Specific Ion Effects in Amphiphile Hydration and Interface Stabilization

Rüdiger Scheu,† Yixing Chen,‡ Hilton B. de Aguiar,† Blake M. Rankin,‡ Dor Ben-Amotz,‡ and Sylvie Roke*†

†Laboratory for Fundamental BioPhotonics (LBP), Institute of Bio-Engineering (IBI), School of Engineering (STI), École Polytechnique Fédérale de Lausanne (EPFL), Station 17, CH-1015 Lausanne, Switzerland
‡Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, Indiana 47907, United States

Supporting Information

ABSTRACT: Specific ion effects can influence many processes in aqueous solutions: protein folding, enzyme activity, bacterial growth, transport across membranes, and colloidal assembly.1−3 The biological relevance of such specific ion effects is undoubtedly linked to the fact that living systems consist of macromolecules and assemblies that contain not only hydrophilic (polar and ionic) groups, but also extended hydrophobic (hydrocarbon) domains. Thus, to investigate specific ion interactions of relevance to such multiscale systems, we compare how different amphiphiles interact with water and oil/water interfaces. More specifically, we focus on single chain amphiphiles of similar structure, but either with negatively (−OSO3−) or positively (−N(CH3)3+) charged head groups. We use oil nanodroplets in water, since such a system enables the in situ preparation of a large amount of clean5 oil/water interface (~3000 cm2/mL). We find that the head groups mentioned above not only interact very differently with bulk water molecules (as confirmed by Raman multivariate curve resolution, Raman-MCR, spectroscopy), but also have a strikingly different influence on scattering oil and water structure (as evidenced by second harmonic scattering, SHS, and sum frequency scattering, SFS). More specifically, we find that the amphiphiles with the −OSO3− head group do not detectably change the conformation of the interfacial oil chains and that they enhance the orientational order of surface water molecules, while those with the −N(CH3)3+ head group strongly change the conformation of the interfacial oil chains and reduce the directionality of interfacial water molecules. Thus, the specific nature of the interaction of the ionic head groups with both water and oil evidently has a major impact on the structure of such complex interfaces.

Here, we first describe the differences in the hydration-shell of isolated octylsulfate (OS−) and octyltrimethylammonium (OTA+) ions obtained with Raman solvation shell spectroscopy. Then, we describe the vibrational sum frequency scattering measurements that were used to determine the structure of dodecylsulfate (DS−) and dodecyltrimethylammonium (DTA+) ions on impenetrable solid nanoparticles and penetrable liquid oil nanodroplets in water. By deuterating the oil phase, we selectively measure the conformation of the amphiphile’s alkyl chains. This is followed by a study of the change in hydrophobic oil conformation at the nanodroplet/amphiphile/water interface upon adsorption of amphiphiles with deuterated alkyl chains. Finally, we describe the change in charge and in interfacial water structure induced by DS− and DTA+. We end with some remarks regarding applications and surface stabilization.

INTRODUCTION

Specific ion effects occur in many biological and chemical phenomena, such as protein folding, enzyme activity, bacterial growth, transport across membranes, and colloidal assembly.1−3 The biological relevance of such specific ion effects is undoubtedly linked to the fact that living systems consist of macromolecules and assemblies that contain not only hydrophilic (polar and ionic) groups, but also extended hydrophobic (hydrocarbon) domains. Thus, to investigate specific ion interactions of relevance to such multiscale systems, we compare how different amphiphiles interact with water and oil/water interfaces. More specifically, we focus on single chain amphiphiles of similar structure, but either with negatively (−OSO3−) or positively (−N(CH3)3+) charged head groups.

