Impact of Counterion on Water Motion in Aerosol OT Reverse Micelles

Ruth E. Riter, Erik P. Undiks, and Nancy E. Levinger*

Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

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Abstract: We have measured the dynamics of water solvation in two different reverse micellar environments with low water content, $w_0 = 1.7$. In the water/Aerosol OT (AOT)/isooctane reverse micelles, the characteristic ultrafast bulk water motion is completely absent. In contrast, when the sodium cation normally complexed to the AOT surfactant head group is exchanged for an ammonium cation, solvation dynamics measurements reveal that the water is significantly more mobile. However, the water present in these modified reverse micelles is still less mobile than bulk water. These studies reveal that the Na^+ ion in normal AOT reverse micelles is responsible for reducing a large fraction but not all of the water motion in these environments.

I. Introduction

Reverse micelles have been invoked frequently in the past to solve a variety of chemical problems. They are effective stabilizers for reactive species that are insoluble in nonpolar phases.[1] They serve as templates for nanomaterials.[2,3] In addition, they have been used as models for biological compartmentalization.[4] As such, they represent a useful alternative heterogeneous medium to standard homogeneous chemistry.

By far, the most common system used for reverse micellar studies is the ternary mixture water/Aerosol OT (AOT)/nonpolar solvent.[5] AOT reverse micelles have been very well characterized spectroscopically and thermodynamically; techniques used to probe the solutions include light scattering, neutron scattering, IR and NMR spectroscopy, and the spectroscopy and dynamics of probe molecules solubilized inside the micelle. AOT micelles have the ability to solubilize large amounts of water and form highly monodisperse solutions. The size of micelles in a suspension, determined through light, X-ray, and neutron scattering,[6−11] has been characterized by the molar ratio of water to AOT

$$w_0 = [H_2O]/[AOT] \quad (1)$$

which has been shown to be directly proportional to the micellar radius. "Dry" AOT micelles, $w_0 = 0$, are slightly nonspherical, but the micelles rapidly convert to a spherical form upon addition of small amounts of water. The smallest micelles possess a hydrodynamic radius of ∼1.5 nm.[10] The aggregation number for the small micelles, $w_0 \leq 2$, is ∼20 AOT molecules/micelle.[5] As water is added to the solutions, the reverse micelles swell solubilizing large amounts of water, $w_0 = 50-70$, in discrete droplets.

The water pools inside the AOT reverse micelles possess some interesting properties. For example, IR absorption spectroscopy shows that water molecules solubilized inside small micelles are in contact with and bound to the polar head group of the AOT molecules.[12−15] This inhibits their ability to form the normal hydrogen bonds found in bulk water. As w_0 increases, the IR spectrum shifts toward that of bulk water indicating the water molecules in the inner pool form bulklike hydrogen bonds. Similar results have been observed with NMR spectroscopy.[16]

In addition to structural differences, experiments measuring dynamics reveal that motion of the water molecules inside the micelles differs from bulk.[17−24] Hasegawa et al. have used molecular probes to measure the microviscosity inside reverse

* Corresponding author. E-mail: levinger@lamar.colostate.edu.

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micelles of varying size.[19] Results from their work indicate that the viscosity of water in small micelles is greater than that in bulk water. The viscosity decreases dramatically up to $\sim w_0 = 10$ and then decreases slowly as the micellar size increases. Zhang and Bright have probed solvent relaxation via steady-state and nanosecond fluorescence properties of the molecular probe 1,8-anilino-8-naphthalenesulfonic acid (ANS).[21] Their measurements reveal two different solvation rates inside the micelles, and they attribute the differing rates to water bound to the polar head groups of AOT and bulk water in the micelles. In an independent study, Cho et al. also probed the fluorescence decay characteristics of ANS solubilized in a range of AOT reverse micellar sizes.[22] Their results were similar to those of Zhang and Bright.

One method for investigating solvent motion in a variety of environments, including reverse micelles, is to measure the solvation dynamics via ultrafast time-resolved spectroscopy. Solvation dynamics experiments measure the dynamic response of polar solvents to an instantaneous electric perturbation. A wide range of bulk solvents have been studied.[25] For all solvents, there exist two different types of solvent motion that result in an ultrafast, sub-100-fs inertial component and slower diffusive components.[26] Solvation dynamics of water have been measured.[27−29] Measurements with the highest time resolution[27,29] show a large (>50%) sub-50-fs inertial component in addition to diffusive components with subpicosecond time constants.

