**

SELF-ORGANIZED molecular assemblies are often found in nature in an aqueous environment. In these systems, the water molecules which are confined within or at the surface of such assemblies have properties which are different from bulk water and these differences are often used in Nature to carry out specific physico-chemical functions[1–6]. Recently, several groups have studied the dynamics of such water molecules by using many different techniques, including dielectric relaxation (DR)[3,4], solvation dynamics (SD)[6–8], 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[9]. This second component decays in hundreds to thousands of a picosecond. 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 understood and is currently a subject of lively debate[2–7].

Experimental studies have shown that the relaxation of water near a micellar surface exhibits a similar slow component. SD in neutral (triton X-100, TX), cationic (cetyl trimethyl ammonium bromide, CTAB) and anionic (sodium dodecyl sulphate, SDS) micelle have been studied using C480 and 4-aminophthalimide (4-AP) as probes[6]. Spectroscopic studies indicate that the probes reside in the water (i.e. the Stern) layer near the micellar surface. The average solvation times for SDS, CTAB and TX are respectively 180, 470 and 1450 ps for C480, and 80, 270 and 720 ps for 4-AP (ref. 6). Thus, SD in the Stern layer of the micelle is *two to three orders of magnitude slower than that in the bulk water*. The ultrafast component of SD in reverse micelle was studied under varied conditions by Levinger and coworkers[10]. DR studies also show the existence of a very slow component. Recently, Ladanyi and coworkers have explored the role of constrained water in SD within reverse micelle[11]. Their interesting study has revealed many aspects of water dynamics in constrained environments. However, the origin of the slow component is not understood at present. In bulk systems, the orientational relaxation of the solvent molecules and the SD of the ion/dipole in question is well understood. This may not be the case in inhomogeneous systems where the underlying surface can play a very important role.

In order 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 water molecules that are far from the surface decay on their usual fast time scale, the ones near the micelle show a *very slow decay*. The SD of counterions that are present near the micellar surface, also shows a dramatic slowing down

compared to those present in bulk solvent. It is further found that this slowing down of the reorientation of water molecules can be attributed at least partly to an interesting transient hydrogen bonding arrangement where two neighbouring hydrogen-bonded water molecules are hydrogen bonded to oxygen atoms of two neighbouring 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 surfactant molecules. Our results thus indicate a possible role of the micellar aggregate in the experimentally observed long time decay of the solvation time correlation function. In addition, simulations reveal a rather strong temperature dependence of orientational dynamics of surface water.

It is important to realize that the water molecules are not permanently bound to the micellar surface and are rather transient to the surface. This aspect raises several interesting issues regarding the role of averaging in the observable properties. Thus, a single particle and collective properties behave differently, as the collective properties, like DR and SD of the system are sensitive to the fraction of (slow) water molecules at the surface.

In the next section, we discuss the simulation details. We then present the results and discuss their significance. The last section contains the concluding remarks.

## Simulation details

In this simulation, the surfactant is pentadecafluoro-octanoate, with cesium being the counterion, commonly referred to as CsPFO. The CsPFO–$H_2O$ system has been well-studied experimentally[12,13] and is regarded as a typical binary to exhibit micellization[14]. The amphiphiles are believed to form disc-shaped (oblate ellipsoid) micelles, stable over an extensive range of concentration and temperature. 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 MD 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[13]. 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[15], 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[16]. The surfactant is modelled with explicit fluorine atoms and interactions between the fluorocarbon tails were obtained from the work of Sprik et al.[17] on polytetrafluoroethylene. Other details of the potential parameters are provided in ref. 18. The equations of motion were integrated with the reversible reference system propagator algorithm (RESPA) scheme[19] using the PINY-MD package[20] with an outer time-step of 4 fs. The bond stretch and bend interactions within molecules were integrated with a time-step of 0.5 fs, while the torsional degrees of freedom were handled at 1 fs interval. The non-bonded interactions were split into two ranges, and the short-range interactions were integrated at 2 fs interval. 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 equilibrated for around 0.5 ns and the micelle was found to be stable, with a total pressure of around 100 atmospheres. The analyses reported here were carried out from different sections of a subsequent 2.3 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 near a micellar interface, 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 neighbouring 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 one of our operating temperatures of 350 K is above ambient conditions, when water is quite mobile. For example, at 350 K, for a time period of 72 ps, only 18 water molecules are present within 6 Å from the headgroup, and no water molecule stays within a distance of 10 Å from any headgroup, continuously, for more than 300 ps.

Thus, both the distance from the headgroup as well as the residence time define the location of a water molecule amongst the different layers. This effectively filters out molecules or ions which relax fast, so that we could focus on only those species with a slow component in their

dipolar or solvation relaxation. In general, we found that water molecules more than 20 Å away from the micellar surface behave identically as those in the bulk.

