Cosurfactant Impact on Probe Molecule in Reverse Micelles

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A wide variety of probe molecules have been used to characterize the environment found within reverse micelles. This manuscript reports on results from steady-state and time-resolved spectroscopies of the probe molecule Coumarin 343. The steady-state spectra for the probe molecule in ternary and quaternary systems are nearly identical. However, the time-resolved studies clearly indicate substantial differences in the probe sensed by the probe molecule. Implications of these results for the interpretation of spectroscopy of probe molecules in confined media are discussed.

I. Introduction

Reverse micelles have recently garnered significant attention as model systems to explore the effects of confinement. Confined environments occur naturally in many biologically important systems as well as a range of physically interesting materials such as porous glasses. The beauty of the reverse micelle is that it is easily created, shows substantial stability, and provides a well-characterized nanoscopic water pool for a range of chemistries.

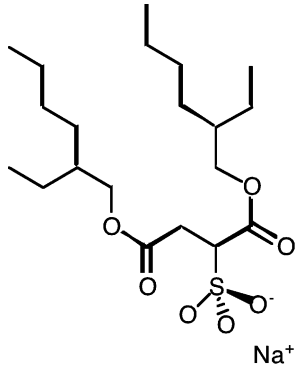
The branched double-chained surfactant Aerosol OT (AOT, sodium di(2-ethylhexyl) sulfoccinate), see Chart 1, has been the surfactant of choice for creating monodisperse reverse micelles and is therefore very well characterized.[1] The size of the reverse micelles is usually given by

$$w_0 = \frac{[H_2O]}{[AOT]} \quad (1)$$

AOT reverse micelles can be formed from $w_0 = 1$ up to $w_0 = 70$ in a range of nonpolar solvents. Many studies have shown that AOT reverse micelles formed in ternary solutions of water, AOT, and nonpolar solvent display a spherical form.[2−9] Because the water defines the volume while the AOT surfactant defines the surface area, for spherical reverse micelles, w_0 is directly proportional to the micellar radius.

One common method to interrogate the interior of a reverse micelle is to follow the spectroscopic characteristics of a probe molecule solubilized in the solution forming reverse micelles.[10] A solute can occupy a variety of locations in reverse micelles, for example in the oil phase, in the water pool, or near the interface of the reverse micelle.[11] Many research groups have employed spectroscopic studies to investigate the microenvironment inside reverse micelles, gauging the environment of the probe by its changing spectroscopy. For example, Correa et al. have estimated the intramicellar polarity through the spectroscopy of standard micropolarity probe molecules inside reverse micelles.[12] Gupta et al. report acidity of reverse micellar interiors based on the various spectral signatures of the indicator dye, acridine orange.[13] Recently, Panja and Chakravorti explored the solubilization of cinnamaldehyde in AOT reverse micelles, correlating its photophysical properties with its location.[14]

CHART 1



Dynamical measurements have also been used to probe the microenvironment of solute molecules in reverse micelles.[15−22] These studies have all found that the water inside the reverse micelles differs from bulk water; most notably, its relaxation is slower. The auramine O probe that Hasegawa et al. used to measure the microviscosity of AOT reverse micelles allowed them to gauge viscosity changes at the inner micellar interface.[20] They found that the microviscosity decreased rapidly for $w_0 < 10$ and then decreased more gradually for larger reverse micelles. Altamirano et al. investigated the fluorescence quenching of pyrene derivatives in AOT reverse micelles.[22] They found the fluorescence quenching increased as w_0 increased for probes located in the water pool, while fluorescence quenching at the interface was much lower than that of water. They attributed this result to the high microviscosity of the interface. Zhong et al. found that pseudohalide ions inside reverse micelles display longer vibrational relaxation times and rotate more slowly than in bulk aqueous solution.[23] Sarkar et al. measured nanosecond components of the water solvation motion.[16] These results indicate that water in AOT reverse micelles moves more slowly than bulk water.

Recently, we and others have utilized ultrafast solvation dynamics to study water in AOT reverse micelles.[15−18,24−26] Polar solvation dynamics is the measure of the polar solvent response to an instantaneous change of the charge distribution in a probe molecule. Solvation dynamics of a wide variety of bulk liquids have been well studied both experimentally and

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theoretically.[27−31] These studies have revealed two different types of solvent motion: an ultrafast time component attributed to an inertial solvent response (<100 fs) and a slower diffusive component (hundreds of femtoseconds to nanoseconds) due to the diffusive solvent motion in response to the probe's new charge distribution. In ternary AOT reverse micelles, there is a time component on the femtosecond time scale and another time component on the nanosecond time scale.[15,16]

One effective method to measure solvation dynamics utilizes time-resolved fluorescence-upconversion spectroscopy to monitor the time-dependent emission spectrum of a fluorescent probe. When the probe is excited, the solvent reorganizes to lower its free energy conforming to the change in charge distribution leading to an increasing red shift of its fluorescence. Measuring the time dependence of the emission frequency of the solute reveals the solvent's motion back to equilibrium and is quantified by the solvent response function (SRF),[27−30] $C(t)$, defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(t) - \nu(0)} \tag{2}$$

where $\nu(0)$, $\nu(t)$, and $\nu(\infty)$ represent the frequency of fluorescence intensity maximum immediately after excitation, at some time t after excitation, and a time sufficiently long enough to ensure the excited solvent configuration is at equilibrium. Thus, one can monitor the interior motion of the microemulsion over time.

