Published in final edited form as:

J Phys Chem B. 2013 August 22; 117(33): 9775–9784. doi:10.1021/jp406725a.

An Ion's Perspective on the Molecular Motions of Nano-confined Water: A 2D IR Spectroscopy Study

Prabhat K Singh^{‡,†}, Daniel G. Kuroda^{‡,*}, and Robin M. Hochstrasser

Ultrafast Optical Processes Laboratory, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104, USA

Abstract

The vibrational population relaxation and the hydration shell dynamics of the symmetric tricyanomethanide (TCM) anion is investigated in AOT reverse micelle as a function of the water pool radius. Two-dimensional infrared spectroscopy in combination with linear absorption and ultrafast IR pump-probe spectroscopy is utilized in this study. Spectroscopic measurements show that the anion has two bands in the 2160 – 2175 cm⁻¹ region, each with its own spectroscopic signatures. Analysis of the vibrational dynamics shows that the two vibrational bands are consistent with the anion located either at the interface or in the water pool. The sensitivity of the TCM anion to the environment allows us to unequivocally monitor the vibrational and hydration dynamics of the anion in those two different environments. TCM anion located at the interface does not show any significant variation of the vibrational dynamics with the water pool size. On the contrary, the TCM anion inside the water pool exhibits a large and non-linear variation of the vibrational lifetime and the frequency-frequency correlation time with the pool radius. Moreover for the solvated anion in water pools of 49 Å in radius ($W_0=30$), the vibrational lifetime reaches the values observed for the anion in bulk water while the frequency-frequency correlation time shows a characteristic time higher than that observed in the bulk. In addition, for the first time a model is developed and used to explain the observed non-linear variation of the spectroscopic observables with the pool size. This model attributes the changes in the vibrational dynamics of the TCM anion in the water pool to the slow and radius dependent water dynamics present in the confined environment of a reverse micelle.

Keywords

ultrafast IR spectroscopy; vibrational echo; tricyanomethanide; hydration dynamics; vibrational dynamics; reverse micelle; water confinement

Introduction

The confinement of water usually occurs in various chemical and biological systems where the close proximity of the water to the interface dramatically affects its behavior compared to the bulk. Since confined water is very important in the different processes occurring in the cell¹, there has been a vast scientific interest in describing the water structure and dynamics in various bio-mimicking confined environments, such as reverse micelles. The reverse

*Corresponding Author, Author to whom correspondence should be addressed. dakuroda@sas.upenn.edu.

[‡]Daniel G. Kuroda and Prabhat K. Singh contributed equally to this work.

[†]On leave from Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India.

ASSOCIATED CONTENT

Additional supporting data and methodology for determining ρ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

micelles are one of the most widely used prototypical systems to study water confinement. They consist of nanometer sized water droplets stabilized by surfactants in a bulk non-aqueous/organic solvent (Scheme 1). In these micellar systems, the size of the water droplet can be systematically modified by varying the molar ratio of water to surfactant molecules ($W_0 = [\text{WATER}]/[\text{SURFACTANT}]$).² One of the most widely used surfactants to make reverse micellar systems is sodium bis(2-ethylhexyl)sulfosuccinate (AOT). AOT is an amphiphilic molecule with two alkane chains and one sulfonate head group (Scheme 2). AOT is an ideal surfactant for reverse micelle formation because it has the appropriate ratio between hydrophobic tail volume and hydrophilic head group surface area.³ Aqueous AOT reverse micelles exhibit a wide range of possible water pool sizes that can range from ~1 nm to ~14 nm in diameter. In particular for reverse micelles with water pool sizes of ~1.7 nm to ~6.9 nm in diameter, a linear relation with W_0 has been observed.⁴ Thus AOT reverse micelles offer the possibility of systematically studying the properties of the confined water over a large range of water pool sizes. Although the water confinement effect in AOT reverse micelles has been widely studied experimentally and theoretically,^{5–9} its effect on the hydration dynamics of ions remains less well described.

Theoretically, it has been shown that the water inside the reverse micelle is strongly perturbed by the presence of the ionic layer.^{8–10} This perturbation has been theorized to arise from the high concentrations of interfacial ions which results in the immobilization of the interfacial water.⁹ Also, it has been shown that the slowdown of water is a function of the radius of the water pool.⁸ Moreover, the water slowdown has been explained by a curvature-induced frustration mechanism in which the extent of the confinement effect over the water dynamics is related to the curvature of the interface.⁸

Experimentally, many different techniques, including nuclear magnetic resonance,^{11,12} fluorescence Stokes' shift,^{13–18} dielectric relaxation,^{19,20} and infrared spectroscopy,^{21–24} have been used to investigate the structure and dynamics of the confined water in reverse micelles. More recently ultrafast infrared (IR) spectroscopy, including 2D IR spectroscopy, has been applied to this problem.^{5,7,25–35} Ultrafast IR spectroscopy has a sub-picosecond time resolution making it a suitable technique for measuring the water configurations and its dynamics. The typical time scale of the water dynamics is that of the hydrogen bond fluctuation and reorganization, i.e. a few femtoseconds³⁶ to picoseconds^{36–38}. The ultrafast IR studies have revealed that confined water has a slower dynamics than the bulk and the magnitude of the slowdown is dependent on the radius of the water pool.^{28,34,35}

Another approach utilized to investigate the dynamics of confined water relies on molecular probes. Ideally, spectroscopic probes must be very sensitive to their location, so the dynamics derived from their spectroscopic measurements can be assigned to certain locations within the reverse micelle such as the interface or the water pool. Notwithstanding the new insights that many probes have provided in the reverse micelle field, spectroscopic probes usually lack the specificity regarding their location especially in the highly heterogeneous environment like the reverse micelles. This uncertainty in location leaves some ambiguity in the interpretation of the spectroscopic measurements. To overcome these shortcomings, the use of vibrational probes has been proposed.

It is well known that the solvation shell of an ion has a significant impact on the properties of the ions.^{39–47} Because of its sensitivity and time resolution, vibrational spectroscopy has been shown to be an excellent method for examining the dynamics and structure of the ions' hydration shell.^{39–47} Earlier efforts to employ ions as vibrational probe in AOT reverse micelles involved the study of the azide ion and the ferrocyanide ion among others.^{48,49} These studies showed that the vibrational energy relaxation of these anions is equal (within the experimental error of the study) to that observed in the bulk. These results were

interpreted in terms of the ion being located in the center of the water pool where the water has bulk like behavior. Thus, the effect of water confinement on the hydration dynamics of ions in reverse micelle remains to be characterized. For this purpose, the present study uses the tricyanomethanide (TCM) anion.