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

$$C_{\mathbf{\hat{\mu}},i} = \frac{\langle \mathbf{\hat{\mu}}_i(t) \cdot \mathbf{\hat{\mu}}_i(0) \rangle}{\langle \mathbf{\hat{\mu}}_i(0) \cdot \mathbf{\hat{\mu}}_i(0) \rangle}, \tag{1}$$

where $\mu_i(t)$ is the dipole moment vector of the $i$th water molecule at time $t$.

The SD is monitored by the decay of solvation time correlation function $C_s(t)$ which is defined as[2],

$$C_s(t) = \frac{\langle \boldsymbol{dE}(t)\boldsymbol{dE}(0) \rangle}{\langle \boldsymbol{dE}(0)\boldsymbol{dE}(0) \rangle}, \tag{2}$$

where $\boldsymbol{dE}(t)$ denotes the fluctuation in the polar part of the potential energy of the tagged cesium ion at time $t$, and the angular bracket is an equilibrium average over different reference zero times, and over cesium ions or water molecules.

$C_s(t)$ was calculated by considering only the polar part of interaction energy, both of a tagged water molecule and of a tagged cesium ion, with the rest of the system. Typically, the coordinates of all the atoms from a MD run were stored at periodic intervals from which the correlation functions were calculated. In order to study both the fast (tens of femtoseconds) and the slow (tens or hundreds of picoseconds) dynamics, we had to store the coordinates at different time resolutions, varying from 4 fs to 1 ps, from different MD runs. For the calculation of $C_s(t)$, the polar energy was calculated using a real space molecular interaction cut-off of 23 Å, with no Ewald sum. Note that our MD simulations were performed with converged Coulomb energies, using the Ewald summation method, and that we used a simple real-space cut-off during data analysis only. In the absence of an Ewald method, the total Coulomb energy of a typical polar system such as water, is believed to converge reasonably only at interaction cut-off distances of about 30 Å. Since the box length in the $z$-direction of our simulation is only 52 Å, we could not extend the inter-action cut-off beyond 26 Å. Hence, the single-particle interaction energies obtained from the analysis of our simulations, may not necessarily be converged. By systematically increasing the cut-off distance from 12 to 23 Å, we have observed that the quantity of interest to us, i.e. $C_s(t)$ remained relatively unchanged. This procedure has helped us to gain confidence in our results.

It is also pertinent to note that the use of an atomic interaction cut-off (i.e. one that is based on atom positions, and not on molecular centre of mass coordinates), leads to a residual charge on the interaction sphere, while in the molecular cut-off method, the interaction sphere is neutral. We have observed that use of the former leads to spurious results which show no slow component in the

solvation time correlation function. We believe that this subtle, but potent error is specific to solvents containing small molecules which have an ultrafast libration component, such as water.

The solvation energy of a tagged cesium ion consists of contributions from cesium ions, the water molecules and the polar headgroups of the surfactant. Thus, the total solvation time correlation function can have contributions from six distinct partial time correlation functions (three pure and three cross-correlations).

The cut-off 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 neighbour 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 cut-off based only on the position of the minimum in the first peak of the pair correlation function might yield only a few (or no) 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 have considerable mobility in the direction perpendicular to the local micellar surface. Wherever possible, we have employed realistic cut-offs for interfacial layers based on the first coordination shell around the headgroup.

We would like to add a comment here regarding the use of solute probe molecules to 'measure' the solvation time correlation function. It would have been ideal to introduce real probe molecules, such as a coumarin dye to study their SD. One could then make a direct comparison to experiments on SD of dipoles. However, such a simulation will have the following difficulties. As only one or two such probe molecules can be introduced in the system (so as to be in the dilute regime of probe concentration), our results will suffer seriously from poor statistics. In real experiments, one has the advantage of many micelles, each with one or two coumarin dyes close to them. We thus use water molecules themselves as a dipolar solute probe. The limitation of using water as a dipolar solute is that it itself is highly mobile. While this self-motion is expected to make the solvation somewhat faster, one could still get a measure of the dipolar SD which is much faster than the self-motion. The case for SD of ions is not so difficult. We could profitably use the existing counterions themselves for this purpose. Cesium too, is reasonably large and massive, so that its translational motion is not quite high. Unlike dipolar solvation, there have been no experiments to study the SD of ions in micellar solutions. Our simulations provide the

first results on ion solvation that exhibits a slow component for ions near the micelle. Note that while SD of a small dipolar solute is expected to be somewhat slower than that of a small ion (especially in the long time[21]) the difference is not expected to be nearly as significant as the difference observed experimentally between the bulk water and micellar surface.

## Results and discussion

We are interested in understanding the dynamics of water molecules and of ions near complex interfaces. The micelle–water interface, while being rich in terms of the interactions involved, is simple enough to probe. In a variety of aspects, it can be a prototype to study complex biological systems. In Figure 1, we provide a snapshot of the micelle at 350 K to illustrate the complexity of the structure and to show that the simulated micellar aggregate is indeed stable.

