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The behavior of hydroxide and hydronium ions at the hexadecane–water interface studied with second harmonic generation and zeta potential measurements†

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By probing the electric potential at the hexadecane–water interface with second harmonic generation and the zeta potential at the surface of a hexadecane droplet in its emulsion, we show that hydronium ions don't have a specific affinity to the oil–water interface although hydroxide ions do. The observed apparent affinity of the hydronium ions to the hexadecane–water interface is more likely a result of the electro-static attraction effect. The adsorption free energy of the hydroxide ions at the oil–water interface was estimated to be $-8.3 \text{ kcal mol}^{-1}$. This study provides more experimental evidence for understanding the behavior of hydronium and hydroxide ions at the oil–water interface.

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Introduction

Exploring the interactions of ions at aqueous interfaces is crucial for understanding phenomena such as emulsion stability, cloud nucleation, catalytic reactions and protein folding.^{1–4} The oil–water interface is one of the most important types of aqueous interface because they are generally involved in the oil industry, food and medicine production, and also in metabolism processes etc.^{4–9} One of the most discussed topics on ionic interactions at oil–water interfaces is the adsorption/depletion of hydroxide and hydronium ions.^{10–12} For example, although it is still a controversial topic,^{13,14} many researchers have reported an enhancement of

surface charge consistent with a surface enrichment of hydroxide ions by electrophoretic analysis or pH-stat experiments.^{15–19} So far theoretical simulations on the behavior of hydroxide and hydronium ions at the oil–water interfaces are still rare, although the interfacial behavior of these ions at other water–hydrophobic interfaces, for instance the air–water interface, has been intensively discussed.^{20–23}

Another technique that can detect interfacial charge/potential is second harmonic generation (SHG) and sum frequency generation-vibrational spectroscopy (SFG-VS) that have been successfully applied in studying the electric potential at water based interfaces.^{9,11,24–31} In an early study on the surface of polystyrene particles in colloids by E. C. Y. Yan *et al.*,²⁴ SHG was used to probe the surface potential of the particles and compared with the zeta potential which reflects the potential at the outer surface of the shear zone, *i.e.*, relatively further away from the polystyrene–water interface. As summarized in our recent work,⁹ although the mechanism behind the changed second order nonlinear signal from the interface at varied interfacial potential and the corresponding molecular structures at the interface are still not completely clarified, it has been accepted that the electric field of the nonlinear signal can be expressed as $E = E_0 + e^{i\phi} E_{\text{induced}}$. Here E_0 is the electric field of the nonlinear signal from the interface with no net electric charge/potential and E_{induced} is the electric field of the nonlinear emission induced by the interfacial potential. The phase difference (ϕ) between the two contributions is normally simplified to be 0° or 180° for the constructive and destructive interference, respectively. The E_{induced} part can be calculated by the electric field induced second harmonic effect which originates from the third-order

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nonlinear susceptibility ($\chi^{(3)}$) of the water molecules, *i.e.*, $E_{\text{induced}} \propto \chi^{(3)}\Phi(0)$, with $\Phi(0)$ being the interfacial potential,^{32,33} or treated as a contribution from reoriented water molecules induced by the interfacial potential as detected by sum frequency generation-vibrational spectroscopy, or from the changed solvation structure of water molecules.^{27–31} In recent reports it has been pointed out that $\chi^{(3)}$ could be influenced by factors that may mix, including the dipole reorientation, the third order nonlinear polarizabilities and the limited coherent length of the measurements.^{33–36} Overall, the application of this “water indicator” in probing the electric charge and the adsorption of ionic species at water interfaces has been generally accepted.^{11,24–27}

For example, K. Bhattacharyya *et al.* used the changed electric field of the SHG emission from the air–water interface to analyze the adsorption of negatively charged phenolate ions with varied alkanes at the interface.³⁷ This approach initiated by Eisenthal’s group has been followed by many researchers and applied in SHG and SFG-VS studies.^{11,25,26,38} C. S. Tian *et al.* probed the amplitude of the imaginary part of the phase sensitive SFG-VS spectra and used it to represent the charge at the water–octadecyltrichlorosilane interface.²⁷ Although the $\chi^{(3)}$ effect on resonant OH stretch measurements was not explicitly accounted for, the data of Tian *et al.* qualitatively show similar effects. Preferential adsorption of OH^- , as well as the adsorption of Cl^- and the subsequent adsorption of H^+ at the octadecyltrichlorosilane–water interface at varied NaOH and HCl concentrations were revealed. In our recent work we have used SHG to study the adsorption of surfactants with different charges, including negatively charged sodium dodecyl sulfate and oleic acid, and positively charged cetyltrimethylammonium bromide (CTAB) and oleylamine, at the hexadecane–water interface.^{9,39} With the analyses of the interfacial potential monitored by SHG measurements, information on the multiple steps in the adsorption of these surfactants has been provided. It was found that the adsorption of negatively charged surfactants at the interface led to enhanced SHG emission from the interface. In contrast, adsorption of positively charged surfactants decreased the SHG intensity.