The TCM anion is a plano-triangular symmetric ion in which each corner of the triangle contains a cyano group and a central carbon atom (Scheme 2). This anion has D_{3h} symmetry and thus has a pair of degenerate asymmetric stretch modes (called A1 and A2 in Ref ⁴³) that are IR active in the nitrile stretch spectral region ($2100\text{--}2200\text{ cm}^{-1}$). These IR transitions are shown to have a very large peak extinction coefficient ($\sim 4380\text{ M}^{-1}\text{cm}^{-1}$)⁴³ which facilitates the use of low concentration and minimizes the multiple occupancy of ions in a single reverse micelle. In addition, it has been shown that the vibrational modes of symmetric molecular ions are very sensitive to the composition and spatial arrangement of its solvation shell⁴². Further, the TCM anion is expected to favor hydration within the water pool of the reverse micelles since the AOT head group is negatively charged (Scheme 2). Thus, TCM anion is an ideal probe for asymmetric solvation perturbation dynamics of water in reverse micelles.

The goal of this study is to explore the vibrational relaxation and hydration dynamics of the TCM anion inside anionic reverse micelle as a function of the water pool size by probing the nitrile stretch region with femtosecond time resolution. For this purpose, linear IR, ultrafast IR pump-probe, and 2D IR spectroscopies are used. Experimental results are explained in terms of a simple model that provides a molecular description of the heterogeneous dynamics of water in the reverse micelle.

Material and Methods

Experimental methodologies

Potassium tricyanomethanide (KTCM, 99%) was purchased from Alfa Aesar and used as received. AOT (Sigma-Aldrich) was used after purification by boiling the methanol solution of AOT with activated charcoal. Charcoal was removed by hot filtration and AOT was recovered by removing methanol under vacuum. Ultrapure grade isooctane was purchased from Sigma-Aldrich and was used as received. Reverse micelles were prepared by mixing AOT, isooctane, and the requisite amount of water. The AOT concentration was kept at 0.2 M throughout the present study. Water was systematically added to the AOT-isooctane solution to prepare the reverse micelle with a given W_0 value. The residual water concentration in AOT-isooctane solution was determined by FTIR measurements to be equivalent to $W_0=0.3$. Reverse micelle samples containing TCM anion with $W_0>30$ were not stable for the time required to perform the photon echo experiments. Concentration of TCM anion was kept at 1.3 mM to minimize the multiple occupancy of TCM anions in each reverse micelle. Samples were held between two CaF_2 windows separated by a $140\text{ }\mu\text{m}$ spacer for the photon echo measurements and a $400\text{ }\mu\text{m}$ spacer for the IR pump-probe measurements. All the measurements presented in this study were done at room temperature.

FTIR experiment

The linear absorption IR spectra were collected in a Thermo Nicolet 6700 FTIR spectrometer with a 0.5 cm^{-1} resolution.

Pump-probe experiment

The details of the ultrafast IR laser system used for the experiment have been described previously.³⁹ In summary, the ultrafast IR source generates near transform limited 75 fs pulses with $\sim 2.5\text{ }\mu\text{J}$ energy centered at 2170 cm^{-1} . The source output is divided into the

pump and the probe pulses. The pump pulse is vertically polarized and has ~500 nJ energy at the sample. A polarizer is used to decrease the intensity of the probe to ~50 nJ and to rotate its polarization to 45° with respect to that of the pump pulse at the sample. Both pump and probe pulses are focused on the sample (spot size of >200 μm) with a parabolic mirror. After the sample, the recollimated probe beam is spectrally dispersed with a 100 grooves/mm grating onto a liquid nitrogen cooled MCT array detector with 32 elements. A polarizer after the sample is used to select the parallel, the perpendicular, and the magic angle polarization components of the probe pulse. The delay between the pump and the probe pulses is varied by a computer controlled translation stage.

2D IR spectroscopy

The detail description of the 2D IR photon echo experimental and data processing methodologies have been discussed in detailed in an earlier publication.⁵⁰ Briefly, Fourier transform limited infrared pulses consisting of 80 fs pulses centered at 2170 cm⁻¹ with 400 nJ energy are split into three replicas (wave-vectors: $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$) and focused at the sample using the box configuration geometry. The photon echo signal, collected in the phase matching direction $-\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$, is heterodyned with a fourth IR pulse (Local oscillator), and detected after dispersion (100 grooves/mm grating) on a liquid nitrogen cooled MCT array detector with 64 elements. In all the experiments, the LO pulse preceded the echo signal by ~1 ps. The rephasing(non-rephasing) echo signal is produced when the pulses with the wave vector $\mathbf{k}_1(\mathbf{k}_2)$ arrived at the sample before those with wave vector $\mathbf{k}_2(\mathbf{k}_1)$. In both sequences, the coherence time interval between $\mathbf{k}_1$ and $\mathbf{k}_2$ is scanned with a 2 fs step for 3.5 ps. The time interval between the second and the third pulse, waiting time (T_w), was varied in steps of 250 fs from 0 to 3 ps. The Fourier transformation of the signal along the coherence () and the detection (t) axes yields the 2D spectrum.

Results and Discussion

Linear IR absorption spectrum

The linear absorption spectra of the TCM anion in different reverse micelle environments (W_0 's) are presented in Figure 1. These spectra were measured in the 2100–2250 cm⁻¹ region and their corresponding solvent background was subtracted. For reverse micelles with $W_0=4$, the linear IR absorption spectrum shows two bands for the TCM anion. However, as W_0 increases the low frequency band becomes gradually less intense such that at $W_0 = 20$ it is almost imperceptible. In addition, the high frequency band shifts towards lower frequencies when W_0 is increased. To quantify the changes in the linear absorption spectrum as a function of W_0 , a fitting of all the linear IR spectra with two Gaussian functions was performed (see SI, Figure S1). Note that TCM in bulk water presents a single band corresponding to two degenerate transitions at 2172 cm⁻¹ (see Ref. 43) that can be approximated with a single Gaussian function (see SI). The most relevant parameters of the Gaussian fitting are presented in Figure 2 as a function of W_0 , but all the spectral parameters are tabulated in Table S1 (see SI).