In comparison with the extensive information that is available about ternary solutions forming AOT reverse micelles, there are relatively few studies of quaternary AOT micellar systems, especially where an alcohol serves as cosurfactant.[8,32−35] Bardez et al. investigated the OH stretching region of water and found that it is quite sensitive to the polarization effects of the polar headgroups of the micelle surface and the presence of alcohol to the micellar system.[33] Nazario et al. investigated the effect of nonionic cosurfactants on AOT reverse micellar interface and micelle/micelle interactions.[8,34] These studies found that the addition of alkanol to the micellar system increases the percolation temperature, has little affect on the hydrodynamic radius of the micelle, and decreases the fluidity of the interface. Finally, Plucinski et al. found that short-chain alkanols accelerate the mass transfer of phenylalanine into reverse micelles while long-chain alkanols inhibit this process.[35]

In the work presented here, we have explored how adding a cosurfactant to AOT reverse micelles impacts the information available from a probe molecule sequestered in the reverse micellar interior. We use steady-state absorption and fluorescence spectroscopy and time-resolved fluorescence upconversion spectroscopy. We have measured solvation dynamics in quaternary solutions forming AOT reverse micelles and contrast the results with solvation studies in ternary solutions forming AOT reverse micelles. Through these experiments, we determine the effect the addition of a cosurfactant has on the dynamics in reverse micelles. We also interpret the results comparing and contrasting the results from steady-state and time-resolved spectroscopic methods.

II. Experimental Methods

IIA. Sample Preparation. To prepare reverse micellar solutions, the water content of AOT (sodium bis(2-ethylhexyl)-sulfosuccinate, Aldrich) was first determined to be 0.43 water molecules per AOT headgroup with NMR. The AOT was then added to isooctane (Acros, ACS spectrophotometric grade) in concentrations ranging from 0.36 to 0.17 M to which water was added to achieve w_0 values of 5, 10, 15, and 40. 1-Heptanol (Fluka, 99% purity) was dried over molecular sieves and added to the solution. A ratio of 1:5 or 3:5 1-heptanol/AOT was used to ensure that the reverse micelles maintained a spherical form. Reverse micellar radii were measured using dynamic light scattering (DLS, DynaPro, Protein Solutions). Micellar sizes measured using DLS showed that, as w_0 increases, the hydrodynamic radius also increases. This confirms that the micellar solutions swell as water is added to the systems. Sizes measured for quaternary solutions forming reverse micelles were similar to those measured for ternary systems with the same water content.

The anionic dye Coumarin 343 (C343, Exciton) was used without further purification. The dye was added in excess to each of the samples and allowed to sit overnight. The samples were then sonicated for a half hour and filtered to remove any excess dye. Absorption spectra were collected using a Hewlett-Packard 8452A diode array spectrophotometer, and fluorescence spectra were collected using an ISA Fluorolog Fluorometer. From the absorption spectrum and information about AOT reverse micelle size and surface area,[1,8] we estimate that the concentration of dye in the sample was 75 μM, which corresponds to approximately one dye molecule per every 100 micelles. The probability of finding one dye molecule in one micelle is 1/100, given by the binomial distribution; the probability of finding two dye molecules in one micelle is $1/4950 = 2.0 \times 10^{-4}$.[36] Thus the measured spectroscopy and dynamics should arise from individual dye molecules rather than from aggregates.

IIB. Time-Resolved Studies. Time-resolved fluorescence Stokes shift experiments investigating solvation dynamics were performed via femtosecond fluorescence upconversion. The experimental apparatus is similar to that reported earlier;[15] only the laser used for the experiment differs. Briefly, the excitation source is a mode-locked Ti:sapphire laser (KM Labs) pumped by a CW intracavity doubled Nd/VO_4 laser (Verdi, Coherent) at 5 W. The Ti/sapphire laser produces an output pulse with a 60-fs duration (full width at half maximum, assuming a Gaussian pulse shape) at an 80-MHz repetition rate. The spectrum of the pulse is centered at 805 nm. The beam is frequency doubled in a 0.5-mm β-barium borate (BBO) crystal. The frequency-doubled beam is separated from the fundamental beam using a dielectric beam splitter. The frequency-doubled light traverses a half wave plate and focuses onto a 1-mm flow cell through which the sample circulates. A small portion of the forward fluorescence is collected and refocused onto a second 0.5-mm BBO crystal using an ellipsoidal mirror. The fluorescence is upconverted with the residual fundamental beam that has been sent through a variable optical delay. All solvation dynamics measurements are made with the excitation beam polarization at 54.6° with respect to the gate beam to eliminate effects from probe molecule rotation on the dynamics. The upconverted light is collimated, isolated from the gate and frequency-doubled beams with an iris, and focused through a UV-transmitting filter (340 nm, Opto-Sigma) into a 0.33-m single monochromator equipped with a 2400 groove/mm grating blazed at 400 nm. The instrument response is determined from the cross correlation of the excitation and gate pulses in the 0.5-mm upconversion crystal. The upconverted photons are detected using a photomultiplier tube at ambient temperature. A personal computer using LabVIEW collects a signal from a photon counter as a function of the optical delay between the excitation and gate pulses. Fluorescence upconversion measurements are obtained

by counting for 1 s at each delay. Scans are collected with high, medium, and low resolution in one scan, that is, 17-fs steps for the first 2.0 ps, followed by 200-fs steps for 58 ps, followed 2.5-ps steps for 453 ps, for a total of a 512 ps scan. Data are collected at 8−10 different wavelengths to monitor the entire fluorescence spectrum.

