

Water reorientation dynamics in colloidal water-oil emulsions

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Abstract

We study the molecular-scale properties of colloidal water-oil emulsions consisting of 20-500 nm oil droplets embedded in water. This type of emulsions can be prepared with low concentrations of surfactants and are usually kinetically stable. Even though colloidal water-oil emulsions are used ubiquitously, their molecular properties are still poorly understood. Here we study the orientational dynamics of water molecules in these emulsions using polarization resolved pump-probe infrared spectroscopy, for varying surfactant concentrations, droplet sizes, and temperatures. We find that the majority of the water molecules reorients with the same time constant as in bulk water, but that a small fraction of the water molecules reorients on a much longer time scale. These slowly reorienting water molecules are interacting with the surface of the oil droplets. The fraction of slowly orienting water molecules is determined by the oil volume fraction, and shows a negligible dependence on the average droplet size. This finding indicates that the total surface area of the oil droplets is quite independent of the average droplet size, which indicates that the oil droplets are quite corrugated, showing large protrusions into the water phase.

Introduction

Emulsions constitute very interesting types of systems, since they combine two immiscible liquids into one solution. Most emulsions either consist of oil droplets dispersed in water, or of water droplets dispersed in oil, where the droplets are often stabilized by surfactant molecules. Emulsions find many applications in the food industry, agrochemical, cosmetics and the pharmaceutical industry, among others.^[1-3]

The droplet size of emulsions can range from a few nanometers to tens of micrometers. The emulsions with the biggest droplet size, the macro-emulsions, contain droplets with diameters between 1 and 100 μm , and are known to be unstable. The emulsions with the smallest droplets, the so-called micro-emulsions, have droplet diameters on the order of 10 to 100 nm. These emulsions are thermodynamically stable, but usually require a high concentration of surfactant, making them unappealing for practical applications. The emulsions with intermediate droplet sizes, from 20 to 500 nm, are sometimes denoted as nano-emulsions (please note that nano-emulsions have bigger droplet sizes than micro-emulsions. The names have different historical origins). These emulsions are not thermodynamically stable, but they are kinetically stable (they usually have a long shelf life time ranging from months to years) and they can be prepared with a low concentration of surfactants. The combination of these factors make these emulsions a very attractive platform for industrial applications.^[1,2,4]

There have been a lot of studies exploring how colloidal water-oil emulsions with intermediate droplet sizes, from 20 to 500 nm, can best be prepared, in particular on how the droplet size can be controlled,^[5-8] and exploring the role of the surfactant in the droplet stabilization,^[9-12] Expanding the knowledge on these emulsions on a molecular level is essential for this field, since the molecular interactions determine the droplet stability. Over the last decades, the molecular-scale dynamics of water in water-in-oil emulsions has been extensively investigated with femtosecond mid-infrared spectroscopy. In these emulsions water is contained in nanometer-size droplets within an oil matrix that are stabilized by surfactant molecules.^[13-20] In these studies it was observed that the molecular reorientation and vibrational relaxation of water molecules interacting with the polar head groups of the surfactants can strongly differ from the corresponding properties of bulk water molecules. Here we report on a study of the reorientation dynamics of water molecules in the reverse system, i.e. oil-in-water emulsions, with intermediate oil droplet sizes, using polarization-resolved infrared pump-probe spectroscopy. These measurements were performed for different surfactant concentrations, droplet sizes and temperatures.