Recently, solvation dynamics measurements have also been performed in a few heterogeneous environments. Yanagimachi et al.[30] examined polar solvation dynamics at the sapphire/1-butanol interface. Bessho et al. explored fluorescence decays from ANS at the water−heptane interface.[31] In both of these studies, the polar solvent response observed was slower at the interface than in bulk. Sarkar et al. probed the solvation of coumarin 480 in oil-in-water micelles[32] and water-in-oil reverse micelles.[24] Their experiments revealed additional long time, nanosecond components to the water dynamics. Solvation dynamics in zeolites measured by coumarin 480 have also been probed.[33] Here the dynamical response from the zeolite cavity has been attributed to the motion of the mobile sodium ions and/or motion of the probe molecules. In all of these solvation dynamics studies described and in the micellar studies described above, the time resolution was >50 ps, hence the ultrafast water solvation dynamics would not be observable. In contrast, Vajda et al. measured the dynamics of water solvation within cyclodextrin cavities using subpicosecond resolution.[34] At short times, <0.2 ps, the solvation dynamics in the cyclodextrin cavity are similar to those of bulk water. At longer times, ≥0.2 ps, the solvation dynamics in the cyclodextrin cavity are observed to be significantly slower compared to those of bulk water displaying additional long time components to the relaxation. These long time components were attributed to probe molecule motion in and out of the cavity as well as to water molecules constrained by binding to the cyclodextrin.[34,35] Recently, we have probed the solvation dynamics of water in AOT reverse micelles as a function of water loading.[36] These experiments show that the water inside the smallest reverse micelles is completely immobilized, but a bulklike component appears as water is added and a core water pool forms. Mittleman et al.[37] have probed the dielectric properties of water in AOT reverse micelles using subpicosecond terahertz spectroscopy. Compared to bulk water, their results reveal reduced amplitude and time scale for the observed relaxation.

The water dynamics in the smallest sized AOT micelles, $w_0 < 7$, have been shown to differ significantly from bulk water.[13−16,38−40] While the mobility of the water molecules is reduced inside the reverse micelles, the source of this reduction is not clear. Possible perturbations could arise from the size restriction of the water pool in the micelles or interactions of water molecules with various parts of the surfactant molecules. These interactions include ion−dipole with the cation/anion, dipole−dipole with the ester moieties, and dispersion forces with the alkyl tails. To separate the role of the cations complexed to the amphiphilic anion from the effect of the small micellar size or interactions involving other parts of the surfactant molecule, we have exchanged the sodium cation for an ammonium cation in AOT and measured the dynamics of polar solvation inside the resulting reverse micelles. The dynamics we observed in the ammonium-exchanged micelles are significantly faster than the sodium counterpart, indicating that the sodium cations play a large role in impeding normal water motion.

II. Experimental Methods

In these experiments, we have used the fluorescence upconversion technique to follow the dynamic fluorescence Stokes shift of the probe molecule Coumarin 343 (C343, see Figure 1) solubilized inside reverse micelles. The time-resolved fluorescence upconversion apparatus has been described in detail elsewhere.[36] Briefly, we use the doubled output (410 nm) from an ultrafast mode-locked Ti:sapphire laser to excite the dye to its first excited state. The resulting fluorescence is mixed with the residual laser fundamental gate pulse in a nonlinear crystal a variable time later, thereby time-resolving the fluorescence. The time resolution of the spectrometer, determined via cross-correlation of the excitation and gate pulses in the nonlinear crystal, was <170 fs, assuming a Gaussian profile. The upconverted fluorescence is dispersed with a prism and sent through a monochromator where it is detected with a cooled photomultiplier tube. The bandwidth of the sum-frequency radiation collected was 8 nm fwhm. Signals are collected via a photon counter interfaced to a computer. The collected time-resolved fluorescence signals are fit to a multiexponential function using a Global variable fit function.