We have measured fluorescence lifetimes for the C343 dye in all environments probed using time-correlated single photon counting.[26] The lifetimes measured for the various systems are all within 10% of 3 ns, very similar to each other and essentially the same as the dye lifetime in bulk water.

IIC. Data Analysis. The spectral reconstruction method was used to determine the SRFs for water in various reverse micellar samples. This method is described in detail elsewhere.[30] The resulting time-resolved fluorescence upconversion decays were normalized to the steady-state spectrum and fit to multiexponential functions. Time-resolved fluorescence spectra were constructed from the multiexponential fits. The resulting spectra were fit to a log normal function to determine the peak maximum $\nu(t)$. The peak maximum was used to calculate the SRF as shown in eq 2. $\nu(\infty)$ was determined from the peak maximum of the steady-state spectrum. $\nu(0)$ is a hypothetical emission spectrum that would be observed if a molecule were to be promoted to its first excited state and allowed to relax vibrationally and emit before any nuclear solvent motion has occurred; the method used to calculate $\nu(0)$ is described in detail elsewhere.[37]

IID. Time-Resolved Fluorescence Anisotropy. Because time-resolved fluorescence anisotropy (TRFA) is an excellent method for tracking the degree and rate of rotation of the probe molecule,[38] we have employed this technique to gauge the environment of the dye molecule in the reverse micellar water pool. TRFA measurements were collected utilizing the same system that is used for time-resolved fluorescence upconversion measurements. To determine the anisotropy of the dye molecule, the polarization of the excitation beam is either set to be parallel or perpendicular with respect to the gate beam. The fluorescence is then mixed with the residual gate pulse as in our fluorescence-upconversion experiment. The anisotropy $r(t)$ was calculated via

$$r(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)} \tag{3}$$

Here $I_{||}(t)$ and $I_{\perp}(t)$ are the time-dependent intensities of the signal from parallel and perpendicular excitation, respectively. The rotation of the dye coupled to the micelle should yield a substantially longer rotational correlation time than free dye. From a simple Debye−Stokes−Einstein analysis[39]

$$\tau_{rot} = \frac{V_m \eta}{k_B T} \tag{4}$$

where V_m is the micellar volume, η is the viscosity of the supporting nonpolar phase, and T is the temperature, we estimate that the rotational correlation time for a reverse micelle with $w_0 = 5$ is approximately 600 ns. Because we collect $r(t)$ data only out to 500 ps, we cannot measure the micellar rotation but we can see if the dye rotation departs from its value in bulk solution indicating it is hindered.

III. Results

IIIA. Steady-State Spectroscopy. We have measured the steady-state absorption and fluorescence of C343 in a range of environments. Figure 1 displays absorption and fluorescence spectra of C343 in quaternary solutions forming AOT reverse micelles for varying hydration levels, w_0. Because the steady-state absorption spectra of C343 follow the same trends as the fluorescence spectra and because the time-resolved measurements are based on fluorescence, we show only the fluorescence spectra in subsequent figures displaying steady-state spectra. The C343 spectra shift to longer wavelengths as w_0 increases, similar to our results for ternary solutions containing AOT reverse micelles.[15] However, even in the reverse micelles with the highest water loading, $w_0 = 40$, C343 spectra in the reverse micelles never overlay the spectrum in bulk water. We have measured the C343 spectrum in a range of environments where the dye could be found in the microemulsion samples, including bulk nonpolar solvent and in an alcohol/nonpolar solvent mixture. These spectra are shown in Figure 2 along with the spectrum for C343 in quaternary reverse micelles with $w_0 = 40$ and in bulk water. The spectra for C343 in the nonpolar solvent and alcohol/nonpolar mixture clearly differ significantly from the spectra of the dye in the reverse micelles. It is clear from the differences in these spectra that the dye resides in the interior of reverse micelles in the quaternary solutions containing reverse micelles. Figure 3 contrasts the spectrum of C343 in quaternary and ternary solutions forming reverse micelles with high water loading, $w_0 = 40$, and bulk water. At this w_0 level,