The fits with Gaussian functions show that the maximum of the high frequency band has a small but gradual redshift towards the value in the bulk water with the increase of W_0 (Figure 2a). On the contrary, the maximum of the low frequency peak remains almost invariant with W_0 . Furthermore, the full width at half maximum (FWHM) of the high frequency band gradually increases with increase in W_0 whereas the FWHM of the low frequency band remains almost constant (Figure 2b). The frequency redshift with W_0 indicates that the high frequency band arise from the TCM anions solvated in the water pool. A comparable gradual redshift of the frequency of a vibrational transition has been previously observed for an analogous experiment performed on the azide ions.⁵¹ In this later

study, the authors suggested that the redshift of the vibrational frequency could arise from the change in the concentration of AOT counterions within the water pool with W_0 .⁵¹ This assignment is also supported by the gradual increase of the FWHM of the higher frequency band with W_0 which, as will be shown later, are directly related to the changes in the vibrational dynamics of the anion due to the variations of the confined aqueous environment. In contrast, the almost negligible change in the transition frequency and FWHM of the low frequency band is a strong indication of the presence of a population of reverse micelles with TCM anions residing at the interface. Moreover, bulk solvent studies for the TCM anion showed that the band center frequency shifts to lower frequencies when the polarity of the solvent is lowered⁵² agreeing with anion located at the interface where low polarity has been measured⁵³. Thus, the central frequency of the low frequency band provides a strong support for the TCM anion being located at the interface. Although it is conjectured that ions having the same charge as that of the surfactant will reside in the water pool, a previous study has shown that ions can reside in non-polar microheterogeneous environments deep inside the interface irrespective of their charge.^{11,54,55} Moreover, it is not possible to exclude the formation of aggregates between the AOT, the TCM anion, and their counter ions at the interface. These aggregates could have similar structures as to those predicted for the guanidinium cation⁵⁶. Thus, one expects that in a reverse micelle a change in W_0 will significantly change the properties of the water pool and the ions within, but will not affect the molecular interactions observed at the interface especially if the ion is located in the region of the interface close to the ester groups and away from the counter ions.

Further support of this molecular picture, in which ions are located either in the water pool or at the interface, is provided by the linear dependence of the ratio of the integrated areas of the two transitions with W_0 (Figure 2c). The change of this area ratio is interpreted as a decrease in the fractional population of the interfacial TCM anions as the size of the water pool is increased or equivalently as a variation in the equilibrium constant. The equilibrium between TCM anions residing at the interface and in the water pool is given by

$$K(W_0) = \frac{[TCM_P(W_0)]}{[TCM_I(W_0)]} \quad (1)$$

where TCM_P and TCM_I are the concentration of the TCM anion in the water pool and at the interface, respectively. Assuming that the interaction between the ion and the environment is negligible, the concentration of anions in each location is directly given by the probability of finding the ion at each location. Thus, for the ion in the interface, the probability of occupancy is proportional to the area of the water pool surface ($P_I \propto r^2$), and for the ions in the pool, is proportional to its volume ($P_P \propto r^3/3$). The equilibrium constant, $K(W_0)$, of this simple model predicts a linear variation of the equilibrium constant with the size of water pool, or equivalently W_0 , as observed experimentally (Figure 2c). In addition, this equilibrium picture is also in full agreement with the observed hydration dynamics for the ions in the interface and the water pool (see below).

Population relaxation dynamics

The water confinement effect on the TCM anion in reverse micelles was also studied by measuring the excited state population relaxation at various W_0 's. Figure 3a shows the transient dynamics of the ground state bleach and stimulated emission signals for the high frequency band of TCM anion measured at 2178 cm^{-1} (see Figure S2 in SI) after the ultrafast excitation. All transient signals for the different W_0 's are well represented by a single exponential decay function (the R^2 for all the fit is > 0.994). The vibrational lifetimes extracted from these fits (Figure 3b) reveal a gradual and non-linear decrease with increase in W_0 . Moreover, at the highest studied W_0 the vibrational relaxation lifetime reaches the

value for the bulk water of 5.3 ps⁴³ (dashed line in Figure 3b). Due to the overlap between the anharmonically shifted new absorption signal of the high frequency band and the stimulated emission/bleach signal of the low frequency band, the vibrational dynamics of the low frequency band could not be determined. The spectral overlap of signals can be clearly observed in the 2D IR spectra (see next section).

The observed behavior for the vibrational lifetime of the TCM anion located in the water pool differs from an earlier investigation of the azide anions in AOT reverse micelle where no variation of the vibrational lifetime with W_0 was observed.⁴⁸ These findings were justified by proposing that azide anions are residing exclusively in the most central region of the water pool where the water behaved as bulk.⁴⁸ However, the results of TCM anions in reverse micelle clearly show that the water confinement influences the vibrational energy relaxation indicating that the ions are not localized in the center of the reverse micelle, but are distributed in its volume. Moreover, it will be shown below that lifetime is less sensitive to the water motions than other spectroscopic observables such as the frequency-frequency correlation function. This lack of sensitivity of the vibrational lifetime might explain the previous results for the azideion⁴⁸.

The observed change in the vibrational lifetime is also supported by the variation of the width of the high frequency transition (Figure 2b). The linear absorption spectrum ($\mathcal{S}(\omega)$) of an IR transition is given by the well-known lineshape function,⁵⁷

$$S(\omega) = 2\text{Re} \int_0^\infty \exp(i(\omega - \langle\omega_{10}\rangle)t) \exp(-g(t) - t/2T_{10} - 2Dt) dt \quad (2)$$

where $g(t)$ is the double time integral of the frequency-frequency correlation function (FFCF, $\langle\delta\omega_{10}(t)\delta\omega_{10}(0)\rangle \approx \frac{1}{2} \exp(-t/\tau_c)$ where τ_c is the correlation time), T_{10} is the vibrational lifetime, and D is the rotational diffusion coefficient. Assuming no significant contribution to the lineshape from rotational diffusion ($D=1/(15.6 \text{ ps})$ for TCM in bulk water⁴³), the lineshape is dominated by the vibrational lifetime and the FFCF correlation time. Thus, it is expected that an increase in either the vibrational lifetime and/or the FFCF correlation time will decrease the width of the transition as observed experimentally (Figure 2b). Although the change of the lineshape can be hindered by a decrease of the correlation time when lifetime increases, as it will be shown in the following section, the lifetime and FFCF correlation time are correlated (Figure 5c) making this possibility very unlikely.

The confinement effect in the reverse micelle might also affect the rotational diffusion of the ion. Although this information can be obtained from the anisotropy of the pump-probe transient signal, our measurement of the rotational diffusion from the anisotropy does not show any statistical difference with W_0 (see SI, Table S2). The lack of any systematic variation of the rotational reorientation time is attributed to the presence of a subpicosecond decay in the anisotropy in TCM, unrelated to the rotational diffusion⁴³, that lowers its amplitude to 0.1 and hinders the observation of a change in the rotational relaxation time with W_0 .

Hydration dynamics

To characterize the hydration dynamics of the TCM anion under confinement, the 2D IR spectra of TCM were also investigated. The 2D IR spectra of the TCM anion in different pools ($W_0=4, 8, 12, 20$ and 30) for two different waiting times ($T_W=0$ and 3 ps) are presented in Figure 4 (for a more complete time series of 2D IR spectra see SI Figure S3). Note that solvent background signal in any of the samples for all the measured waiting times is found to be negligible (see SI, Figure S4).

