Slow Solvation Dynamics near an Aqueous Micellar Surface

S. Balasubramanian*,† and Biman Bagchi*,‡

Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064, India, and Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Solvation dynamics of an ion near an aqueous micellar interface are studied in an atomistic molecular dynamics simulation of cesium pentadecafluorooctanoate (CsPFO) in water. The long time part of the polar solvation energy time correlation function ($C_s(t)$) of a tagged cesium ion at the micellar surface is found to *decay very slowly—the long time decay at the surface is slower by 2−3 orders* of magnitude compared to that in bulk water. Through an analysis of partial solvation time correlation functions, we find that the slow decay originates mostly from the interaction of the cesium ions with the polar headgroups; the slow orientational dynamics of water molecules on the surface seem to play only a secondary role. The probability distribution of the polar energy of ions show a *non-Gaussian distribution* with a tail toward the low-energy states.

1. Introduction

Solvation dynamics of tagged polar probes has emerged as an important time-resolved technique to investigate dynamics in restricted geometries.[1−5] The advantage of solvation dynamics over many other techniques is that it offers both spatial and temporal resolution.[5] Naturally, solvation dynamics have been used to study the dynamics in self-organized assemblies and biological systems, which are subjects of great current interest.[4−9] These systems are quite complex, containing not only macromolecules, like surfactants or proteins, but also water as an essential ingredient. For example, water molecules are present within reverse micelles, at the surface of micelles[1,4,6−9] and also at the surface of biomolecules such as proteins and DNA.[2,6] It has been known for a long time that dynamics (rotation, translation) of such water molecules are quite different from water in the bulk. For example, it is known that aqueous solutions of proteins exhibit a slow dielectric relaxation with a time constant in the range of hundreds of picoseconds—a decay which has been attributed to the water molecules bound to the hydrophilic groups at the protein surface.[4] More recently, several groups have studied dynamics of such water molecules by using many different techniques, including dielectric relaxation,[7,8] solvation dynamics,[1−3] NMR relaxation dispersion (NMRD),[8] and intermolecular water-solute NOE studies.[9] All these studies have reinforced the existence of a second, *very slow*, component in the dynamics, which decays in the hundreds to thousands of picosecond, in such restricted environments.[5] The slow second component appears to be unique to complex systems whose origin is not understood and is currently a subject of lively debate.[1,2,4,7−10] Although it is straightforward to attribute the origin of the slow decay to water molecules for orientational relaxation, the same is certainly not true for solvation dynamics of ions and dipoles because here, the heterogeneous surface can directly participate in the solvation process.

We briefly mention the experimental studies on solvation dynamics of a solute probe located near an aqueous micellar surface. Solvation dynamics (SD) in neutral (triton X-100, TX), cationic (cetyl trimethylammonium bromide, CTAB), and anionic (sodium dodecyl sulfate, SDS) micelles have been studied using C480 and 4-aminophthalimide (4-AP) as probes.[1] Spectroscopic studies indicate that the probes reside in the water (i.e., the Stern) layer near the micellar surface. The average solvation times (of the slow component) for SDS, CTAB, and TX are respectively 180, 470, and 1450 ps for C480 and 80, 270 and 720 ps for 4-AP.[1] Thus, the long time part of the solvation dynamics in the Stern layer of the micelles is *two to 3 orders of magnitude slower than that in bulk water*. These studies missed the initial ultrafast part of solvation dynamics. Thus, the relative weight of the slow relaxation has not been clearly established, but it is expected to be between 5 and 20%.[2]

It has been proposed that the dynamic exchange between bound and free water molecules could provide a general explanation of the slow component observed in diverse systems.[4,5,8,9] A quantitative version of this explanation has recently been worked out which is based on a reaction−diffusion equation for the orientational motion of the water molecules near the micellar/protein surface.[4] If it is further assumed that the water molecules completely randomize their orientation on desorption from the surface, then one can explain the slow decay by using reasonable values of the substrate-water hydrogen bond. Thus, although one can envisage the bound water as the primary reason for the slow orientational relaxation, as observed by NOE and dielectric relaxation, the situation, as mentioned earlier, could be quite different for solvation dynamics because the polar headgroups present on micellar or protein surface are expected to play an important role, and they can give rise to a decay component in the time scale of hundreds of picosecond or even nanosecond range. Very little work has been done on these aspects.

