Structure of micelles and micro-emulsions probed through the molecular reorientation of water

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Abstract

We study the structural properties of dodecyltrimethylammonium bromide (DTAB) micelles and micro-emulsions by probing the molecular reorientation of water with polarization-resolved infrared pump-probe spectroscopy. For all systems studied, we observe that a fraction of water reorients on a much slower timescale than bulk water. This slow water fraction increases sublinear with increasing DTAB concentration, indicating an increase of the micelle size and enhanced micelle aggregation with concentration. We observe that the addition of oil to the micelle solutions, leading to the formation of a micro-emulsion, does not lead to a significant change of the fraction of slow water, showing that the added oil molecules are well solvated within the core of the micelles, and thus completely shielded from water.

1. Introduction

Emulsions are mixtures of water and oil, stabilized by surfactants. These can either be a mixture of oil droplets in water (oil-in-water) or water droplets in oil (water-in-oil). The surfactant molecules that stabilize emulsions are amphiphilic molecules (consisting of a hydrophilic moiety and a hydrophobic moiety). Without oil, the surfactant molecules tend to form spherical aggregates denoted as micelles. When micelles are swollen with oil, a micro-emulsion is formed. The use of emulsions is widespread: in food industry, as carriers of pharmaceuticals and in oil recovery [1–4]. Emulsions can degrade over time [5]. Water can be expelled from the emulsion and phase separation can occur, a process known as syneresis. Syneresis is thus an important issue in the long term stability of emulsions.

Micelles and micro-emulsions have been intensely studied with a variety of techniques such as Dynamic Light Scattering, rheology, titrations and conductivity measurements [6–9]. These techniques give insight in the overall properties and structure of these systems, but they do not provide information about their molecular properties. The details of the molecular properties can provide insight into the process of syneresis, since this process involves the breaking and reorganization of hydrogen bonds. The molecular properties of micelles and micro-emulsions can be studied with methods like pump-probe infrared spectroscopy, optical Kerr effect spectroscopy and Raman spectroscopy, [10–15]. Up to now, these techniques have been mostly applied to the study of reverse micelles: small water droplets surrounded by surfactants dispersed in oil. [10–13] These reverse micelles are considered to be a good model for water in confinement [10–13].

Recently, the hydration of normal micelles was studied using multivariate-curve-resolution (MCR) Raman spectroscopy [15]. Evidence was found that water molecules penetrate deeply into the micelle. Using the same method, it was found that alkane molecules added to the micelles, thus forming a micro-emulsion, are largely adsorbed in the dry core of the micelles.

In this paper, we study the reorientation dynamics of water molecules interacting with dodecyltrimethylammonium bromide (DTAB) micelles, and of water molecules in a micro-emulsion system of toluene droplets stabilized by DTAB in water. We measure the reorientation dynamics with polarization-resolved infrared pump-probe spectroscopy (fs-IR). With this technique we can determine the fraction of water molecules that reorients like bulk water molecules, and the fraction of water molecules for which the dynamics are changed by the micelles and surfactant-covered oil droplets.

2. Experimental methods

We measure the reorientation dynamics of water in micelle solutions and micro-emulsions using polarization-resolved femtosecond infrared spectroscopy. The micelle solutions are prepared by dissolving different concentrations of dodecyltrimethylammonium bromide (DTAB, 99%, Sigma-Aldrich) or sodium dodecyl sulfate (SDS, 99%, Sigma-Aldrich) in 4% D_2O (99.9%D, Cambridge Isotope Laboratories) in H_2O (ultrapure milli-Q grade). Micro-emulsions are prepared by first dissolving different concentrations of DTAB in 4% D_2O in H_2O, and then adding a certain amount of toluene (99.8%, anhydrous, Sigma-Aldrich), benzene (99.9%, Sigma-Aldrich), *p*-xylene (99%, anhydrous) or hexane (95%, anhydrous, Sigma-Aldrich). The solutions were mixed with a vortex mixer and the micro-emulsions formed spontaneously, forming a transparent solution.