Absorption spectra were obtained with a Cary 2400 UV/vis/IR spectrophotometer. Static emission spectra were measured with a

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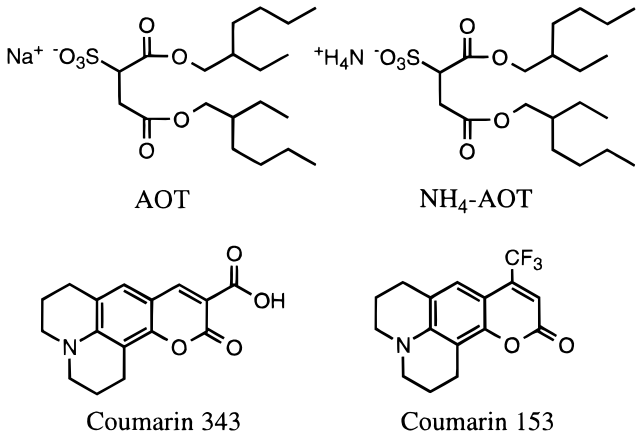

Figure 1. Molecular structures for Aerosol OT, NH_4-AOT, Coumarin 343, and Coumarin 153.

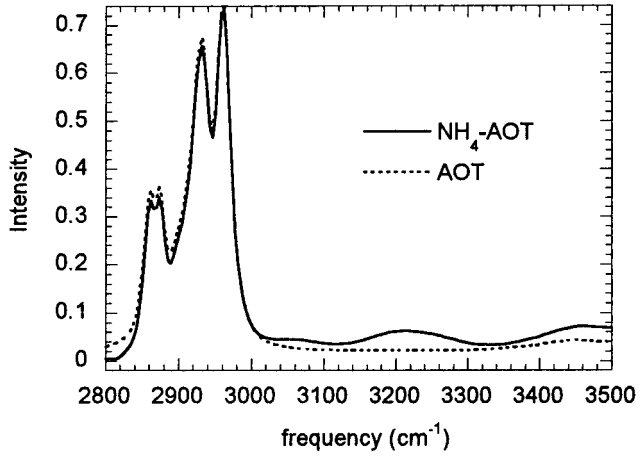

Figure 2. FTIR spectrum of AOT and NH_4-AOT in the region showing the ammonium symmetric and asymmetric stretch peaks.

home-built fluorometer.[41] Fluorescence lifetimes for the C343 probe molecule in the various milieus were determined via time-correlated single photon counting (TCSPC).[42]

The reverse micellar samples were prepared from high-purity water (Milli-Q filtered, 18.2 MΩ/cm^2)/surfactant/isooctane (2,2,4-trimethylpentane, HPLC grade, Aldrich). Samples were prepared with AOT (sodium bis(2-ethylhexyl)sulfosuccinate, Aldrich) and ammonium bis-(2-ethylhexyl)sulfosuccinate (NH_4-AOT). The structures for each are shown in Figure 1. To prepare the NH_4-AOT, the sodium cation in the AOT was exchanged for ammonium using a procedure similar to those reported in the literature for exchanging sodium with other atomic cations, as follows:[43−45] Thirty-three grams of AOT in 100 mL of ether and 30 g of NH_4Cl (Sigma) dissolved in 100 mL of water (Milli-Q distilled, filtered, deionized, >18.2 MΩ/cm) was stirred vigorously for several hours. The solution was allowed to phase-separate, and the ether phase was extracted and dried over molecular sieves (Sigma, 3A) after which the ether was pumped off the sample. Electrospray mass spectra of the ion-exchanged surfactant revealed quantitative removal of the sodium from the sample. Infrared spectra of the ion-exchanged sample revealed new bands peaking at 3050 and 3200 cm^{-1}, shown in Figure 2. These peaks are associated with the ammonium ion symmetric and asymmetric stretches and are absent in spectra of the AOT samples, shown in Figure 2 for comparison. Samples for upconversion experiments were prepared by dissolving the surfactant in isooctane to which water was added. Volume fractions of surfactant and water in the isooctane are given by the following relation:

$$\phi = [V_{H_2O} + n_{AOT}(\upsilon_{AOT} + n_{H_2O}\upsilon_{H_2O})]/V_{total} \quad (2)$$

where V_{H_2O} is the volume of water, n_{AOT} is the number of moles of AOT, υ_{AOT} is the volume of one AOT molecule,[46] n_{H_2O} is the number of water molecules per AOT molecule, υ_{H_2O} is the volume of one H_2O molecule, and V_{total} is the total volume of the solution. The volume fraction for these experiments was $\phi < 0.20$, and the ratio of water to surfactant was $w_0 = 1.7$. The probe molecule was added to the ternary mixtures containing the reverse micelles; as it is highly insoluble in the isooctane, it was preferentially solvated inside the micelles.[47] From the concentration of surfactant and absorbance of the samples, we estimate that there were fewer than one C343 molecule per 50 micelles.

