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Evidence of the adsorption of hydroxide ion at hexadecane/water interface from Second Harmonic Generation study

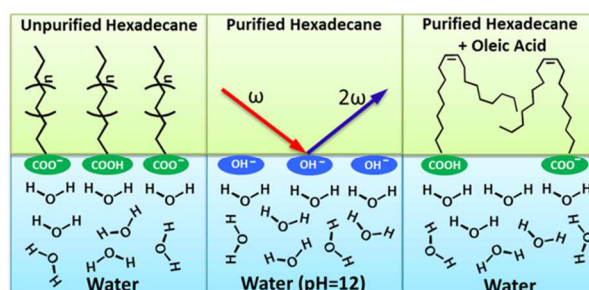
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The effect of hydroxide ion, impurities and oleic acid on molecular structure at hexadecane/water interface studied with second harmonic generation.

ABSTRACT: The electric potential and water molecular orientation at oil/water interfaces, as well as the origin of the interfacial potential have been intensively investigated recently. In some reports, the purity of hexadecane and its influence to the origin of the negative charge at hexadecane/water interface was in debating. In the debate the reliability of Sum Frequency Generation - Vibrational Spectroscopy in evaluating the influence of chemical impurities on the electric potential and molecular structure at the hexadecane/water interface was called into question. Here we revisited this system using another second order nonlinear spectroscopic technique, Second Harmonic Generation (SHG). The SHG results sensitively reflected the influence of the impurities in hexadecane. As a representative long-chain carboxylic acid, which is generally considered to be the principle impurity in hexadecane, oleic acid at a concentration of several micromolar caused a notable change in the SH intensity of the hexadecane/water interface. The presence of carboxylic-type impurities was confirmed in the as-received hexadecane with 99% purity. After purification with alumina columns, the concentration of the impurities was substantially reduced and the influence on the SH signal was barely detectable. The effect of the hydroxide ion on the structure of water molecules at the hexadecane/water interface was also confirmed, which strongly supports the adsorption of hydroxide ions at oil/water interfaces.

Introduction

At oil/water interfaces, processes such as molecular adsorption, transportation and chemical reaction, as well as the role of interfacial charge, chemical composition and molecular structure played in these dynamic processes have been intensively studied because they are closely related to important interfacial phenomena in chemistry, physics, engineering, biology and life sciences.¹⁻⁴ Although techniques such as surface tension measurements,⁵⁻⁶ surface potential measurements,⁷⁻¹⁰ X-ray photoelectron spectroscopy,¹¹ X-ray reflectivity study,¹²⁻¹³ small angle neutron scattering,¹⁴⁻¹⁵ and in particular, second order nonlinear optical techniques¹⁶⁻³⁰ have been demonstrated to be able to probe liquid interfaces, it is still a challenge to understand oil/water interfaces at the molecular level because the composition, molecular structure, interfacial charge (potential) and the molecular dynamic processes at the interface are interdependent.

An intensively discussed example is the interfacial charge (potential), the orientational structure of water molecules at oil/water interfaces and the chemical component of these interfaces. It has been reported that oil/water interfaces are negatively charged without the addition of any ionic surfactant based on the observation of the electrophoretic mobility of oil droplets towards the anode.³¹⁻⁴⁰ The existence of this interfacial charge was challenged by molecular dynamics (MD) simulations, which suggested that electrophoretic mobility could originate from factors other than surface charge at the

oil/water interface, such as preferential orientation of surface molecules or surface roughness.⁴¹⁻⁴³ However, Bonthuis et al. pointed out possible errors in these MD simulations with an analytical theory based on a generalized Navier-Stokes equation in their own MD simulation.⁴⁴⁻⁴⁵ O'Brien et al. also proved the existence of negative interfacial charge by experimentally observing the decreased dynamic mobility of a hexadecane droplet in water at increased electrolyte concentrations.¹⁰

