Vibrational Relaxation of Azide in Formamide Reverse Micelles

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Static and ultrafast infrared spectroscopy have been used to measure absorption spectra and vibrational energy relaxation (VER) times for the antisymmetric stretching vibrational band of azide, N_3^-, in formamide-containing reverse micelles (RMs). RMs were formed in *n*-heptane using the surfactant AOT, sodium bis(2-ethylhexyl) sulfosuccinate. The VER times were found to be significantly longer than in bulk formamide. The VER times became longer as the molar ratio of formamide to AOT, ω_F, was decreased. Decreasing ω_F also resulted in substantial blue shifts of the azide static absorption band compared to the frequency in bulk formamide. The ω_F dependent studies are consistent with expected size trends, where a larger RM results in more bulklike polar solvent and faster VER rates. These results are in contrast to aqueous AOT RMs where VER times were indistinguishable from those in the bulk and the static spectral shifts were much smaller. The differences between the static and dynamic behavior in aqueous and formamide RMs are related to differences in structural changes upon confinement in RMs.

Introduction

The properties of molecules are often affected when confined to regions with diameters about a few molecular radii. In particular, confined water has received a great deal of attention because of its relevance to biological systems.[1−3] Nanoporous glasses[4] as well as cyclodextrin cavities[5] have been studied as model systems of confinement. Another method of confinement is the use of reverse micelles. Reverse micelles are nanosized droplets of water, or another polar solvent, in a nonpolar solvent stabilized with surfactants. Aqueous reverse micelles have been thoroughly studied and are often monodisperse with the size determined primarily by the ratio of water to surfactant, ω, where $\omega = [H_2O]/[\text{surfactant}]$.[6−8] This allows easy control of the reverse micelle size and the extent of confinement. A wide variety of aqueous reverse micelles using anionic, cationic, and nonionic surfactants have been characterized.[6−8] Reverse micelles using other polar solvents are much less well characterized. Most nonaqueous studies have been limited to the anionic surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT).[9−17] For the remainder of the paper, "micelle" will refer to an AOT reverse micelle unless otherwise indicated

Unlike aqueous micelles, formamide-containing micelles have shown a size dependence on both ω_F, [formamide]/[surfactant], and the surfactant concentration, or volume fraction of polar constituents, with a larger surfactant concentration resulting in a larger micelle size.[9−11] Formamide-containing micelles are in general much larger than aqueous micelles with similar molar ratios of polar solvent to surfactant. In isooctane, for $\omega_F = 1.1$, the diameters of formamide-containing micelles range from 50 to 230 Å depending on the AOT concentration, while the corresponding aqueous micelle has a diameter of 30 Å.[11] The same study of nonaqueous micelles also demonstrated that when the polar and nonpolar solvents are miscible (e.g., acetonitrile, methanol, and *N*-methylformamide in isooctane) the micelle size is nearly independent of the amount of polar solvent with additional polar solvent going into the nonpolar phase.[11] For highly immiscible solvents (formamide and ethylene glycol in isooctane), the micelle size does depend significantly on the amount of polar solvent as well as on the volume fraction of polar components. Another significant difference is that aqueous micelles are stable up to $\omega \sim 40$, while formamide micelles are only stable up to $\omega_F = 2$.[18] This may be due to the increased attractive interactions between droplets.[9]

In general, aqueous micelle studies have concluded that the confined water is less polar and contains fewer hydrogen bonds than bulk water.[19−26] In contrast, for formamide, IR spectroscopy of the C═O and N−H stretch regions has suggested that the overall structure is much less disrupted by confinement in a micelle.[11,18] Other nonaqueous solvents have shown varying levels of perturbation by micelle confinement, and the amount of structural perturbation has been correlated with the amount of hydrogen bonding.[13−17] In general, more hydrogen bonding results in a greater structural disruption.