We performed pump probe spectroscopy on the micelle and micro-emulsion solutions. A detailed description of the experiment is given elsewhere [16]. We excite the OD stretching vibrations of HDO molecules with an intense femtosecond pump pulse at 2500 cm^{-1}. The resulting absorption changes are detected with a weaker delayed probe pulse, also at 2500 cm^{-1}, which is polarized parallel or perpendicular with respect to the pump pulse. Initially, the parallel transient absorption ($\Delta\alpha_\parallel$(v,t)) will be larger than the perpendicular transient absorption ($\Delta\alpha_\perp$(v,t)), because the pump excites the OD vibrations that are oriented parallel to the pump pulse most efficiently. At longer probe delay times, the signals measured with the parallel and perpendicular probe pulse polarization become equal due to the reorientation of the HDO molecules. From the parallel and perpendicular signals we construct the isotropic signal, which is independent of the reorientation:

$$\Delta\alpha_{iso}(v,t) = \frac{1}{3}(\Delta\alpha_\parallel(v,t) + 2\Delta\alpha_\perp(v,t))$$

The isotropic signal decays with the vibrational lifetime. We also construct the anisotropic signal R, which is independent of the vibrational relaxation:

$$R(v,t) = \frac{\Delta\alpha_\parallel(v,t) - \Delta\alpha_\perp(v,t)}{\Delta\alpha_\parallel(v,t) + 2\Delta\alpha_\perp(v,t)}$$

The anisotropic signal decays with the rate of molecular reorientation.

3. Results and Discussion

3.1 Micelles

Figure 1A shows isotropic transient absorption spectra measured at different pump-probe delay times for a solution of 2.2 molal DTAB in isotopically diluted water. At short delay times (0.5 ps) we observe a ground-state bleach, and at long delay times (>10 ps) we observe a thermal-difference spectrum, indicating that the vibrational relaxation is complete and that the energy of the pump pulse has become thermal over the focus of the pump pulse. In Figure 1B we show pump-probe transients at three different probe frequencies. At all three frequencies we observe a bleaching that decays on a picosecond time scale. Depending on the probe frequency, the decay ends in a residual bleaching or in an induced absorption, reflecting the frequency dependence of the eventual heating effect on the absorption spectrum of the OD stretch vibration.

In order to determine the anisotropy of the transient absorption signal associated with the excitation of the OD stretch vibration, the ingrowing heating contribution to the transient absorption signal needs to be subtracted. To this end, the spectra are fitted to a kinetic model describing the vibrational relaxation and the resulting rise of the heating contribution. Previous studies showed that the vibrational relaxation of the OH and OD stretch vibrations of HDO molecules strongly depends on the nature of the donated hydrogen bond of the OH/OD group[17–19]. For OD/OH groups donating a hydrogen bond to large halide anions like Br$^-$ and I$^-$ the vibrational lifetime is substantially longer than for OH/OD groups donating a hydrogen bond to the oxygen atom of a D_2O or H_2O molecule. The micelle solution contains water molecules donating hydrogen bonds to other water molecules and to Br$^-$ ions. We thus model the relaxation with a kinetic model in which we consider two populations of excited OD vibrations, OD vibrations hydrogen bonded to H_2O molecule, and OD vibrations hydrogen bonded to Br$^-$ ions. The excited OD vibrations decay to an intermediate state, and the intermediate state to the hot ground state [20]. We use the transient spectrum and the relaxation time constants that have been determined before for neat water (1.7 ps for the vibrational lifetime and 1.2 ps for the relaxation time constant of the intermediate state). The initial populations of the two excited OD vibrations are determined from the concentration of Br$^-$ ions. We find a vibrational lifetime of the excited OD vibration of HDO molecules hydrogen bonded to Br$^-$ ions of 8±2 − 5.2±0.4 ps for 0.36 − 2.2 molal DTAB.
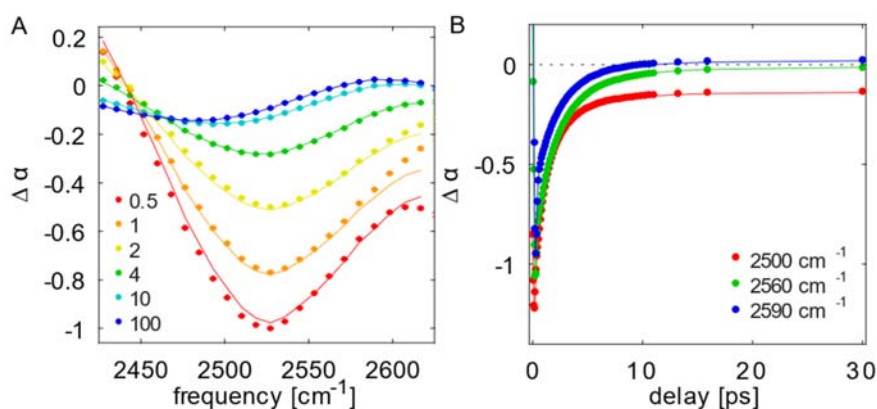

Figure 1. (A) Isotropic transient absorption change of the OD stretch vibration of HDO molecules for a solution of 2.2 molal DTAB in isotopically diluted water for six different delay times. The solid lines results from a fit to the model described in the text. (B) Isotropic transient absorption change as a function of delay time, measured for a solution of 2.2 molal DTAB in isotppically diluted water, for three different probe frequencies.