It was widely believed that this negative surface charge originated from preferential adsorption of hydroxyl ions (OH^-) at the oil/water interface based on the fact that the electronic mobility of the oil droplet increased with increasing pH of the aqueous phase of oil-in-water emulsions.^{31-37,40} The mechanism of OH^- adsorption was interpreted as being related to the unbalanced hydrophobic/hydrophilic properties of the OH^- and hydronium (H^+) ions,⁴⁶ the influence of the preferentially oriented water molecules in the first two layers from the oil interface,⁴⁷ or the suppression of collective dipole-moment fluctuation of the water molecules.^{37,48} However, the influence of chemical impurities in the oil used in the experiments, with hexadecane as an example, was highlighted and used to exclude the role of OH^- adsorption at “pristine” oil/water interfaces.^{8,49} It was suggested that the existence of impurities such as long-chain carboxylic acids was the origin of the negative charge on the oil droplet surface in hexadecane-water emulsions. This called into question the validity of the widely accepted OH^- effect,³¹⁻³⁷ as well as other interpretations of the negative surface charge at oil/water interfaces.⁵⁰

To prove that surface impurities were not the origin of the surface charge at the hexadecane/water interface, Jena et al. performed Sum Frequency Generation - Vibrational Spectroscopic (SFG-VS) measurements of hexadecane-D₂O emulsions prepared from hexadecane of 99% and 99.8% purity, respectively, as well as a hexadecane/D₂O emulsion with hexadecanoic acid as a representative carboxylic acid.⁵¹ They found that the spectra measured from the emulsions prepared with hexadecane of 99% and 99.8% purity were the same, whereas the spectra from the emulsion containing 5 mM hexadecanoic acid displayed a clear feature attributed to the surface-adsorbed hexadecanoic acid. These experiments demonstrated that long-chain carboxylic acids in hexadecane, which could be detected with SFG-VS, were not present in the 99% hexadecane used and were not responsible for the negative charge at the oil/D₂O interface. Roger and Cabana then pointed out that these SFG-VS experiments only proved its capability to probe impurities at very large concentration (e.g., 5 mM in an emulsion, which corresponds to 0.5 M in hexadecane when the emulsion is prepared with an oil-to-volume ratio of 1%).⁴⁹

Although the reliability of SFG-VS was questioned in the aforementioned study, the application of SFG-VS and other second order nonlinear spectroscopic methods to probe the molecular structure at liquid surfaces and interfaces with surface selectivity and sub-monolayer sensitivity is well established.¹⁶⁻³⁰ Particularly in the study of the behavior

of ions at surfaces/interfaces of water or electrolyte, the adsorption behavior of OH^- , H^+ and chloride ions (Cl^-) at a hydrophobic solid/water interface was revealed by measuring the SFG-VS spectra of the interfacial water molecules.⁵² The enhanced H^+ concentration at the surface of a HI solution was deduced from the enhanced iodide concentration measured at the surface with another second order nonlinear spectroscopic technique - Second Harmonic Generation (SHG).^{22,53-54} The strong attraction of H^+ to and weak repulsion of OH^- from the air/water interface was also reported with evidence from SFG-VS measurement and MD simulation.⁵⁵

From the discussion above, one could notice the quite different interfacial affinities of H^+ and OH^- at interfaces between water and hydrophobic liquid (oil), solid and gas; thus, more experimental evidence is required before one may reach a clear view on the charge and molecular structure at water surfaces/interfaces. In this work, we revisited the charge, molecular structure and chemical composition of the hexadecane/water interface using SHG. The experiments performed with total internal reflection geometry, which was demonstrated to be able to greatly enhance the SH intensity at liquid/liquid interfaces,⁵⁶⁻⁵⁷ showed that SHG was able to sensitively detect the influence of impurities in hexadecane. With oleic acid as a model impurity, concentrations as low as several micromolar resulted in notable SHG changes at the hexadecane/water interface. Hexadecane purified with basic alumina columns was examined and found to have a negligible effect on the SHG signal, although the as-received sample with 99% purity had a pronounced effect. Based

on these results and the pH-dependent SH signal from the hexadecane/water interface, it was concluded that interfacial water molecules were preferentially oriented with their hydrogen atoms directed toward the oil phase upon the addition of NaOH. The observation of the orientational structure change in the water molecules strongly supports the preferential adsorption of OH⁻ at the oil/water interface.