At any waiting time and water pool size, the 2D IR spectrum shows a negative peak/s (blue) and its/their corresponding positive peak/s (red) along the diagonal. While the negative peak is assigned to the bleach of the ground state and the stimulated emission signals, the positive peak arises from the excited state absorption signals. As previously seen in the linear IR spectra, the 2D IR spectra also consist of two peaks along the diagonal. Moreover, the low frequency band gradually gets less intense as the size of the water pool increases and becomes almost undetectable at $W_0 > 20$. In particular, for reverse micelles with $W_0=4$, two transitions are clearly observed in either the positive or the negative peaks of the 2D IR spectra. Although in all the samples, both negative peaks are elongated along the diagonal at $T_w=0$ ps, the 2D IR spectra also shows that only the high frequency negative peak exhibits a waiting time evolution, as the peak becomes more circular and acquires a more up-right position. The waiting time evolution of the high frequency peak becomes more evident for samples with higher W_0 . On the contrary, the low frequency negative peak does not change its shape with waiting time and remains elongated along the diagonal even at higher W_0 .

To extract and quantify the dynamics of the FFCF for both bands, the inverse of the nodal line slope, referred to as slope from here onwards, separating the corresponding negative and positive peak was measured from all the spectra⁵⁸ (see SI for the slope determination procedure and examples). Although both bands correspond to a set of degenerate transition, it has been shown in Ref 43 that the nodal line describes appropriately the FFCF even in the simultaneous presence of vibrational population exchange and hydration dynamics. Figure 5a shows the variation of the logarithm of the slope with waiting time for the high frequency transition in reverse micelles with $W_0=4, 6, 8, 12, 20$, and 30. Interestingly, the high frequency transition displays a significant change of the slope, while the slope of the low frequency transition does not vary with waiting time, T_w (see SI, Figure S5). As observed from the experimental data, the slope of the high frequency transition decays linearly on a logarithmic scale indicating that its waiting time evolution is well represented by a single exponential decay of the form $Slope(T_w) = Ae^{-T_w/\tau_c}$ where τ_c is the FFCF correlation time.

The dependence of the FFCF correlation time, τ_c , for the high frequency peak as a function of W_0 is presented in Figure 5b. From these results, it is evident that as W_0 increases the FFCF correlation time becomes faster, i.e. the characteristic time decreases. Moreover, the correlation time shows a non-linear and gradual decrease with increase in W_0 , but without reaching the correlation time of the TCM anion in bulk water ($\tau_c=1.1\text{ps}$ ⁴³) for the sample with the highest W_0 ($\tau_c(W_0=30)=1.5 \pm 0.1$ ps) as shown in Figure 5b (dashed line). The variation of the FFCF correlation time for the high frequency peak with W_0 is consistent with the picture proposed from the linear FTIR measurements where the high frequency peak is assigned to the TCM anion in the water pool.

Another feature of the 2D IR spectra which shows a quite apparent change as a function of W_0 is the anti-diagonal width of the high frequency band at $T_w=0$. The 2D IR anti-diagonal width of the high frequency transition shows an initial value of $\sim 5\text{ cm}^{-1}$ ($W_0=4$) and increases non-linearly with W_0 to a value of $\sim 7\text{ cm}^{-1}$ (see SI, Figure S6). The anti-diagonal width of the 2D IR spectrum contains the information of all the homogeneous contributions to the lineshape.⁵⁷ In particular, it contains the lifetime, rotational diffusion as well as all those components of the FFCF that are sufficiently fast to contribute homogeneously to the lineshape, i.e. pure dephasing T_2^* .⁵⁷ In water, these extremely fast components of the FFCF have been attributed to the fast librations of water.³⁶ Thus the change in the experimental anti-diagonal width with W_0 not only reflects the changes in the lifetime, but also reveals changes in the water dynamics with the size of the water pool. In the present case, numerical simulations of the anti-diagonal width with the standard response functions⁵⁹ show that the pure lifetime component accounts for less than 1 cm^{-1} of width including a maximum

increment of $\sim 0.1 \text{ cm}^{-1}$ for $W_0=20$. Thus the lifetime ($\sim 1 \text{ cm}^{-1}$ in bandwidth) alone does not explain either the change ($\sim 2 \text{ cm}^{-1}$) or the total anti-diagonal width ($\sim 5\text{--}7 \text{ cm}^{-1}$) observed in the 2D IR spectra. This implies that a significant part of the anti-diagonal width and its variation arise from very fast inhomogeneous processes of the hydration dynamic and from its growing contribution as the water pool becomes larger. This observation further supports the idea that changes in the dynamics of water are the source of the observed effects in the vibrational dynamics of the TCM anion in AOT reverse micelle.

Another important observation is that the FFCF does not reach the bulk values for $W_0=30$ which is in contrast with the measured vibrational lifetime where a bulk characteristic time is observed. This indicates that the FFCF is more sensitive to subtle changes in the environment compared to the vibrational lifetime. Although the FFCF measures the autocorrelation of the vibrational frequency fluctuations⁵⁷ and the lifetime measures the power spectrum of the bath potential fluctuations over the vibrational mode⁶⁰, these two observables which are intimately related to the fluctuations of the hydration shell might not necessarily share the same molecular mechanism. For example, the FFCF is inherently independent of the fast fluctuations of the water, such as librations, because they appear as homogeneous components.⁵⁷ In contrast, the vibrational lifetime is very susceptible to these motions as it has been shown for the azide ion.⁶¹ Although a rigorous theoretical analysis should be performed to confirm this hypothesis, the change of the anti-diagonal width of the 2D IR spectrum supports this idea. For $W_0 \gg 20$ the anti-diagonal width has little variation indicating that the ultrafast inhomogeneous process of hydration, such as librations, almost have the same contributions as in the bulk. However, the collective motions of water necessary for producing a fluctuation of the frequency of the vibrational mode might remain perturbed by the confinement effects as seen in the FFCF. Thus, the different contributions of the “fast” and “slow” inhomogeneous process to the lifetime might explain the difference in sensitivity observed for the TCM anion as well as the lack of change in the vibrational energy relaxation for the azide anion as observed by Owrutsky and coworkers⁴⁸.

