Novel Reverse Micelles Partitioning Nonaqueous Polar Solvents in a Hydrocarbon Continuous Phase

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Reverse microemulsions have been characterized in isooctane and decane using the surfactant Aerosol-OT (AOT) and the polar solvents formamide, ethylene glycol, acetonitrile, methanol, *N*,*N*-dimethylformamide, and 1,2-propanediol. Dynamic light scattering (DLS) experiments show that reverse micelles form in these solutions. The DLS data and steady-state absorption spectra of Coumarin 343 in these solutions reveal that the character of these reverse micelles depends partially upon the solubility of the polar solvent in the hydrocarbon. For formamide and ethylene glycol, which are highly immiscible in the hydrocarbon solvents, changes in micellar size occur for variations in the volume fraction ϕ of the polar solvent and surfactant in the continuous phase as well as for the traditional changes in *w*. These reverse micelles with $w = 1.1$ and $\phi = 0.006-0.051$ exhibit diameters ranging from 5.0 to 26.1 nm. For the solvents acetonitrile, methanol, *N*,*N*-dimethylformamide, and 1,2-propanediol, which are slightly miscible with isooctane and decane, micelles form and solubilize some of the polar solvent. However, these solutions do not support micelles with large diameters. Reverse micelles with mole fractions of polar solvent to AOT, *w*, ranging from 1.1 to 5 exhibit diameters ranging from 2.7 to 9.0 nm, respectively.

Introduction

Reverse micelles have attracted significant attention in the recent past. Their utility has been demonstrated in various chemical systems. Reverse micelles are used as size-controlling microreactors for a variety of aqueous chemical reactions.[1–3] They have been shown to stabilize species that are insoluble in nonpolar phases. They facilitate reactions by stabilizing reactants, especially radicals, in nonpolar media and by increasing the local concentration of reactants prior to reaction.[1–4] These systems are also excellent models for biological membranes and compartmentalization.[5] In general, reverse micelles are formed from a surfactant or surfactant and cosurfactant pair dissolved in a nonpolar phase. Often water is solubilized inside the micelle which can swell the micelles to many times their empty size.[6]

The distinction between reverse micelles and reverse microemulsions is often ill-defined. For this work, we use the convention given by De and Maitra[6] defining reverse microemulsions as solutions containing a ternary or higher order mixture that display a single phase. These microemulsions can exhibit various structures, for example, discrete spherical droplets, interconnected bicontinuous water channels, liquid crystals, etc. We define reverse micelles as noncontinuous, noninteracting aggregates of surfactant molecules that delineate a polar phase from a nonpolar phase.

Much is known about reverse micelles solubilizing water.[1–3] However, many reactions that one might want to scale down to the microreactor scale occur in nonaqueous polar solvents. Some nonaqueous, highly polar solvents used commonly in chemistry include acetonitrile, methanol, and *N*,*N*-dimethylformamide (DMF). While these solvents all show miscibility gaps with nonpolar solvents,[7] there have been no reports of reverse micelles, as defined above, created using these solvents as the polar phase. For many chemical reactions, water is not the

solvent of choice as the medium in which the reaction occurs. An attractive alternative for reactions in restricted geometries would be to isolate solvents other than water inside the micelles.

A common surfactant used to create reverse micelles is Aerosol-OT (AOT). The characteristics of AOT reverse micelles in nonpolar solvents have been the focus of many studies.[6] AOT is used in part because the micelles formed with this surfactant can solubilize a large quantity of water in a nonpolar solvent. While there are entire volumes describing microemulsions of nonpolar solvents, water, and AOT, there exist only a few references to microemulsions where the polar phase is something other than water.[8–16] Polar solvents used include formamide, DMF, dimethylacetamide, ethylene glycol, propylene glycol, and glycerol. These few studies report only information about phase behavior and reactions occurring in the microheterogeneous environment; none of these reports include information about reverse micelle formation, micellar size, or characteristics of the micelles.