In this work we report our experiments showing that hydronium ions don’t have a strong affinity to the hexadecane–water interface, although specific adsorption of hydroxide ions at the hexadecane–water interface does exist, irrespective of the species of alkali used in the experiments.

Experimental section

Deionized water with a resistivity of 18.2 M Ω cm was obtained from a water purifier (WP-UP-UV-20, Sichuan Water Technology Development Co. Ltd, China). Hexadecane (99%, Sigma-Aldrich) was purified by passing through basic alumina (100–200 mesh, Aladdin) columns for up to six times with procedures reported previously.¹¹ NaOH (99.99%, Sigma Aldrich), KOH (99.999%, Aladdin), HCl (AR reagent, 37% solution in water, Tianjin Baishi Chemical Co. Ltd, China) and HNO_3 (GR, *ca.* 65% solution in water, Xi’an Chemical Reagent Factory, China) were used after

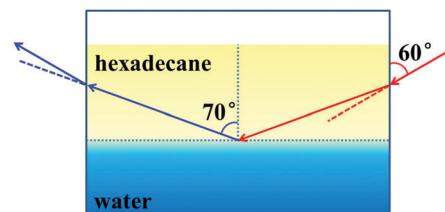


Fig. 1 Illustration of the sample cell and the laser direction in SHG measurements.

being dissolved/diluted in deionized water. NaCl (>99%, Sigma Aldrich) was used after purification following the procedures reported before.^{4,11} Briefly, it was calcined at 500 °C for 10 hours to eliminate the organic contaminants, dissolved in deionized water and then filtered with a membrane (0.025 μm, Merck Millipore Ltd).

SHG measurements were performed at 22 ± 1 °C with an 810 nm femtosecond laser, which was generated from a broadband Ti:sapphire oscillator (Coherent, Mira-900f) with a pulse width of ~ 130 fs and a repetition rate of 82 MHz. An oil/water interface was formed in a rectangular shaped quartz cell as shown in Fig. 1. As we pointed out before,⁹ using a square cell in total internal reflection (TIR) SHG measurements is more accurate than using a cylindrical cell. The incident angle of the fundamental laser was set to 70° from the interface normal to achieve TIR geometry for the oil–water interface. The polarization of the input laser was controlled by a half-wave plate (Thorlabs, WPH05M-808, 808 nm) and a polarizing cube beam splitter (Thorlabs, PBS202, 620–1000 nm, extinction ration 1 : 1000) to the *p* direction, *i.e.*, with its electronic field parallel to the plane defined by its propagating direction and the interface normal. A high pass filter (Thorlabs, FEL0750, >750 nm) was placed before the sample to suppress the second harmonic light from the oscillator or other optics. The reflected light and the SHG signal from the interface were filtered by using a bandpass filter (Thorlabs, BG-39, 300–600 nm) to eliminate the residual fundamental laser. The *p* polarized signal was selected by a polarizing cube beam splitter (Thorlabs, PBS201, 420–680 nm, extinction ratio 1 : 1800 at 405 nm) and focused in the monochromator (Andor SR-500I). The output signal at 405 nm wavelength was detected by using a photomultiplier tube (Hamamatsu R-1527p, -1000 V) and amplified by a factor of 5 with a preamplifier (Stanford Research, SR445A). After being analyzed by a photon counter (Stanford Research, SR400), the data was recorded by a computer.

In the preparation of hexadecane–water emulsions, 200 μL purified hexadecane was mixed with 10 mL water in a homogenizer (Omni, TM125-220, 8000 rpm) for 1 min and stirred at 500 rpm in a thermostatic water bath (25 ± 1 °C) for 15 min. The mixture was then sonicated (KQ-300DE, 300 W, 40 kHz, Kunshan Ultrasonic Instrument Co. Ltd, China) for 10 min at 25 ± 3 °C.