Experimental

Sample preparation

The studied emulsions consist of deionized water (ultrapure milli-Q grade, prepared using MILLIPORE Synergy 185 system), Econa oil containing 80 wt% of diacylglycerols and 20 wt% triacylglycerols (Kao, Tokyo, Japan), and the surfactant sodium dodecyl sulfate (Sigma Aldrich, Schnellendorf, Germany). The emulsions are prepared according to the recipe presented in Ref. ^[5]. All chemicals are used as received. In order to create the emulsions, an aqueous solution of the desired SDS concentration (116 mM, 87 mM and 58 mM, which equals to 3.4, 2.5 and 1.7 wt% respectively, as described in Ref. ^[5]) was prepared by adding SDS slowly to the water while stirring using a rotor-stator mixer (Silverson L4RT-A) until full dissolution was reached. Subsequently 53 wt% of oil was added slowly to the aqueous solution, while stirring at 8000 rpm using a stator grating with 2 mm holes. The emulsion was then mixed for 5 minutes to obtain a macro-emulsion. Emulsions with oil droplet sizes on the order of a few hundred nanometers were created by further processing using an ultra-high-pressure impinging jet mixer (Microfluidizer M-110S, Microfluidics), with a maximum inlet pressure of 120 MPa. A Y-type ceramic chamber (F20Y) was used with a minimum passage of 75 μm . Different droplet sizes were obtained by using different inlet pressures. The temperature of the emulsion was controlled with a water bath to not exceed room temperature. The thus prepared emulsions were stored at 4°C until further use.

Droplet size characterization

The droplet size of the emulsions was measured using dynamic light scattering, using a Zetasizer Nano ZS (Malvern Instr., Malvern, UK) in backscattering geometry. Before the measurement, the emulsions were diluted with demineralized water to minimize multiple scattering and to make the bulk viscosity very similar to that of water. One ml of the diluted emulsion was pipetted into a plastic cuvette and placed into the instrument. The size of the particles is characterized by the surface-mediated mean particle size $D[3,2]$ of the dominating peak, which is defined as:

$$D[3,2] = \left[\sum_i^M \frac{\phi_i}{d_i} \right]^{-1} \quad (1)$$

The size distribution as measured involves the diameter d_i and relative percent-based volume fraction ϕ_i for each size class i . The sum over all relative volume fractions in the distribution is 1.

Pump-probe spectroscopy

For the transient absorption (pump-probe) experiments D_2O (99.9%D, Cambridge Isotope Laboratories) was added to the solutions to achieve a water phase containing 4% of D_2O . A detailed description of the pump-probe experiment has been reported before^[21]. In brief, we excite the OD stretch vibrations of HDO molecules in isotopically diluted water (4% D_2O in H_2O) with an intense femtosecond pump pulse centered at 2500 cm^{-1} . This excitation leads to changes in the absorption, $\Delta\alpha$, that are probed with a second, weaker probe pulse, which is also centered at 2500 cm^{-1} . We measure the absorption changes both with a probe pulse with a polarization direction parallel and a probe pulse with a polarization direction perpendicular with respect to the polarization direction of the pump pulse. The pump pulse excites vibrations that have their transition dipole moment aligned parallel to the polarization of the pump most efficiently. This means that at short delay times between the pump and probe pulse, the absorption change probed in the parallel direction

($\Delta\alpha_{\parallel}(v,t)$) will be larger than the absorption change probed in the perpendicular direction ($\Delta\alpha_{\perp}(v,t)$). At larger delay times between the pump and probe pulses two processes take place that influence the absorption changes: the excited vibrations will relax and the molecules are reorienting, eventually causing the signals in parallel and perpendicular direction to be the same. From the parallel and perpendicular probe signals, we construct the reorientation independent isotropic signal:

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

that decays with the vibrational lifetime, and the vibrational relaxation independent anisotropy R:

$$R(v, t) = \frac{\Delta\alpha_{\parallel}(v, t) - \Delta\alpha_{\perp}(v, t)}{\Delta\alpha_{\parallel}(v, t) + 2\Delta\alpha_{\perp}(v, t)} \quad (3)$$

that decays with the rate of molecular reorientation. The reorientation of the HDO molecule is representative for the reorientation dynamics of all water hydroxyl groups present in the solution.

Results

We prepared emulsions with different surfactant concentrations and using different processing pressures. All these emulsions were prepared with the same amount (53 wt%) of oil. Figure 1 shows the oil droplet diameter of the emulsions, including the droplet sizes of the emulsions that were not processed using the impinging jet mixer (shown at 0 bar). For the processed emulsions the droplet size no longer depends on the surfactant concentration. In addition, it is observed that the droplet size is inversely proportional to the surfactant concentration, meaning that at higher processing pressures, smaller droplets are formed. The diameter of the droplets of the emulsions ranges between ~ 120 and ~ 290 nm. We find that the droplet size hardly changes over a 30-day period (see Supplementary Information).