Experimental Section

All water (18.25 MΩ·cm) used was prepared from water purification system (Water Purifier, WP-UP-UV-20, Sichuan water technology development co. ltd, China). Hexadecane (99%, Sigma-Aldrich) was used as received or purified with up to six passes through basic alumina columns with procedure presented in previous reports.^{5,36} Briefly, 100 g alumina (Aladdin, 100-200 mesh) was filled in a column shaped valval funnel with fritted disc. 75 ml hexadecane to be purified was used to wash the column, then the column was used to purify no more than 1000 ml hexadecane with a flow speed of approximately 2 ml·min⁻¹. This process was counted as one pass through a basic alumina column. Oleic acid (99%, Sigma-Aldrich) was used after being dissolved in purified hexadecane. Sodium Hydroxide (NaOH, 99.99%, Sigma Aldrich) was used after being dissolved in water. Sodium chloride (NaCl, >99 %, Sigma Aldrich) was used after purification following the procedure in literatures.⁵⁸⁻⁵⁹ Briefly, the as-received NaCl was calcined at 500 ± 1 °C for 10 h to eliminate possible organic impurities, dissolved in

water and then filtered through a membrane (Merck Millipore Ltd.; pore size: 0.025 μm).

All glassware used was cleaned with piranha solution ($\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ with a volume ratio of 3:7), then thoroughly rinsed with water and dried before each experiment. *Caution! Piranha solution is strongly oxidizing and must be handled with care.*

In the SHG measurements, a broadband Ti:sapphire oscillator laser (Coherent, Mira-900f) with a pulse width of approximately 130 fs and a repetition rate of 82 MHz was used. The laser wavelength was centered at 810 nm. The ambient temperature was 22 ± 1 $^\circ\text{C}$ during the experiment.

A cylindrical quartz cell was used to form an oil/water interface for the total internal reflection (TIR) SHG measurements, as described by Conboy et al.⁵⁶ The incident angle of the 810-nm fundamental laser was set at 70° , which is slightly greater than the TIR angle of the hexadecane/water interface to ensure the TIR-SHG measurement. A high pass filter (>750 nm) was used to eliminate the second harmonic light in the laser. The polarization of the input laser was controlled by a half-wave plate and polarizing cube beam splitter. The reflected SH signal at 405 nm was passed through a filter (BG-39, 300–600-nm band pass) to eliminate the reflected light at the fundamental frequency. The signal was then passed through another polarizing cube beam splitter and monochromator (Andor SR-500I), before being detected with a photomultiplier tube (PMT, Hamamatsu

R-1527p). The output of the PMT was amplified by a factor of five with a preamplifier (Stanford Research, SR450A) and analyzed with a photon counter (Stanford Research, SR400). The obtained photon counts were then delivered to a computer and recorded with a program developed in-house. With a laser power of 150 mW and high-voltage supply for the PMT of -1000 V, the dark noise level was 1–2 counts s⁻¹, well below the SH signal at the hexadecane/water interface. The polarization of the pump laser and the SH signal was set as the *p* direction, with the electric field of the light parallel to the incident plane of the laser. To ensure that the SH intensity was recorded under equilibrium conditions, after adjustment of the chemical composition in the oil or water phase, the sample was left for 30–60 min until the SH intensity became stable.

Results and discussion

A SH intensity at the hexadecane/water interface affected by carboxylic acid and chemical impurities

The debate concerning the chemical composition, charge and molecular structure at the hexadecane/water interface is focused on whether the negative potential arises from the pure hexadecane/water interface or is induced by long-chain carboxylic acid impurities in the hexadecane, which may be present as a result of slow oxidization or through contamination.^{8,39,49,51,60} If carboxylic acids were present at the oil/water interface, the partly ionized carboxylic groups would impart a negative charge at the interface. It is known from SFG-VS studies that positive or negative charges at the water surface can

induce certain orientational ordering of water molecules in the surface layers.^{20,24,61-65}

The addition of oleic acid into hexadecane also resulted in change of the SH signal from hexadecane/water interface. This change in the SH intensity can be used to evaluate the purity of the hexadecane in our experiment, which was used as received, or after several times passing through basic alumina columns. Figures 1 and 2 show the change in the SH intensity of the purified hexadecane/water interface with the addition of oleic acid and less-purified hexadecane to the organic phase, respectively. Here “purified hexadecane” refers to hexadecane that had been passed through the basic alumina columns six times (denoted as “Hexadecane6”). “Less-purified hexadecane” refers to hexadecane that had been passed through the basic alumina columns zero to five times (i.e., “Hexadecane0” to “Hexadecane5”).