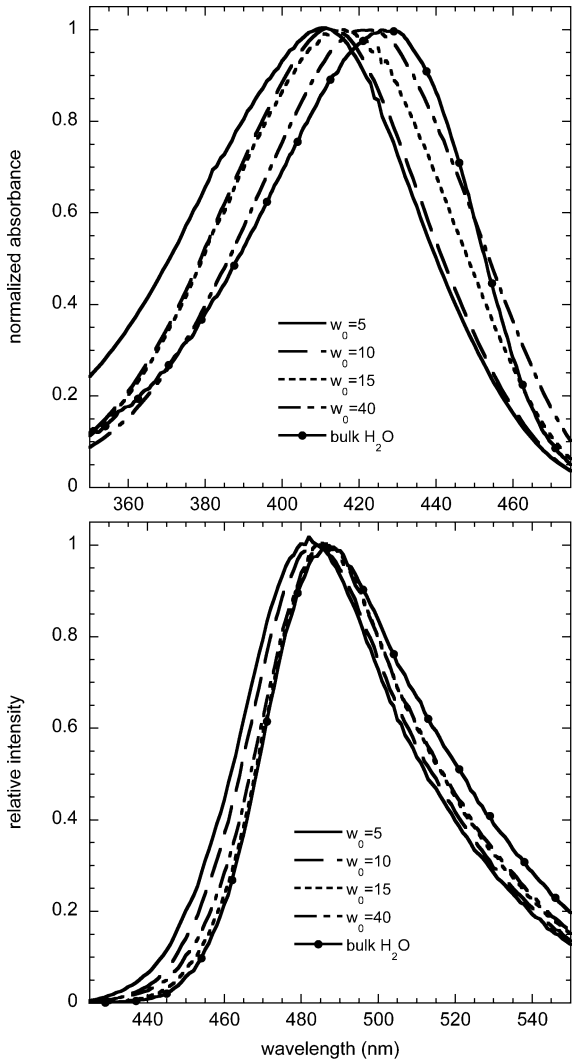

Figure 1. Steady-state absorption (a) and fluorescence (b) spectra of Coumarin 343 in water/1-heptanol/AOT/isooctane quaternary reverse micelles as a function of w_0.

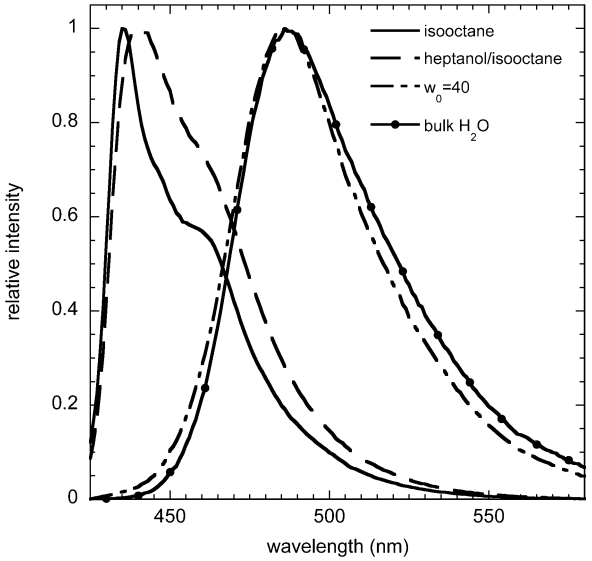

Figure 2. Steady-state fluorescence spectra of C343 in bulk isooctane (solid line), 1-heptanol-isooctane mixture (long-dashed line), ROH/AOT reverse micelles, $w_0 = 40$ (dashed line), and bulk water (dots and solid line).

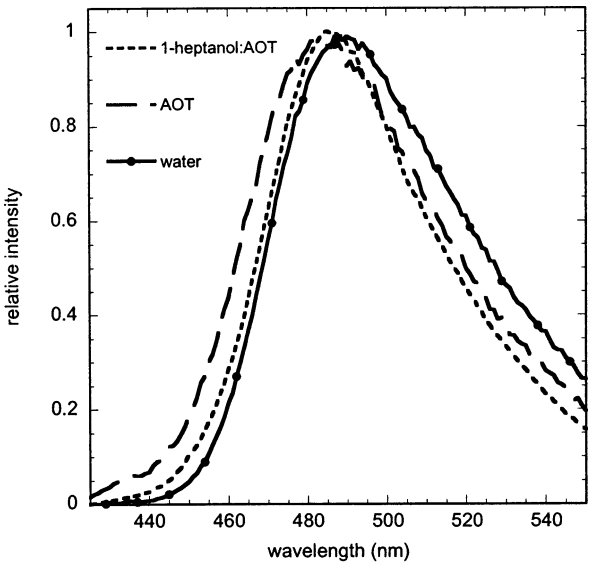

Figure 3. Steady-state fluorescence spectra of C343 in ternary AOT/isooctane/water $w_0 = 40$ (long-dashed line), quaternary AOT/1-heptanol/isooctane/water $w_0 = 40$ (dashed line), and bulk water (solid line).

there is a substantial water pool formed inside the reverse micelles. We estimate that there a reverse micelle of this size should contain more than 100 000 water molecules,[4] which should be large enough to behave like bulk water. Steady-state infrared spectroscopy indicate bulk-like hydrogen-bonding characteristics for the water inside reverse micelles with $w_0 > 10$,[40−47] but recent studies utilizing THz spectroscopy[48] have challenged the view that the reverse micellar water pool behaves bulk-like even at very high water loading. While they are similar, the C343 spectra in the reverse micelles peak at shorter wavelengths compared to the spectrum in bulk water. Also, the C343 spectrum in the ternary system peaks at shorter wavelength and is slightly narrower than the quaternary system. These results indicate that the alcohol cosurfactant, while present in relatively small proportion compared to the AOT surfactant, impacts the environment sensed by the C343 probe molecule.