In a handful of references, researchers have invoked nonaqueous reverse microemulsions to affect chemistry in polar nonaqueous but restricted environments. In particular, organic reactions such as the Diels–Alder addition of methyl acrylate to cyclopentadiene have been carried out in reverse microemulsions of formamide/cetyltrimethylammonium bromide (CTAB)–1-butanol/isooctane.[14,17] Mukherjee et al.[18] measured alkaline hydrolysis of crystal violet in aqueous and nonaqueous ethylene glycol microemulsions with AOT and isooctane. In this work, the rate of the reaction the ethylene glycol microemulsion exceeded any of the aqueous environments and was postulated to result from a better stabilized activated state of the reaction. Zinc oxide and $BaFe_{12}O_{19}$ nanoclusters have been formed in dry ethanol/metal bis(2-ethylhexyl) sulfosuccinate/isooctane reverse microemulsions.[19,20] In all these studies, the alternative polar solvents facilitated the desired chemistry. However, the characteristics of the microemulsions responsible for the chemistry were not reported or apparently known. With improved understanding of this type of heterogeneous environ-

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ment, the possibilities for new chemistry are endless. The work presented here demonstrates the nature of these milieus, particularly focusing on creating reverse micellar environments, and provides the framework for developing new chemical reaction media.

We have made reverse microemulsions in isooctane (i-C_8H_{18}) and decane using AOT as a surfactant solubilizing several different polar solvents. Dynamic light scattering measurements confirm that these solutions contain reverse micelles. We report the first size characterization for these novel reverse micelles. Direct comparisons for micelles solubilizing water are made. This work also represents the first report of AOT microemulsions that use acetonitrile or methanol as the polar phase.

Experimental Methods

Reverse microemulsions were made with isooctane (2,2,4-trimethylpentane, HPLC grade, Aldrich) or decane (Aldrich, HPLC grade), Aerosol-OT (sodium bis(ethylhexyl) sulfosuccinate, Aldrich) and one of several polar solvents: acetonitrile, methanol, formamide (FA), N,N-dimethylformamide (DMF), ethylene glycol (EG), and 1,2-propanediol (propylene glycol, PG) (all from Aldrich). All solvents were of the highest grade available (spectral or HPLC grade) and were used without further purification. Micelles solubilizing water used filtered, deionized Milli-Q water (18.2 MΩ/cm). AOT of the highest grade available was also used without further purification. Electrospray mass spectrometry of the AOT revealed no contamination by other species. However, the AOT is not completely dry; a Karl Fisher titration revealed 0.617 wt % water. The laser dye Coumarin 343 (C343) was purchased from Exciton and used without further purification. Solvents were filtered twice with 100 nm Teflon filters prior to sample preparation, and samples were filtered twice with a 100 nm Teflon filter prior to light scattering measurements. All glassware used to handle and store the samples was acid washed, rinsed with distilled water three times, then rinsed three times with high-purity water (Milli-Q filtered, 18.2 MΩ/cm), and thoroughly dried.

Microemulsions and micellar samples were prepared from a stock solution of AOT in the hydrocarbon solvents. Samples with various volume fractions were probed. The volume fraction of the sample is given by

$$\phi = \frac{V_{polar} + V_s c(\nu_{AOT} + 0.15\nu_{H_2O})}{V_{total}} \quad (1)$$

where V_{polar} is the volume of the polar solvent, V_s is the volume of the AOT stock solution in the hydrocarbon solvent, c is the concentration of the stock solution, ν_{AOT} is the volume of one AOT molecule, and V_{total} is the total volume of the solution. To account for the fact that the AOT is not completely dry, we have included $0.15\nu_{H_2O}$, the volume of 0.15 water molecules for each AOT molecule, as indicated by the Karl Fisher titration, in the calculation of the volume fraction.

Solubilities of the polar solvents in the nonpolar phases were measured by adding 0.01 mL aliquots of the polar solvent into the nonpolar phase, shaking or ultrasonicating, and looking for phase separation or turbidity. The solubility of a given solvent pair was consistent with similar solvent pairs in hexane or heptane, as reported in ref 7. All solubility measurements were carried out at ambient temperature, 21 ± 1 °C.