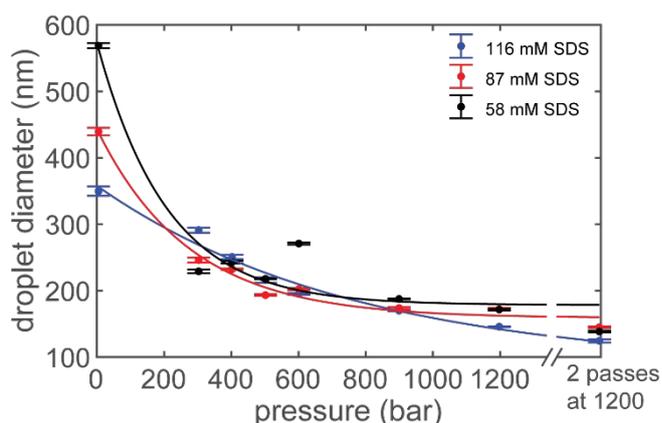


Figure 1. Droplet diameter as a function of processing pressure of the ultra high-pressure impinging jet mixer, for different surfactant concentrations. The values at 0 bar are the droplet sizes of emulsions that were not processed using the ultra high-pressure impinging jet mixer. The values reported at the highest pressure correspond to emulsions that passed through the impinging jet mixer twice at a pressure of 1200 bar. The solid lines are guides to the eye.

Figure 2A shows isotropic transient absorption spectra at different delay times, resulting from pumping and probing the OD stretch vibration of HDO molecules in an emulsion consisting of 53% econa oil droplets with a diameter of 145 ± 0.6 nm (processed at 1200 bar) and 116 mM SDS in isotopically diluted water. At early delay times a decreased absorption is observed due to the bleaching of the ground state and stimulated emission out of the first excited vibrational state back to the ground state. At long delay times, a thermal difference spectrum is observed. Figure 2B shows the transient absorption signals at 2520 cm^{-1} measured in parallel and perpendicular polarization configuration as a function of delay time, and the isotropic signal that is constructed from these signals using equation 2. The isotropic signal decays with a time constant of 1.8 ± 0.1 ps which represents the vibrational relaxation time T_1 of the OD stretch vibration of HDO in the emulsions.

The isotropic, parallel and perpendicular signals do not decay completely to zero, because of the long-lasting thermal difference signal that is also shown in the transient absorption spectrum of Figure 2A. This final thermal difference signal has the same magnitude in the parallel and perpendicular polarization configuration, meaning that the thermal difference signal is isotropic. To distinguish the signal of the OD stretch vibrational excitation from the total transient absorption signal, we fit the isotropic signal to a kinetic model that describes the vibrational relaxation of the OD oscillators and the ingrowing heating signal. The result of this fit is shown as the solid lines in Figure 2A. After subtracting the isotropic heating contribution to the signal, the pure OD vibrational excitation signal is obtained. We determine the anisotropy of this pure OD vibrational excitation signal by correcting both $\Delta\alpha_{\parallel}(v, t)$ and $\Delta\alpha_{\perp}(v, t)$ for the ingrowing heating signal, and by filling out

the thus corrected parallel and perpendicular absorption changes in equation (2) to construct the anisotropy parameter R.