### Translational diffusion and reorientational dynamics of water

As in any micellar system, water does penetrate up to a couple of $CF_2$ groups from the headgroup. The water

molecules are preferentially found at 3.7 Å away from the headgroup carbon, with an average coordination number of 6.5. We have calculated the mean square displacement of water molecules at different distances away from the micellar surface. These are shown in Figure 2. 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 is 'bound' to the micellar headgroups. At a temperature of 350 K, we have found water molecules to stay within a 10 Å shell from the headgroup up to about 300 ps, and not any longer. This gives us an idea of the lifetime of bound water molecules.

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, determines the response in DR experiments. Figure 3 shows the dipolar orientational correlation function ($C_m(t)$) 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 behaviour – after a transient period, its decay is nearly exponential with a time constant close to 3 ps
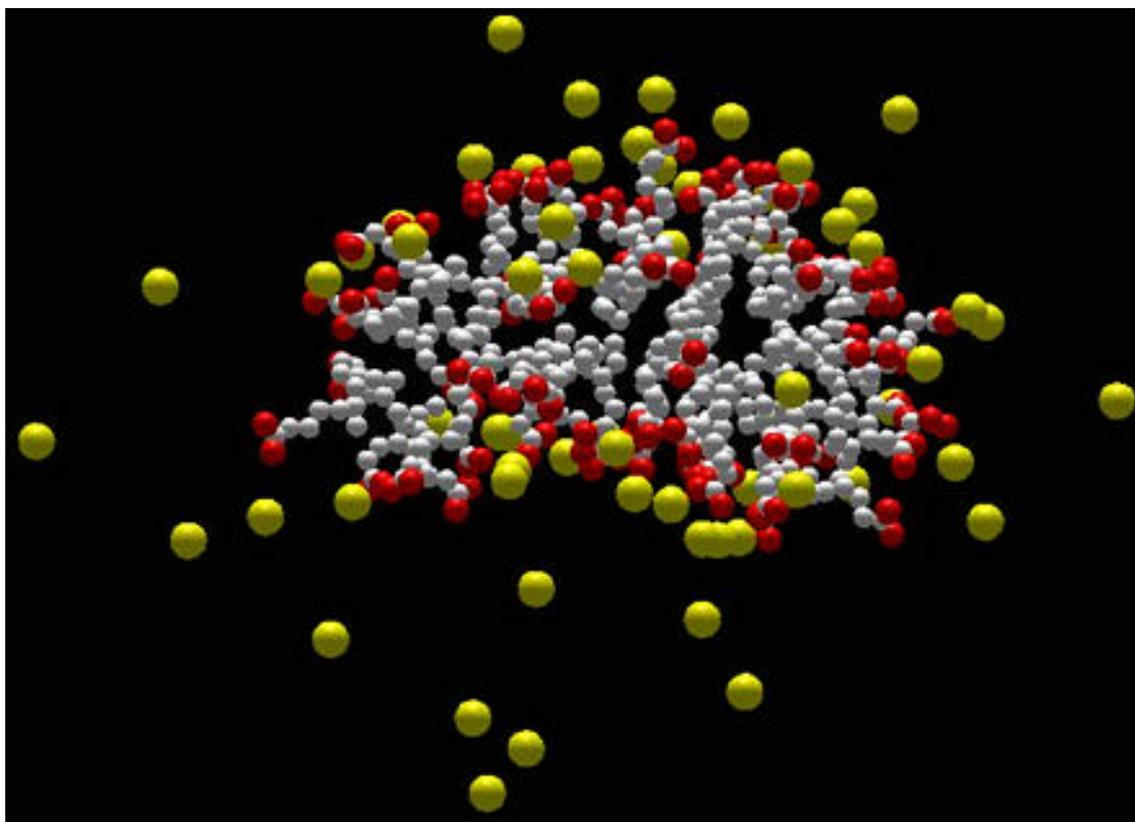


**Figure 1.** Snapshot of the micelle evolved after 3 ns from the initial configuration at 350 K. Red spheres denote the oxygens in the carboxylate headgroup, while white ones are carbon atoms along the perfluoroctonate chain. Yellow spheres are cesium ions and water molecules surrounding the micelle are not shown for clarity. Distance between headgroups in the core of the micelle along the vertical direction (bilayer) is around 24 Å.