Overall, the experimental results indicate that in small water pools (low W_0) the processes that allow the TCM anion to sample the different hydration shells (hydration dynamics), or equivalently frequencies (spectral diffusion), are slower. This effect can be attributed to the slowdown of water molecules in the water pool produced by the water confinement.^{8,9,34,35} Both theoretically and experimentally it has been shown that water interacting with the interface is highly perturbed leading to a slowdown of the water orientational relaxation and FFCF correlation time of the OH/OD stretch.^{8,9,34,35} Moreover, it has been suggested from molecular dynamics simulations that the slowdown is produced by the interface and is transferred to the other water layers by curvature induced frustration mechanism.^{8,9} In this mechanism, the thickness of this dynamically slow water layer changes with the curvature (radius) of the water pool and is larger for smaller water pools. As it is shown in the next section, a model based on this mechanism can be used to explain the experimental non-linear dependence of the FFCF correlation time with W_0 .

Model of the water structure inside reverse micelle

To extract a physical picture of the water structure inside the reverse micelle, a model that takes into account the heterogeneity of the water dynamics was developed and used. This model is based on a molecular dynamics study by Skinner and coworkers,⁸ in which the value of orientational correlation function of the water was found to be dependent on the distance between the probed water and the surface of the water pool. Moreover, this study showed that the water dynamics gets exponentially slower as it approaches the surface. Physically, this model indicates that the water motions get faster towards the center of the water pool where depending on the pool size a bulk water behavior can be observed at

different distances from the surface.⁸ Our model uses the same functional form for describing the changes in the correlation function as a function of the distance,

$$\tau_c(r) = \tau_B + \tau_0 e^{(r-R_{WP})/\tau_0(R_{WP})} \quad (3)$$

where τ_B and τ_0 are the correlation times of the water in the bulk and in the layer closest to the interface, respectively, r is the distance from the center of the water pool, R_{WP} is the radius of the water pool, and $\tau_0(R_{WP})$ is the characteristic length of the decay of the FFCF correlation time. The characteristic length of the decay has the following functional form:

$$\tau_0(R_{WP}) = r'_0 e^{-R_{WP}/r_c} + r_\infty \quad (4)$$

where $r'_0 + r_\infty$ is the limiting value of τ_0 (pool size infinitely small), r_c is the characteristic radius decay constant of τ_0 , and r_∞ is the minimum value of τ_0 (pool size infinitely large). Also our model assumes a spherical water droplet with equal probability of finding the ion at any position of the pool, i.e. $P(r) = 4\pi r^2 dr$. The later approximation is based on the theoretical studies in which the density of water⁸ as well as an organic co-solvent⁶² was found to be constant within the nanopool. Moreover, a comparable probability function has been computed for I_2^+ and I_2^- solvated in AOT reverse micelles.⁶³ In addition, as it will be shown afterwards, this probability distribution provides a reasonable description of the system.

Experimentally, the value of the measured correlation time for the high frequency transition is an average over all possible ion locations in the water pool. Thus in the context of this model, the mean FFCF correlation time measured by the 2D IR experiment is represented by:

$$\langle \tau_c(R_{WP}) \rangle = \frac{\int_0^{R_{WP}} P(r) \tau_c(r) dr}{\int_0^{R_{WP}} P(r) dr} = \frac{\int_0^{R_{WP}} 3r^2 \tau_c(r) dr}{R_{WP}^3} \quad (5)$$

Equation 5 is used to fit our data. In the fitting procedure, it is assumed that the correlation time of the water layer closest to the interface (τ_0) and at the bulk (τ_B) are constant for all water pool sizes and that only the characteristic length of the correlation decay time (r_0) changes with the radius of the water pool as in Equation 4. For the fitting of the experimental data, τ_0 and τ_B are selected to be $\tau_0 = 26.6$ ps (see SI) and $\tau_B = 1.1$ ps (bulk water⁴³). The fit of the experimental mean FFCF correlation time using the model in Equation 5 is presented in Figure 6. A good agreement between the experimental data and the model is observed ($R^2 = 0.992$, solid line in Figure 6) for $r'_0 = 21.4$ Å, $r_c = 5.3$ Å, and $r_\infty = 0.4$ Å. Note that a model where r_0 is a constant value does not fit properly the experimental data ($R^2 = 0.771$, dashed line in Figure 6).

The parameters obtained from this modeling support a molecular picture in which the reverse micelle water pool has a distribution of hydration dynamics as represented by the characteristic length $\tau_0(R_{WP})$ as a function of the pool radius (Figure 7). From this parameter, it can be observed that the water does not reach the bulk behavior in reverse micelles of $W_0 < 4.4$. This estimation is achieved by calculating when the correlation time reaches the bulk value ($\tau_c - \tau_B$) at the center of the pool ($r = 0$) for 5 times the characteristic radius from the surface ($5r_0(R_{WP}) \approx R_{WP}$). Moreover, the minimum width of the water layer, where slow dynamics can be observed, corresponds to $5r_\infty = 2.0$ Å. This thickness of

the water layer can be observed in all micelles with $W_0 = 14.4$ where $5r_c \approx R_{WP}$. In addition the dimension of this water layer agrees well with the molecular dimension of a water molecule (2.8 Å) indicating that irrespective of the water pool size the layer of water close to the interface will always have a slow dynamics.

From the modeling of the mean FFCF correlation time, it can be seen that the smaller the water pool size, the larger the distance from the interface at which the bulk value of the correlation is observed (Figure 7 top and lower panels). This result of the model agrees well with the previously proposed curvature-induced frustration mechanism⁸ in which the lower the radius of the water pool, the farther is the distance from the interface where water will have bulk dynamics (Figure 7). In terms of the hydration dynamics in a reverse micelle, this modeling predicts that in bigger reverse micelle ($W_0=8$) the center of the water pool hydrates the ion as in bulk water (Figure 7 right top panel). However, in a small reverse micelle ($W_0=4$), the TCM anion never experiences the water dynamics of the bulk even at the center of the water pool (Figure 7 left top panel).

The strong correlation observed between the lifetimes and the FFCF correlation times for different pool sizes (Figure 5c) shows that the two processes share a mutual hydration mechanism for the TCM anion. Thus, the proposed model can be used to explain the variations of either the lifetime or the FFCF correlation time with the pool radius. In addition, this molecular picture, deduced from the modeling of our experimental data, might provide the basis for explaining previous studies in which an analogous nonlinear behavior of the average value of observables, such as fluorescence lifetime,^{64–68} fluorescence quantum yield^{64,65} of the optical probes and solvation correlation time^{13–15,17} has been observed.