To understand the origin of the slow decay, we have performed extensive atomistic molecular dynamics (MD) simulations of a micelle in water. This is a large-scale simulation where the system consists of 10 562 water molecules and 62 surfactants. The simulations have been carried out for about 3 ns. They reveal that although the dipolar correlation function

---

† Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research.
‡ Solid State and Structural Chemistry Unit, Indian Institute of Science.

of the 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*. This slow decay can indeed be traced to the existence of bound water. This surprising result has been reported recently.[11] In the present study, we report results of our study on the solvation dynamics on micellar surface, using the naturally present cesium ions as the probe of the dynamics. We calculate their polar energy-energy time correlation function. The solvation dynamics of Cs^+ ions show a dramatic slowing down near the micellar surface as compared to that in bulk solvent. Through an analysis of the contributions to the total solvation time correlation function, we have established that the dynamics of the micelle plays an important role in determining the solvation dynamics of the cesium ions. Thus, in addition to establishing the role of bound water in the solvation process, our results also indicate a possible role of the micellar aggregate in the experimentally observed long time decay of the solvation time correlation function.

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[12−14] and is regarded as a typical binary to exhibit micellization.[15] The amphiphiles are believed to form disk shaped (oblate ellipsoid) micelles over a critical micelle concentration of 0.02 weight fraction of CsPFO in water. The micelles are 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. 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 at a temperature of 350 K, for an aggregate of 62 CsPFO molecules in 10 562 water molecules, i.e., at a weight fraction of 0.15. The average aggregation number of micelles in this system increases as a function of decreasing temperature. For instance, at room temperature, the aggregation number is around 200. In the isotropic phase, the intermicellar interaction is negligible. To be consistent with this, one needs to use a large amount of water around the micelle, so that the micelle in the central box of the simulation does not interact with any of its image in the neighboring boxes. Thus, a simulation of a micellar aggregate with 200 surfactants at 300 K would involve a commensurate increase in the number of water molecules, making the MD simulation prohibitively expensive. We have thus chosen to perform our simulations at 350 K, where the micelle is found to be stable in experiments.

The initial configuration of the micelle was built to mimic experimental data pertaining to its size and shape.[14] This configuration for the micelle with linear dimensions of 45, 45, and 25 Å along its principal axes, was placed in a box of water with linear dimensions of 84, 84, and 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,[16] and the counterions (Cs) carry a unit positive charge. The headgroup of our system is identical to that in sodium octanoate

TABLE 1: Table of Lennard−Jones Parameters for Self Interactions

atom type[a]	ϵ [K]	σ [Å]
Ch	13.20	4.437
Ct	38.50	3.35
O	87.94	3.083
F	37.00	2.95
Cs	50.39	3.886
OW	78.198	3.166
HW	0.0	-

[a] Ch, Ct, and O stand for the headgroup carbon, tail carbon and headgroup oxygen of the perfluoroctanoate surfactant respectively. These parameters were obtained from refs [17−19]. OW and HW denote oxygen and hydrogen sites in the SPC/E water model [16]. All cross interactions were obtained using Lorentz−Berthelot combining rules.

micelles modeled earlier.[17] These potentials have been known to provide a good representation of the hydrogen bonding between water molecules and the headgroup. The charge on the cesium ion 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.[17] The surfactant is modeled with explicit fluorine atoms and interactions between the fluorocarbon tails were used without modifications from the work of Sprik et al on poly(tetrafluoroethylene).[18] The cesium−water interactions were obtained from the work on aqueous ionic solutions.[19] All nonbonded interaction potentials used in our simulation have the Lennard−Jones form, along with the Coulombic term. The atomic Lennard−Jones parameters are listed in Table 1. The equations of motion were integrated with the reversible reference system propagator algorithm (RESPA) scheme[20] using the PINY-MD package[21] 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. A snapshot of the micelle taken after 3.0 ns from the initial configuration is shown in Figure 1 to demonstrate that the micelle is indeed stable.