RESULTS AND DISCUSSION

Hydration-Shell Structure. Raman-MCR8 is used to decompose experimental spectra into solvent and solute-correlated (SC) components. The SC spectrum contains
and OTA+ ions (solid green curve), each normalized to the surfactant CH band area. These OH stretch bands clearly differ significantly from each other, as well as from the OH band of bulk water (dashed black curve), as a result of amphiphile-induced water structure changes. The contribution from the Br− counterion of OTA+ has been removed by including an equal concentration of NaBr in the surfactant-free water reference spectrum, as previously described.14b Note that Na+ ions have no observable effect on the water OH band,15 and so no such procedure was required to correct for the Na+ counterion of OS−. Thus, the OTA+ and OS− spectra in Figure 1 arise only from the hydration-shell of the surfactant itself, with little or no contribution from the corresponding counterion. Differences between the spectra are due primarily to the different head groups, since the alkyl tails are of equal length (and similar results are obtained for surfactants with shorter tails, and the same head groups).

The hydration-shell spectrum of OTA+ consists of two lobes, peaked at ∼3250 and ∼3450 cm−1. The OTA+ OH spectrum has a more prominent lower frequency OH stretch lobe than the bulk water spectrum, indicating that there is enhanced tetrahedral ordering of water molecules around the OTA+ ions, as previously observed in the hydration-shells of nonpolar groups, such as the hydrophobic tails of alcohols (including neopentanol) and of tetraalkylammonium ions (including tetramethylammonium).11,12 The small peak at ∼3660 cm−1 is due to an increase in the number of free (dangling) OH groups in the hydration-shell of OTA+ (again as previously observed in aqueous alcohol and tetraalkylammonium solutions).9,12 The hydration-shell spectrum of OS− ions is more intense and looks quite different, as it is likely dominated by water OH groups that are H-bonded to the anionic sulfate head group, as a similar SC OH band is seen in the hydration-shells of halide anions,13 as well as the SC spectra of aqueous sulfate ions. Thus, the differences between OS− and OTA+ hydration-shell spectra are consistent with the formation of hydrogen bonds between water and the sulfate head group, while the OTA+ head group has a hydration-shell structure that is similar to that around neutral hydrophobic solutes that are not hydrogen bonded to water. We now turn to the molecular structure of the surfactant stabilized oil/water interface.

**Interfacial Conformation.** Surfactants at the planar oil/water interface have been studied with various methods including neutron scattering, X-ray scattering, and sum frequency (SF) generation.16−25 The molecular surface structure of the nanoscopic oil droplet/water interface has received much less attention. Recent developments that combine light scattering and second-order nonlinear optics26 have opened up the possibility to retrieve molecular structure and conformation from nanoparticle/droplet interfaces in water. Apart from providing molecular level details to the nanomaterial, it also increases the detection sensitivity for liquid interfaces and reduces impurity issues that are always linked to surface studies.6 The surface composition of nanodroplets can be measured with vibrational sum frequency scattering (SFS), a vibrational coherent surface spectroscopy that measures the combined IR and Raman spectrum of molecules in noncentrosymmetric environments such as interfaces.27−30 Selective deuteration allows to independently probe both the surfactant and the oil molecules, since C−D and C−H modes vibrate at different frequencies.31 The C−H stretch spectral region contains valuable information about the alkyl chain conformation and geometry. The amplitude ratio (d+/r+) of the symmetric methylene (d+, at ∼2850 cm−1) and the symmetric methyl (r+, at ∼2874 cm−1) stretch vibrational modes is a common indicator for the conformation of alkyl chains.32−35 A value of d+/r+ ≪ 1 is associated with a stretched all-trans alkyl chain conformation, whereas a value of d+/r+ > 1 indicates that gauche defects dominate the measured SF spectra. When we compare the spectra, we focus on this d+/r+ ratio. d+/r+ ratios were obtained from a global fitting procedure,36 in which the weak nonresonant background is taken into account by using a measured SF signal from an all-deuterated sample. This is done because the nonresonant background varies per oil/surfactant/water interface and polarization direction.