Molecules generally exhibit longer time constants for dynamical processes in micelles than in bulk solution. This has been seen for solvation dynamics in both aqueous and nonaqueous micelles, where at least part of the solvent response can be several orders of magnitude slower than in the bulk.[27,28] Similar rate reductions have been observed in rotational dynamics as well.[27,29] More recently, studies of vibrational energy relaxation (VER)[30−33] and vibrational spectral diffusion[34] of solutes in aqueous micelles have been performed. In most cases, rate reductions have been observed, although the effects of confinement are much smaller than in solvation dynamics. This is primarily due to the local nature of the vibrational relaxation process, which is less affected by confinement than by the long-range interactions important in solvation dynamics. For most cases, the rates become faster and closer to bulk values with increasing micelle size. Studies of organic solvents in normal micelles have revealed confinement effects on ultrafast dynamics that depend on the solvent polarity.[35,36]

The small ion azide, N_3^-, serves as a useful benchmark for VER processes. The antisymmetric stretching vibrational band

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of azide exhibits fast VER and has a large IR tranisiton dipole moment, making it a relatively easy system to study.[37,38] The VER of azide has been studied in a variety of bulk solvents[38−40] as well as in cationic, anionic, and nonionic aqueous micelles[31,32,41] and has shown a significant dependence on the solvation environment. In addition, the position of the antisymmetric stretch also shows a significant dependence on the solvation environment. Azide VER is a good measure of the local solute−solvent interaction strength. In this study, we use femtosecond IR spectroscopy to extend the VER studies of azide to nonaqueous micelles using formamide as the polar solvent. Studies in bulk formamide are included for comparative puposes. A primary purpose of this study is to investigate if the confinement effects on vibrational spectra and dynamics in aqueous micelles are similar in nonaqueous micelles. A related goal is to explore how the short-range solute−solvent interactions of a nonaqueous solvent, rather than the long-range interactions important in solvation dynamics, are modified upon confinement in a micelle.

Experimental Section

Details of the laser system can be found in a previous publication.[31] Briefly, the laser system consists of a regeneratively amplified titanium sapphire oscillator that pumps an optical parametric amplifier. Mid-IR pulses are generated by difference frequency mixing of the signal and idler pulses in a type I $AgGaS_2$ crystal (1 mm) after traveling through a quartz time plate. This provides ~200 fs IR pulses with a pulse energy of ~4 μJ at 5 μm. The mid-IR beam is split into pump and probe (10%) components. The pump beam is directed to a chopper. The probe beam polarization is controlled with a wire grid polarizer after the sample and is sent to a monochromator with ~5 cm^{-1} resolution and is detected with a HgCdTe infrared detector. The signal is processed with a gated integrator and a pair of lock-in amplifiers to determine the transient signals. FTIR spectra were taken with a Mattson 7020A spectrometer using 25 scans with 1 cm^{-1} resolution.

AOT samples were prepared by adding the appropriate amount of a solution of NaN_3 in formamide, usually 1 M, to a nominally $\omega = 0$ solution of AOT in *n*-heptane. The sample was then shaken until a clear solution resulted. Sample path lengths were 500 μm for the micelle solutions using a static Harrick variable path length cell with CaF_2 windows and Teflon spacers. To minimize water contamination, AOT/*n*-heptane solutions and formamide were dried over molecular sieves (4 Å) and NaN_3 was dried in a vacuum oven for several days.

Results

FTIR. FTIR spectra and peak positions of the azide antisymmetric stretch region are shown in Figure 1. Results are shown with several ω_F values (0.5−2.0) for 0.25 M AOT in *n*-heptane and for bulk formamide, in which the formamide micelle or solvent spectra have been subtracted. The spectral peak locations and widths derived from Gaussian fits are provided in Table 1. A significant blue shift from the bulk value is apparent in the micelles. As ω_F increases, the peak position approaches, but does not reach, the bulk value, with the blue shift decreasing from 32 cm^{-1} at $\omega_F = 0.5$ to 17 cm^{-1} at $\omega_F = 2$. Reduction of the AOT concentration up to a factor of 5 resulted in peak positions that differed by less than 1 cm^{-1}. The vibrational bands are significantly broader in the micelles (~38 cm^{-1}) than in bulk formamide (~25 cm^{-1}), but the widths show little dependence on ω_F or the AOT concentration. All reported spectra are of solutions made using 1 M NaN_3 in formamide.