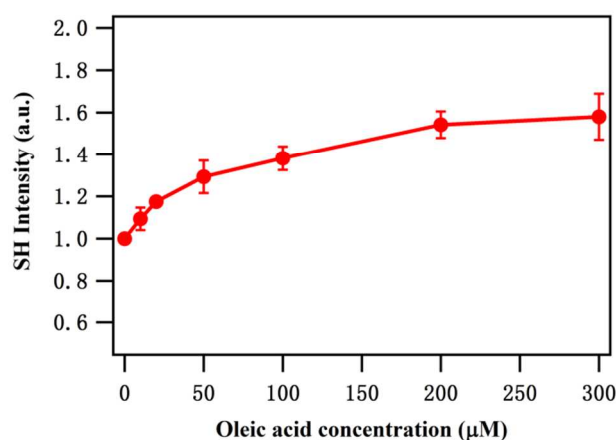


Figure 1. SH intensity from the hexadecane/water (pH=7) interface as a function of oleic acid concentration in the hexadecane phase. The intensity

was normalized with respect to the intensity at an oleic acid concentration of zero, which was approximately $2000 \text{ counts s}^{-1}$. The line joining the data points tracks the change.

The increase in the SH signal shown in Figure 1 from the Hexadecane6/water interface with the addition of oleic acid proves that changes in the molecular structure (in particular, of water molecules, as discussed latter) at the oil/water interface can be easily detected with this surface-sensitive spectroscopic method. An oleic acid concentration of the order of $10 \mu\text{M}$ in hexadecane caused a notable intensity change in the SH signal from the hexadecane/water interface.

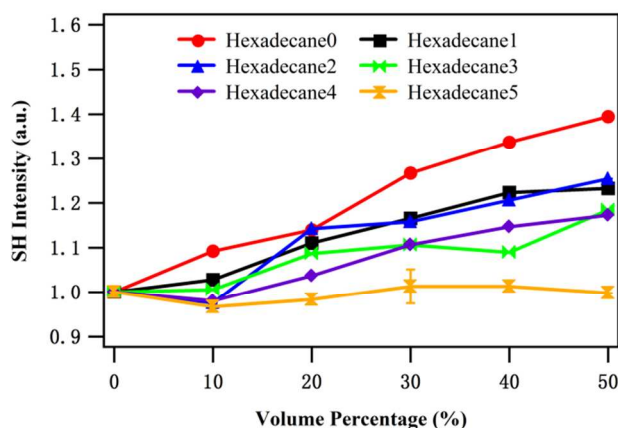


Figure 2. Normalized SH intensity from the purified hexadecane/water (pH=7) interface as a function of the volume percentage of the less-purified hexadecane (Hexadecane0 to Hexadecane5) added to the purified hexadecane. For clarity, only one typical error bar is shown.

Figure 2 shows the SH signal from the Hexadecane6/water interface after the addition of less-purified hexadecane as a function of the volume percentage up to 50%. The general trend of the SH intensity increasing with the addition of Hexadecane0-Hexadecane4 reflects the presence of chemical impurities, which are believed to be mostly long-chain carboxylic acids, in these less-purified hexadecane samples. This trend becomes less prominent each time the hexadecane is purified through a basic alumina column. No such effect could be detected with the addition of Hexadecane5 to Hexadecane6. This implies that the amount of chemical impurities in Hexadecane5 was substantially reduced during the purification process.

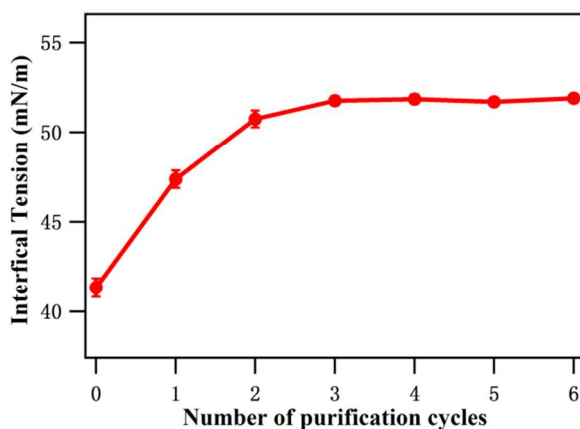


Figure 3. The change of the interfacial tension of the hexadecane/water interface with the purification of the hexadecane sample by alumina columns.