Differences in the spectral region above 2900 cm−1 are not immediately useful for determining the chain conformation,31,36 as it contains a number of modes that are not well-resolved, some of which consist of couplings to overtones. The methyl groups in the OTA+ head group vibrate at higher frequencies:37 The symmetric stretch mode appears at ∼2985 cm−1, and the...
The symmetric stretch mode appears at 3040 cm\(^{-1}\) in the Raman spectrum.\(^{38}\) They do not influence our observed \(d' / r'\) ratios. The antisymmetric stretch mode appears in our SF spectra as a very weak and broad feature at \(\sim 3045\) cm\(^{-1}\). Since the signal is very close to our detection limit, it cannot be used here. The DS\(^{-}\) head group does generate a strong signal (close to that of the pure sulfate ion\(^{39}\)), and it has been used in conjunction with the C–H signal to determine an upper limit for the amount of surface adsorbed DS\(^{-}\).\(^{39}\)

To critically test whether or not a given charged amphiphile penetrates into or perturbs the liquid oil interface we have measured (i) the surface structures of DS\(^{-}\) ions and DTA\(^{+}\) ions adsorbed on 150–250 nm diameter liquid deuterated oil nanodroplets, on impenetrable polytetrafluoroethylene (PTFE) and polystyrene (PS) particles, and (ii) the conformational changes of the oil surface molecules at the droplets by selectively deuterating the surfactant ions. Both bare particles do not generate SF signal in the C–H stretch region below 2900 cm\(^{-1}\) (as we confirmed experimentally).\(^{40}\) Although the chemical structures of oil, PTFE, and PS are different, we use the three systems to compare surfactant alkyl chain conformations on a liquid (penetrable) and solid (impenetrable) interface. It is expected that if chain penetration plays an important role, the different state of matter (solid vs liquid) will be more important than the chemical differences such as between the PTFE and PS surfaces.

The following discussion begins with a description of our measurements of the structure of DS\(^{-}\) on PS and PTFE and DTA\(^{+}\) on PTFE nanoparticles. Then, we follow the adsorption of both surfactants on \(d_{15}\)-hexadecane oil droplets. Next, we describe measurements performed using alkyl-deuterated surfactants in order to elucidate amphiphile-induced changes in the interfacial structure of the liquid oil droplets. We end with monitoring the changes in the electrokinetic mobility (representative of the interfacial charge) and water structure.

**Amphiphile Chain Conformation.** Figure 2 shows SFS spectra of the alkyl tails of DTA\(^{+}\) ions on PTFE nanoparticles (A) and on \(d_{15}\)-hexadecane oil droplets (C), and of DS\(^{-}\) ions on PTFE and PS nanoparticles (B), and on \(d_{15}\)-hexadecane oil droplets (D). The particles/droplets were dispersed in solutions of SDS and DTAB in D\(_2\)O. The surfactant concentrations are given in the caption and are all below their respective cmc’s. SF spectra of surfactants on the oil droplets are plotted in panels C and D, for two different concentrations. It can be seen in panels A and B that the spectra for the C\(_{12}\) alkyl chains of DTA\(^{+}\) and DS\(^{-}\) on PTFE resemble each other closely, with both having very large \(d' / r'\) ratios (3.6 and 4.5 for DTA\(^{+}\) and DS\(^{-}\), respectively). The spectra for DS\(^{-}\) ions on PTFE/PS and on the hexadecane oil droplet are also very similar (B,D), with \(d' / r'\) amplitude ratios of 4.5 and 3.7, indicating the predominance of gauche defects on the spectra shown in panels A, B, and D. The spectra in panel C of DTA\(^{+}\) on \(d_{16}\)-C\(_{16}\) however, are clearly quite different from the others, with approximately equal amplitudes for both \(d'\) and \(r'\) modes, indicating that the alkyl chains have more all-trans character. The increasing SF intensity with increasing bulk concentrations in panels C and D indicates that more surfactant molecules adsorb to the interface when the bulk concentration is raised.

Thus, it is clear that the chain conformation for the DS\(^{-}\) alkyl chains is not very different on solid PTFE particles, PS particles, and liquid oil droplets. The chain conformation of DTA\(^{+}\) ions, however, is very different on solid PTFE and liquid oil droplets.