It is often impossible to objectively define different interfacial layers precisely, as there is a constant exchange of ions between notionally defined interfacial layers. Our interest here is to observe the slow solvation dynamics of cesium ions near the interface. We have identified these cesium ions in terms of their residence times near the headgroups. It is natural to expect slow solvation dynamics for ions with the largest residence time near the micellar interface. In our study, the solvation time correlation functions were calculated by following only those ions which stayed within a given distance from the micellar surface throughout that particular run. Although this curtails the number of qualifying ions, in practice, we have found that a statistically significant number of cesium ions (about twelve) are present within 10 Å from any headgroup over an entire time period of 660 ps.

Thus, in our analyses, both the distance from the headgroup as well as the residence time define the location of an ion among 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 solvation relaxation.

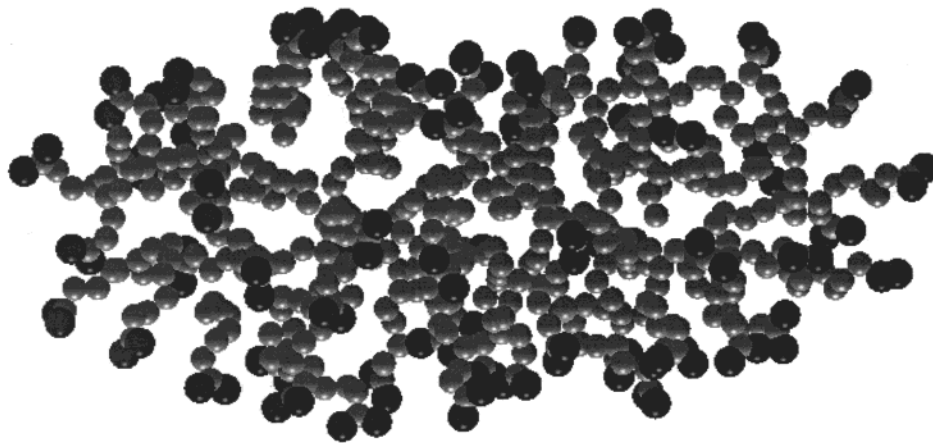The solvation dynamics is monitored by the decay of solvation time correlation function, $C_s(t)$ which is defined as[4]

Slow Solvation Dynamics

J. Phys. Chem. B, Vol. 105, No. 50, 2001 **12531**

Figure 1. Snapshot of the micelle evolved after 3 ns from the initial configuration. The darker spheres denote the oxygens in the carboxylate headgroup, whereas the lighter ones are carbon atoms along the perfluoroctonate chain. Other atoms in the simulation are not shown for clarity. The distance between headgroups in the core of the micelle along the vertical direction (bilayer) is around 24 Å.

$$C_s(t) = \frac{< \delta E_i(t) \delta E_i(0) >}{< \delta E_i(0) \delta E_i(0) >} \tag{1}$$

where $\delta E_i(t)$ 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, {i}, that qualify the distance and residence time criteria, outlined above.

$C_s(t)$ was calculated by considering only the polar part of interaction energy of tagged cesium ions with the rest of the system. Typically, the coordinates of all the atoms from a molecular dynamics run were stored at periodic intervals of 1 ps from which the correlation functions were calculated. For the calculation of $C_s(t)$, the polar energy was calculated using a real space molecular interaction cutoff of 21 Å, with no Ewald sum. Note that our molecular dynamics simulations were performed with converged Coulomb energies, using the Ewald summation method, and that we used a simple real space cutoff for data analysis only. By systematically increasing the cutoff distance from 12 Å to 21 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.

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 solvation dynamics. One could then make a direct comparison to experiments on solvation dynamics 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. In our simulations, 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 solvation dynamics 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 although solvation dynamics of a small dipolar solute is expected to be somewhat slower than that of a small ion (especially in the long time[22]) the difference is not expected to be nearly as significant as the
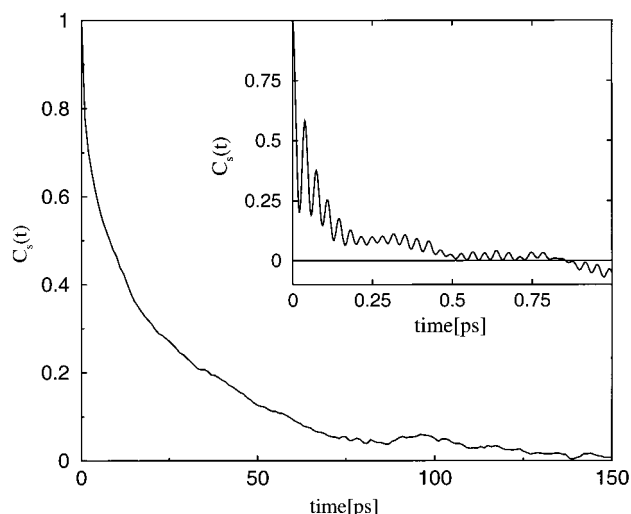

