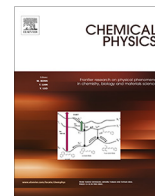




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# Structure of micelles and micro-emulsions probed through the molecular reorientation of water

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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.

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## 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<sub>2</sub>O (99.9%D, Cambridge

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Isotope Laboratories) in H<sub>2</sub>O (ultrapure milli-Q grade). Micro-emulsions are prepared by first dissolving different concentrations of DTAB in 4% D<sub>2</sub>O in H<sub>2</sub>O, 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<sup>-1</sup>. The resulting absorption changes are detected with a weaker delayed probe pulse, also at 2500 cm<sup>-1</sup>, 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 anisotropy  $R$ , which is independent of the vibrational relaxation:

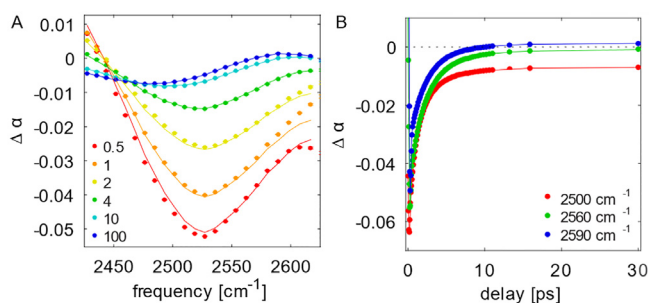
$$R(v, t) = \frac{\Delta\alpha_{\parallel}(v, t) - \Delta\alpha_{\perp}(v, t)}{\Delta\alpha_{\parallel}(v, t) + 2\Delta\alpha_{\perp}(v, t)}$$

The anisotropic signal decays with the rate of molecular reorientation. The reorientation of the OD group of the HDO molecule is representative for the reorientation dynamics of all hydroxyl groups, since the reorientation of water molecules is determined by the collective hydrogen-bond dynamics of the solution [17].

### 3. Results and discussion

#### 3.1. Micelles

Fig. 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



**Fig. 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 isotopically diluted water, for three different probe frequencies.

the vibrational relaxation is complete and that the energy of the pump pulse has become thermal over the focus of the pump pulse. In Fig. 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 [18–20]. For OD/OH groups donating a hydrogen bond to large halide anions like Br<sup>-</sup> and I<sup>-</sup> the vibrational lifetime is substantially longer than for OH/OD groups donating a hydrogen bond to the oxygen atom of a D<sub>2</sub>O or H<sub>2</sub>O molecule. The micelle solution contains water molecules donating hydrogen bonds to other water molecules and to Br<sup>-</sup> ions. We thus model the relaxation with a kinetic model in which we consider two populations of excited OD vibrations, vibrations of OD groups hydrogen bonded to H<sub>2</sub>O molecule, and vibrations of OD groups hydrogen bonded to Br<sup>-</sup> ions. The excited OD vibrations decay to an intermediate state, and the intermediate state to the hot ground state [17]. In the modeling 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 types of excited OD vibrations are determined from the concentration of Br<sup>-</sup> ions. We find a vibrational lifetime of the excited OD vibration of HDO molecules hydrogen bonded to Br<sup>-</sup> ions of  $8 \pm 2$ – $5.2 \pm 0.4$  ps for 0.36–2.2 molal DTAB solutions.

Fig. 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 those of neat isotopically diluted water. The anisotropy of neat water decays exponentially with a time constant of  $\tau_r = 2.5$  ps, in agreement with previous work [17]. 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,  $R = R_0 e^{-t/\tau_r} + R_{slow}$ . For all DTAB solutions (0.36–2.2 molal) we find a reorientation time  $\tau_r = 2.1 \pm 0.1$  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. The offset  $R_{slow}$  is attributed to water molecules interacting with DTA<sup>+</sup> and Br<sup>-</sup> ions. Previous work showed that the orientation dynamics of water molecules hydrogen bonded to halide ions like Br<sup>-</sup> contain a slow component [19]. Measurements of the anisotropy dynamics for solutions of 0.8 to 2.2 molal KBr show that the amplitude of this component is  $0.011 \pm 0.002$  per molal Br<sup>-</sup> (See SI1).

Fig. 2B shows the offset as a 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<sup>-</sup> contribution, we can determine the number of slow water hydroxyl groups  $N_{slow}$  per surfactant molecule by dividing the fraction of slow water  $R_{slow}/(R_{slow} + R_0)$  by the DTAB concentration  $c$  (in

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