This difference might stem from the fact that DTA\(^{+}\) penetrates into the oil phase which would also result in a perturbed conformation of the interfacial oil molecules. In the following experiment, we will show that the oil phase is indeed perturbed by the presence of DTA\(^{+}\) ions, but not detectably by the presence of DS\(^{-}\) ions. In the Supporting Information we compare the spectra to previously published work on related systems and relate the spectral shapes to possible chain conformations.

**Oil Chain Conformation.** Having measured the difference in alkyl chain conformation of DS\(^{-}\) and DTA\(^{+}\) ions on the liquid oil droplets, we now describe the response of the interfacial oil molecules to test whether their conformation is perturbed by the surfactant ions. Figure 3 shows SFS spectra of the C–H stretch modes of \(h\)-hexadecane droplets dispersed in D\(_2\)O to which different bulk concentrations of alkyl chain deuterated \(d, DS^{-}\) (A, 0.0, 0.06, 0.25, 0.98 \(\times\) cmc) and \(d, DTA^{+}\) (B, 0.0, 0.03, 0.25, 0.93 \(\times\) cmc) were added. The intensities can be compared within each panel, but not between panels, as the average droplet size and size distribution of these two sample series are different (which here influences the spectral intensity but not the spectral shape\(^{41}\)). From Figures 2C–D it is clear that up to the cmc the interfacial coverage is increased if more surfactant is added to the solution. Figure 3A shows that adding \(d, DS^{-}\) does not detectably change the hexadecane SF spectra. This implies that, within our detection limit, no significant changes

![Figure 2](image-url)
in the amount of surfactant at the oil/water interface (which agrees with the increasing SF signals of Figure 2C,D). The zeta potential of bare hexadecane droplets in ultrapure water is $\sim-50$ mV (not shown), a value that is in agreement with previous studies.44

**Interfacial Water.** The interfacial water around our nanoscopic droplets can be measured with second harmonic45 (SH) scattering,46–49 a process that occurs only in non-centrosymmetric regions. The SH signal reports on the difference in orientational directionality of the water molecules in the interfacial region compared to the orientational directionality of the bulk solution45,50–52 (on a femtosecond time scale). The Supporting Information contains additional details on the origin of the signal. The change in directionality can be induced by chemical interactions (such as H-bonding), or by electrostatic interactions of the dc field from the surfactant ions that interact with the water dipoles in the surface region ($\chi^{(3)}$ effect) as discovered by the Eschenfeld lab45. Both effects can act together and give rise to SH electric field contributions that interfere constructively or destructively, which can lead to an increasing or decreasing SH intensity. Figure 4B displays the SH intensity obtained at a scattering angle of 35° in PP polarization (i.e., all beams polarized in the horizontal scattering plane), and around the angle of maximum intensity53 for solutions with oil droplets and different concentrations of SDS and DTAB. The measured intensity was corrected for hyper Rayleigh scattering from the same solution without droplets, and then divided by the (isotropic) hyper Rayleigh scattering intensity in SS polarization of pure water for normalization purposes (following ref 54).

It can be seen that the SH intensity changes for both surfactants, but in a very different manner. For DS$^-$ the intensity increases sharply (starting at 0.07 mM/8.6 × 10$^{-3}$ cmc), then levels off (0.1 mM/0.012 cmc), and then drops again (1 mM/0.12 cmc). For DTA$^+$ the intensity decreases sharply, and for concentrations greater than 0.3 mM (0.02 cmc), there is no detectable difference between the SH intensity coming from the droplet solution and the droplet free solution. For both the zeta potential and SH intensity a similar trend is observed for DTAC, with the difference that the magnitude of the zeta potential increases to larger values, and the SH intensity vanishes at even lower concentrations.