III. Results and Discussion

Previous experiments have probed the nature of micelles created with the NH_4-AOT surfactant.[48,49] Small-angle neutron scattering and conductivity measurements have shown that the NH_4-AOT aggregates form spherical micelles with virtually the same size as AOT reverse micelles with the same w_0 and volume fraction, ϕ (R_h = 2.0 nm for w_0 = 2). We have measured the size of both NH_4-AOT and AOT micelles using dynamic light scattering and also find that both systems yield micelles of the same size for the same hydration level, w_0. While the size of the hydrated ammonium cation is slightly smaller than the sodium ion, largely because it complexes fewer water molecules, this does not appear to impact the micelle size or shape. As such, the NH_4-AOT micelles provide an excellent system to compare the effect of the counterions on the mobility of water solubilized inside the micelles.

Normally the interior of the AOT reverse micelles is quite basic.[5] However, for the NH_4-AOT micelles, we estimate that the interior pH is <4.[50] The absorption and fluorescence spectra of the C343 probe molecule are sensitive to the pH of the surroundings. Because the interior of the AOT and NH_4-AOT micelles have significantly different pH, we have investigated the spectroscopy of C343 as a function of pH to ensure that the observed dynamics arise from a dynamic Stokes shift due to solvent equilibration and not from ultrafast protonation or deprotonation of the dye.

Static absorption and fluorescence spectra for C343 in acidic, neutral, and basic environments are shown in Figure 3a. The absorption and fluorescence spectra for C343 in neutral and basic solution are indistinguishable. However, the peak of the absorption spectrum shifts from 428 nm in neutral or basic solution to 456 nm in acidic solution. The peak of the fluorescence spectrum also shifts, albeit much less, from 487 nm in neutral or basic solution to 494 nm in acidic solution. These shifts are commensurate with absorption and fluorescence spectral shifts of C343 in normal and basic methanol solution measured by Tominaga and Walker,[51] that is, the absorption spectrum exhibits a substantial shift while the fluorescence spectrum exhibits a smaller shift. These results indicate that the dye is anionic at neutral and basic pHs and in the neutral, protonated form in acidic solution. Via spectrophotometric

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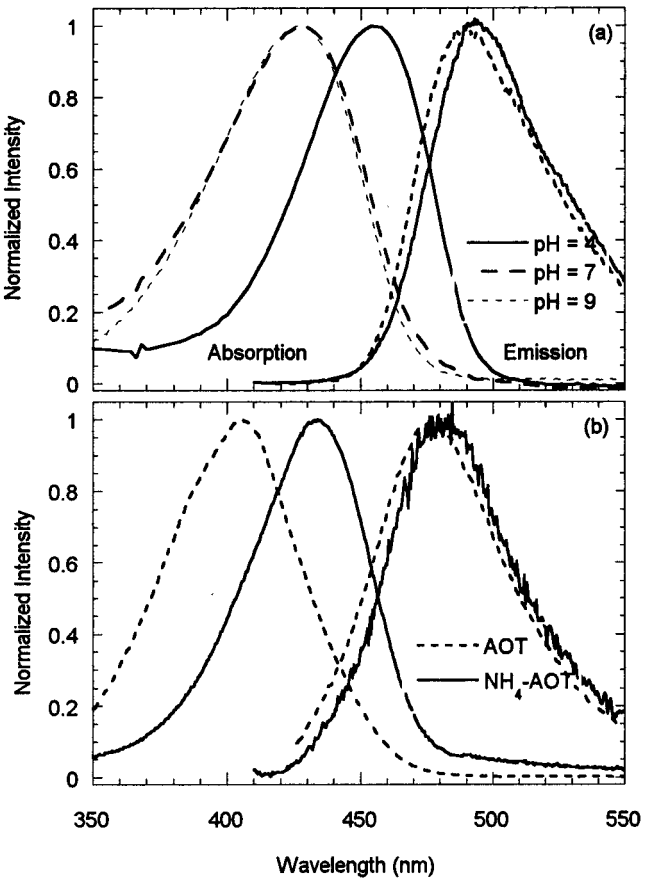