(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. Data for near water are for those molecules which stayed within 10 Å from the headgroup. Even with such a liberal cut-off distance, we
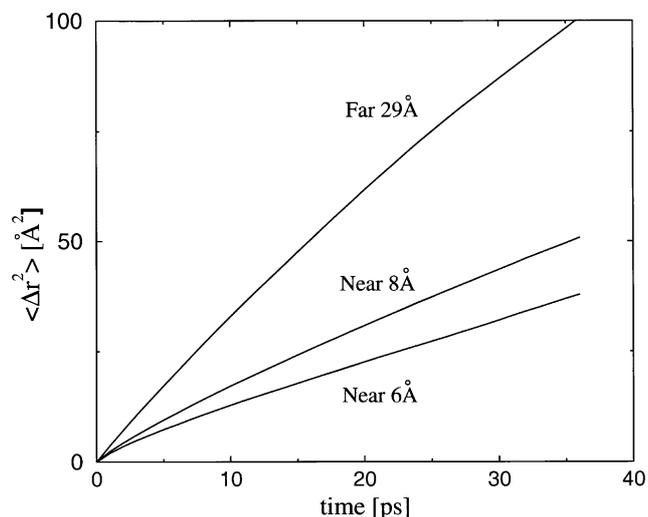


**Figure 2.** Mean square displacement for water molecules near and far away from the micellar headgroups at 350 K. *Near* molecules are those which stay within the specified distance from the headgroups for a time period of 72 ps, and *far* are those which stay beyond the specified distance for the same time period.
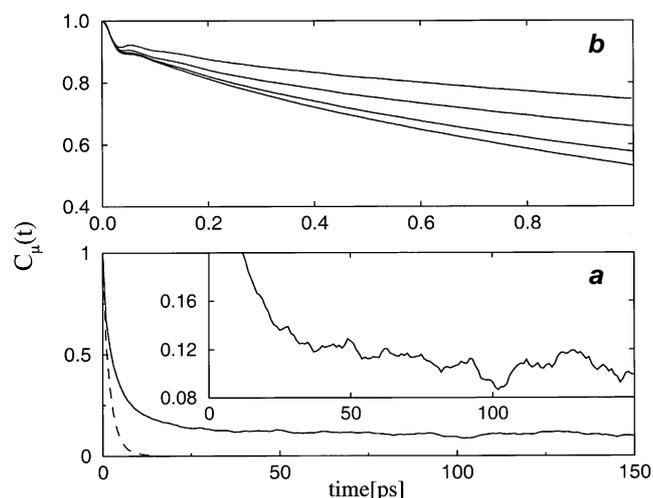


**Figure 3.** Dipolar time correlation function for water molecules at 350 K. Only those molecules which are located within (*near*) or beyond (*far*) the specified distance for the period of time mentioned have been considered for this calculation. *a*, Continuous line, molecules within 10 Å; dashed line, molecules beyond 25 Å. These were obtained by averaging over five independent trajectories each of length 330 ps. (Inset) Near-constancy of the time correlation function for water molecules within 10 Å from the micellar surface in expanded scale; *b*, Short time decay of the same function for water molecules in various regions for trajectories of length 2.4 ps (Top to bottom), Near 4.5 Å, Near 6 Å, Near 10 Å, Far 28 Å.

could clearly see the presence of slow orientational dynamics. This feature is accentuated as one approaches the interface. In Figure 3 *b*, we also show the decay of $C_m(t)$ 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.

Figure 4 shows the dipolar time correlation function at a lower temperature, of 300 K. Here the effect of the heterogeneous surface on the orientational dynamics is rather dramatic. Now, almost 40% of the decay falls under the slow region. This graph is perhaps the first demonstration of such a dramatic slowing down of orientational dynamics near a surface which interacts strongly with the water molecules. From Figures 3 and 4, it can be observed that $C_m(t)$ for water molecules near the micellar interface does not decay to zero, as opposed to its decay to zero for water molecules in bulk. Also, note that the function exhibits a nearly constant value at long times, spanning over 100 to 200 ps. The decay to zero of this function for bulk water is a consequence of the water dipole being able to explore all possible orientations in space. For water molecules near an interface, this exploration is restricted to a cone, due to the fact that they are hydrogen-bonded to the micellar headgroups, and that micellar dynamics is much slower. Thus the long time value of this function is a direct indicator of the extent of this restriction, with larger values signifying a more restricted environment for molecular reorientation. It is now natural to ask if the reorientation of water is hindered or slowed down within this cone. This information can be obtained by studying the time correlation function of the fluctuation in dipole moment, rather than the dipole moment itself. This function is defined as,
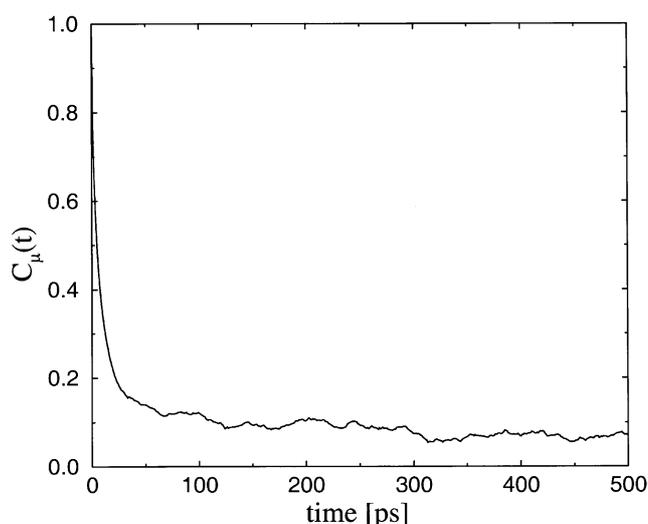