We have increased the relative heptanol concentration in the sample to explore its effect on the C343 spectroscopy in reverse

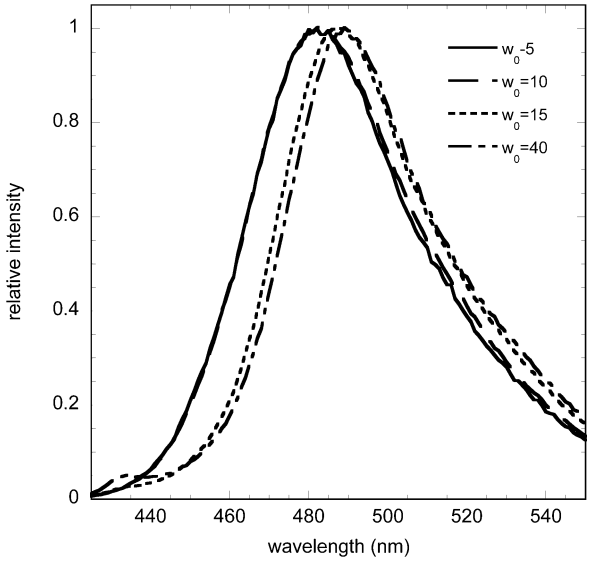

Figure 4. Steady-state fluorescence spectra of C343 in 1-heptanol/AOT 3:5 reverse micelles.

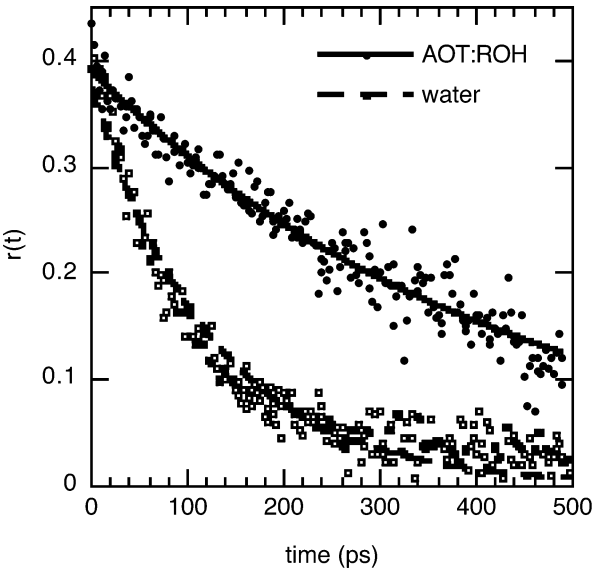

Figure 5. Time-resolved fluorescence anisotropy of C343 in AOT/1-heptanol/isooctane/water 1:5 $w_0 = 10$ (dots and solid line) and in bulk water (dots and dashed line). Symbols represent data while lines indicate fits.

micelles. Figure 4 shows the absorption spectra of C343 in quaternary reverse micelles where we increased the ratio of 1-heptanol/AOT from 1:5 to 3:5. Plotted on the same graph, these spectra would nearly overlay the spectra collected for lower 1:5 cosurfactant/surfactant ratio. The similarity in the steady-state spectra for C343 in both quaternary reverse micellar environments suggests that adding more alcohol to the system does not change the local environment sensed by the dye.

IIIB. Time-Resolved Fluorescence Anisotropy. In addition to steady-state spectroscopy, we can gauge the local environment sensed by the dye through its rotational motion. Time-resolved fluorescence anisotropy compares the decay of the fluorescence resulting from excitation with differing polarizations and, hence, can be used to measure rotational diffusion of a probe molecule as given in eq 3.[38] The anisotropy decay for the C343 dye in quaternary microemulsions is significantly slower than in bulk water, as shown in Figure 5. For C343 in bulk solution, $r(t)$ fits well to a single-exponential decay with a relaxation time 87 ps.[15] In contrast, the anisotropy decay for C343 in AOT/1-

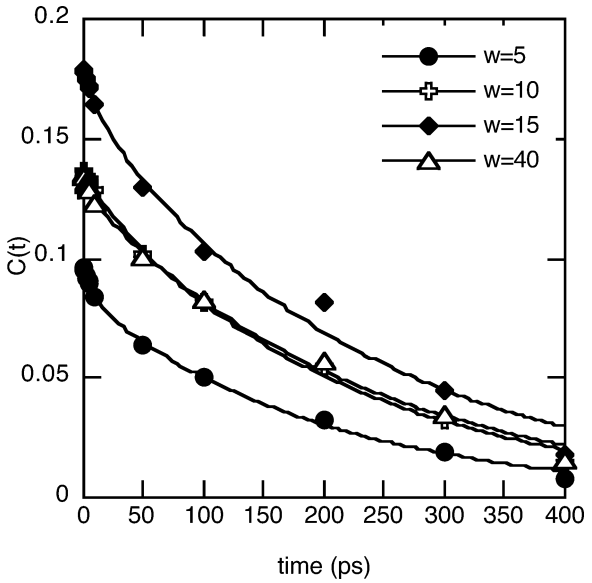

Figure 6. SRFs, $C(t)$, and fits to biexponential decays for AOT/1-heptanol 1:5 reverse micelles. Symbols are experimental data while lines represent a best fit to the data.

heptanol 1:5 $w_0 = 10$ fits to a single-exponential decay with a time constant of 430 ps plus a long time offset. Anisotropy decays we have measured in ternary solutions forming AOT reverse micelles with $w_0 \geq 7.5$ display biexponential behavior;[15] because the short time component of those decays was similar to the value for the dye in bulk water, we interpreted the results as indicative of the C343 dye residing in a range of locations from the interface to the water pool. The core of a spherical reverse micelle with a water content of $w_0 = 10$ should present some water with bulk-like characteristics.[49,50] The single 430-ps rotational correlation time measured for the quaternary reverse micelles here indicates that the dye environment is not like bulk water. As discussed in section IID, the overall rotation time for the reverse micelles should be substantially longer than what can be measured with these experiments. The long time offset displayed by the data most likely arises from rotation of the micelle.