Conclusion

The vibrational energy relaxation and the hydration shell dynamics of the TCM anion has been investigated in the nano-confined water pools of anionic AOT reverse micelle as a function of the pool radius. Linear FTIR and 2D IR spectra indicate and differentiate two populations of reverse micelles with different solute occupancy: one that has the anion at the interface and the other that has it in the water pool. Experimental data strongly suggest a dynamically slow equilibrium between locations exist. Moreover, the anion in each of these locations presents its own spectroscopic signatures. While the TCM anion located at the interface show invariant vibrational parameters, the TCM anions in the water pool display strong dependence of the vibrational lifetimes and FFCF correlation times with the water pool radius. The non-linear dependence of the FFCF correlation time is explained with a new model. This novel model takes into account the heterogeneous dynamics of the water of the pool for different pool radius and attributes the changes of the FFCF to the slow dynamics of the water in the pool due to confinement. In addition, the proposed model not only verifies previous theoretical findings on the radius dependent heterogeneity of the water dynamics in AOT reverse micelles, but also might provide a theoretical framework for explaining earlier experimental investigations where similar non-linear variation of average spectroscopic properties in reverse micelles have been observed.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Funding Sources

This research was supported by grants to RMH from NIH-GM12592, and NIH-9P41GM104605 for instrumentation.

We would like to thank Ms. Ileana Pazos for providing us the AOT samples, Dr. Tom Troxler for many helpful discussions, and Prof. Feng Gai for many helpful discussions and advice.

REFERENCES

1. Rasaiah JC, Garde S, Hummer G. Water in Nonpolar Confinement: From Nanotubes to Proteins and Beyond. *Annu Rev Phys Chem.* 2008; 59:713–740. [PubMed: 18092942]
2. De TK, Maitra A. Solution Behavior of Aerosol Ot in Nonpolar-Solvents. *Adv Colloid Interfac.* 1995; 59:95–193.
3. Mitchell DJ, Ninham BW. Micelles, Vesicles and Micro-Emulsions. *J Chem Soc Farad T 2.* 1981; 77:601–629.
4. Kinugasa T, Kondo A, Nishimura S, Miyauchi Y, Nishii Y, Watanabe K, Takeuchi H. Estimation for Size of Reverse Micelles Formed by AOT and SDEHP Based on Viscosity Measurement. *Colloids Surf., A.* 2002; 204:193–199.
5. Moilanen DE, Levinger NE, Spry DB, Fayer MD. Confinement or the Nature of the Interface? Dynamics of Nanoscopic Water. *J Am Chem Soc.* 2007; 129:14311–14318. [PubMed: 17958424]
6. Moilanen DE, Fenn EE, Wong D, Fayer MD. Geometry and Nanolength Scales versus Interface Interactions: Water Dynamics in AOT Lamellar Structures and Reverse Micelles. *J Am Chem Soc.* 2009; 131:8318–8328. [PubMed: 19449867]
7. Piletic IR, Tan HS, Fayer MD. Dynamics of Nanoscopic Water: Vibrational Echo and Infrared Pump-probe Studies of Reverse Micelles. *J Phys Chem B.* 2005; 109:21273–21284. [PubMed: 16853758]
8. Pieniazek PA, Lin YS, Chowdhary J, Ladanyi BM, Skinner JL. Vibrational Spectroscopy and Dynamics of Water Confined inside Reverse Micelles. *J Phys Chem B.* 2009; 113:15017–15028. [PubMed: 19842648]
9. Faeder J, Ladanyi BM. Molecular Dynamics Simulations of the Interior of Aqueous Reverse Micelles. *J Phys Chem B.* 2000; 104:1033–1046.
10. Levinger NE. Ultrafast Dynamics in Reverse Micelles, Microemulsions, and Vesicles. *Curr Opin Colloid In.* 2000; 5:118–124.
11. Crans DC, Rithner CD, Baruah B, Gourley BL, Levinger NE. Molecular probe location in reverse micelles determined by NMR dipolar interactions. *J Am Chem Soc.* 2006; 128:4437–4445. [PubMed: 16569021]
12. Wong M, Thomas JK, Nowak T. Structure and State of H₂O in Reversed Micelles .3. *J Am Chem Soc.* 1977; 99:4730–4736.
13. Sarkar N, Das K, Datta A, Das S, Bhattacharyya K. Solvation Dynamics of Coumarin 480 in Reverse Micelles. Slow Relaxation of Water Molecules. *J Phys Chem.* 1996; 100:10523–10527.
14. Banerjee D, Pal SK. Solvation Dynamics of LDS 750 in Micelles, Reverse Micelles and Proteins. *Chem Phys Lett.* 2008; 451:237–242.
15. Pant D, Riter RE, Levinger NE. Influence of Restricted Environment and Ionic Interactions on Water Solvation Dynamics. *J Chem Phys.* 1998; 109:9995–10003.
16. Riter RE, Undiks EP, Levinger NE. Impact of Counterion on Water Motion in Aerosol OT Reverse Micelles. *J Am Chem Soc.* 1998; 120:6062–6067.
17. Riter RE, Willard DM, Levinger NE. Water Immobilization at Surfactant Interfaces in Reverse Micelles. *J Phys Chem B.* 1998; 102:2705–2714.
18. Levinger NE, Swafford LA. Ultrafast Dynamics in Reverse Micelles. *Annu Rev Phys Chem.* 2009; 60:385–406. [PubMed: 18999990]
19. D'Angelo M, Fioretto D, Onori G, Palmieri L, Santucci A. Dynamics of Water-Containing Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) Reverse Micelles: A High-frequency Dielectric Study. *Phys Rev E.* 1996; 54:993–996.