**Figure 4.** Dipolar time correlation function for water molecules that stay within 10 Å from the micellar surface throughout a time period of 1.1 ns at 300 K.

$$C'_{\mu,i}(t) = \frac{\langle d\mu_i(t) \cdot d\mu_i(0) \rangle}{\langle d\mu_i(0) \cdot d\mu_i(0) \rangle},$$   (3)

where $d\mu_i(t) = \mu_i(t) - \langle \mu_i(t') \rangle$ is the fluctuation in the dipole moment, and the average in the second term is taken over all times, $t'$. This quantity is plotted for water molecules near the micellar surface at 350 K and at 300 K in Figure 5. The reorientation of water molecules near the interface is not only restricted to a cone, but the motion within this cone is also considerably slowed down.

### Solvation dynamics

For SD of dipoles in pure water, experimental studies find a dominant sub-50 fs Gaussian component and a slow biexponential decay with time constants 126 fs and 880 fs, respectively[22]. It is believed that the initial ultrafast response comes from the intermolecular O...O vibrational mode of water, while the slowest one from the reorientational dynamics of water[23]. As the latter is most affected by the presence of the micellar surface, we expect the slower component of SD to be really affected. In the absence of a probe dipole, we have looked at the SD of a tagged water molecule. The results are shown in Figure 6. The SD of a water molecule shows signatures of slow dynamics near a micellar interface, but it is not as dramatic as is observed for a dye molecule in experiments. This could primarily be due to the presence of the fast librational mode of water, and could also be due to the fact that a water molecule is much more mobile than a typically large dye molecule. Thus in this case, the
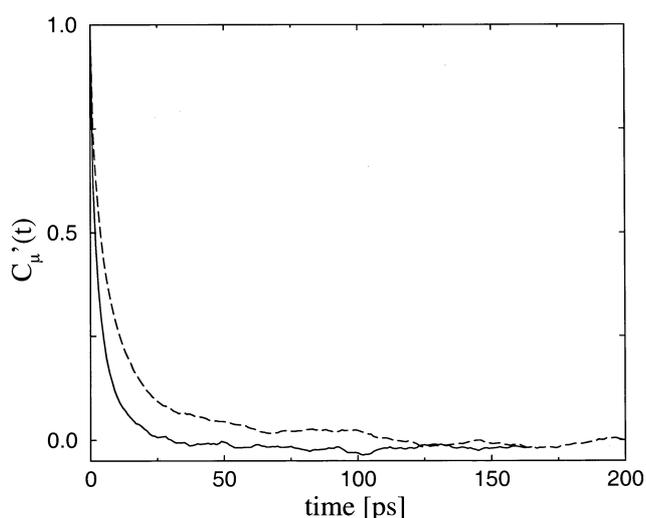
solvation decay is not a good indicator of the relaxation happening in the solvent due to the 'creation' of the tagged water molecule, but rather is a consequence of the fast mobility in orientational and translational space of the probe.

We now turn our attention to the SD of cesium ions, which are a lot heavier than a water molecule, and thus present themselves as a natural probe to study the solvent relaxation. Cesium ions are present predominantly near the micelle–water interface. The pair correlation function between the headgroup carbon and cesium is shown in Figure 7. The first coordination shell is well defined with
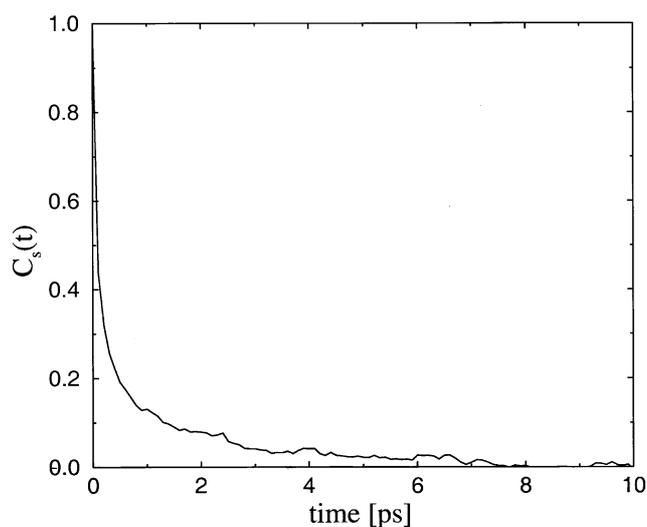


**Figure 6.** Total correlation function of $E_{\text{water}}$ for water molecules within 6 Å from the headgroup carbon for a trajectory of length 71 ps at 350 K.