Figure 2A shows the anisotropy of the transient absorption change measured for solutions of different concentrations of DTAB in isotopically diluted water. The anisotropy is constructed from the parallel and the perpendicular probing signal, that are both corrected for the ingrowing heating signal of which the dynamics is determined from the fit to the kinetic model. We compare the anisotropy dynamics of the DTAB solutions with that of neat isotopically diluted water. The anisotropy of neat water decays exponentially with a time constant of τ_r=2.5 ps, in agreement with previous work [20]. For the micelles we observe that the anisotropy transients contain a fast and a slow component. We thus fit these transients with an exponential function with an offset, $R_0 = e^{-t/\tau_r} + R_{slow}$. For all DTAB solutions (0.36-2.2 molal) we find a reorientation time τ_r=2.1±0.1 ps, similar to the time constant of neat isotopically water. This fast component is attributed to the reorientation of water molecules interacting with other water molecules and showing bulk-like behaviour. The offset R_{slow} is attributed to water molecules interacting with DTA$^+$ and Br$^-$ ions. Previous work showed that the orientation dynamics of water molecules hydrogen bonded to halide ions like Br$^-$ indeed contain a slow component[18]. Measurements of the anisotropy dynamics for solutions of 0.8 to 2.2 molal KBr show that the amplitude of this component is 0.011±0.002 per molal Br$^-$ (See SI1).
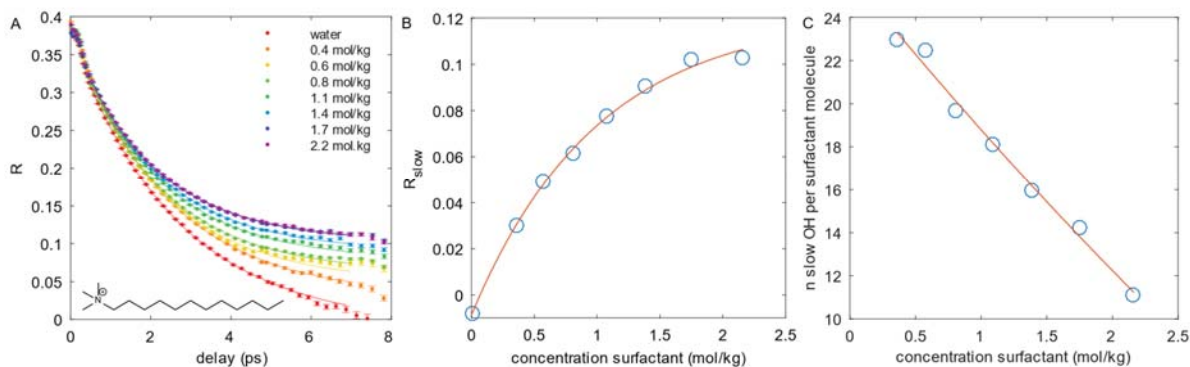

Figure 2. (A) Anisotropy decay as function of delay time for different solutions of DTAB in isotopically diluted water and neat isotopically diluted water. The solid lines are fits to an exponential function with an offset. (B) Offset of the anisotropic decay as a function of DTAB concentration. (C) Number of slow water molecules per surfactant ion as a function of DTAB concentration. The number of slow water molecules per surfactant ion is obtained after subtraction of the part of R$_{slow}$ that can be attributed to water molecules hydrating Br$^-$ ions. The solid lines in (B) and (C) are a guide to the eye.