The changes in the SH intensity originate from chemical or electrostatic changes in the interfacial region. Increasing the DS$^-$ ion concentration increases both the number of sulfate groups as well as the magnitude of the electrostatic potential. With an increasing number of surface sulfate groups, the number of sulfate H-bonded water molecules also increases (as was shown in Figure 1). H-bonded water molecules have their dipoles oriented toward the sulfate ions. The presence of the alkyl chain most likely results in a larger number of H-bonded water molecules with their dipoles directed toward the surface plane. With an increasing electrostatic field that is directed toward the surface ions, more water molecules will have their dipoles oriented toward the surface. Thus, with an increasing concentration of SDS the H-bonding and the dc field increase the orientational directionality of the interfacial water in the same direction, both favoring water dipoles pointing toward the surface. The combination of both effects ensures that the coherent SH signal increases. The decreasing intensity beyond 0.12 cmc can be explained by an increase in electrostatic screening45,53 because the increased ionic strength of the solution results in a more effective screening of the surface.

Figure 3. Effect of DS$^-$ and DTA$^+$ ions on the interfacial structure of the oil phase. The graphs show SFS spectra in the CH-region of hexadecane nanodroplets in solutions containing various concentrations of DS$^-$ (A, 0, 0.06, 0.25, 0.98 cmc) and DTA$^+$ ions (B, 0, 0.03, 0.25, 0.98 cmc) with deuterated alkyl chains. All spectra are recorded in SSP polarization combination. Intensities have not been scaled within each panel.

are observed in the interfacial oil chain conformations. Figure 3B shows that adding d-DTA$^+$ changes the hexadecane SF spectra significantly. The total spectral intensity and the $d^*/r^*$ ratio of the vibrational modes of the interfacial oil molecules increase with an increasing surface concentration of d-DTA$^+$ ions. Note that the spectra of the surfactant free samples ("0 mM") in panels A and B have the same shape to within the experimental error, as both have the same $d^*/r^*$ ratio to well within the 0.4 uncertainty in our $d^*/r^*$ ratio measurement (as we determined previously42 from 11 different samples prepared and measured under identical conditions). These results clearly imply that the surface structure of the interfacial oil molecules is altered by the DTA$^+$ ions. No such conclusion can be drawn for the DS$^-$ ions, however.

**Electrostatic Properties.** To determine the electrostatic properties of the interface, we performed electrokinetic mobility measurements.53 Figure 4A displays the absolute zeta potential for a solution of 0.01 v/v% hexadecane droplets in aqueous solutions against different concentrations of SDS and DTAB. It can be seen that for both solutions the zeta potential increases in magnitude, from +63 (0.005 × cmc) to +87 mV (0.93 × cmc) for DTA$^+$ and from −68 (0.006 × cmc) to −108 mV (0.93 × cmc) for DS$^-$ with increasing surfactant concentration. The observation can be explained by an increase...
electric field, the amount of water that is orientationally affected decreases, and so does the SH intensity.

We now turn to the DTA’ ions. From the Raman hydration-shell measurements (in Figure 1) it is likely that DTA’ ions are surrounded by water molecules that have a similar Raman response as water molecules around hydrophobic solutes. When such ions adsorb to the interface, it may be expected that this results in a loss of water dipolar orientation along the surface normal. The adsorption of DTA’ ions also results in a more positive surface potential, which will tend to orient some water molecules with their dipoles pointing away from the surface, resulting in a reduction of the orientational directionality compared to that of a surfactant free droplet. Since both the change in H-bond configuration and the positive surface charge change the initially present directionality of the water molecules adjacent to the neat oil/water interface, the SH field decreases. At higher concentrations one may also expect that electrostatic screening reduces the SH signal. However, since the SH signal is already below the detection limit, this is not observed. Thus, DS− ions enhance the directionality of surface water molecules, while DTA’ ions reduce the directionality of surface water molecules.