Samples yielding microemulsions were determined by visually inspecting of the ternary mixtures for phase separation and sample turbidity. Tests for microemulsion formation were all done at ambient temperature, 21 ± 1 °C. The reverse microemulsions were probed for regions displaying micelles

TABLE 1: Solvent Combinations Yielding Microemulsions; Measurements Taken at Room Temperature (21 ± 1 °C)

continuous phase (1)	polar solvent (2)	solubility of 2 in 1 (mole fraction)
2,2,4-trimethylpentane	acetonitrile	0.08
	methanol	0.21
	N,N-dimethylformamide	0.081
	formamide	<0.0002
	ethylene glycol	0.0004
	1,2-propanediol	0.004
	water[a]	0.00059
decane	acetonitrile	0.03
	methanol	0.09
	N,N-dimethylformamide	0.07

[a] From ref 7 at 20 °C.

using dynamic light scattering (DLS). Measurements were made with a Coulter N4Plus particle sizer. The light source in the N4Plus was a 10 mW HeNe laser. This unit could collect data at multiple angles ranging from 10° to 90°. The instrument was calibrated before and during the course of experiments using several different size standards. Measurements of 19 ± 1.5 nm diameter polystyrene spheres in water (Duke Scientific) yielded a diameter of 18.4 ± 0.7 nm, and 38 nm poly(vinyltoluene) spheres in water (Coulter) yielded 38.4 ± 0.4 nm. Also, size measurements of AOT micelles containing water reproduced literature values well.[21−25] Multiple samples at each size and volume fraction were made, and eight independent size measurements were made for each individual sample. Most measurements were made at a 28° scattering angle though other angles yielded the same size results. We measured particle sizes for solutions at various volume fractions ranging from 0.63 to 41%. The temperature of the samples was held at a constant 21 °C in the spectrometer.

For samples revealing reverse micelles, we measured the characteristic absorption spectra of an anionic laser dye, Coumarin 343 (C343), dissolved in the solution. Absorption spectra were collected with a Cary 2400 UV/vis/IR spectrophotometer. Most of the spectra were collected with 1 cm path length cuvettes; occasionally, the absorbance of a sample was large enough to require shorter pathlength cuvettes, 1 or 2 mm, for accurate measurement.

Results and Discussion

We have investigated reverse microemulsions using AOT and isooctane or decane solubilizing various nonaqueous polar solvents and water for comparison. Solutions yielding microemulsions are listed in Table 1 along with the solubility of the polar solvent in the hydrocarbon. Most of the microemulsions were prepared at concentrations where the solvent pairs normally phase separate, but some were also probed at lower concentrations. In one case, we found that FA/AOT/i-C_8H_{18} formed microemulsions, that is, ternary mixtures yielding a single phase, at concentrations conflicting with published reports.[15]

For some of the samples, notably acetonitrile, methanol, and DMF, the solvents were somewhat soluble in the nonpolar phase. As shown in Table 1, these solvents were determined to be significantly more soluble in nonpolar solvents like i-C_8H_{18} than water.[7] For these solvents, microemulsions were prepared using i-C_8H_{18} and decane at concentrations that were high enough to display phase separation in the absence of the surfactant. Addition of the surfactant to the solutions changed the sample from two separate phases to a single phase. We prepared microemulsions in both i-C_8H_{18} and in decane, because all the polar solvents probed are less soluble in decane as shown in Table 1.[7]