Figure 2B shows the offset as function of the surfactant concentration. It is seen that the slow water fraction increases sublinearly with the surfactant concentration. After correcting R$_{slow}$ for the Br$^-$ contribution, we can determine the number of slow OH groups per surfactant molecule, as is depicted in Figure 2C. We see that at low surfactant concentration, 23±1 OH groups per surfactant molecule are slowed down. These slow OH groups are probably located near the three methyl groups of the DTA$^+$ surfactant head group. Previous work on slow water surrounding hydrophobic groups showed that every methyl group slows down ~5 water OH groups, meaning that probably ~15 of the slow OH groups is slowed down due to their close position to the methyl groups of the DTA$^+$ head group [21,22]. The remaining ~8 OH groups are probably slowed down due their interaction with the hydrophobic tails, which implies that these OH groups belong to water molecules that penetrate into the micelle. At higher surfactant concentrations, we observe a decrease of the number of slowed down water molecules per surfactant molecule, from 23±1 slowed down OH groups per surfactant molecule to only 11±1 slowed down OH groups per surfactant molecule.
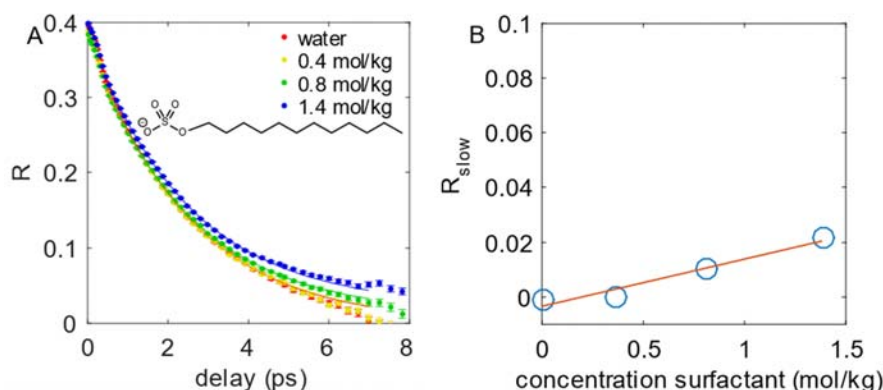
Figure 3. (A) Anisotropy decay as function of delay time of neat water and different SDS concentrations. The solid lines are fits to an exponential function with an offset. (B) Offset of the anisotropic decay as a function of SDS concentration. The solid line is a guide to the eye.

For comparison, we also measured the anisotropy dynamics of water in SDS solutions, as shown in Figure 3A. SDS has a different head group, without methyl groups. In the case of SDS, we find much smaller offsets, as illustrated in Figure 3B. For SDS at 0.8-1.4 molal, we find only 4.0±0.5 slowed down water OH groups per surfactant molecule. This finding supports the assignment of the main fraction of slow water molecules in the DTAB solutions to water molecules hydrating the methyl groups of the DTA$^+$ head group.

For the DTAB micelle solutions the number of slow OH groups per surfactant molecule strongly decreases with increasing surfactant concentration. There are several explanations for this: at higher concentrations, the micelles become larger, or the hydration shells of the micelles start to overlap (and thus there is competition for solvating water molecules). The latter effect will be enhanced if the micelles aggregate.

It is known that for micelles the aggregation number (number of surfactants per micelle, N_{agg}) and thus the micelle size, increase with increasing concentration [23–27]. This change in size leads to a change in surface area. The increase in N_{agg} of DTAB with concentration has been described with a power law by Bales and Zana, $N_{agg} = N^0 \left(C_{aq}/cmc_0 \right)^{\gamma}$, where N^0 is the aggregation number at cmc$_0$, cmc$_0$ is the critical micelle concentration (which is 14.9 mM) in the absence of salt and C$_{aq}$ is the concentration of the surfactant counterion in the aqueous phase and γ is 0.146 [24,27]. From this equation we find that N$_{agg}$ increases from 73 for 0.4 mol/kg to 109 for 2.2 mol/kg. The corresponding change in surface-volume ratio leads to a decrease from 23 to 20 slow OH groups per surfactant molecule. It thus follows that the growing of the micelle size with concentration only partially accounts for the observed decrease of the number of slow OH groups per surfactant molecule: we observe only 11 slowed down OH groups at 2.2 mol/kg DTAB.

The number of slow OH groups per surfactant molecule will further decrease if there is a competition for solvation water molecules at high concentrations, which implies that the hydration shells of the DTA$^+$ ions start to overlap. To calculate if this effect could explain the further decrease of the number of slow OH groups per surfactant, we followed the approach of Petersen et al. [28], in which the effect of the competition for hydration water is described with a chemical equilibrium, under the assumption that there is no specific interaction between the solutes, i.e. the solutes are statistically distributed over the solution. We find that this effect cannot account for the strong further decrease of the number of slow water molecules, because the competition for solvation water molecules leads to a decrease of only 2-4 slow OH groups at the highest concentration of surfactant. From this we conclude that there must be a

much stronger overlap of the micelle hydration shells than would be expected for a statistical distribution of micelles in the solution. This means that the micelles aggregate, and thereby strongly reduce the total micelle surface area that is exposed to water. Micelle aggregation implies that the head groups of the DTA$^+$ surfactant ions of different micelles aggregate. This finding is in line with other studies of aqueous solutions of quaternary ammonium ions (that constitute the head group of DTA$^+$). Aqueous solutions of tetra-*n*-alkylammonium salts also show strong aggregation at higher concentrations, leading to a strong decrease of the number of hydrating water molecules per tetra-*n*-alkylammonium ion [18].