**Figure 5.** Time correlation function of fluctuations in water dipole for water molecules near the micelle surface at 350 K (continuous line) and at 300 K (dashed line), corresponding to the distance and time criteria specified in Figures 3 and 4.
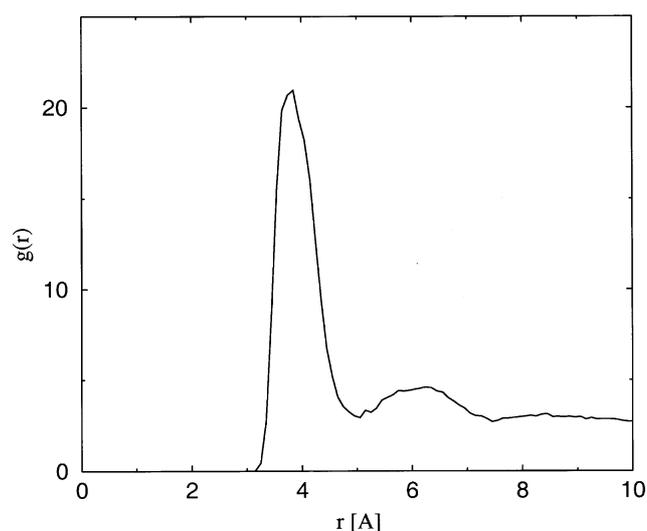


**Figure 7.** Pair correlation function for headgroup carbon–cesium pairs at 350 K. The function does not attain a value of one at large distances, as nearly all the cesium ions 'condense' onto the micellar surface to form the Stern layer.

a peak at 3.8 Å, with an average coordination of 0.67. Thus a headgroup carbon is surrounded by six water molecules and about 0.67 cesium ions in its first coordination shell.

There is, however, an important distinction to be made in terms of residence times between water molecules and cesium ions – the latter have significantly longer residence times near the micellar interface than the former. The cesium ions nearly 'condense' on top of the micelle, to presumably form the Stern layer. This gives us a much wider time window to study their long time dynamics, which was not possible in the case of water molecules, due to their relatively rapid exchange between interfacial layers.

Figure 8 shows the decay of the solvation time correlation function of a cesium ion near the micellar surface. As remarked earlier, the dynamics is really fascinating. We plot the solvation time correlation function for cesium ions within 10 Å from the headgroups with residence time 660 ps. In this case, we notice a strong slow component to the relaxation of the solvation energy, in good agreement with experimental data. In addition, there is a clear trend of ions with longer residence times exhibiting a relatively slower SD, signalling the important role of the interaction with the micelle. We need to compare this result against the SD of a cesium ion in bulk water. Unfortunately, not many cesium ions are present far away from the micelle for us to study this dynamics within the present simulation. We have thus performed MD simulations of one cesium ion in a bath of 5712 water molecules within a periodic box of linear dimensions, 63 Å, 63 Å, 44 Å, at a temperature of 300 K.
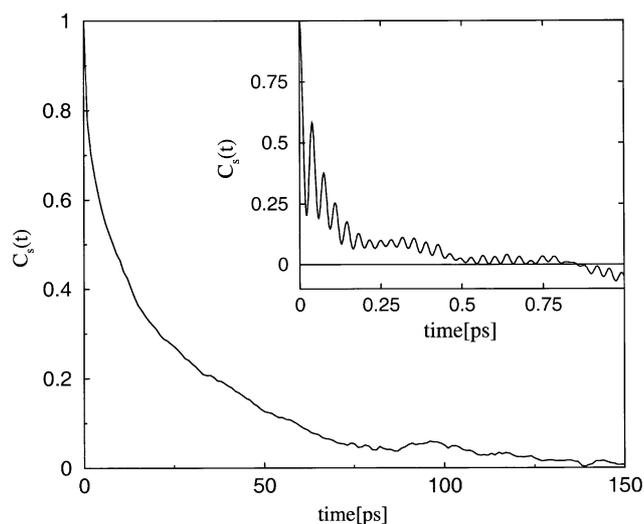
Figure 8 shows the solvation time correlation function for this cesium ion in pure bulk water (inset). In agreement with earlier non-equilibrium simulations of Maroncelli et al.[22,24], and Skaf and Ladanyi[25], the solvation relaxation decays within 2 to 3 ps at 300 K. A comparison of the data against solvation data for cesium ions near the micelle tells us that the long time part of the SD is slowed down by at least two orders of magnitude near the interface.