SCHEME 1

C343
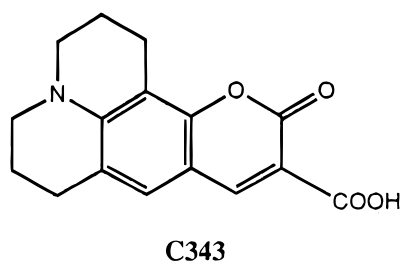
We have used DLS to detect the presence of reverse micelles and to measure their size. Not all the microemulsions could be measured with the apparatus available because some samples did not scatter strongly enough. Although all the samples measured were weak scatterers, reproducible results were routinely obtained. DLS measurements yielded similar sizes for a variety of detection angles. This indicates that the shape of the particles detected is relatively spherical. Initially, we characterized the size of the micelles using the volume to surface area ratio,

$$w = [\text{polar solvent}]/[\text{AOT}] \qquad (2)$$

commonly used for micelles containing water. However, as discussed below, w may not be a good measure of micellar size in the nonaqueous solutions.

The micelles are also characterized by the absorption spectra of the probe molecule Coumarin 343 (C343) in various reverse micellar solutions. The structure of the dye is shown in Scheme 1. The absorption spectrum of the dye is sensitive to its environment; hence, we discuss its spectroscopy in various bulk environments before showing its behavior in the micelles. UV−vis absorption spectra of C343 in bulk water methanol, acetonitrile, FA, DMF, EG, and PG are shown in Figure 1a,b. We have measured the dye's pK_a to be ∼4.5. Therefore, in aqueous solution, the dye exists in its anionic form. At acidic pH, the peak of the absorption spectrum shifts approximately 20 nm to longer wavelength than at neutral or basic pH. Previous reports have shown that, in basic methanol and ethanol solution, the peak of the absorption spectrum shifts to significantly higher energy[26,27] and attribute the shift to deprotonation and anion formation. While other coumarin dyes are quite soluble in nonpolar solvents,[28] the carboxylic acid group on the dye molecule renders it quite insoluble in hydrocarbon solvents. This is evident from its absorption spectrum in i-C_8H_{18}. When i-C_8H_{18} is saturated with C343 and filtered to remove the excess undissolved dye, the absorption spectrum shows the complete absence of spectral features associated with the dye. When any of these polar solvents that are sparingly soluble in alkane solvents is added to neat i-C_8H_{18}, a small amount of the dye dissolves into the solution. The resulting absorption spectrum, shown in Figure 1c for FA in i-C_8H_{18}, is much narrower than in a bulk FA and displays coarse vibrational structure on the high-energy side of the spectrum.