3.2 Micro-emulsions

We prepared micro-emulsions by swelling the DTAB micelles with toluene. The added toluene is completely dissolved in the DTAB solution (see SI2). Figure 4A shows the anisotropy decay of a solution of 1.4 mol/kg DTAB and different toluene concentrations in water. Surprisingly, we observe that the offset of the anisotropy decay does not change significantly when changing the oil concentration. This is surprising, because at the highest oil concentration, the volume of oil added to the micelles is 1.8 times the volume of the micelles.
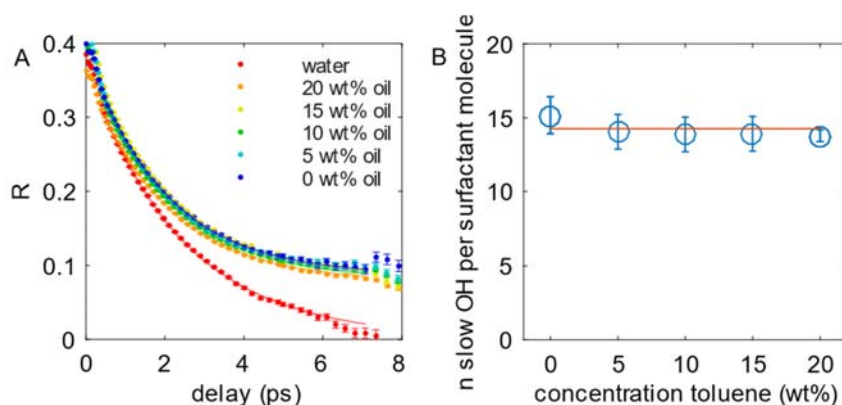

Figure 4. (A) Anisotropy decay as function of delay time for emulsions with a DTAB surfactant concentration of 1.4 mol/kg and different concentrations of toluene. The solid lines are fits to an exponential function with an offset. (B) Number of slow water molecules per surfactant molecule as a function of toluene concentration. The solid line is a guide to the eye.

Using the offset of the anisotropy decay, we calculated the number of slow OH groups per surfactant molecule, as shown in Figure 4B. The number of slow OH groups per surfactant molecule does not change with increasing concentrations of oil. Apparently, the added oil molecules are well embedded within the core of the surfactant covered oil droplets, and thus completely shielded from water.

In Figure 5A we show the anisotropy dynamics of solutions containing a constant oil concentration of 10 wt%, and different surfactant concentrations. We observe that at all surfactant concentrations the offset of the anisotropy is similar for the micro-emulsion and the micelle with the same surfactant concentration.
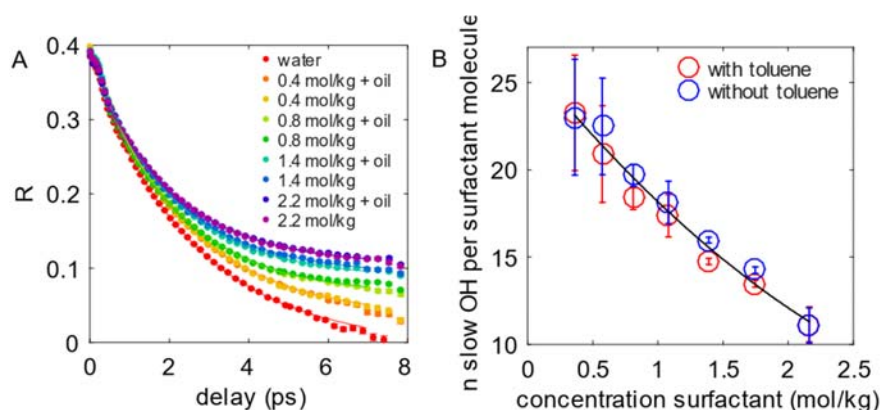
Figure 5. (A) Anisotropy decay as a function of delay time for micelle solutions and emulsions with 10 wt% oil for four different surfactant concentrations. The solid lines are fits to an exponential function with an offset. (B) Number of slow water molecules per surfactant of emulsions with different surfactant concentrations, with and without oil. The solid lines are a guide to the eye.