Figure 2. Decay of the solvation time correlation function, $C_s(t)$, of a cesium ion near the micellar surface at 350 K. Here, the solvation tcf is shown for only those Cs$^+$ cesium ions which stay within 10 Å from any headgroup during the whole of 660 ps. For comparison, the solvation time correlation function of a cesium ion in pure, bulk water at 300 K, is shown as inset. Note the difference in time scales between the two figures.

difference observed experimentally between dipolar solvation in bulk water and on a micellar surface.

3. Results

Cesium ions are present predominantly near the micelle-water interface. The first shell of cesium ions with respect to the headgroup carbon is well defined at a distance of 3.8 Å. We find that, on average, a headgroup carbon is surrounded by six water molecules and about 0.67 cesium ions in its first coordination shell. Details of the structure at the micelle-water interface has been discussed elsewhere;[11] here, we shall focus on solvation dynamics.

In Figure 2, the decay of the solvation time correlation function (tcf) of a cesium ion near the micellar surface is shown and the observed dynamics is really fascinating. Here, we plot the solvation tcf for cesium ions within 10 Å from the headgroups, and with a residence time of 660 ps. Note the strong, slow component to the relaxation of the solvation energy, in good agreement with experimental data.[1-3] We need to compare this result against the solvation dynamics of a cesium
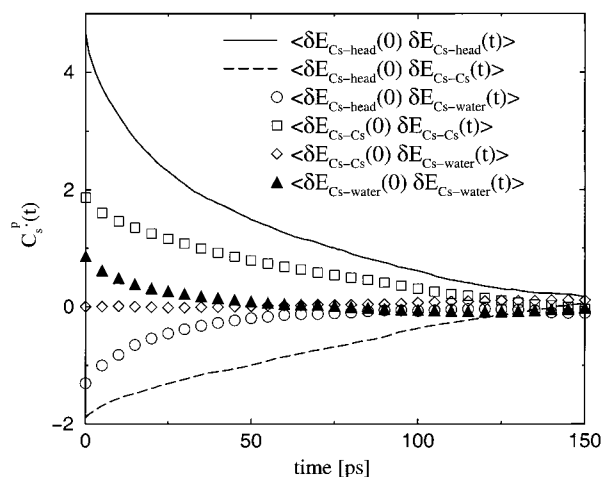
Figure 3. Partial solvation time correlation functions $C_s^p(t)$, of cesium ions for those ions which remained within 10 Å from any headgroup carbon throughout a trajectory of length 660 ps. These are "normalized" by the $t = 0$ value of the *total* time correlation function, $\langle \delta E_{Cs}(0) \delta E_{Cs}(0) \rangle$ and hence will not start from a value of one, at $t = 0$. All the six contributions are shown. The details are given in the legends to the figure. 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.

Figure 4. Time averaged distribution of the polar contribution to the potential energy of cesium ions with large residence times, as discussed in Figure 2.

ion at distances far away from the micelle. 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 5711 water molecules within a periodic box, at a temperature of 300 K. The solvation time correlation function for this cesium ion in pure, bulk water is shown as inset to Figure 2. This correlation function has been obtained by averaging over 16 runs. In agreement with earlier nonequilibrium and equilibrium simulations of Maroncelli,[23,24] and of Ladanyi,[25] the solvation relaxation decays within 1 to 2 ps at 300 K. A comparison of these data against solvation data for cesium ions near the micelle tells us that the longtime part of the solvation dynamics is slowed by at least 2 orders of magnitude near the interface.

Note that the slow component of solvation dynamics in experimental studies[1,7,8,2] is believed to arise from the solute probes immobilized at the micellar surface. The present study agrees with this conjecture. In order for the slow decay to persist over such a long time as 200−300 ps, the probes must remain at the surface. As discussed earlier, we have ensured this by employing a filter that selects cesium ions with the longest residence times at the micellar interface.