IIIC. Solvation Dynamics. We have used our TRFSS measurements to create SRF from eq 2. The experimentally derived SRFs and fits to biexponential decays are shown as a function of w_0 in Figure 6. To demonstrate the impact that the alcohol cosurfactant has on the solvation dynamics in the reverse micelles, we plot solvent response functions, including the predicted inertial response from time zero analysis,[37] for both ternary and quaternary solutions forming AOT reverse micelles in Figure 7. Solvation relaxation times from multiexponential fits to the data are given in Table 1 along with those for bulk water for comparison. Excluding the data point obtained from time zero analysis, the SRFs for quaternary AOT micellar systems fit well to a biexponential decay with time components of approximately 10 and 200 ps. Excluding the inertial component, the SRFs for ternary AOT systems require a biexponential decay for adequate fitting with time components on the 200-fs and 3-ps time scale for all hydration levels as seen in Table 1.

To explore the role of the heptanol cosurfactant on the solvation dynamics, we measured the SRF in AOT reverse micelles with $w_0 = 5$ for differing alcohol fractions, that is, in systems with the AOT/alcohol ratio equal to 1:5 and 3:5. Similar to the solvation response in the quaternary reverse micelles with lower alcohol content, when we exclude the point from the time zero analysis, the data fit well to a biexponential decay; parameters for the fit are given in Table 1. The response seen in this system is quite similar to the time components of the solvent response in the quaternary AOT micellar systems with the lower cosurfactant/surfactant molar ratio of 1:5 (see Table 1). The addition of a cosurfactant to AOT micellar systems has an enormous effect on the observed solvation dynamics. Unlike ternary systems we have studied, the time-resolved fluorescence traces for quaternary solutions forming AOT micelles lack a

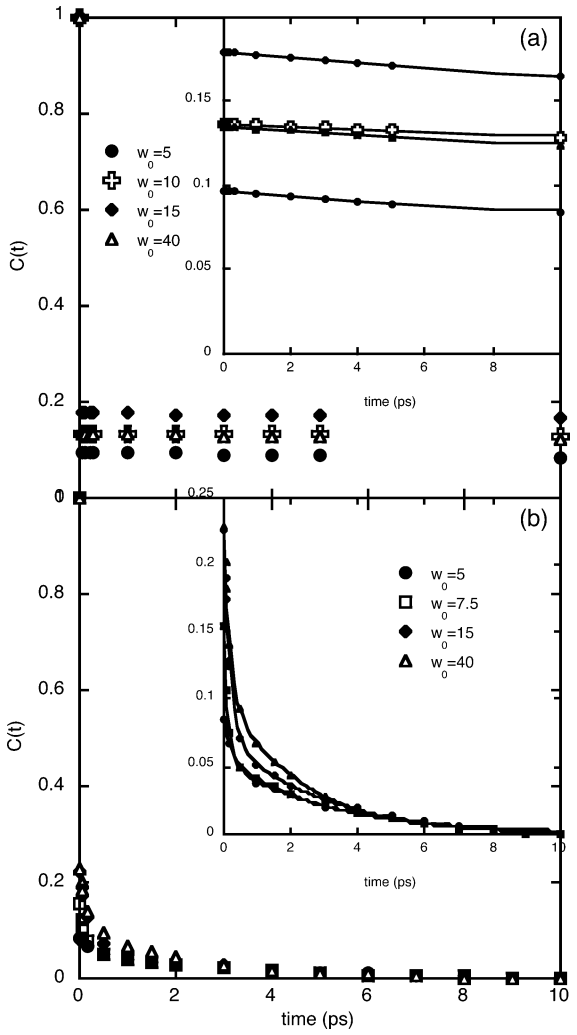

Figure 7. SRFs, $C(t)$, and biexponential fits for (a) AOT/1-heptanol/isooctane/water reverse micelles, AOT/ROH = 1:5, and (b) AOT/isooctane/water reverse micelles without cosurfactant. Insets show response without $t = 0$ point.

TABLE 1: Fit Parameters of the Ultrafast Components of the Solvent Correlation Functions for Water in Various Micellar Environments

1-heptanol/AOT ratio	w_0	Stokes shift (cm^{-1})	$C(t)$[a] a_1	τ_1 (ps)	a_2	τ_2 (ps)
1:5	5	3845	0.13	11	0.08	200
	10	2895	0.01	21	0.13	210
	15	2555	0.15	15	0.16	230
	40	2666	0.008	8	0.13	230
3:5	5	4022	0.001	8	0.05	190
no alcohol	5		0.04	0.25	0.05	3.3
	7.5		0.13	0.11	0.06	3.0
	15		0.18	0.17	0.07	2.8
	40		0.15	0.16	0.10	2.3

[a] We estimate error of 10% on all values.

decay component occurring on the hundreds of femtosecond to ones of picoseconds time scale.

While the transients from quaternary solutions containing reverse micelles lack diffusive relaxation on a sub-picosecond or picosecond time scale, we predict a large inertial response in the quaternary reverse micelles when we apply the time zero analysis. Thus, it appears that there is a significant portion of the solvent response that occurs on a time scale significantly shorter then we can measure. Reanalysis of ternary AOT micellar systems with time zero analysis reveals that the inertial component also comprises a significant part of the relaxation, approximately 90% of the total solvent response. Thus, even though we observe solvent motion on the 2-ps time scale in the ternary systems containing AOT micelles, we also miss a large portion of the solvent response occurring on the sub-100-fs time scale.