Figure 3. Static absorption and fluorescence spectra of C343 in (a) acidic, neutral, and basic bulk aqueous solution and (b) AOT and NH_4−AOT reverse micelles with $w_0 = 1.7$.

titration, we have determined that the ground- and excited-state pK_a's of C343 are both 4.65.

There are several sites on the C343 molecule that could potentially accept a proton, the carboxylic acid group, the cyclic ester, and cyclic amine moieties. To determine what site on C343 protonates in acidic solution, we investigated the spectroscopy of the related dye, coumarin 153 (C153, shown in Figure 1). This dye shares two of the three potential proton acceptor sites on C343, the cyclic amine and cyclic ester, but does not include the carboxylic acid group. The absorption spectrum of C153 showed no spectral shift in highly acidic, pH ∼ 0, methanol solution. (These experiments were carried out in methanol rather than water because C153 is virtually insoluble in water but highly soluble in methanol.) Therefore, neither the amine nor the ester group on the C153 molecule protonate at low pH. In contrast, the near-UV band in the C343 absorption spectrum shifts readily to longer wavelength at pH < 4.5. At pH < 2, the near-UV absorption band of the C343 spectrum disappears completely. The crystal structure of C343[52] shows that the carboxylic acid proton is in close proximity to the ester carbonyl. This suggests that the proton interacts with the carbonyl through a hydrogen bond. While the pK_a values for common organic acids usually lie in the 1−2 range,[53] the hydrogen-bonding interaction of the carboxylic acid hydrogen on C343 would raise the pK_a. Thus, the 4.65 pK_a value we measure for this site is appropriate. Therefore, by analogy with the C153 results, and in accordance with the crystal structure, we conclude that the C343 molecule protonates on the carboxylic acid moiety. This interpretation is supported by our observation that the protonated dye is significantly less soluble in water than the deprotonated dye. This is an important finding for this work; it demonstrates that protonation and deprotonation of the C343 molecule occur at the carboxylate and do not involve the chromophore responsible for the S_0-S_1 transitions of the dye molecule.

The absorption and fluorescence spectra for C343 also reveal marked spectroscopic shifts in the AOT and NH_4−AOT micelles, see Figure 3b. In the $w_0 = 1.7$ AOT reverse micelles, the C343 absorption spectrum shifts ∼20 nm to shorter wavelength relative to the spectrum in neutral or basic water, pH > 4.65. The dye's emission spectrum also displays a spectral blue-shift compared to in neutral or basic water. In contrast, the absorption spectrum of C343 in the NH_4−AOT reverse micelles peaks at longer wavelength than the dye in aqueous solution above pH = 4.65. However, the absorption spectrum blue-shifts ∼20 nm relative to the absorption spectrum in *acidic* water, pH < 4.5. The emission spectrum of C343 in the NH_4−AOT reverse micelles exhibits a shift commensurate with spectrum in the AOT reverse micelles. Therefore, we conclude that C343 is protonated in the NH_4−AOT micelles but exists as an anion in the AOT micelles.

Dynamics measured by fluorescence Stokes shift of C343 in either the neutral, protonated or the anionic form reflect solvation dynamics. Tominaga and Walker[51] investigated the response of the C343 anion in methanol and found that it was virtually the same as the related nonionic probe molecule C153. Because the excited-state pK_a of C343 is identical to that of the ground state, in a given micellar environment, the dye should exist in the same form in both the ground and excited states; protonation or deprotonation is no more likely to occur in the excited state than it is in the ground state. Therefore, while the dye does exist in two different forms within the different micellar environments, it does not interconvert between these forms during the course of the time-resolved fluorescence experiments. The dynamics that we observe for these experiments do not arise from ultrafast excited-state protonation or deprotonation.