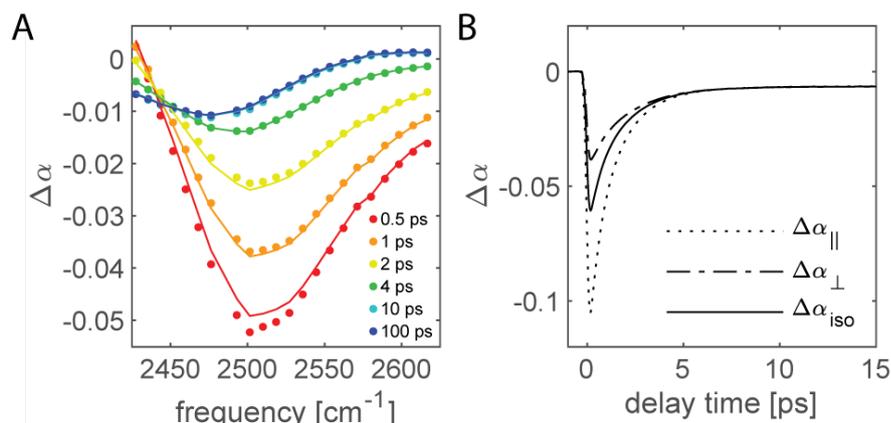


Figure 2. (A) Isotropic transient absorption spectrum of the OD stretch vibration of HDO molecules for a colloidal water-oil emulsion composed of 50% econa oil and 116 mM SDS, and a diameter of 145 ± 0.6 nm in isotopically diluted water, for different delay times. (B) Transient absorption change as a function of delay time at 2520 cm^{-1} , for the parallel, perpendicular and isotropic signal, for a colloidal water-oil emulsion composed of 50% econa oil and 116 mM SDS, and a diameter of 145 ± 0.6 nm in isotopically diluted water.

Figure 3A shows the anisotropy decay of solutions of different concentrations of SDS in isotopically diluted water. For neat water, we fit the anisotropy decay with an exponential function, extracting a reorientation time of 2.5 ± 0.2 ps. In the case of the SDS solutions, the anisotropy does not decay to zero, and we thus fit the anisotropy decays of these solutions with an exponential decay with an offset. The extracted reorientation time for the SDS solutions is 2.3 ± 0.2 ps, and the offset increases with increasing SDS concentration. This means that a large fraction of the water molecules is reorienting with the same reorientation time as bulk water, and a small fraction is reorienting on a time scale that is longer than ~ 7 ps, which defines the time window in which we can determine the anisotropy of the OD vibrational excitation signal with a sufficient signal-to-noise ratio. This time window is limited by the relaxation of the OD vibration. After a delay time corresponding to 4-5 times the vibrational relaxation time constant T_1 , the OD vibrational excitation signal becomes too weak to determine its anisotropy reliably.

For these solutions of SDS in isotopically diluted water, we assign the slow water molecules to water molecules that are in direct contact with the SDS solute molecules. From the offset, we derive that each surfactant molecule slows down 25 ± 2 water OH groups (see Supplementary Information). Figure 3B shows the anisotropy decay of three emulsions, with the same surfactant concentrations as shown in Figure 3A. The oil droplets of the three emulsions displayed all possess a diameter of ~ 195 nm (195 ± 2 , 202 ± 2 and 187 ± 0.7 for 116, 87 and 58 mM SDS, respectively). We fit the anisotropy decay of the three emulsions with the same exponential reorientation time constant of 2.3 ps that was found for the SDS solutions. A larger offset was observed for the emulsions than for solutions that only contain SDS, which means that for the emulsions more water molecules are slowed down in their reorientation. For the emulsions, we assign the slow water molecules to two contributions: to water molecules interacting with SDS, and the larger fraction of slow water of the emulsions is explained from water molecules interacting with the oil molecules. The offset of the anisotropy of the emulsions increases with increasing surfactant concentration, as was the case for the solutions only containing the surfactant.