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).

An analysis of the partial solvation time correlation functions (Figure 3) 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 tcf also exhibits a very slow component which is the leading cause of the slow decay of the total solvation energy time correlation function. In contrast, the contribution from the interaction with water molecules is much less dominant. Thus, it appears that the slow part of the polar solvation of the cesium ions may have more
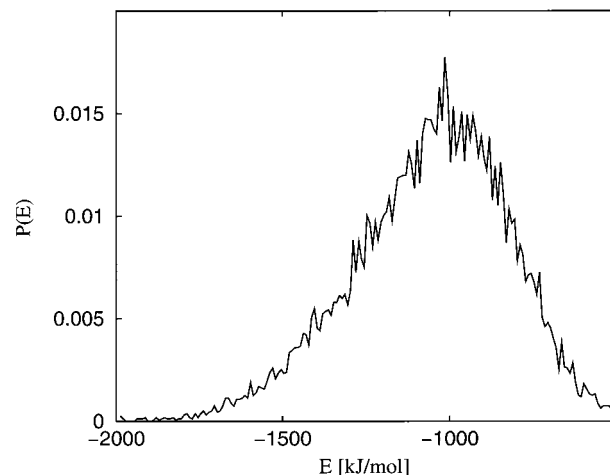
to do with micellar dynamics than with the solvent (i.e., water). If this is indeed true, then the slow solvation of ions and dipoles and the slow orientational relaxation of the solvent at the surface are indeed probes of interaction with the micelle. This is a rather interesting result that has emerged from this study, which needs to be confirmed from further simulations.

The energy-energy time correlation function presented in Figure 2 has been obtained from a subset of cesium ions that satisfy the residence time criterion described earlier. It is reasonable to expect that these cesium ions are in a more favorable environment energetically, than those ions which solvate faster. It is thus imperative that we study the energy distribution of the former. In Figure 4, we provide the time averaged distribution of the polar contribution to the potential energy of such cesium ions. First note that the distribution is non-Gaussian, with a tail toward low energy states. The large width of this distribution tells us that there could be a wide variety of sites for the cesium ions to be present near the micelle. Cesium ions which contribute to the low energy tail could contribute predominantly to the slow decay of the solvation time correlation function. We are studying further the nature of this tail in the energy distribution and its relation to the slow dynamics. Note that this probability distribution of polar energy of an ion can be useful in the study of electron-transfer reactions at the micellar surface.

4. Conclusions

The main result of the present work is the appearance of the slow component in the ion solvation time correlation function, with a relaxation time 2−3 orders of magnitude slower than that in the corresponding bulk solvent. This aspect seems to be in agreement with the experimental results on micelles and reverse micelles. We further find that the slowing down of the solvation time correlation function comes from the interaction of the ion with the polar headgroups of the micelle and not from the slow reorientational motion of water. This is a new result that emphasizes the point that solvation dynamics on a heterogeneous aqueous surface could arise from the specific probe−surface interaction. Thus, this slow *cannot* be explained by invoking something like a continuum model which uses the orientation of water molecules as the main mechanism of solvation dynamics.

The appearance of the slow component in solvation dynamics of ions, due primarily to their interaction with the micelle, agrees

Slow Solvation Dynamics

J. Phys. Chem. B, Vol. 105, No. 50, 2001 **12533**

with experiments, and also throws open the question of the nature of ion solvation. Is the ion really solvated by the solvent, or by the micellar headgroups? 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 ion solvation, and water reorientation. One would of course need to worry about the stability of the micelle itself. Work in this direction is under progress.

We have also presented the probability distribution of the polar solvation energy of the ion. This distribution is asymmetric, with a tail toward the low energy side. The origin of this asymmetry deserves further attention.

References and Notes

(1) (a) Sarkar, N.; Datta, A.; Das, S.; Bhattacharyya, K. *J. Phys. Chem.* **1996**, *100*, 15 483. (b) Datta, A.; Mandal, D.; Pal, S. K.; Bhattacharyya, K. J. *Mol. Liq.* **1998**, *77*, 121.

(2) Jordanides, X. J.; Lang, M. J.; Song, X.; Fleming, G. R. *J. Phys. Chem.* **1999**, *103*, 7995.