20. Fioretto D, Freda M, Onori G, Santucci A. Effect of Counterion Substitution on AOT-based Micellar Systems: Dielectric Study of Cu(AOT)(2) Reverse Micelles in CC14. *J Phys Chem B*. 1999; 103:8216–8220.
21. Onori G, Santucci A. IR Investigations of Water-Structure in Aerosol Ot Reverse Micellar Aggregates. *J Phys Chem*. 1993; 97:5430–5434.
22. Maekawa H, Ohta K, Tominaga K. Spectral Diffusion of the Anti-symmetric Stretching Mode of Azide Ion in a Reverse Micelle Studied by Infrared Three-pulse Photon Echo Method. *Phys Chem Chem Phys*. 2004; 6:4074–4077.
23. Nucci NV, Vanderkooi JM. Temperature Dependence of Hydrogen Bonding and Freezing Behavior of Water in Reverse Micelles. *J Phys Chem B*. 2005; 109:18301–18309. [PubMed: 16853355]
24. Temsamani MB, Maeck M, El Hassani I, Hurwitz HD. Fourier Transform Infrared Investigation of Water States in Aerosol-OT Reverse Micelles as a Function of Counterionic Nature. *J Phys Chem B*. 1998; 102:3335–3340.
25. Piletic IR, Moilanen DE, Spry DB, Levinger NE, Fayer MD. Testing the Core/Shell Model of Nanoconfined Water in Reverse Micelles using Linear and Nonlinear IR Spectroscopy. *J Phys Chem A*. 2006; 110:4985–4999. [PubMed: 16610816]
26. Tan HS, Piletic IR, Fayer MD. Orientational Dynamics of Water Confined on a Nanometer Length Scale in Reverse Micelles. *J Chem Phys*. 2005; 122:174501. [PubMed: 15910039]
27. Tan HS, Piletic IR, Riter RE, Levinger NE, Fayer MD. Dynamics of Water Confined on a Nanometer Length Scale in Reverse Micelles: Ultrafast Infrared Vibrational Echo Spectroscopy. *Phys Rev Lett*. 2005; 94:057405. [PubMed: 15783696]
28. Dokter AM, Woutersen S, Bakker HJ. Anomalous Slowing Down of the Vibrational Relaxation of Liquid Water upon Nanoscale Confinement. *Phys Rev Lett*. 2005; 94:178301. [PubMed: 15904342]
29. Dokter AM, Woutersen S, Bakker HJ. Inhomogeneous Dynamics in Confined Water Nanodroplets. *P Natl Acad Sci USA*. 2006; 103:15355–15358.
30. Dokter AM, Woutersen S, Bakker HJ. Ultrafast Dynamics of Water in Cationic Micelles. *J Chem Phys*. 2007; 126:124507. [PubMed: 17411144]
31. Cringus D, Bakulin A, Lindner J, Vohringer P, Pshenichnikov MS, Wiersma DA. Ultrafast Energy Transfer in Water-AOT Reverse Micelles. *J Phys Chem B*. 2007; 111:14193–14207. [PubMed: 18047308]
32. Cringus D, Lindner J, Milder MTW, Pshenichnikov MS, Vohringer P, Wiersma DA. Femtosecond Water Dynamics in Reverse-Micellar Nanodroplets. *Chem Phys Lett*. 2005; 408:162–168.
33. Moilanen DE, Fenn EE, Wong D, Fayer MD. Water Dynamics at the Interface in AOT Reverse Micelles. *J Phys Chem B*. 2009; 113:8560–8568. [PubMed: 19485407]
34. Fayer MD. Dynamics of Water Interacting with Interfaces, Molecules, and Ions. *Accounts Chem Res*. 2012; 45:3–14.
35. Fenn EE, Wong DB, Giammanco CH, Fayer MD. Dynamics of Water at the Interface in Reverse Micelles: Measurements of Spectral Diffusion with Two-Dimensional Infrared Vibrational Echoes. *J Phys Chem B*. 2011; 115:11658–11670. [PubMed: 21899355]
36. Loparo JJ, Fecko CJ, Eaves JD, Roberts ST, Tokmakoff A. Reorientational and Configurational Fluctuations in Water Observed on Molecular Length Scales. *Phys Rev B*. 2004; 70:180201.
37. Laage D, Hynes JT. A Molecular Jump Mechanism of Water Reorientation. *Science*. 2006; 311:832–835. [PubMed: 16439623]
38. Laage D, Hynes JT. On the Molecular Mechanism of Water Reorientation. *J Phys Chem B*. 2008; 112:14230–14242. [PubMed: 18942871]
39. Vorobyev DY, Kuo CH, Chen JX, Kuroda DG, Scott JN, Vanderkooi JM, Hochstrasser RM. Ultrafast Vibrational Spectroscopy of a Degenerate Mode of Guanidinium Chloride. *J Phys Chem B*. 2009; 113:15382–15391. [PubMed: 19905022]
40. Vorobyev DY, Kuo CH, Kuroda DG, Scott JN, Vanderkooi JM, Hochstrasser RM. Water-Induced Relaxation of a Degenerate Vibration of Guanidium Using 2D IR Echo Spectroscopy. *J Phys Chem B*. 2010; 114:2944–2953. [PubMed: 20143800]

41. Kuroda DG, Hochstrasser RM. Two-Dimensional Infrared Spectral Signature and Hydration of the Oxalate Dianion. *J Chem Phys.* 2011; 135:204502. [PubMed: 22128938]
42. Kuroda DG, Hochstrasser RM. Dynamic Structures of Aqueous Oxalate and the Effects of Counterions Seen by 2D IR. *Phys Chem Chem Phys.* 2012; 14:6219–6224. [PubMed: 22314844]
43. Kuroda DG, Singh PK, Hochstrasser RM. Differential Hydration of Tricyanomethanide Observed by Time Resolved Vibrational Spectroscopy. *The Journal of Physical Chemistry. B.* 2013; 117:4354–4364. [PubMed: 22934602]
44. Ji MB, Park S, Gaffney KJ. Dynamics of Ion Assembly in Solution: 2DIR Spectroscopy Study of LiNCS in Benzonitrile. *J Phys Chem Lett.* 2010; 1:1771–1775.
45. Moilanen DE, Fenn EE, Lin YS, Skinner JL, Bagchi B, Fayer MD. Water Inertial Reorientation: Hydrogen bond Strength and the Angular Potential. *P Natl Acad Sci USA.* 2008; 105:5295–5300.
46. Park S, Ji MB, Gaffney KJ. Ligand Exchange Dynamics in Aqueous Solution Studied with 2DIR Spectroscopy. *J Phys Chem B.* 2010; 114:6693–6702. [PubMed: 20426448]
47. Park S, Odelius M, Gaffney KJ. Ultrafast Dynamics of Hydrogen Bond Exchange in Aqueous Ionic Solutions. *J Phys Chem B.* 2009; 113:7825–7835. [PubMed: 19435307]
48. Sando GM, Dahl K, Owrutsky JC. Vibrational Relaxation Dynamics of Azide in Ionic and Nonionic Reverse Micelles. *J Phys Chem A.* 2004; 108:11209–11217.
49. Sando GM, Dahl K, Owrutsky JC. Surfactant Charge Effects on the Location, Vibrational Spectra, and Relaxation Dynamics of Cyanoferrates in Reverse Micelles. *J Phys Chem B.* 2005; 109:4084–4095. [PubMed: 16851467]
50. Kim YS, Wang JP, Hochstrasser RM. Two-Dimensional Infrared Spectroscopy of the Alanine Dipeptide in Aqueous Solution. *J Phys Chem B.* 2005; 109:7511–7521. [PubMed: 16851862]
51. Zhong Q, Steinhurst DA, Carpenter EE, Owrutsky JC. Fourier Transform Infrared Spectroscopy of Azide Ion in Reverse Micelles. *Langmuir.* 2002; 18:7401–7408.
52. Weidinger D, Houchins C, Owrutsky JC. Vibrational Dynamics of Tricyanomethanide. *Chem Phys Lett.* 2012; 525–26:60–63.
53. Silber JJ, Biasutti A, Abuin E, Lissi E. Interactions of Small Molecules with Reverse Micelles. *Adv Colloid Interfac.* 1999; 82:189–252.
54. Crans DC, Trujillo AM, Bonetti S, Rithner CD, Baruah B, Levinger NE. Penetration of Negatively Charged Lipid Interfaces by the Doubly Deprotonated Dipicolinate. *J Org Chem.* 2008; 73:9633–9640. [PubMed: 19053583]
55. Singh PK, Kumbhakar M, Pal H, Nath S. A Nano-Confined Charged Layer Defies the Principle of Electrostatic Interaction. *Chem Commun.* 2011; 47:6912–6914.
56. Mason PE, Dempsey CE, Neilson GW, Brady JW. Nanometer-scale Ion Aggregates in Aqueous Electrolyte Solutions: Guanidinium Sulfate and Guanidinium Thiocyanate. *J Phys Chem B.* 2005; 109:24185–24196. [PubMed: 16375411]
57. Hamm, P.; Zanni, MT. *Concepts and Methods of 2D Infrared Spectroscopy.* Cambridge, UK: Cambridge University Press; 2011.
58. Kwac K, Cho MH. Molecular Dynamics Simulation Study of N-methylacetamide in Water. II. Two-Dimensional Infrared Pump-probe Spectra. *J Chem Phys.* 2003; 119:2256–2263.
59. Ge NH, Zanni MT, Hochstrasser RM. Effects of Vibrational Frequency Correlations on Two-Dimensional Infrared Spectra. *J Phys Chem A.* 2002; 106:962–972.
60. Oxtoby DW. Vibrational-Relaxation in Liquids. *Annu Rev Phys Chem.* 1981; 32:77–101.
61. Li SZ, Schmidt JR, Skinner JL. Vibrational Energy Relaxation of Azide in Water. *J Chem Phys.* 2006; 125:244507. [PubMed: 17199355]
62. Pomata MHH, Laria D, Skaf MS, Elola MD. Molecular Dynamics Simulations of AOT-Water/Formamide Reverse Micelles: Structural and Dynamical Properties. *J Chem Phys.* 2008; 129:244503. [PubMed: 19123513]
63. Faeder J, Ladanyi BM. Solvation Dynamics in Reverse Micelles: The Role of Headgroup-Solute Interactions. *J Phys Chem B.* 2005; 109:6732–6740. [PubMed: 16851757]
64. Satpati AK, Kumbhakar M, Nath S, Pal H. Influence of Confined Water on the Photophysics of Dissolved Solutes in Reverse Micelles. *Chemphyschem.* 2009; 10:2966–2978. [PubMed: 19810081]