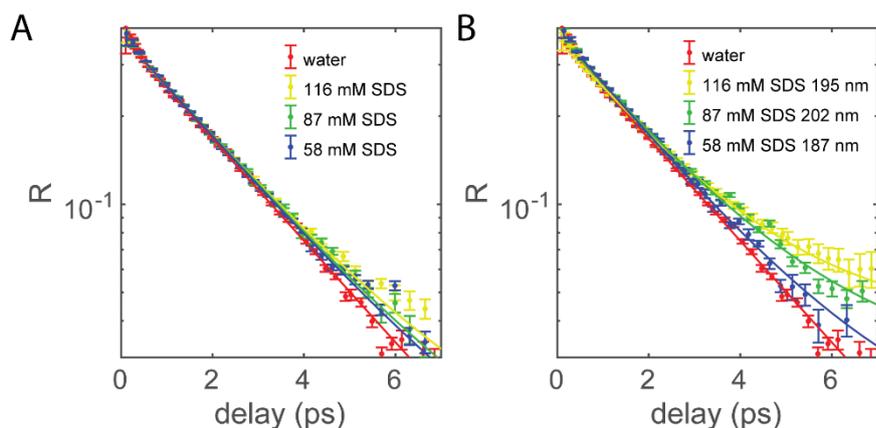


Figure 3. (A) Anisotropy decay as a function of delay time for solutions of 116, 87 and 58 mM SDS in isotopically diluted water. (B) Anisotropy decay as a function of delay time for colloidal water-oil emulsions containing 50% econa oil and 116, 87 and 58 mM SDS in isotopically diluted water. All emulsions have a similar droplet diameter between 187-202 nm. The solid lines are fits to an exponential function with an offset.

To get a better understanding of the influence of the surfactant concentration and droplet size on the amount of slow water, we measured the anisotropy decay for a series of droplet sizes at different surfactant concentrations. The concentration of oil is kept constant throughout the whole experiment. Figure 4A shows the anisotropy decay of emulsions with different droplet diameters at 116 mM SDS concentration. As in Figure 3, the offset of the emulsion is higher than that of the solution only containing the surfactant. Interestingly, there is no significant difference between the offsets of emulsions with different droplet sizes. At the other surfactant concentrations, shown in Figure 4B, we also do not observe a significant effect of droplet size on the offset. This observation is surprising: the slow water molecules are water molecules interacting mainly with the oil and surfactant on the droplet surface. If the droplets would have a smooth spherical surface, the total surface area of the droplets is expected to decrease when the droplet diameter increases while the total oil fraction is kept constant. However, the results show that the amount of water interacting with the droplets stays more or less the same for droplets with average diameters ranging from 124 ± 3 to 291 ± 4 nm. This indicates that the surface area of the droplets interacting with water stays more or less the same for all these droplet sizes.

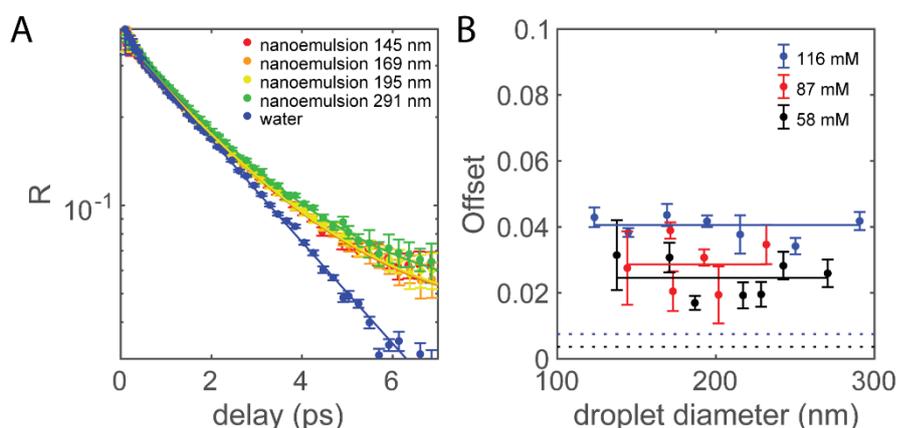


Figure 4. (A) Anisotropy decay as a function of delay time for colloidal water-oil emulsions composed of 50% econa oil and 116 mM SDS in isotopically diluted water, with different oil droplet diameters. The solid lines are fits to an exponential function with an offset. (B) Offset of the anisotropic decay for colloidal water-oil emulsions at different SDS concentrations

as a function of droplet diameter. The solid lines are the average of each SDS concentration series. The dashed lines represent the offsets observed for solutions only containing SDS.

We also measured the influence of temperature on the water reorientation dynamics for a 116 mM 123 nm diameter emulsion, in a range of 20-60°C. In this temperature interval there is no effect of temperature on the droplet size (see Figure SI6 of the Supplementary Information). We could not measure at higher temperatures, because then the emulsion became strongly scattering in the mid-IR, indicating a strong change of the composition of the emulsion. Figure 5A shows the anisotropy dynamics of the emulsion at different temperatures in the range 20-60°C. It is clearly seen that the anisotropy decay becomes faster with increasing temperature.