Because the C343 is insoluble in isooctane, it is selectively solubilized within the micelles. While the cavity inside both AOT and NH_4−AOT reverse micelles is sufficiently large, the dye molecule is not necessarily found in a well-defined water pool. (On the basis of crystallographic data,[52] the C343 molecule is approximately $9 \times 4 \times 2$ Å^3. Empty AOT reverse micelles possess a 15 Å radius, while micelles with $w_0 = 2$ swell to a radius of ∼20 Å.[5] Therefore, even if the cavity in a $w_0 = 1.7$ micelle is slightly smaller than that for $w_0 = 2$, there is still ample space for the C343 dye molecule to be contained completely within the micellar interior.) Rather, it is possible that the probe resides partially embedded in the micellar interface. To ascertain the probe location in the reverse micelles, we have measured the time-resolved depolarization of the dye in the micelles. Rotational reorientation times for C153 have been measured in a wide range of solvents.[54] These measurements show that, in nonviscous solvents, the rotational reorientation time for C153 is ∼20 ps. The rotational reorientation time for C343 in 0.5 M aqueous Na_2SO_4 is ∼90 ps.[36] In contrast, the rotational reorientation time for dry AOT micelles has been shown via electron spin resonance (ESR) to be 1.18 ns.[55] The rotational reorientation times we have measured for C343 in a series of AOT reverse micelles with increasing w_0

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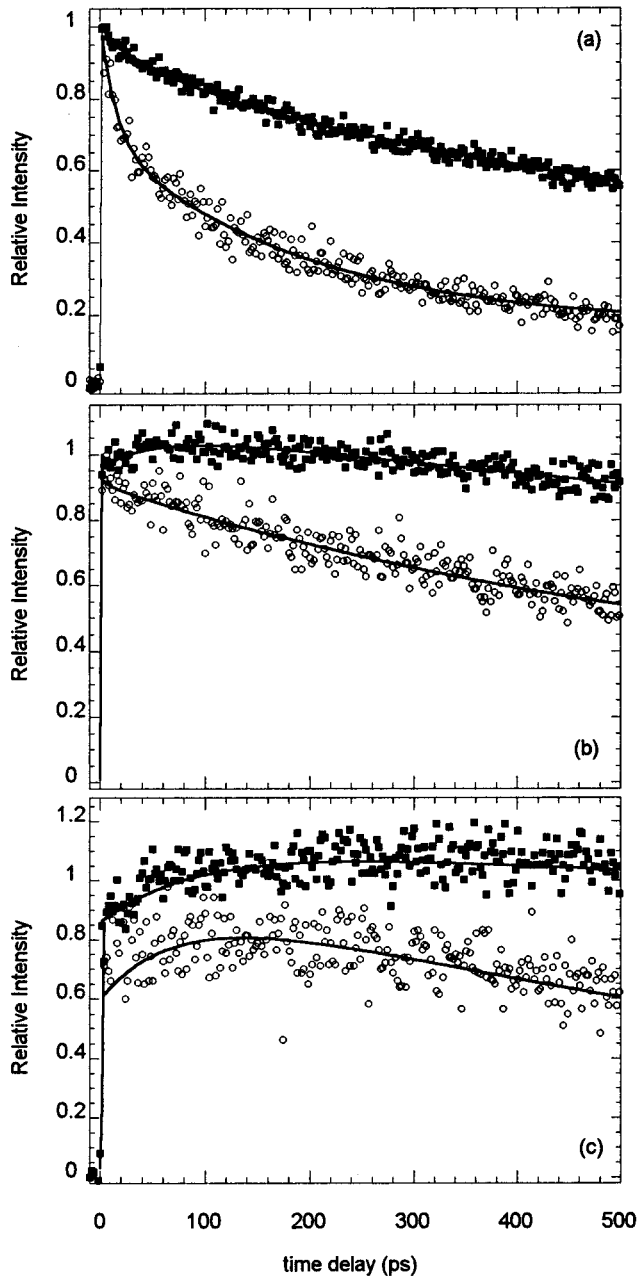

Figure 4. Fluorescence decays for Coumarin 343 in AOT (■) and NH_4−AOT (○) reverse micelles, $w_0 = 1.7$, at (a) 440 nm, (b) 480 nm, and (c) 520 nm. Signals in part c are offset to clarify the difference.

are all dominated by a 1.3-ns component.[36] The similarity between our measurement and the ESR measurement leads us to conclude that the dye molecule interacts strongly with the micellar interface and does not rotate freely within the water pool in AOT reverse micelles of any size.