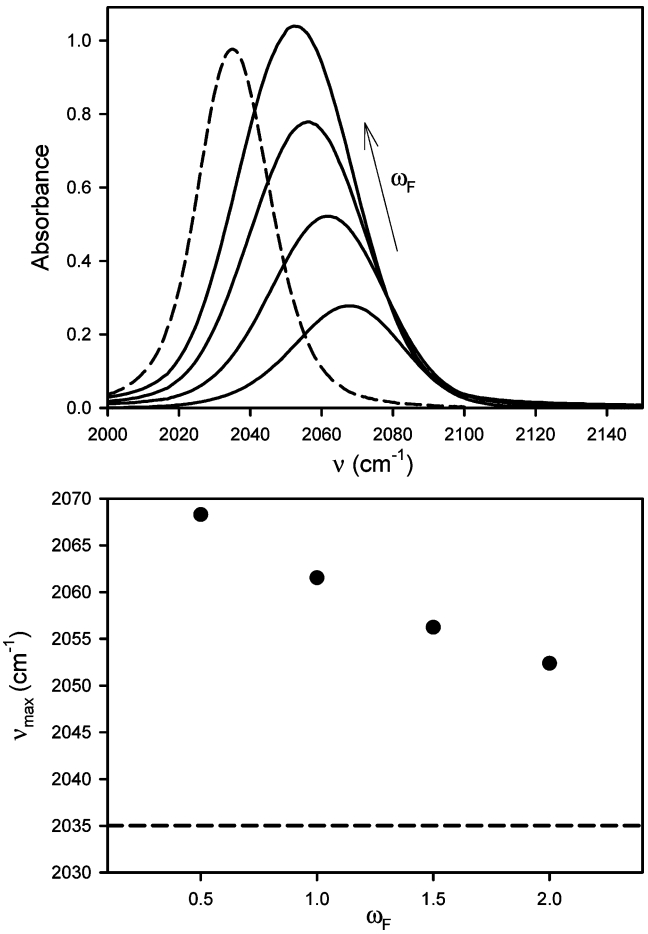

Figure 1. FTIR spectra (top) and peak positions (bottom) of the antisymmetric stretch of azide in formamide-containing AOT reverse micelles as a function of ω_F (solid lines and points) and in bulk formamide (dotted lines). The AOT concentration is 0.25 M. Reverse micelles are made with 1 M NaN_3 in formamide. Five hundred micrometer spacers are used for micelle samples, and no spacers are used for the bulk formamide sample. For all the spectra, the spectrum of the appropriate solvent or micelle solution without azide are subtracted.

TABLE 1: Vibrational Frequencies, Band Widths, and T_1 Times of N_3^- in Formamide-Containing AOT Reverse Micelles with 0.25 M AOT in *n*-Heptane[a]

ω_F	ν_{max} (cm^{-1})	$\Delta\nu$ (cm^{-1})	T_1 (ps)
0.5	2067.2	36.6	10.5 ± 0.5
1.0	2061.5	37.8	8.1 ± 0.5
1.5	2056.1	38.2	6.8 ± 0.4
2.0	2052.9	37.7	6.3 ± 0.3
bulk formamide	2035.4	24.6	3.6 ± 0.2

[a] The uncertainty in the vibrational frequencies and the bandwidths is 0.3 cm^{-1}.

The FTIR peak positions were within 1 cm^{-1} for spectra obtained using 0.3 M NaN_3.