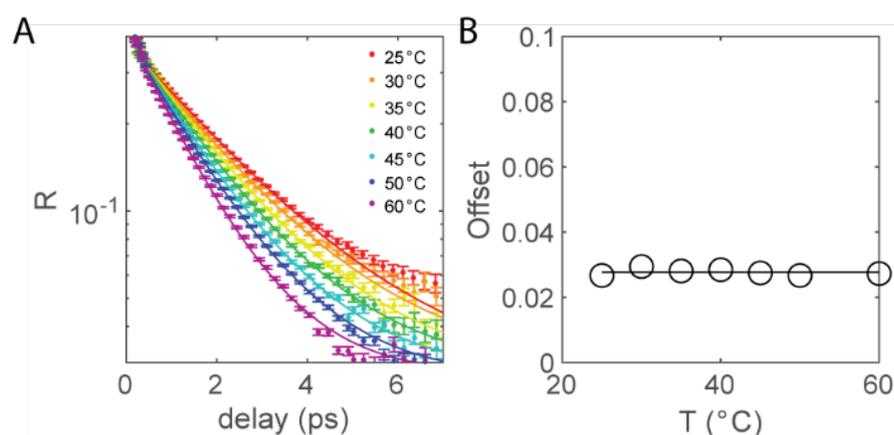


Figure 5. (A) Anisotropy decay as a function of delay time at different temperatures, for a colloidal water-oil emulsion composed of 50% econa oil and 116 mM SDS in isotopically diluted water with a diameter of 123 nm at room temperature. The solid lines represent fits of the data to an exponential function with an offset. (B) Offset of the anisotropic decay as a function of temperature, for a colloidal water-oil emulsion composed of 50% econa oil and 116 mM SDS in isotopically diluted water with a diameter of 123 nm at room temperature. The solid line shows the average of the offsets.

To analyze the anisotropy decay curves of the emulsion at different temperatures, first the reorientation time τ_r of neat isotopically diluted water at different temperatures in an independent set of measurements was determined, which are shown in the Supplementary Information. Figure SI4A shows the anisotropy decay of isotopically diluted water as a function of delay time for different temperatures. These anisotropy decays can be fitted well with an exponential function without an offset. The obtained exponential time constants are shown in figure SI4B, where they are plotted on a logarithmic scale as a function of inverse temperature. The time constant decreases with increasing temperature, and this temperature dependence can be well described with the following Arrhenius equation:

$$\frac{1}{\tau_r} = Ae^{-E_{act}/RT}$$

Where A is the pre-exponential factor, E_{act} is the activation energy (in J/mol), and R is the gas constant. We find the activation energy to be 14 ± 1 kJ/mol for isotopically diluted water, in agreement with previous findings.^[22-24]

Subsequently, the anisotropy decays of the emulsion at different temperatures were fitted to an exponential decay with an offset, where the exponential time constant was fixed to a value that follows from the Arrhenius fit of the time constants observed for neat (isotopically diluted) water. Figure 5B shows the offset that is obtained with this procedure. The resulting offset is constant,

which means that temperature has a negligible effect on the amount of water molecules that is interacting with the oil droplets.