Adding AOT above the critical micelle concentration, that is, the concentration at which micelles begin to form, to the hydrocarbon solvents also brings the dye into the solution. However, as shown in Figure 2 for acetonitrile/AOT/i-C_8H_{18}, the absorption spectrum in the i-C_8H_{18}/AOT solution is broad and blue-shifted compared to the case of C343 in bulk solvents. The spectrum peaks in the vicinity of the peak of the anionic form of the dye discussed in refs 21 and 22. We believe the polar head groups on the AOT molecules lead the micellar interior to be basic and cause deprotonation of the dye. Thus, when C343 is absorbed into the i-C_8H_{18}/AOT solution, the dye
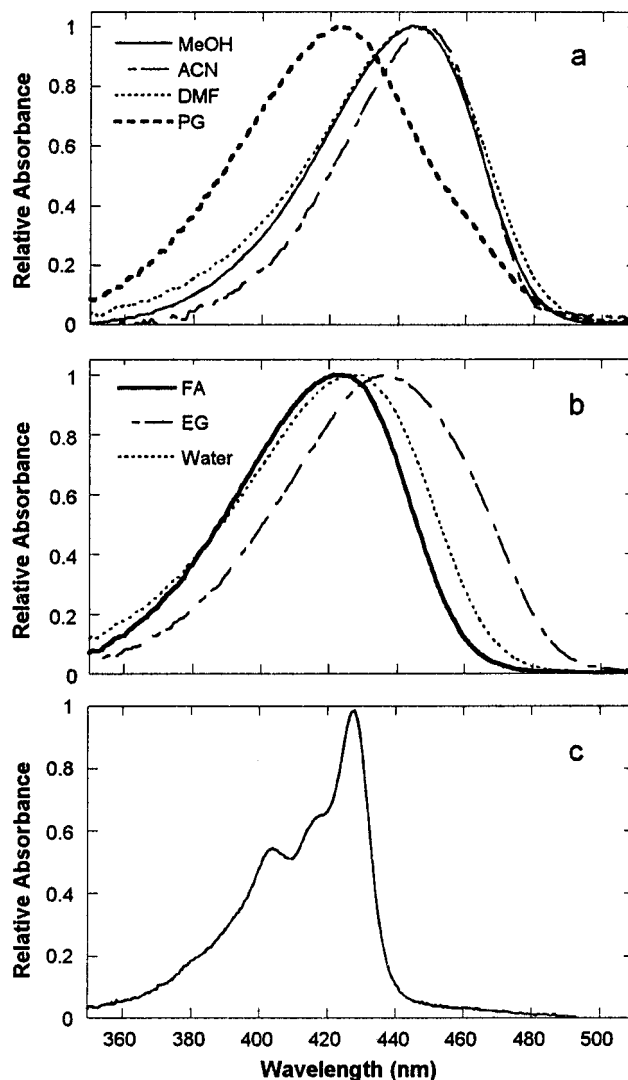
Figure 1. Absorption spectra of Coumarin 343 in (a) acetonitrile, methanol, 1,2-propanediol, and dimethylformamide, (b) formamide, ethylene glycol, and water, and (c) 0.001 mole fraction formamide in isooctane.
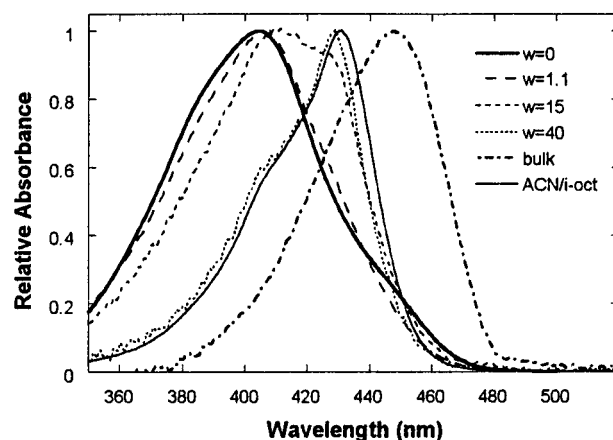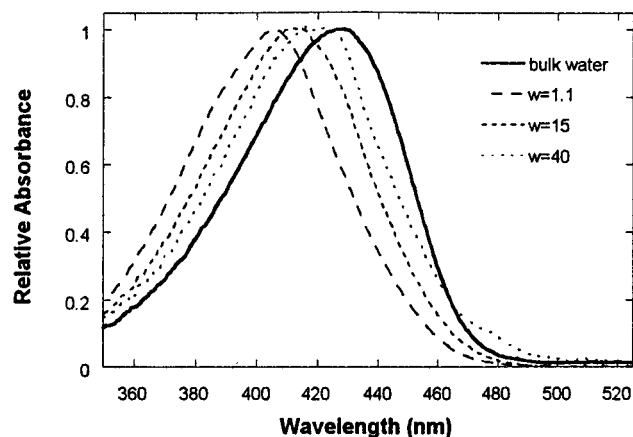

Figure 2. Absorption spectra of Coumarin 343 in "empty" micelles, acetonitrile/AOT/isooctane micelles, acetonitrile in isooctane, and bulk acetonitrile.

molecules are solubilized inside the micelles and exist in the anionic form. Therefore, it is easy to distinguish the dye molecules that are solubilized within the micelles from those outside and to compare how much of the polar solvent is solubilized in the micelles and how much is merely dissolved in the nonpolar phase.