An analysis of the partial solvation time correlation functions (Figure 9) for the micellar system shows that the contribution from the polar interaction of the cesium ion with the micelle headgroups is the most dominant. This partial time correlation function also exhibits a very slow component which is the leading cause for the slow decay of the total solvation energy time correlation function. In contrast to this partial time correlation function, the contribution from the interaction with water molecules is much less dominant. In effect, it appears that the slow part of the polar solvation of the cesium ions may have more to do with the micellar dynamics than with the solvent (i.e. water). If this is indeed true, then the slow solvation and slow orientational relaxation at the surface are indeed probes of interaction with the micelle. This is a rather interesting result that has emerged from this study, which needs to be confirmed from further simulations.
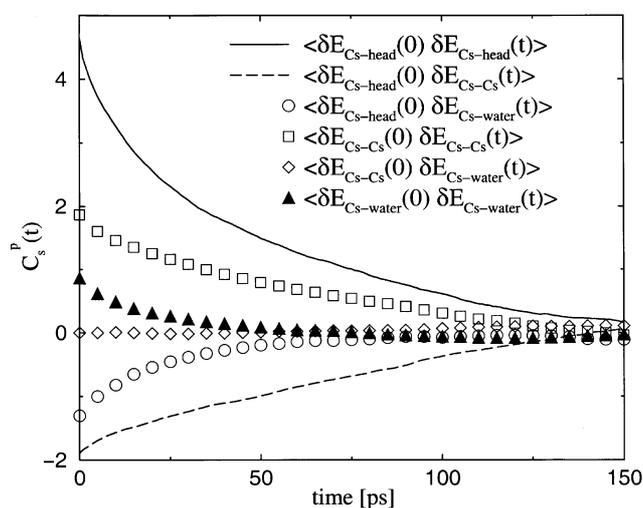


**Figure 8.** Decay of the solvation time correlation function (tcf), $C_s(t)$ of a cesium ion near the micellar surface at 350 K. Here the solvation tcf is shown for only those cesium ions which stay within 10 Å from any headgroup during the whole of 660 ps. For comparison, the solvation time correlation function of a cesium ion in pure bulk water at 300 K is shown (inset).



**Figure 9.** Partial solvation time correlation functions $C_s^p(t)$ for those cesium ions which remained within 10 Å from any headgroup carbon throughout a trajectory of length 660 ps. These are 'normalized' by the $t = 0$ value of the *total* time correlation function, $\langle dE_{Cs}(0) dE_{Cs}(0) \rangle$, and hence will not start from a value of one at $t = 0$. All the six contributions are shown. This analysis shows that the contribution from the polar interaction of the cesium ion with the micelle headgroups is the most dominant. This partial tcf also exhibits a very slow component which is the leading cause of the slow decay of the total solvation energy time correlation function. Time resolution for all tcfs is 1 ps. For tcfs plotted with symbols, data points every 5 ps are shown for clarity.

## Hydrogen bonding

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, the usual hydrogen-bonded network between water molecules 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 H-bonds with the same headgroup or only one. Not much is known about the structure and hydrogen bonding of water molecules at the micellar surface.

Classical MD 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 10. 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 configuration 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 ion of the headgroup, unlike in say, 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 three-fold coordination has been reported in simulations of other macromolecular systems[16]. Another interesting observation is that while a water molecule is bonded to one headgroup by one hydrogen bond, the same water molecule is H-bonded to another water molecule which is H-bonded to a neighbouring 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. It is still an open question whether the breaking of these hydrogen bonds gives rise
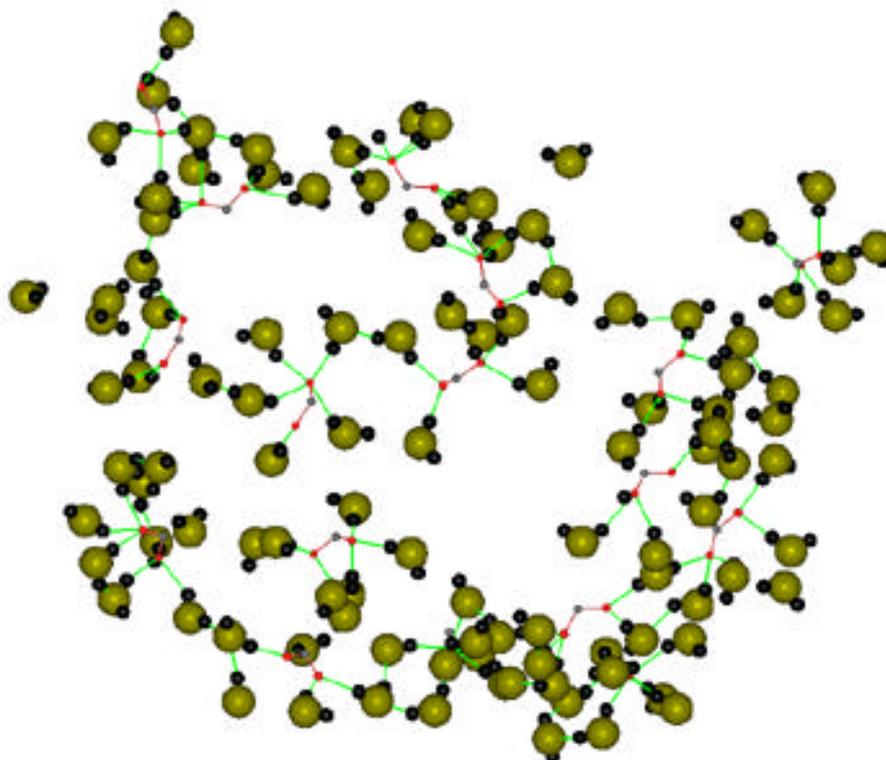


**Figure 10.** Snapshot of a part of the micelle configuration along with water at 350 K. Water molecules in the first coordination shell of the headgroup oxygens are shown, i.e. these water molecules are within a distance of 4.3 Å away from the headgroup carbon. Greenish yellow, water's oxygen; black, water's hydrogen; grey, headgroup carbon; red, headgroup oxygen. Green-coloured bonds denote hydrogen bonding between the headgroup oxygen and water's hydrogen and are obtained using a distance criterion.

to the observed time scale, as predicted in theoretical studies.