Discussion

Comparison emulsions with different droplet sizes

Figures 3 and 4 clearly show that the emulsions containing Econa oil plus SDS possess a larger fraction of slow water molecules than solutions that only contain the same amount of SDS. This extra amount of slow water is attributed to water molecules that are interacting with the oil.^[13–15,18] In this respect, the properties of emulsions with oil droplet sizes between 100 and 300 nm are different from those of micro-emulsions that we investigated with the same technique before.^[25] In that study, we performed a similar experiment, -emulsions with much smaller oil droplets, possessing diameters <10 nm. With these micro-emulsions, adding apolar oil to the surfactant solutions did not change the anisotropy offset and thus did not change the fraction of slowly reorienting water molecules. This means that for these emulsions, the water phase is not in direct contact with the oil phase. There is thus a clear difference between the two types of emulsions, where in the case of micro-emulsions, the surface of the oil droplets is completely covered with surfactant molecules shielding the oil surface, while in the present case of emulsions with 100-300 nm size droplets, the surface of the oil droplets is not completely covered with surfactant molecules, thus allowing the water molecules to interact with the oil. For a solution containing only 116 mM of SDS and no oil, the anisotropy offset is ~ 0.0015 ^[25], which implies that the fraction of water of which the reorientation is slowed down by interacting with SDS is $\sim 5\%$ of the total amount of slowed-down water. Hence, for $\sim 95\%$ of the water molecules that are slowed down in their reorientation, this slowing down results from their interaction with econa oil molecules, most likely at the surface of the oil droplets. It should be noted at this point that the amount of slowed down water molecules may also depend on the precise nature of the oil molecules. This potential influence will be investigated in a future study.

Independence of slow water fraction on droplet size

Figure 4 shows that the fraction of slowly reorienting water is not dependent on the droplet size. This is surprising, because the amount of slow reorienting water is dependent on the amount of droplet surface with which the water interacts. If the oil droplets would possess a smooth spherical shape, their total surface is expected to increase with decreasing droplet size and thus the amount of slowly reorienting water.

The total droplet surface exposed to water can be estimated from the fraction of slow water and a reasonable assumption about the thickness of the hydration layer that is affected in its reorientation dynamics by the near presence of the oil droplet surface. The emulsion contains $\sim 50\%$ of oil and $\sim 50\%$ of water. From Fig. 4 it follows that a fraction of $\sim 0.03/0.4 = \sim 0.075$ of the water is slow for all studied droplet sizes, which corresponds to 0.038 m^3 in 1 m^3 emulsion. Hydrophobic hydration effects have been found to be short range. If we estimate the thickness of the affected water layer to be $\sim 0.5 \text{ nm}$, the affected water volume corresponds to a total surface of $\sim 0.038/5 \cdot 10^{-10} = \sim 7.5 \cdot 10^7 \text{ m}^2$. It is interesting to compare this surface with that of perfect spherical nanodroplets with a diameter of 150 nm. The volume of such a nanodroplet is $1.77 \cdot 10^{-21} \text{ m}^3$ and its surface is $7.07 \cdot 10^{-14} \text{ m}^2$. In 1 m^3 emulsion there are $0.5/1.77 \cdot 10^{-21} = 2.83 \cdot 10^{20}$ droplets with a total surface area of $2 \cdot 10^7 \text{ m}^2$, which is thus ~ 4 times smaller than the surface area that is derived from the fraction of slowed down water.

A possible explanation for the enhanced fraction of slow water is that the emulsion contains a significant fraction of very small droplets with diameters <10 nanometer that are rich in surfactant (swollen micelles), and that would dominate the total exposed surface area to the water solvent. In a previous study of the properties of Tween 80 and medium chain triglycerides, such a co-existence of large oil droplets and small swollen micelles has been observed.^[26] In the present case such a co-existence of large droplets with much smaller swollen micelles is not very likely because the slow water fraction, and thus the inferred surface area of the droplets, does not depend on temperature (see Figure 5). In case the surface area would be dominated by swollen micelles, the total surface is expected to depend on temperature, as these micelles would constitute a thermodynamic stable phase, meaning that their composition and size are expected to be strongly temperature dependent. Moreover, the DLS measurements do not show any indication for the presence of small droplets with a diameter <10 nm, even when the emulsion is strongly diluted. Hence, a more likely explanation for the observation of a ~4 times larger fraction of slow water surface area than expected from the total area of perfectly spherical oil droplets, is that the oil droplets do not possess a perfectly spherical shape, and are in fact quite corrugated, showing large protrusions into the water phase.