Vibrational and Rotational Dynamics. T_1 times were determined from decay curves obtained with the relative polarizations of the probe and pump beams oriented at the magic angle (54.7°) to eliminate rotational contributions to the signal. The measured signals were fit to a single-exponential decay convoluted with a Gaussian pulse (~350 fs). Sometimes, an additional instrument-limited component due to coherence or multiphoton processes was observed and was fit by an additional Gaussian term. T_1 times were determined from both transient bleach and absorption measurements, which agreed within the experimental uncertainties. The peaks of the transient absorptions were ~25

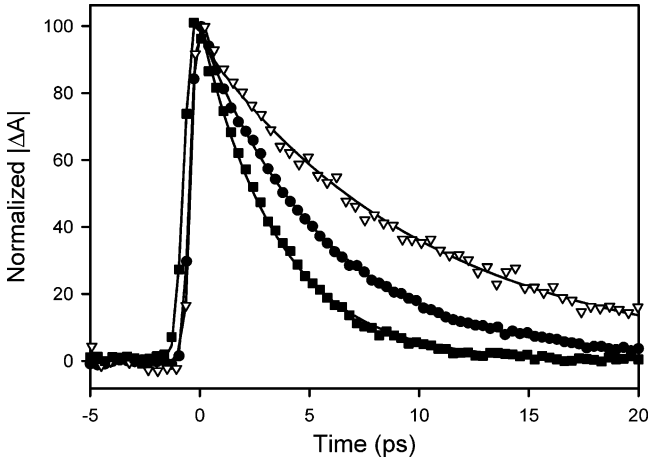

Figure 2. Representative normalized transient decays of azide antisymmetric stretch in formamide-containing AOT reverse micelles. Transients correspond to 0.25 M AOT at $\omega_F = 2$ (circles) and $\omega_F = 0.5$ (open triangles) as well as bulk formamide (squares). The decays are transient bleaches at 2065, 2070, and 2032 cm^{-1}, respectively. The solid lines are fits to a single-exponential decay convoluted with a Gaussian pulse.

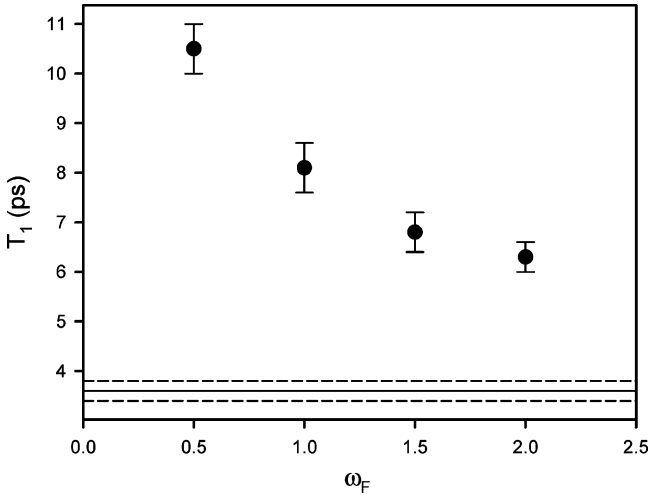

Figure 3. T_1 times for antisymmetric stretch of azide in formamide-containing AOT reverse micelles as a function of ω_F. AOT concentration is 0.25 M in *n*-heptane. Solid lines are the bulk formamide value with uncertainty represented by the dashed lines.

cm^{-1} to the red of the static absorption, consistent with a standard anharmonic shift for the excited-state absorption frequency relative to the fundamental band. Representative transients are shown in Figure 2. In bulk formamide, the T_1 time is 3.6 ± 0.2 ps. The bulk spectral peak position and VER rate are consistent with the frequency−rate correlation seen for azide in a series of bulk solvents.[37−39] The T_1 times are summarized in Table 1 and Figure 3. The T_1 time is 10.5 ps for $\omega_F = 0.5$ and approaches, but does not reach, the bulk value with increasing ω_F, reaching 6.3 ps for $\omega_F = 2$. The T_1 time remains significantly longer than the bulk. Reducing the AOT concentration by a factor of up to 5 resulted in T_1 times that were indistinguishable from the 0.25 M case. The micelle size in formamide-containing isooctane micelles was determined by dynamic light scattering to increase with increasing AOT concentration.[11] For this reason, experiments were repeated using isooctane as the nonpolar phase, and the results were indistinguishable from the *n*-heptane results.