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TABLE 2: Size and Volume Fraction ϕ for Water/AOT/Isoctane Reverse Micelles

w	ϕ	diameter (nm)	w	ϕ	diameter (nm)
1.1	0.01	3.2 ± 0.4	15	0.069	10.6 ± 0.4
5	0.22	9.7 ± 0.2	40	0.075	20.6 ± 0.4
10	0.14	10.0 ± 0.1			

Figure 3. Absorption spectra of Coumarin 343 in a range of water/AOT/isooctane reverse micelles from $w = 1.1$ to 40. The spectrum of C343 in pure water is also included.

The DLS data and spectral differences allow us to characterize the nature of the microemulsion solutions and the micelles in the solutions. We have found that the character of reverse micelles is partially dependent upon the solubility of the polar solvent in the hydrocarbon phase. This leads to a natural separation between the results for the solvents that are highly immiscible (FA and EG) and those that are slightly miscible with the nonpolar phase (methanol, acetonitrile, DMF, and PG) as shown in Table 1. We first discuss our results for aqueous micelles and then follow with results for slightly miscible and highly immiscible solvents in the following sections.

Micelles Solubilizing Water. To ensure our capability for making and characterizing reverse micelles solubilizing nonaqueous polar solvents, we created and characterized a range of aqueous micellar environments. Using DLS, we measured the sizes of these micelles; results are shown in Table 2. Our size results agree well with results reported in the literature.[21−24,29]

We have also characterized the micelles solubilizing water using the spectroscopy of the probe molecule, C343. Absorption spectra are shown in Figure 3. These spectra show a range of absorption maxima from small to large sized micelles. All the micellar spectra peak at wavelengths blue of the peak in aqueous solution. The lack of an obvious isosbestic point in the spectra indicates that the spectral shifting arises from a changing environment rather than from competition between two different forms of the dye, such as the protonated and deprotonated form. The dye exists in its anionic form in all the micelles.

Slightly Miscible Solvents. For the polar solvents methanol, acetonitrile, DMF, and PG, we have observed reverse micelles in solution in equilibrium with a polar solvent dissolved in the continuous phase. Size data from DLS measurements are shown in Table 3. The reversed micelles observed in i-C_8H_{18} and decane maintained a small size even as w was increased. Representative absorption spectra of C343 in AOT reverse micelles in i-C_8H_{18} with acetonitrile as the polar solvent are shown in Figure 2. These spectra show that at small values of w the polar solvent appears to be inside the micelles; the spectrum is broad and peaks at wavelengths close to, but shifted from, the peak of the dye in "empty" reverse micelles, $w = 0$. As w increases, the absorption spectrum of the dye begins to

TABLE 3: Size and Volume Fraction ϕ for Polar Solvent/AOT/Isooctane Reverse Micelles[a]

polar solvent	w	ϕ	diameter (nm)
acetonitrile	1.1	0.035	3.4 ± 0.8
	5	0.041	3.3 ± 1.5
methanol	1.1	0.25	3.1 ± 1.0
	1.1	0.41	2.8 ± 1.2
	5	0.12	2.7 ± 2.7
	5	0.14	3.4 ± 0.9
	5	0.17	3.4 ± 1.0
	5	0.19	3.3 ± 1.2
	10	0.094	4.6 ± 1.4
	15	0.062	3.4 ± 1.2
N,N-dimethylformamide	1.1	0.029	4.6 ± 0.1
	1.1	0.11	3.5 ± 0.2
	2.5	0.13	5.9 ± 0.4
	5	0.033	3.5 ± 1.1
	5	0.014	9.1 ± 0.3
1,2-propanediol	1.1	0.030	3.2 ± 1.1

[a] The polar and nonpolar solvents are slightly miscible.

reveal two distinct peaks. One peak is near the wavelength characteristic of the dye solubilized in the micelles. Another peak appears at approximately the same frequency as the peak of the spectrum in the solvent mixture with no surfactant. This indicates that the dye is present in two different environments within the solution, one inside the micelle and one outside. As the polar solvent is added to the solution, its concentration outside the micelles increases while the concentration in the micelle interiors remains constant. This trend continues until the hydrocarbon becomes saturated with the polar solvent, at which point the solution becomes biphasic.