Time-resolved fluorescence transients contrasting the dynamics of water in AOT and NH_4−AOT reverse micelles are shown at three wavelengths in Figure 4. We selected the displayed wavelengths, 440, 480, and 540 nm, because they bracket the peak of the equilibrium fluorescence and, therefore, reveal information about the dynamic fluorescence Stokes shift of the C343 molecule, hence the relative solvation dynamics. The time constants for the decays are reported in Table 1. The dynamics presented by these individual fluorescence decays agree well with the solvent correlation function of water in AOT reverse micelles of varying size we have recently observed.[36] Data obtained with higher time resolution revealed no dynamics occurring on a subpicosecond time scale. Unfortunately, the time resolution of the apparatus precludes observation of the inertial component.

Table 1. Normalized Amplitudes (a_i) and Time Constants for Multiexponential Fits of Fluorescence Decays of Coumarin 343 in AOT and NH_4−AOT Reverse Micelles, $w_0 = 1.7$, at Various Wavelengths (Time Constants Are Given in Picoseconds)

wavelength (nm)	a_1	τ_1	a_2	τ_2	a_3	τ_3
			NH_4−AOT Reverse Micelles			
440	0.33	15	0.52	192	0.17	4500[a]
480	0.02	8	0.57	570	0.34	4500[a]
540	−0.33[b]	65	1.0	1170		
			AOT Reverse Micelles			
440	0.12	77	0.86	1200		
480	−0.12[b]	51	0.96	2600		
540	−0.27[b]	92	0.88	4500		

[a] Value fixed for the lifetime of the dye. [b] A negative value for the amplitude indicates a rising rather than a decaying component.

In the AOT micelles with $w_0 = 1.7$, the fluorescence decay is dominated by a nanosecond component, nominally the lifetime of the dye. One other component is observed with a much smaller amplitude and time constant on the order of 50−100 ps. Motion on this time scale is most certainly not due to free water molecules. Most likely, motion on this time scale reflects collective motion of water and the micellar interface and is due to the fact that the water molecules that are strongly bound to the surfactant head group.

In contrast, the NH_4−AOT micelles show additional shorter time components to the observed fluorescence decays at all wavelengths investigated. The decay characteristics for C343 are faster in the NH_4−AOT reverse micelles than the AOT reverse micelles at all the reported wavelengths. The most dramatic departure of decay characteristics is evident at the shortest wavelength, 440 nm. Here the C343 fluorescence transient from the NH_4−AOT sample displays a substantial 15-ps component. In contrast, the shortest component of the fluorescence decay in the AOT sample is 77 ps and has approximately one-third the relative amplitude. This indicates that the water molecules in the interior of the NH_4−AOT reverse micelles can respond to the large excited-state dipole of C343 much more quickly than water molecules in the AOT reverse micelles.

One significant difference between the dynamics observed in the two different micellar environments is the multiexponentiality of the NH_4−AOT decays. In the AOT reverse micelles, the decays are dominated by a single long time relaxation component. In contrast, the fluorescence decays from the NH_4−AOT environment exhibits two or three relaxation components. This may be due to water residing in multiple, nonequivalent sites, some of which allow for significant water motion in the NH_4−AOT reverse micelles, whereas water in the AOT systems appears to reside in equivalent but immobilized sites.

We attribute the major difference in the solvation dynamics in the two micellar environments to cation−water interactions. The interaction of water with ions in solution has been previously shown to alter the observed solvation dynamics. We have measured the solvation dynamics of a strongly electrolytic aqueous solution.[36] Our measurements reveal that the faster ultrafast diffusive component of the water solvation dynamics remains unaffected by the sodium ions in the 1 M solution while

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the relaxation time of the slower diffusive component increases from approximately 0.6 ps in neat water to 1.3 ps in the aqueous electrolyte solution. Additional longer time components to the relaxation are also observed. We attribute the longer time scale for the second diffusive component and the additional longer relaxation components to water−ion interactions that effectively retard the water motion.