The interfacial tension of the hexadecane/water interface was also measured by the platinum slice method with an automatic tension meter (Shanghai Fangrui Instrument Co. Ltd., QBZY-2). As shown in Figure 3, a constant interfacial tension was reached after the third purification round. This result is consistent with that of a previous report, which systematically studied this impurity effect in *n*-alkanes.⁵ In addition, this proves that the interfacial tension, which tells no difference between Hexadecane3, Hexadecane4, Hexadecane5 and Hexadecane6, was less sensitive to the impurities in hexadecane compared with the SHG signal, as shown in Figure 2.

B Enhanced change of the SH intensity under basic aqueous environment

To further investigate the influence of the impurities in hexadecane on the SH intensity, we increased the pH of the water phase to 12. A more sensitive enhancement in the SH intensity of the Hexadecane6/water interface was observed after the addition of oleic acid or the less-purified hexadecane samples into Hexadecane6.

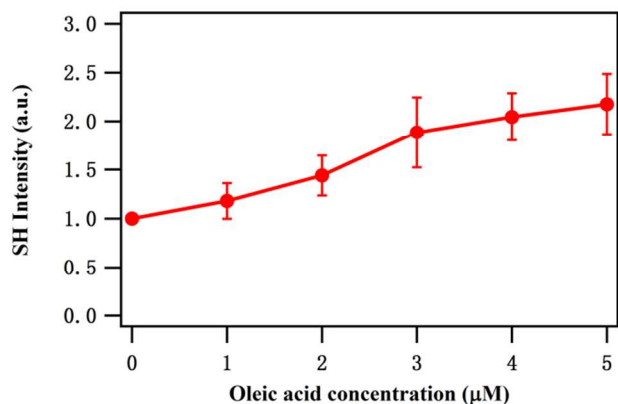


Figure 4. SH intensity of the purified hexadecane/water (pH=12) interface

as a function of the concentration of oleic acid added to the hexadecane. The intensity was normalized with respect to the intensity at an oleic acid concentration of zero, which was approximately $4000 \text{ counts s}^{-1}$.

Figure 4 shows that oleic acid concentrations as low as several micromolar caused large increases in the interfacial SH signal. Similarly, the addition of unpurified hexadecane to the purified hexadecane caused a relatively large enhancement of the interfacial SH intensity (Figure 5). It can be seen that the addition of Hexadecane5 into Hexadecane6 did not cause an appreciable increase in the SH intensity. This proves that the impurities in Hexadecane5, if evaluated with oleic acid as a reference impurity, are at the micromolar level or lower.

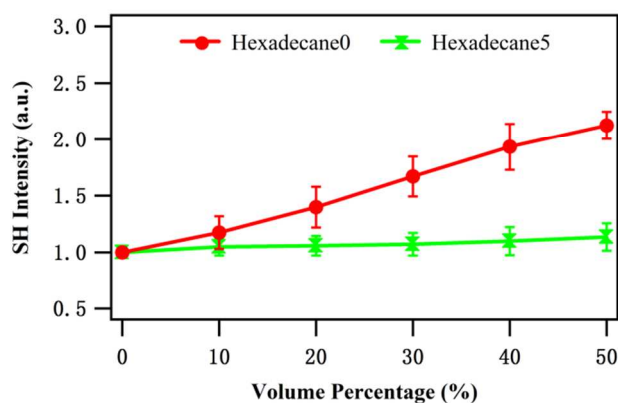


Figure 5. Normalized SH intensity of the purified hexadecane/water (pH=12) interface as a function of the volume percentage of less-purified hexadecane (Hexadecane0 and Hexadecane5) added to the purified hexadecane.