**Interfacial Structural Implications.** The above results reveal striking differences between the interfacial structure of anionic DS− and cationic DTA’ amphiphiles. Water molecules are H-bonded to DS− sulfate head groups. Upon adsorbing to a hydrophobic/water interface the interfacial DS− hydrophobic tails do not have very different chain conformations when adsorbed on either a solid or a liquid hydrophobic interface. They also do not detectably change the conformation of the surface oil molecules (as concluded from vibrational sum frequency spectroscopy data). The orientational directionality of the surface water is strongly increased with respect to the bare oil/water interface, which can be explained by H-bonding and electric field effects that orient water molecules in the same direction.

Water molecules around the DTA’ ions have a structure similar to that around hydrophobic solutes. DTA’ ions have a significantly different alkyl chain conformation when adsorbed on a liquid hydrophobic interface or on an impenetrable solid/water interface. DTA’ strongly perturbs the structure of the oil molecules at the droplet/water interface. The orientational directionality of water compared to that at a neat oil/water interface is strongly reduced. Thus, DS− and DTA’ ions clearly interact very differently with water and the oil/water interface.

Schweighofer et al. simulated a single SDS molecule on the water/air and water/CCl4 interface and found that on the water/air interface the DS− ion has the head group immersed in the water phase and the tail bent along the surface plane. Such a conformation is similar to the one that would give rise to the observed SF spectra in Figure 2. The DS− ion on the CCl4/water interface has an alkyl tail that is pointing into the oil phase under an angle. Such a tail structure would give rise to d2/dr2 < 1 (see Supporting Information for more details, and this would not explain our results). In a subsequent study Schweighofer et al. simulated SDS and a charge reversed equivalent on the CCl4 water interface at high surfactant concentrations (0.45 nm²/molecule). Here, the alkyl tails are immersed in the CCl4 phase, and the positively charged head group is further down into the water phase than the negatively charged head group. Simulations by Abranko-Rideg et al. simulated two different concentrations (1.66 nm²/molecule and 0.45 nm²/molecule) of DS− and DTA’ on the air/water interface and found that at lower concentrations the head groups penetrate deeper into the water phase. Furthermore, they found that the sulfate head group is immersed somewhat deeper than the trimethyl ammonium head group. This finding is in agreement with our results. Simulations by Vacha were done of DS− at decane/water and air/water interfaces at low concentrations (1.0 nm²/molecule). It was found that air/water and decane/water interfaces are very different with the air/water interface displaying surfactant aggregation, in contrast to the decane/water interface, which displayed no aggregation. The DS− head groups distort the water orientational distribution down to a distance of ~3.5 nm away from the Gibbs dividing plane. From an experimental point of view it is further interesting to note that it is not possible to generate stable CCl4/water emulsions with only SDS or DTAB. Thus, our results are partly in agreement with simulations, but since complete oil nanodroplets cannot be simulated in water and an explanation for the large negative electrokinetic potential is yet to be found, comparisons are probably not definitive.

**Interfacial Stabilization.** It is interesting to consider the relationship between the remarkably different interfacial structures of the above cationic and anionic amphiphiles, the concentration dependence of the interfacial structure, and the resulting different molecular mechanisms by which they might lower the interfacial free energy of the oil/water interface. Anionic DS− amphiphiles are directly H-bonded, and decorate the oil/water interface with hydrated sulfate groups. The water orientational directionality also increases when more surfactants adsorb. The oil structure on the other hand does not display detectable changes. Thus, water is likely to play a major role in the stabilization of the interface. The cationic DTA’, on the other hand, is very weakly hydrated, and when it is added to the interface, the conformational flexibility of the oil changes. The water structure changes as well, but the orientational directionality is decreased. Thus, the molecular actors have different roles in both surface structures and are concentration dependent, and consequently the molecular mechanism by which the interfacial energy is lowered might also be different. This difference could be verified by additional temperature dependent measurements and/or molecular dynamics simulations performed to elucidate entropic, energetic, and molecular contributions to the corresponding amphiphile stabilized surface free energy.