These micelles do not support significant amounts of these polar solvents. Both the spectroscopy of C343 and the DLS results show that some solvent is solubilized inside the micelles. Spectra of C343 in the micellar solutions with nonaqueous polar solvents always display a small red shift compared to the empty micelles. DLS data show that addition of the polar solvent to solutions of AOT in i-C_8H_{18} increases the size of the micelles, albeit slightly. Therefore, the polar solvent molecules do not appear to behave as a cosurfactants which would increase the surface area leading to smaller micelle sizes.[30] Also, if the added solvent behaves as a cosurfactant, it should increase the relative concentration of micelles in the solution and lead to increased light scattering. DLS measurements reported here always display a reduction in intensity upon addition of polar solvent to the solution, which supports the hypothesis that the additional polar solvent adds directly to the nonpolar phase and yields a net dilution to the micellar sample.

Highly Immiscible Nonaqueous Solvents. In contrast to the micelles formed with slightly miscible solvents, microemulsions using EG and FA could be formed with various w values, yielding different reverse micellar sizes as observed for water-containing reverse micellar solutions. DLS results are shown in Table 4. With EG and FA solvents, the micellar size varies as w is varied but also as the volume fraction of AOT and polar solvent in the hydrocarbon phase is varied. This differs considerably from AOT reverse micelles containing water where the micellar size remains essentially constant as the volume fraction of the dispersed phases is varied as shown in Table 2 and reported in the literature.[23] For AOT reverse micelles containing water at volume fractions less than 1%, one study shows that the micellar radius actually increases as the volume fraction decreases.[31]

Because the micellar sizes are derived from measurements of the diffusion constant, one possible explanation for this phenomenon is that intermicellar attractive forces reduce the

TABLE 4: Size and Volume Fraction ϕ for Polar Solvent/ AOT/Isooctane Reverse Micelles[a]

polar solvent	w	ϕ	diameter (nm)
formamide	0.126	0.088	7.1 ± 0.2
	0.198	0.072	5.0 ± 0.5
	0.198	0.14	5.0 ± 0.6
	0.252	0.080	8.6 ± 0.1
	0.504	0.069	12.6 ± 0.1
	0.504	0.075	12.6 ± 0.1
	0.553	0.028	9.4 ± 0.2
	0.553	0.057	12.1 ± 0.1
	0.553	0.086	15.5 ± 0.3
	1.007	0.054	13.9 ± 0.1
	1.100	0.0063	5.2 ± 2.6
	1.100	0.013	9.3 ± 0.3
	1.100	0.025	15.5 ± 0.2
	1.100	0.038	18.4 ± 0.4
	1.100	0.051	23.1 ± 0.1
ethylene glycol	0.86	0.047	5.2 ± 0.1
	0.85	0.094	9.6 ± 0.4

[a] The polar and nonpolar solvents are highly immiscible.
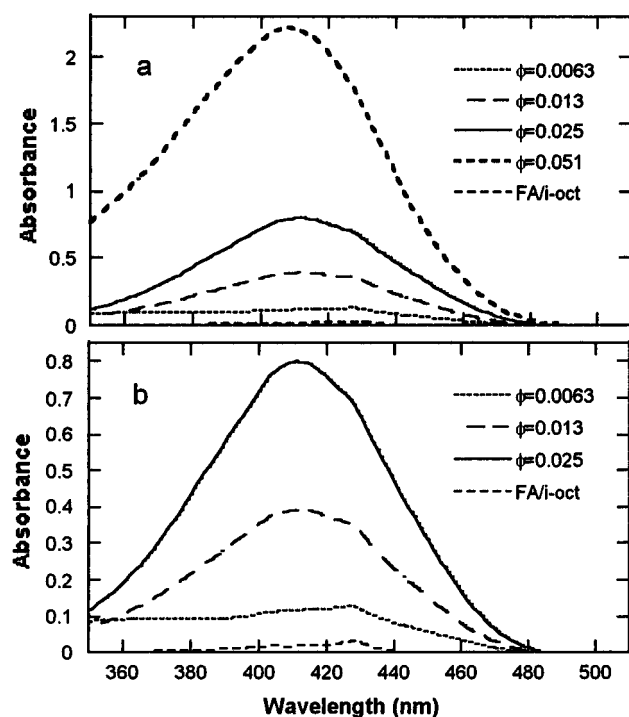
Figure 4. Absorption spectra of Coumarin 343 in formamide/AOT/ isooctane micelles, $w = 1.1$, for different volume fractions of formamide and AOT in isooctane and C343 in formamide in isooctane: (a) volume fractions from 0.0057 to 0.000 71; (b) volume fractions from 0.0028 to 0.000 71 showing the contribution from dye molecules outside the micelles.