To evaluate the influence of OH^- at the oil/water interface, we investigated the SH intensity from the Hexadecane6/water interface with the addition of NaOH to the aqueous phase. A large enhancement of the interfacial SHG was observed with increasing NaOH concentration, as shown in Figure 6. The same change was also observed with the addition of KOH instead of NaOH (For clarity, data not shown). However, the addition of NaCl to the aqueous phase at concentrations up to 10 mM only caused SHG change close to the experimental uncertainty. This implies that the increase in the SH intensity is attributable mainly to the effect of OH^- and not Na^+ .

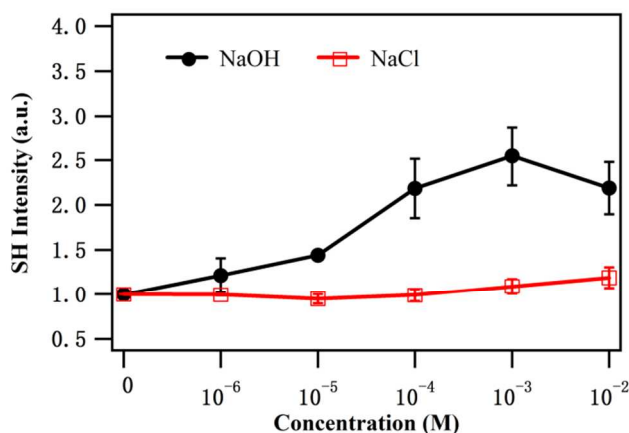


Figure 6. Normalized SH intensity of the purified hexadecane/water interface as a function of the concentration of NaOH or NaCl added to the aqueous phase.

C Understanding of the changed SH intensity and the molecular structure at the hexadecane/water interface

With the use of surface-sensitive, second-order nonlinear spectroscopic techniques, including SHG and SFG-VS, polar ordering of both water molecules and n-alkane molecules at oil/water interfaces has been suggested.^{50,56,66-68} Therefore, it is not easy to determine if the SHG radiation from the hexadecane/water interface is from ordered water molecules, hexadecane molecules, or from both. Although both SHG and SFG-VS belong to second order nonlinear spectroscopic technique, which make them with interface selectivity,⁶⁹⁻⁷⁰ they probe the interfacial molecule/material differently. SHG is performed with one beam as the pump (fundamental) laser by detecting the output beam, which is double the fundamental frequency (second harmonic). In the SHG method, when one of the light beams is close to the electric resonance of the interfacial molecules/materials, the output signal is enhanced. This gives SHG the capability of molecular recognition under certain conditions and allows the origin of the SH signal to be ascertained with relative ease.^{54,71-74} SHG can also be observed in the absence of such resonance; in such cases, the origin of the signal needs to be analyzed more thoroughly and the signal intensities are relatively weaker. In contrast, SFG-VS is performed with one visible beam and one infra-red (IR) beam as the pump laser and the output beam detected is the sum frequency of the two pumping lasers. In the SFG-VS method, when the IR beam is close to the vibrational resonance of the interfacial molecules, the output signal is enhanced. Under most conditions, SFG-VS is capable of molecular recognition,^{18,21,75-76} because the use of vibrational spectra in recognizing molecular groups is well established in Raman and IR studies. The advantages of using polarization

analysis and experimental configuration analysis in surface SFG-VS studies for the assignment of vibrational spectra of methyl groups and methylene groups had also been demonstrated.⁷⁷⁻⁷⁸ In SFG-VS experiments, the transmission of the IR beam through the bulk material can adversely affect the measurement; this needs to be avoided by the appropriate selection of solvent or by using deuterated samples. Although the SHG measurements in this work were not affected by this problem, the distinguishing of the origin of the SH signal and direct orientational analysis of the interfacial molecules is challenging.