The finding that charged amphiphiles with different head group structures might have different roles in both surface structures, and consequently in surface stabilization, is of chemical importance in, e.g., nanosynthesis and emulsification. In biochemistry it has consequences for vesicle and membrane assembly, protein/peptide folding, aggregation, and stabilization.

**CONCLUSIONS**

By combining hydration-shell Raman spectroscopy, vibrational sum frequency scattering, electrokinetic mobility, and second harmonic scattering measurements, we have discovered the strong influence of specific ion–water interactions on the structure of surfactant stabilized oil/water interfaces. The weakly hydrated DTA’ surfactant has a different conformation on the oil droplet/water interface than on an impenetrable solid hydrophobic particle/water interface. In addition, DTA’ induces a change in the oil surface structure. The surface water structure changes as well, displaying a reduction in the number of water molecules whose dipoles are orientationally
directed along the surface normal, up to the point where no detectable difference with the bulk solution exists (at (0.02 × cm/c)). In contrast, the strongly hydrophobic DS surfactant has a very similar chain conformation on the impenetrable solid hydrophobic particle/water interface and on the oil droplet/ water interface. At the same time, it does not induce a detectable change in the oil surface structure. The surface water structure changes significantly, displaying a growing number of water molecules that are orientationally directed along the hydrophobic particle/water interface and on the oil droplet/ water molecules that are orientationally directed along the interfacial oil.

### MATERIALS AND METHODS

n-Hexadecane (C16H34, 98.8%, Sigma-Aldrich), h-DTAB (99%, Sigma-Aldrich), d4-hexadecane (C16D32, 98% d, Cambridge Isotope), d5-DSDS (99% d, Cambridge Isotope), d5-DTAB (99% d, Cambridge Isotope), and D2O (99%, Sigma-Aldrich) were used as received.

The spectral resolution of the Raman system is ∼4 cm⁻¹ (35) (35) (35) at a repetition rate of 1 kHz. The focused laser beams were overlapped under an angle of 20° in a sample cuvette with a path length of 200 μm. At a scattering angle of 60°, the scattered SF light was collimated using a plano-convex lens (f = 15 mm, Thorlabs LA1540-B) and passed through two short wave pass filters (Third Millenium, 3RD770SP). The SF light was spectrally dispersed with a monochromator (Acton, SpectraPro 2308) and detected with an intensified CCD camera (Princeton Instruments, PI-Max3) using a gate width of 10 ns. The acquisition time for a single spectrum was set between 150 and 300 s. A Glan-Taylor prism (Thorlabs, GT15-B), a half-wave plate (EKSMA, 460 °), and a polarizer (Thorlabs, WP25H-B) were used to control the polarization of the SFG, VIS, and IR beams, respectively. All shown SFS spectra were normalized by an SFG spectrum obtained in refection geometry from a z-cut quartz crystal. Concentration series were measured against a reference sample that was inserted between every other measurement, to detect and correct for possible fluctuations during the course of the experiment.

**S Supporting Information**

49

**ASSOCIATED CONTENT**

Relationship between the SFG signal and the molecular conformation of DS surfactant alkyl chains, and more details regarding the interpretation of the origin of the SH intensity. This material is available free of charge via the Internet at http://pubs.acs.org.
concluded that at least 97% of the droplet surface is clean.

We have


2009

reduces the unwanted e

sample with a 1 vol % concentration of 100 nm droplets greatly

Slipchenko, L. V.; Ben-Amotz, D.

2008

167

59

12230.

106

122

13

1805

102

82

135

160

24

191

10775.

117

10801.

10

82

138

3793.

117

103.

1805

112

1093.

113

14146.

191

379.

135

8818.

160

255.

1. 1

Faraday Discuss.

2013

167

177.

Faraday Discuss.

2013

158

303.

Faraday Discuss.

1993

158

303.

Faraday Discuss.

1993

59

153.

Rev. Chem. B

2000

104,

606.

J. Phys. Chem. B

2000

25,

3953.

J. Langmuir 2009,

21


6724.


6724.


2122.


10801.