65. Singh PK, Kumbhakar M, Pal H, Nath S. Ultrafast Torsional Dynamics of Protein Binding Dye Thioflavin-T in Nanoconfined Water Pool. *J Phys Chem B*. 2009; 113:8532–8538. [PubMed: 19485371]
66. Kim J, Lee M. Excited-state Photophysics and Dynamics of a Hemicyanine Dye in AOT Reverse Micelles. *J Phys Chem A*. 1999; 103:3378–3382.
67. Kitamura N, Sakata N, Kim HB, Habuchi S. Energy Gap Dependence of the Nonradiative Decay Rate Constant of 1-anilino-8-Naphthalene sulfonate in Reverse Micelles. *Anal Sci*. 1999; 15:413–419.
68. Hunt NT, Jaye AA, Meech SR. Reactive Dynamics in Confined Water Droplets: Auramine O in AOT/Water/Heptane Microemulsions. *Chem Phys Lett*. 2005; 416:89–93.

Figure 1.

Linear IR spectra of TCM anion in reverse micelles of various sizes. Normalized and background subtracted FTIR spectra of TCM ion in reverse micelle of $W_0=4$ (black), 6 (red), 8 (blue), 12 (pink), 20 (green), and 30 (orange). The dotted black line represents the IR spectrum of TCM anion in bulk water.

Figure 2.

Parameters of the FTIR spectra Gaussian fit. (a) Peak frequency as a function of W_0 for the high frequency band (grey open circles) and the low frequency band (black filled squares). The right side caption (grey) corresponds to the high frequency band. (b) FWHM as a function of W_0 for the high frequency band (grey open circles) and the low frequency band (black filled squares). (c) Change of the area ratio of the high frequency band to the low frequency band with W_0 . The black open triangles are the data points and the solid black line is its linear fit. The top axis of the panel (a) shows the equivalent water pool radius for the different W_0 's used in the experiment.⁴

Figure 3.

Vibrational dynamics of TCM anion as function of W_0 . (a) Transient bleach/stimulated emission signal for the TCM anion at 2178 cm^{-1} in reverse micelle of $W_0=4, 6, 8, 12, 20$, and 30 . (b) Variation in vibrational lifetime with W_0 . The dashed line corresponds to the vibrational lifetime in bulk water (5.3 ps^{43}). Error bars are too small to be included (Error $< \pm 0.05\text{ps}$ for all samples).

Figure 4.

Absorptive 2D IR spectra of TCM ion in reverse micelles of different size. Columns from left to right correspond to $W_0=4, 8, 12, 20$, and 30 respectively. Rows correspond to $T_w=0$ ps (second row) and 3 ps (third row). The top row shows their corresponding linear IR spectra and fit with two Gaussian functions.

Figure 5. FFCF dynamics for TCM anion in water pools of different size. (a) Logarithm of slope, $S(T_w)$ vs waiting time, T_w , for $W_0=4$ (filled squares), 6 (open circles), 8 (filled triangles), 12 (filled stars), 20 (filled rhombus), and 30 (open squares) of the high frequency band. (b) Variation of correlation time with W_0 . The dashed line shows the correlation time for the TCM anion in bulk water. (c) Correlation plot of the FFCF correlation time (high frequency band) with vibrational lifetime. The filled squares represent the data points and the solid black line is a linear fit.

Figure 6.

Fitting of the experimental FFCF correlation time with the model described in the text.

Black solid line show the fitting the model when $r_0(R_{WP})$ varies as in Equation (5) and the dash line when $r_0(R_{WP})$ is kept constant.

Figure 7.

Heterogeneous hydration dynamics of water in a reverse micelle. Top: Schematic presentation for the variation of the FFCF correlation time of TCM as a function of distance from the interface for $W_0=4$ (left) and $W_0=8$ (right). Bottom: Variation of the characteristic length of the decay of the correlation time (r_0) as a function of W_0 obtained from the fitting parameters and Equation 5.

Scheme 1.

Cartoon representation of an AOT reverse micelle. The light blue area (A) represents the water pool and the grey area (B) represents the interface. Note that in our definition of water pool, the layer of counter ions at the interface is not included. Green, yellow, and blue circles represent the sulfonate head groups, sodium ions, and the ester groups, respectively.

Scheme 2.

Chemical structures of AOT surfactant (left) and the tricyanomethanide anion (right)