Discussion

Previous studies on small anions in aqueous reverse micelles have revealed static vibrational spectra and VER dynamics that depend on the surfactant charge.[30−32,41] For nonionic and cationic surfactants, static red-shifts and slower VER rates were observed, which are consistent with a less polar solvation environment than in bulk water. Bulk behavior is approached as the micelle size increases for the nonionic surfactants but not for the cationic surfactant CTAB.[30−32,41] Anionic probes in anionic AOT micelles behave differently. The vibrational bands are slightly blue shifted, possibly because of ionic strength effects.[6,30] In addition, the VER dynamics are indistinguishable from the bulk.[30,41] The differences in anion spectroscopic properties for differently charged micelles have been attributed to Coulombic interactions determining the probe location within the micelle.[30,41]

The frequency of the antisymmetric stretching band of azide in formamide micelles is significantly higher than in bulk formamide. The blue shift is larger in formamide micelles than in aqueous micelles.[6,41] Increasing the ionic strength in bulk formamide does slightly blue shift the azide IR band in bulk formamide. However, increasing the azide concentration from 0.03 to 1 M only results in a 1.5 cm^{-1} shift, a much smaller shift than the comparable blue shift in aqueous systems. This is much smaller than the >15 cm^{-1} blue shift in the micelles, so that it is unlikely that ionic strength effects account for most of the blue shift. In addition, the VER rates are reduced significantly in formamide-containing micelles, while in aqueous micelles the VER times were indistinguishable from the bulk water values. This suggests a more significant change in the azide solvation environment in going from bulk to micelles in formamide than in the corresponding aqueous case. This is somewhat surprising since compared to water the structure of formamide is reputed to be less affected by encapsulation in micelles. Previous studies have suggested that the solvation of surfactant headgroups is much less extensive in formamide micelles than in aqueous micelles.[10,16] IR spectroscopy has shown that the hydrogen-bonding network of formamide is relatively unaffected in micelles,[11,18] while the hydrogen-bonding network is severely disrupted in aqueous micelles.[19,20] However, these results are not consistent with the larger changes in the static spectra and dynamics of the azide stretching band in formamide. There is no correlation between the spectral widths and VER rates, but the increased width in the micelles when compared to bulk formamide suggests a possible inhomogeneous distribution that is independent of micelle size. However, we see no effect of any inhomogeneity on the VER dynamics.

Studies of solvation dynamics have shown that the solvent response in formamide micelles is basically frozen on the time scale of the VER process,[42] although this has also been reported for aqueous micelles with similar ω values.[29] The rotational motion of probe molecules in formamide micelles has also been shown to be frozen on the VER time scale.[43] This is consistent with the results of our attempts to measure reorientation times in which we observed no decay in the anisotropy over the VER lifetimes. Solvation dynamics in the nanosecond regime for formamide micelles have been reported to be independent of ω_F for $\omega_F \leq 1$,[15] but a dependence is seen for larger ω_F.[44] Solvation dynamics in dimethylformamide (DMF) micelles are independent of the micelle size.[44] This difference has been attributed to the difference in hydrogen-bonding characteristics of formamide and DMF, with a larger structural change and stronger dynamics dependence on micelle size for the hydrogen-bonding formamide, although the effects in formamide are smaller than those seen for aqueous systems. Similar results

have been reported for acetonitrile and methanol (MeOH), with the hydrogen-bonding MeOH showing a dependence on the amount of polar solvent while acetonitrile does not.[13−15]

The static spectra and dynamics of azide in the 0.25 M AOT micelles with formamide approach bulk behavior as ω_F increases. This is not surprising since more bulklike behavior is expected for larger micelles. However, the rate-shift correlations are opposite of those typically seen for azide, except in AOT micelles and bonded to metals in ion pairs[40] and proteins.[45] Generally, for bulk solvents and aqueous micelles, the degree to which a band is blue shifted coincides with the increase in VER rate.[31,32,38,41] The aqueous AOT micelle results are exceptional because the rates are the same as the bulk, but the spectra are slightly blue shifted. However, in the formamide-containing AOT case reported here, the results are opposite from the typical rate-shift behavior because there is a significant blue shift from the bulk and there is a slower VER rate. It is unlikely that the large blue shift is due to water contamination. We initially studied some micelles without drying, and water was apparent in the IR spectra. The VER rates were significantly faster in the wet micelles, but the peak positions were very similar to the dry micelles.