Figure 5B depicts the number of slow OH groups per surfactant molecule as a function of surfactant concentration for surfactant solutions with 10 wt% oil (micro-emulsions, red) and without oil (micelles, blue). Even at the highest oil to surfactant ratio (10% oil in 0.36 molal DTAB, V_{oil}/V_{DTAB}=2.4), there is no significant difference in number of slowed down OH groups. This indicates that at the measured surfactant concentrations, the oil molecules are completely embedded in the core of the surfactant covered oil droplets.

The results above show that in toluene-based emulsions with the surfactant DTAB, the oil is completely embedded in the emulsion core, leading to no observable change in the anisotropy and thus in the fraction of slowed-down water molecules. To test the generality of this result, we also measured the anisotropy of emulsions with other oils. To this end we prepared emulsions consisting of 1.4 mol/kg DTAB and 10 wt% xylene, benzene or hexane. The anisotropy of these different emulsions is depicted in Figure 6.
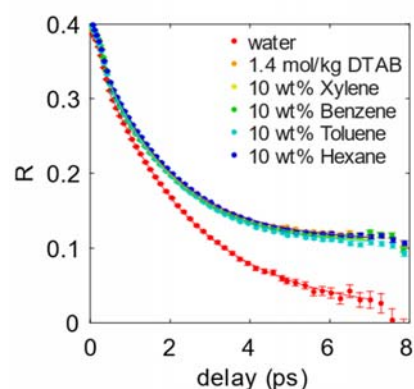

Figure 6. Anisotropy decay as function of delay time for emulsions with 10 wt% of different oils, at a 1.4 mol/kg surfactant concentration. The solid lines are fits to an exponential function with an offset.

We observe that the anisotropy dynamics of the emulsions with different oils is remarkably similar to each other, and more importantly, similar to the anisotropy dynamics of a 1.4 mol/kg DTAB solution without oil. The observation that the added oil molecules are well embedded in the core of the droplet and completely shielded from the surrounding water is thus a quite general result, independent of the

nature of the oil. For all emulsions and the DTAB solution without oil, we find that 16.9±0.6 water OH groups are slowed down.

3.3 Comparison with other work

Recently, similar micellar systems were studied using multivariate-curve-resolution (MCR) Raman spectroscopy [15]. The group of Ben-Amotz found that water molecules penetrate into micelles, and over 20% of the surfactant tail methylene groups stay in contact with water. We find similar results for micelles composed of DTAB surfactant molecules. For SDS micelles we observe that only 4 water OH groups are slowed down, which means that not more than 10% of the surfactant methylene groups can be in contact with water. Bales and Zana studied the hydration of DTAB micelles using electron paramagnetic resonance (EPR), and find that the number of hydration water molecules per surfactant molecule decreases with increasing N_{agg} and thus increasing DTAB concentration, which is in agreement with our findings [24].

The group of Ben-Amotz also studied the the uptake of hydrophobic oil molecules by micelles, similar to our approach of creating micro-emulsions by adding oil to the micellar systems. Based on the vibrational frequencies of the CD stretch vibration of the hydrophobic probes, they found that the added hydrophobic probes are well solubilized within the dry oil-like core of the micelle [15]. This is in perfect agreement with our present results, in which we also see no change in slow water fraction upon adding oil to micelles. In a previous EPR study it was also found that the number of hydrating water molecules per surfactant molecule does not change upon adding heptane to SDS micelles [29].

Conclusions

We studied the reorientation dynamics of water molecules surrounding micelles and micro-emulsions using polarization-resolved femtosecond pump-probe spectroscopy. We observed that a fraction of the water molecules has very slow reorientation dynamics. For micelles, the number of slow OH groups per surfactant molecule decreases with increasing surfactant concentration, from 23±1 slow OH groups per surfactant molecules at low concentrations to 11±1 slow OH groups at high concentrations. This decrease results in part from an increase in size of the micelles with increasing surfactant concentration, and in part from the increase in overlap of the hydration shells of the micelles. The latter contribution is much stronger than would be expected in case the micelles would be statistically distributed over the solution, which indicates that the micelles aggregate at high surfactant concentration. For micro-emulsions we find no significant difference in the number of slow OH groups per surfactant upon the addition of oil, even in case the volume of oil added to the micelles is 1.8 times the volume of the micelles. This indicates that in micro-emulsions, the oil molecules are very well embedded in the inner core of the droplet.

Acknowledgements

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