IV. Discussion

It is clear from the data presented above that the dynamics recorded by the C343 probe molecule in the quaternary solutions forming reverse micelles differ drastically from both ternary AOT reverse micelle systems and from bulk water despite the similarities in the steady-state spectra. Because the steady-state spectra shift as a function of water content, w_0, we expected that the TRFSS response would show a size-dependent trend similar to our results for ternary solutions containing reverse micelles. While we have observed changing solvation dynamics as a function of w_0 for ternary solutions forming AOT reverse micelles,[15] the solvation dynamics in the quaternary reverse micelles appear relatively insensitive to the amount of water solubilized in the micellar interior, as shown in Figure 6. In addition, in both ternary and quaternary reverse micellar systems, we predict an enormous ultrafast response, significantly higher than what is observed for bulk water. At the same time, the time scale for diffusive relaxation in the quaternary reverse micelles is substantially slower than it is for the ternary reverse micelles. These results strongly suggest that the alcohol cosurfactant present in the quaternary reverse micelles plays a substantial role in determining the solvation dynamics. However, the concentration of heptanol in the AOT micellar systems does not appear to have a strong impact of the solvation dynamics.

Because the alcohol cosurfactant affects the observed solvation dynamics, we considered the possibility that the solvation dynamics merely reflect bulk alcohol relaxation. Indeed, longitudinal relaxation times from dielectric relaxation studies suggest that the solvation dynamics observed in 1-heptanol should have a characteristic relaxation time of $\sim$150 ps.[30,51−53] Previous reports in the literature show that alcohol molecules added to solutions containing reverse micelles associate with the self-assembled structures rather than existing dispersed or as aggregates in the supporting nonpolar solvent, especially in systems such as the ones presented here where the overall concentration of alcohol in the reverse micellar solutions is quite low compared to other components, particularly the surfactant. In addition, the steady-state fluorescence spectrum of C343 in a mixture of heptanol dissolved in alkane solvent possesses a distinctly different shape from the steady-state spectra measured in samples containing reverse micelles, as shown in Figure 2. Hence, it is highly unlikely that the dynamics observed arise from solvation by the heptanol alone.

In another possible scenario, the heptanol molecules would aggregate in to "rafts" at the reverse micellar interface. In the smallest reverse micelles we measure, we estimate only 15 heptanol molecules per micelle. Aggregates of heptanol molecules in the reverse micellar interface would cause the micellar surface curvature to change leading to ellipsoidal rather than spherical droplets. We measure similar particle sizes and polydispersities for reverse micelles in ternary and quaternary solutions of a given w_0 value, which shows that the added heptanol does not cause significant changes in micelle shape. Thus, it is unlikely that the heptanol cosurfactant present in these reverse micelles exists aggregated in the interface. We are confident that the long time relaxation component observed for the reverse micelles formed in quaternary systems is not due to solvation by bulk heptanol or by heptanol aggregates in the micellar interface.

Because the diffusive relaxation observed does not vary substantially from sample to sample, and shows essentially no trend with the water content inside the reverse micelles, one possible way that the addition of alcohol could influence the measured solvation dynamics would be by facilitating the C343 dye probe to partition into the reverse micellar interface. This should provide a reasonably similar environment for the dye regardless of the w_0 value. If the dye were embedded in the interface, the environment experienced by the dye in the interface could reflect ordered alkyl chains and thus could be similar to the environment present in an ordered liquid crystal. Rau et al. report solvation dynamics experiments performed in alkylcyanobiphenyl liquid crystal solutions.[54] They observe multiple time scales for the solvation dynamics, ranging from tens of picoseconds to nanoseconds. They attribute the dynamics occurring on the tens of picoseconds time scale as characteristic of the liquid crystalline interactions. Saielli et al. measured solvation dynamics in a nematic liquid crystal mixture.[55] Their results suggest that the local environment rather than long-range order dominates the observed dynamics. The results presented here do not resemble results of either liquid crystal work, suggesting that the environment sensed by the C343 dye probe is not like a liquid crystal. Addition of an alkanol such as heptanol to AOT reverse micelles has been shown to increase the rigidity of the interface.[8,35] Researchers hypothesize that this results from the alcohol partitioning into the alkyl chain region, increasing the curvature of the interface. Increased interfacial rigidity should reduce the propensity for the dye to intercalate into the interfacial region. Thus, it seems unlikely that the dye resides intercalated into the micellar interface.

The overall fluorescence Stokes shift can also reveal information about the location of the probe molecule. Stokes shifts are given in Table 1. There is a large difference in the Stokes shift in the smallest reverse micelles, $w_0 = 5$, compared to the larger ones. For the larger reverse micelles, $w_0 = 10$, 15, and 40, the Stokes shifts are all similar. Thus, the Stokes shifts observed for the larger reverse micelles follows the same trend seen for the dynamics.