On the basis of dynamic light scattering measurements, the micelle size should increase with increasing AOT concentration when ω_F is kept constant.[9−11] The static spectrum does not depend on the AOT concentration from 0.05 to 0.25 M. In addition, the dynamics are indistinguishable upon changing the AOT concentration. This is somewhat surprising since the expected increase in micelle size should lead to more bulklike behavior. The dynamic light scattering results were performed on micelles using isooctane rather than *n*-heptane as the nonpolar phase.[9−11] In light of this, we repeated the static and dynamic experiments in micelles using isooctane as the nonpolar phase, and the results were indistinguishable in terms of the ω_F and AOT concentration dependence on the band positions and T_1 times from those in the *n*-heptane micelles. This suggests that at least for aliphatic hydrocarbons, the nature of the micelles does not depend strongly on the solvent used for the nonpolar phase. The results also suggest that it is the relative amounts of formamide and AOT that determine the solvation environment of azide rather than the hydrodynamic radius of the micelle. This could be related to structural changes that occur upon changing the AOT concentration that have a larger effect on the hydrodynamic radius of the micelle than on the structure of the formamide pool.

The results demonstrate that formamide is different than water in that the interactions determining the VER rate and the vibrational frequency are affected in different ways upon confinement in a micelle. In the aqueous micelle case, the VER of azide is unchanged and the spectral blue shifts are much smaller, while in formamide micelles the VER rate is significantly reduced and a large blue shift is observed. The rate−frequency correlation observed in bulk solvents is roughly followed in aqueous micelles, although ionic factors are also important for ionic surfactants, especially AOT.[41] In formamide micelles, a rate−frequency correlation is observed that is the opposite of what is seen for bulk solvents and aqueous micelles. The structure of formamide in the micelles is similar to that of bulk formamide, but the motions are frozen on the VER time scale.[42,43] This is different than in aqueous micelles, where the structure of water is significantly altered, with less hydrogen bonding and significant headgroup solvation, but lateral movement of solvent molecules is less restricted than in formamide micelles.[43] The effects of confinement in formamide from vibrational spectroscopy appear to be different and more pronounced for solute vibrational spectra than for the formamide spectra. This is another difference with aqueous micelles where the solute and solvent vibrational spectra suggest similar structural changes, that is, reduced hydrogen bonding. It is possible that the static and dynamic differences are related. Additional studies of nonaqueous micelles would be helpful to clarify how the local interactions change upon confinement for nonaqueous solvents. We have preliminary results in nonionic microemulsions, where a slight red shift and slightly longer T_1 times are measured that are independent of ω_F. However, these microemulsions are not well-characterized, and it is unknown if reverse micelles are formed and how they depend on solution composition. Studies are underway to characterize these systems. Studies in other characterized nonaqueous micelles with solvents of varying hydrogen-bonding abilities would also be useful in characterizing the effect of confinement on the local solute−solvent interactions and how these effects are related to the accompanying static structural changes.

Conclusions

We have studied the static IR spectroscopy and VER dynamics of the antisymmetric stretching band of azide in formamide-containing AOT reverse micelles. Upon confinement, significant blue shifts in the static spectra and reductions in VER rates are observed. Both the spectral peak position and the VER rate approach bulk values as the micelle size is increased for a constant AOT concentration. This is different than the effects on the azide vibrational band in aqueous micelles in which there are smaller spectral blue shifts and the VER rates are indistinguishable from the bulk. The rate−frequency correlations in the formamide micelles are opposite of those observed for bulk solvents and aqueous micelles. This is possibly related to the differences between the solvent structures of water and formamide within the micelle and in bulk solution. Further studies are needed to understand the effects of confinement on the local interactions important for VER and vibrational frequencies in nonaqueous solvents.

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