However, with the experiments performed in this work, the change in the SH signal from the hexadecane/water interface after the addition of oleic acid or less-purified hexadecane could be analyzed. The changes observed in the SH signal may be attributed to changes in the surface potential and the orientational order of the interfacial molecules or the adsorbed oleic acid (or other carboxylic acids and other impurities in hexadecane). From the results presented in Figures 1 and 4, the oleic acid concentration–SH intensity curves measured at pH 7 and pH 12 varied significantly. At pH 12, the concentration required to enhance the interfacial SH signal was about two orders of magnitude smaller than that required at pH 7. Similarly, as shown in Figures 2 and 5, the SHG enhancement with the addition of unpurified hexadecane also differed depending on the acidity of the aqueous phase. This is evidence that the nonlinear polarizability of the oleic acid itself (or other carboxylic acids or other impurities) is not the main contributor to the increased SH

intensity; rather, this is most likely caused by changes of the interfacial potential and/or reoriented interfacial water molecules, induced either by oleic acid or chemical impurities in hexadecane (Figures 1 and 2), or by NaOH in the aqueous phase (Figure 6). The orientational structure change in the interfacial hexadecane molecules was not considered because it is unlikely that a pH change in the aqueous phase could influence hexadecane molecules, which have much smaller dipole moments compared with water molecules.

The drastic difference (ca. two orders of magnitude) in the oleic acid concentration–SHG intensity curves in Figures 1 and 4 requires further discussion. The results imply that in the aqueous phase at neutral pH, the majority of interfacial oleic acid molecules are in their neutral form, whereas at pH 12, the ionized form dominates. The ionization of the carboxylic acid at the oil/water interface may be very different from that happened in the bulk solution because it is determined by the localized acidity of the interface, the surface pK_a of the carboxylic acid and the interaction between carboxylic acid molecules at the interface.^{20,79-82} With these factors considered, Konek et al. demonstrated that oriented carboxylic groups at the liquid/solid interface may be laterally hydrogen bonded and have a higher interfacial pK_a value of around 9, compared with 5.6 for non-hydrogen bonded groups.²⁰ Accordingly, the oleic acid molecules at the hexadecane/water interface may also be well oriented and partly hydrogen bonded to each other, similar as that reported on silica/water interface and silicon/water interface.^{20,82}

D Further discussion on the pH dependent SH intensity and the adsorption of OH⁻ at the hexadecane/water interface

The observed changes in the SH intensity due to changes in OH⁻ concentration may come from a change in the interfacial potential, known as the electric field induced second harmonic (EFISH) effect,^{17,20,79-80,83} and/or a change in the orientational ordering of the interfacial molecules, because both these factors contribute to the nonlinear radiation of the interface. As presented in the introduction, the molecular orientation of water and electric potential at the oil/water interface has been widely investigated. If there is a change in the potential at the oil/water interface resulting from OH⁻ adsorption, there should also be a change in the orientational order of the water molecules because of their relatively large dipole moment, which enables them to align with the electric field, as has been confirmed by the SFG-VS studies.^{20,24,61-64} It was more complicated conversely. It has been suggested that a change in the orientational order of water molecules at the interface would not result in “real” interfacial potential change,⁴²⁻⁴³ while other researchers have demonstrated with MD simulations that preferential orientation of the water molecules could result in preferential adsorption of OH⁻ at the hydrophobic/water interface.⁴⁷ Intuitively, the electric attraction and repulsion of positive or negative ions/molecular moieties should occur in both directions; thus, changes in the interfacial charge and the orientational ordering of water molecules are most possibly connected.

In order to evaluate if the changed SH intensity is solely originated from the EFISH effect, or also from the reorientational ordering of interfacial water molecules induced by the electric field, we performed SHG experiments as that reported by Zhao et al.⁷⁹ In the experiment NaCl was introduced in the hexadecane/water system after the pH value of the aqueous phase had been changed from 7 to 12 by the addition of NaOH. The enhanced SH field induced by the addition of NaOH was found to be partly (~20%) eliminated by the addition of NaCl at 1 M concentration.

In Zhao et al.'s work, almost all the changed SH field induced by the positive or negative charges at the air/water interface could be eliminated by the introducing of 1M KCl. So, EFISH effect was considered to be the dominant contribution of the changed SH field. In this work, we could only attribute part of the observed SH enhancement to the EFISH effect; the rest part of the changed SH field should be contributed to the change of the orientational ordering at the oil/water interface. As we mentioned above, the later explanation, which involves an electric field induced orientational ordering of interfacial water molecules, was also supported by recent SFG-VS investigations at other water based interfaces.^{20,24,61-65}