*Sensitivity to time window*

In view of the complexity of the simulations that we have performed, it is important to pause here and reflect on the results that we have obtained. Macromolecular assemblies in general and micellar systems in particular, present a challenging task in their characterization. This is mainly due to the structural roughness of their hydrophilic surface which provides a heterogenous environment for the molecules of the solvent and the counterions. It is thus rather difficult to capture the variety of relaxation processes that might take place in such a system. For instance, one cannot label a set of molecules or ions as *belonging* to the interfacial layer, as such labels are valid only for the time duration of their existence within the interfacial layer. In these fluxional aqueous systems, water molecules in the interfacial layer are in constant exchange with molecules in neighbouring regions and in the bulk. Hence, the calculation of any time-dependent quantity of the water molecules or ions in the interfacial layer will necessarily have to be performed within this time window of their existence within the interfacial layer. This situation might create artifacts in the results in such a way as to make time correlation functions of quantities with an expected zero mean, not to reach the zero value exactly, at long times. Such artifacts will necessarily occur in calculations of time correlation function of quantities from a data set that is of a duration shorter than the timescale of the decay of the correlation function itself. Hence one ought to be careful in such analyses. In the simulations reported here, we have taken adequate care to calculate the time correlation functions over times much longer than the relaxation times of the functions. Due to the heterogeneous nature of the hydrophilic surface, all the ions or molecules that satisfy the residence criteria in the interfacial layer need not be in similar environments. Hence, in the calculation of time correlation functions of fluctuating quantities, we have subtracted the time average of the quantity of interest corresponding to each particle separately (as in eq. (3)), instead of subtracting the average over both time and particles. The latter type of averaging might lead to quantitatively erroneous results in heterogenous environments.

## Conclusions

The appearance of the slow component in the dipolar orientational correlation function, with a relaxation time that is two orders of magnitude slower than that in the corresponding bulk solvent, is certainly a main result of this study. This aspect seems to be in agreement with the experimental results on reverse micelle, even though our simulations have been performed on regular micelle. This indicates that the slowing down of the reorientational motion of water need not necessarily arise from its confinement, and could be a much general property of water present at hydrophilic interfaces. The nearly stationary polar groups on the substrate can profoundly slow down the dynamics of water molecules at the surface.

The present simulation also reveals the existence of extended hydrogen bonding with the headgroups of the micellar assembly and this appears to be responsible for the observed slow orientational relaxation. The two hydrogen bonds seem to form a bridge between the neighbouring polar headgroups. Such bridges have been observed in hydrated jet-cooled biomolecules[26]. Such bridges, once formed, gains stability from the cooperative strengthening of the bonds. Here we show that this strengthening leads to slowdown of the water molecule's rotation. Another equally interesting result is the emergence of a slow component in the SD of ions, in good agreement with experimental data on dipolar solvation.

The reorientational motion and diffusion of water molecules in different hydration shells was earlier examined in micelles of sodium octanoate using the MD method by Watanabe and Klein[16]. In the timescales of a *few* picoseconds, they also observed slow reorientational and translational dynamics of water near the micelle. Recently, Faeder and Ladanyi[11a] reported results of MD simulations of model reverse micelle taking into account many experimental quantities explicitly. They found that both the translational and the rotational mobility of the trapped and bound water were significantly slower than those of free water. Interestingly, their preliminary results did not indicate significant slowing down of the SD in the water pool, which is in disagreement with the present study[11b]. It would be interesting to compare the results of the two simulations, especially the role of the partial time correlation functions.

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 3). Unlike the case of reverse micelle where water molecules are confined in a space of nanometric dimensions, the water molecules near a regular micellar surface as studied here, can exchange themselves with bulk water. This introduces an additional complexity and richness to the problem of studying solvent and ion dynamics. The exchange of water molecules between regions surrounding a micelle causes the overall system to exhibit a variety of relaxational timescales. This would directly determine the collective

properties such as the DR spectrum of the aqueous macromolecular assembly.

The appearance of the slow component in SD of ions, due primarily to their interaction with the micelle, agrees with experiments. 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 show that micellar dynamics gets seriously restrained at ambient conditions, which leads to a further slowing down of water reorientation.

Another point of interest is the role of the slow relaxation on the chemical reactions at the micellar surface. It is clear that the rates of electron transfer reactions can be affected by this slow component[27]. This is a problem of future interest.

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