Interfacial microviscosity can be estimated from time-resolved fluorescence anisotropy. Our results from time-resolved fluorescence anisotropy of C343 in water/AOT/heptanol/isooctane reverse micellar systems yield a single rotational correlation time with a time constant significantly longer than what we measure in bulk aqueous solution.[15] Our previous measurements of time-resolved fluorescence anisotropy in ternary solutions forming AOT reverse micelles showed a bimodal response for the dye, with one component similar in time scale to the dye in bulk solution and one that was much slower. We interpreted these data as suggesting the dye resided in a range of locations within the reverse micelles, sometimes at the inner interface (but not embedded) and sometimes diving into the micellar core.[15] In

contrast, the anisotropy decay we observe in the quaternary solutions forming AOT reverse micelles displays only a single, long time component and a baseline offset. Furthermore, the decay time matches neither the rotation time for C343 in water nor the rotation time of the reverse micelle. This suggests that the rotation of the dye molecule is hindered. By comparison of the results for the rotation of C343 in bulk water and use of the Debye−Stokes−Einstein treatment, eq 4, we predict that the local viscosity sensed by the dye is nearly 5 times that of bulk water. Andrade et al. suggest that microviscosity inside the reverse micelles is 6−9 times lower than in bulk water.[56]

Various solvation dynamics studies have considered the relation of solvent viscosity and solvation dynamics or dielectric friction. Recently, researchers measuring polar solvation dynamics in ionic liquid solutions have found a direct connection between viscosity and the observed dynamics.[57−62] In particular, Maroncelli and co-workers observe a slower component of the solvation dynamics relaxing on the hundreds of picoseconds time scale that tracks the viscosity of the ionic solution and a very fast component, shorter than 5 ps, that is too fast for them to resolve.[57,58] They interpret the slow component of the observed relaxation as due to translational motion of molecules in the ionic liquid and the fast, unresolvable motion as due to small local fluctuations that effectively relax the local environment. The slow response we observe in our reverse micelles that is interdependent of micelle water content could reflect increased solvent viscosity at the micellar interface. Abuin et al. measured the impact of adding alcohol cosurfactants to AOT reverse micelles through the spectroscopy of several molecular probes.[63] They observed decreasing fluorescence lifetimes for fluorescent probe molecules solubilized in AOT when alcohol cosurfactants, such as hexanol, were added to the reverse micelles. Comparisons of micropolarity and fluorescence lifetime data led Abuin et al. to suggest that the interfacial microviscosity increases upon alcohol cosurfactant addition to the AOT reverse micelles.[63] The similarity of the dynamics observed in ionic liquids to what we observe for solvation dynamics in the quaternary solutions containing reverse micelles, evidence of increased interfacial viscosity from other experiments on reverse micelles, and our own time-resolved fluorescence anisotropy experiments lead us to hypothesize that the solvation dynamics reported by the C343 probe molecule reflects a viscous environment that has characteristics similar to ionic liquids. Given the high concentration of ion pairs expected at the interface, it is not surprising that the interfacial region resembles an ionic liquid. At the same time, it is interesting that adding heptanol to the interfacial region appears to impact the interfacial viscosity and also causes the probe molecule to reside in this region of increased viscosity. Garcia-Rio et al. report that addition of alkanol to the interface causes the interface to become more hydrophobic as alkanol molecules replace water molecules at the interface.[64] For our solvation dynamics experiments, this should create a more favorable environment for C343.

In the measurements reported here, we miss a large portion of the solvation dynamics because our apparatus cannot resolve dynamics on a time scale shorter than 100 fs. We predict a substantial portion of the relaxation occurs on this time scale. Ultrafast relaxation at lipid interfaces has been observed in other systems. Most specifically, Bursing et al. observed a substantial 9-fs component to the relaxation in three-pulse photon−echo spectroscopy measurements at the surface of phospholipid vesicles.[65] Apparently, small amplitude, very fast fluctuations present at the interface are sufficient to relax the nonequilibrium milieu created when the probe molecule is promoted to the excited state.

Finally, these studies indicate the importance of multiple measurements to characterize a system. To assess the environment of a probe molecule in a heterogeneous system, coupling steady-state experiments with dynamical studies can help to fully understand the local environment of a probe molecule. A perusal of our steady-state spectroscopy data alone might cause one to conclude that the dye molecule migrates into the free water pool as the hydration level increases. This hypothesis is further supported by the IR spectroscopic results by Bardez et al. that show three distinct types of water in quaternary solutions forming AOT reverse micelles for which the probe molecule to reside.[33] In addition, our steady-state spectroscopy results suggest that there is a change in micropolarity of the dye molecule as a function of w_0 in direct opposition to the dynamical results that show that the micropolarity as well as the microviscosity of the dye environment does not change with water loading.

V. Conclusion

These experiments reported here show how the addition of heptanol to AOT reverse micelles significantly slows solvent reorganization in the reverse micelles, suggesting that the probe molecule, C343, is located in a highly viscous environment at the reverse micellar interface regardless of w_0. In addition, the solvation dynamics in these quaternary systems exhibit no bulk-like water diffusive relaxation as previously observed in the ternary systems.[15] While steady-state absorption and fluorescence spectra of C343 in the quaternary solutions forming AOT reverse micelles show similar red shifts as a function of increasing w_0 as do the steady-state spectra of C343 in the ternary solutions forming AOT reverse micelles, dynamical measurements clearly show that the dye molecule samples significantly different environments in the related microemulsion systems. Hence, steady-state spectroscopy alone may not be sufficient when using a molecule to probe properties in these heterogeneous systems.

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