A SFG-VS study by Vacha et al. showed that the C-H spectra of the hexadecane/D₂O interface (in a hexadecane-D₂O emulsion) was independent of the acidity of the aqueous

phase, implying that the orientational structure of the interfacial hexadecane molecules was unchanged.⁵⁰ This supports our argument above, which attributes the change in the SH signal to the changed structure of the water molecules rather than the hexadecane molecules. They also reported that the orientational order of interfacial D₂O molecules was unchanged when the aqueous phase was changed from neutral to pH 12.5, based on the interference of the high-frequency component of the O–D stretching modes with the C–H stretching modes of the hexadecane molecules.⁵⁰ So, the conclusion Vacha et al. made based on charge transferring effect is quite different from the preferentially adsorption of OH[−] at the oil/water interface drawn in previous reports.^{31-37,40}

In our experiment, the addition of OH[−] to the aqueous phase and the addition of carboxylic acid to hexadecane resulted in similar increases in the SH intensity. Therefore, an explanation involves the reorientation of water molecules with their hydrogen atoms directed toward the oil phase because of the increased negative interfacial potential could be introduced, similar as has been demonstrated at other hydrophobic/water interfaces with SFG-VS studies.^{52,61-62} This discrepancy between the aforementioned SFG study and the present SHG study might have arisen from the fact that the changes in the interfacial potential and the orientational order of water molecules being relatively low in this system. As can be seen in Figures 4 and 6, the enhancement of the SH signal with the addition of 10 mM OH[−] is comparable to the addition of only several micromolar oleic acid in hexadecane. This effect is less pronounced than that induced by the addition of

millimolar concentrations of sodium dodecyl sulfate or cetyl trimethylammonium bromide used in other studies.^{50,61,63} The increase in the SH intensity because of the reorientation of water molecules induced by the negative surface potential (*i.e.* more water molecules with hydrogen atoms pointing to hexadecane) is in line with most reports on water interfaces that suggested preferential orientation of the water molecules with hydrogen atoms pointing to the hydrophobic phase in neutral acidity condition.^{7,41,52,62,84}

The behavior of H^+ and OH^- at hydrophobic/water interfaces, including gas (air)/water, solid (polymer or organic monolayer on substrate)/water and liquid (oil)/water interfaces has been intensively studied both experimentally and theoretically.^{22,31-39,50,53,55,85-91} At the air/water interface, as reviewed by Peterson and Saykally,⁵³ macroscopic electrophoretic measurements with air bubbles in water suggested a negative surface potential,^{85-86,88} whereas studies of the microscopic interfacial structure with spectroscopic measurements or theoretical simulations suggested preferential adsorption of H^+ instead of OH^- at the water surface.^{22,53,55,87,89} At hydrophobic liquid or solid interface, macroscopic electrophoretic measurements with oil-water emulsion or streaming potential and streaming current measurement of solid surface also suggested a negative surface potential,^{31-39,90-91} spectroscopic measurements supported the preferential adsorption of OH^- ,⁵² or at least supported preferential orientation of water molecules with both hydrogen atoms pointing to the hydrophobic solid/liquid phase,⁵⁰ which was consistent with the picture of a negative charged interface. The SHG measurements in this work are

in line with these observations and support the adsorption of hydroxide ion at the oil/water interface.

Conclusions

The reliability of Sum Frequency Generation – Vibrational Spectroscopy for evaluating the influence of chemical impurities on the interfacial charge and molecular structure at oil/water interfaces has recently been called into question.^{8,49} In the present work, Second Harmonic Generation, which is also a second order nonlinear technique, was used to detect the presence of carboxylic acid in hexadecane at concentrations as low as several micromolar. It was found that impurities in the as-received hexadecane (99%) affected the molecular structure at the hexadecane/water interface. The SH intensity from this interface was notably affected by the addition of the unpurified sample to the purified sample. After purification through alumina columns, the concentration of the impurities was substantially decreased such that there was no detectable influence on the SHG radiation from hexadecane/water interface.

The SH intensity from the hexadecane/water interface increased significantly when the acidity of the aqueous phase was changed from neutral to pH 12, thereby confirming the effect of OH^- on the interfacial charge and molecular structure of water. The increase of the negative potential at the oil/water interface and the reorientation of water molecules

with their hydrogen atoms directed toward the oil phase best fits our observation. The results provide new evidence that support the specific adsorption of OH^- at oil/water interfaces.

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