The presence of a non-spherical, corrugated shape of the oil droplets also provides an explanation for the observation that the amount of slow water does not depend on the average droplet size (as shown in Fig. 4). The experimentally derived effective surface area of $\sim 7.5 \cdot 10^7 \text{ m}^2$ to a characteristic radius. A volume of 1 m^3 of emulsion contains $n = 0.5 / ((4/3)\pi R^3)$ droplets with a total surface area of $n \cdot 4\pi R^2 \text{ m}^2$. It follows that $R = 1.5 / 7.5 \cdot 10^7 = 20 \text{ nanometer}$, which can thus be interpreted as the characteristic curvature of the protrusions of the nanodroplets, that is independent of the overall size of the nanodroplet. This independence of the characteristic radius of the protrusions on the average droplet size, implies that larger nanodroplets will show more protrusions than nanodroplets with a small diameter, with the result that the surface of the nanodroplet increases proportional to the third power of the diameter (the volume, see figure 6), instead of the square of the diameter, as would be the case for a perfect sphere. As a result, the total surface area of the oil droplets is not dependent on the average droplet size, and only depends on the oil volume fraction.

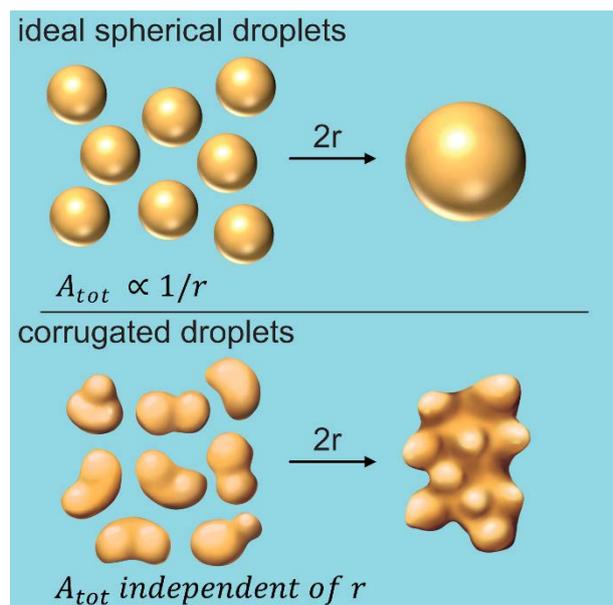


Figure 6. Schematic picture of oil droplets of different average sizes following from polarization-resolved femtosecond measurements of the water dynamics. The measurements show that the total surface area of the oil droplets does not

depend on the average droplet size, indicating that the surface of the oil droplets is corrugated with a correlation length that is similar for small and large oil droplets.

Conclusions

We studied the reorientation dynamics of water molecules surrounding oil droplets in colloidal water-oil emulsions using polarization-resolved femtosecond pump-probe spectroscopy. The studied oil droplets have average diameters ranging from 120 to 290 nm, as determined with dynamic light scattering (DLS). A fraction of the water molecules in these emulsions shows a much slower reorientation than the water molecules in bulk liquid water. This fraction of slow water is higher for emulsions than for solutions that only contain surfactant molecules at the same concentration. This indicates that, contrary to what we found before for micro-emulsions containing very small oil droplets (<10 nanometer),^[25] water is in contact with oil molecules at the surfaces of the emulsion droplets.

For a colloidal water-oil emulsion consisting of 50% oil and 50% water, the fraction of slow water amounts to ~7.5% of the total water volume. We also observe that the amount of slowed-down water is independent of the average droplet size. The volume fraction of slow water of ~7.5% corresponds to a total oil droplet surface of $\sim 7.5 \cdot 10^7 \text{ m}^2$ per m^3 of emulsion, assuming an affected water layer thickness at the oil droplet surface of ~0.5 nanometer. This surface would correspond to perfectly smooth spherical droplets with a diameter of 40 nanometer, which is significantly smaller than the average droplet size of the nanodroplets that were determined with DLS. This finding indicates that the droplets do not have a smooth spherical shape but are highly corrugated showing large protrusions into the water.

The observation that the slow water fraction does not depend on the nanodroplet diameter, indicates that the surfaces of the droplets are corrugated with a correlation length that is similar for small and large oil droplets. Due to this similarity of the surface corrugation length scale, the surface of the nanodroplets increases proportional to the third power of the diameter (their volume), instead of proportional to the square of their diameter, as would have been the case for perfectly spherical nanodroplets.

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