(3) Levinger, N. E. *Curr. Opin. Coll., & Interface Science* **2000**, *5*, 118. Riter, R. E.; Willard, D. M.; Levinger N. E., *J. Phys. Chem. B* **1998**, *102*, 2705.

(4) Nandi, N.; Bhattacharyya, K.; Bagchi, B. *Chem. Rev.* **2000**, *100*, 2013. Nandi, N.; Bagchi, B. *J. Phys. Chem.* **1997**, *101*, 10 954. Nandi, N.; Bagchi, B. *J. Phys. Chem.* **1998**, *102*, 8217.

(5) Bhattacharyya, K.; Bagchi, B. *J. Phys. Chem.* **2000**, *104*, 10 603.

(6) See, for example: Hydration Processes in Biological and Macromolecular systems, Faraday Discuss. **1996**, *103*, 1−394.

(7) (a) Fukuzaki, M.; Miura, N.; Sinyashiki, N.; Kunita, D.; Shiyoya, S.; Haida, M.; Mashimo, S. *J. Phys. Chem.* **1995**, *99*, 431. (b) Belton, P. S. *J. Phys. Chem.* **1995**, *99*, 17 061.

(8) (a) Halle, B.; Denisov, V. P.; Venu, K. in Biological Magnetic Resonance, Volume 17, Ramakrishna, N.; Berliner, L. J. ed. (Kluwer Academic: New York, 1999) p 419. (b) Denisov, V. P.; Peters, J.; Horlein, H. D.; Halle, B. *Nature Struct. Biol.* **1996**, *3*, 505.

(9) (a) Otting, G. in Biological Magnetic Resonance, Volume 17, Ramakrishna, N.; Berliner, L. J. ed. (Kluwer Academic: New York, 1999) p 485. (b) Otting, G.; Liepinsh, E. *Acc. Chem. Res.* **1995**, *28*, 171.

(10) Faeder, J.; Ladanyi, B. M. *J. Phys. Chem. B* **2000**, *104*, 1033; Preprint.

(11) Balasubramanian, S.; Bagchi, B. *J. Phys. Chem. B* (communicated); Balasubramanian, S. (unpublished results).

(12) (a) Boden, N.; Jackson, P. H.; McMullen, K.; Holmes. M. C. *Chem. Phys. Lett.* **1979**, *65*, 476 (b) Boden, N.; Jolley, K. W.; Smith, M. H. *J. Phys. Chem.* **1993**, *97*, 7678.

(13) Boden, N.; Corne, S. A.; Holmes. M. C.; Jackson, P. H.; Parker, D.; Jolley, K. W. *J. Physique* **1986**, *47*, 2135.

(14) Iijima, H.; Kato, T.; Yoshida, H.; Imai, M. *J. Phys. Chem.* **1998**, *102*, 990.

(15) Gelbart, W. M.; Ben-Shaul, A. *J. Phys. Chem.* **1996**, *100*, 13 169.

(16) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. *J. Phys. Chem.* **1987**, *91*, 6269.

(17) Watanabe, K.; Klein, M. L. *J. Phys. Chem.* **1989**, *93*, 6897; Watanabe, K.; Klein, M. L. *J. Phys. Chem.* **1991**, *95*, 4158.

(18) Sprik, M.; Röthlisberger, U.; Klein, M. L. *Mol. Phys.* **1999**, *97*, 355.

(19) Lee, S. H.; Rasaiah, J. C. *J. Phys. Chem.* **1996**, *100*, 1420.

(20) Tuckerman, M. E.; Berne, B. J.; Martyna, G. J. *J. Chem. Phys.* **1992**, *97*, 1990.

(21) Tuckerman, M. E.; Yarne, D. A.; Samuelson, S. O.; Hughes, A. L.; Martyna, G. J. *Comp. Phys. Comm.* **2000**, *128*, 333.

(22) Bagchi, B.; Biswas, R. *Adv. Chem. Phys.* **1999**, *109*, 207.

(23) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1988**, *89*, 5044.

(24) Jimnez, R.; Fleming, G. R.; Kumar, P. V.; Maroncelli, M. *Nature* **1994**, *369*, 471.

(25) Skaf, M. S.; Ladanyi, B. M. *J. Phys. Chem.* **1996**, *100*, 18258.