apparent diffusion constant, leading to an overestimation of micelle size.[32] However, we do not believe that this occurs here for the following reasons: (a) For the smallest values of w measured, we found that the size remains constant as the volume fraction is doubled, as shown in Tables 4, and (2) for the volume fractions used, the micelles in these solutions should be at least three diameters apart. Under these conditions the micelles should be noninteracting.[25]

Our results suggest that some of the nonaqueous polar solvent is dissolved in the i-C$_8$H$_{18}$, causing the apparent constant volume to surface area ratio, w, to vary. The micellar diameter varies both as a function of the volume to surface area ratio, w, and as a function of the volume fraction, ϕ. This indicates that while the micelles solubilize some of the polar solvent, a fraction of the polar solvent exists in the i-C$_8$H$_{18}$ outside the micelles.

Related lecithin microemulsion studies have shown that the critical concentration for forming an organogel depended not only on the concentration of polar solvent, in this case ethylene glycol, but also on the surfactant concentration.[16] This is consistent with our observation that the phase of the solution depends on both the fraction of polar solvent solubilized in the micelles *and* the overall concentration of the surfactant in solution. Interestingly, but not surprisingly since the molar volume is considerably larger, the micelles containing small amounts of FA and EG are larger than comparable reverse micelles containing similar amounts of water.[21−24]

Spectroscopy of C343 in the micelles supports the interpretation that some of the solvent exists outside the micelles. A representative spectrum, shown in Figure 4, contrasts absorption spectra in various FA micelles. In samples containing a very small volume fraction of AOT and FA, two peaks are evident. As the volume fraction is increased, the peak associated with solubilized anionic C343 grows in. The narrow longer wavelength peak changes first into a shoulder and finally becomes indistinguishable, overwhelmed by the other peak. We interpret this to mean that a small fraction of the polar solvent always exists in the continuous phase. However, unlike the solvents that are slightly miscible, the micelles solubilize a considerable amount of polar solvent, swelling in size as they do. Eventually, for high volume fractions and w values, the solutions become biphasic.

Conclusions

We have made measurements of reversed micelles containing nonaqueous polar solvents. For polar solvents that are slightly miscible in the hydrocarbon continuous phase the micelles form and solubilize some solvent, but they do not support large micellar sizes. For polar solvents that are highly immiscible in the hydrocarbon continuous phase, changes in micellar size are observed for variation of the polar solvent/surfactant ratio, w, and for variations in the volume fraction of polar solvent and surfactant in the continuous phase, ϕ. These results agree with the recent work of Shchipunov and Shimilina, who found that the ability of a lecithin solution to support organogel formation depended almost completely on the ability of the nonaqueous polar solvent to form a high degree of hydrogen bonds.[16] In spite of the small values for w, the results for the highly immiscible solvents reported here show the size of the micelles can actually be quite large, e.g., >200 Å diameter, which is comparable to the largest reverse micelles solubilizing water. These results show that it is possible to create microenvironments for controlled chemistry with nonaqueous polar solvents. Experiments are currently underway using static FTIR and NMR spectroscopy and time-resolved fluorescence of the C343 probe molecule to interrogate the nature of the solvents in these unique reverse micellar systems.

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