Molecular dynamics calculations have probed the influence of ions on water motion. In the presence of sodium ions, molecular dynamics calculations have shown decreased water mobility.[56,57] The reorientation time for water in contact with sodium ions is slowed by a factor of 6.[56] In comparison, motion of water in contact with ammonium ions remains essentially unchanged.[58] A molecular dynamics calculation of the water inside a model reverse micelle revealed that the motion of water in contact with interior sodium ions has significantly smaller amplitude and slower librational motion than bulk water.[59]

These results mirror solvation dynamics in nonaqueous ionic solutions that have been investigated both experimentally and theoretically. Experiments using TCSPC[60−63] measured solvation dynamics for a variety of electrolytic solutions over a range of ion concentrations. While details of their interpretations differ, both groups observed additional slow components to the dynamics that were absent from the pure solvents. In addition, while the solvation response was strongly influenced by the nature of the cations in solution, the solvation dynamics appeared to be relatively insensitive to the anions. Both analytical theoretical studies and simulations have been used to probe the effect of ions in solvation dynamics. Chandra and Patey[64] developed a microscopic theory of ion solvation in electrolyte solutions. They showed that the short time dynamics are governed by an inertial response very similar to that of the pure solvents. At long times, there is an additional feature not present in pure solvents that is postulated to arise from ion−ion relaxation. Chandra[65] has also made a detailed study of the solvation dynamics dependence on salt concentration. This work showed that the inertial component of the dynamics depends only weakly on the salt concentration, indicating that it arises from the solvent motion, while the long time decay depends strongly the amount of salt in the solution. This component also showed a dependence on the organization of the ion atmosphere. Employing molecular dynamics simulations, Neria and Nitzan modeled solvation dynamics in a model electrolytic solution.[66,67] Their simulations confirmed that the slow dynamical component observed in experiments arises from ion exchange interactions between the first solvation shell and the solute. They also reported a high correlation of the motion between the ions and the solvent molecules.

Because water interactions with ions can alter solvation dynamics in bulk, it follows that specific interactions of water molecules with various micellar components such as the countercation and sulfonate head group should affect the water mobility inside the reverse micelles. Various studies of AOT reversed micelles have shown that water molecules in contact with the AOT head group do not possess normal hydrogen-bonding characteristics.[12,13,15,16,38] FTIR spectroscopic studies have suggested that the first three to four water molecules interacting with an AOT molecule bridge the sulfonate and sodium ions because the sulfonate vibrational frequency shifts concomitantly with the addition of up to three to four water molecules.[15,68] Hydration beyond three to four water molecules per AOT shows no further shifting. Consequently, in AOT reverse micelles, three to four water molecules appear to be strongly bound to the micellar interface.

While the direct interaction of water with anions in solution has shown only minimal perturbation, the proposed bridging structure for water between the AOT sulfonate and countercation appears to have an enormous impact on water mobility. The decay times in the NH_4−AOT micelles are much faster than the regular AOT reverse micelles, but they are still substantially slower than the corresponding decays in bulk water.[27−29,36] Therefore, reductions of water motion in *either* the AOT or NH_4−AOT reverse micelles cannot be attributed solely to water−cation interactions.

In summary, we show that water motion is not restricted solely by the size of AOT reverse micelles. In fact, the sodium cation in small standard AOT reverse micelles appears key for eliminating most of the water motion, but only in conjunction with the rest of the micellar interior. In contrast, the interaction of the water with ammonium in NH_4−AOT reverse micelles is significantly weaker. This makes it possible for the water to move more than when it is complexed with sodium. The weakened interaction could also be the source of the multiexponentiality observed for the fluorescence decays. That is, the water interacting with the ammonium ions could reside in a variety of different sites leading to more or less immobilization. The results reported here also demonstrate that the sulfonate by itself is not particularly effective at restricting the water motion. Furthermore, these results show that specific interactions with the surfactant head group play a major role in impeding water motion. This work indicates that AOT reverse micelles may not be as good a mimic for biological membranes as previously proposed because much of the water dynamics is due to interactions of the water with the positive counterions rather than the restricted environment.

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