The size and electrophoretic mobility of the oil droplets in emulsions at varied pH were measured with dynamic light scattering equipment (ZS90, Malvern, UK). For this measurement

the emulsions were diluted 100 times with deionized water. The pH of the emulsions was adjusted by NaOH or HCl solutions. The used laser wavelength was 633 nm and the measuring angle was 90°. All the measurements were performed with temperature set at 25 °C. The average diameter of the oil droplets in the emulsions was measured to be 200–300 nm during the electrophoretic mobility measurements. The pH values of the emulsions were obtained using a Mettler Toledo acidometer (PE20K, electrode: LE438).

Results and discussion

We measured the SHG intensities from the hexadecane–water interface with the addition of acids (HCl and HNO_3). As shown in Fig. 2, the electric fields of the SHG intensities decreased with the increased concentration of HCl or HNO_3 . The first consideration from this result may be that hydronium ions preferentially adsorb at the hexadecane–water interface and cause decreased SHG fields, because a decreased SHG signal has been observed with the adsorption of positively charged CTAB and oleylamine.⁹ However, it needs to be noticed that for the CTAB and oleylamine cases, the SHG intensities decreased to a value close to zero at a relatively low surfactant concentrations and then increased at a higher surfactant concentration, in accordance with a reverse of the interfacial potential at the hexadecane–water interface from negative to positive. Here the SHG fields only decreased to approximately 70% of the original values at acids concentrations as high as 0.1 M, indicating that the electric potential at the hexadecane–water interface was not reversed.

The decrease in the SHG fields with acid addition was close to the SHG decrease with salt addition which has been reported before⁹ and plotted in Fig. 2 for comparison. As we have pointed out,⁹ the decrease of the SHG field at the hexadecane–water interface with the salt addition comes from the screening effect: the increased concentration of sodium ions close to the interface at increased electrolyte concentration weakens the negative potential of the interface. Our observation here shows that the hydronium ions have the same effect. These results show the affinities of Na^+ and H^+ to a negatively charged interface. However, no evidence of a strong specific affinity for hydronium

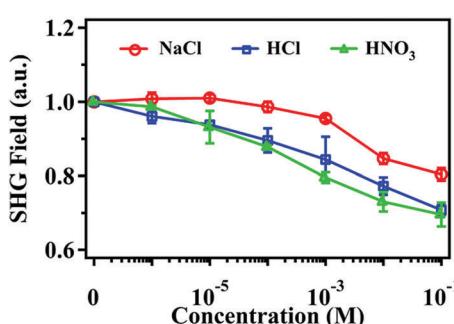


Fig. 2 Electric fields of the SHG intensities from the hexadecane–water interface as a function of the concentration of NaCl (red), HCl (blue) and HNO_3 (green) in water. All data points have been normalized to the first point.

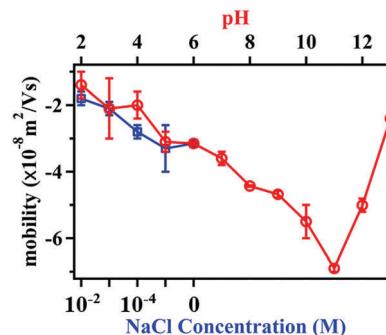


Fig. 3 Measured electrophoretic mobilities of the oil droplets in hexadecane–water emulsions with the adjustment of pH (red line) or the ionic strength (blue line).

ions to a hydrophobic phase can be deduced from these experiments.

Electrophoretic measurements at the surface of oil droplets in hexadecane–water emulsions support the above analyses. As shown in Fig. 3, the absolute value of the electrophoretic mobility, which was generally considered to be proportional to the zeta potential of the surface,^{39–41} decreased with the decrease of the pH value of the emulsions. However, at pH 2 the electrophoretic mobility was close to zero rather than significantly positive. This observation indicates that hydronium ions don't have a higher affinity to the oil–water interface over the counter ions (Cl^-). The previously reported pH dependent electrophoretic mobility curves measured in hexadecane–water emulsions varied with the change of ionic strength of the emulsions and the purities of the hexadecane samples.^{14,17} However, all measurements with hexadecane–water emulsions or other alkane–water emulsions showed electrophoretic mobilities below zero or only slightly larger than zero at relatively high acid concentrations.^{14–18} These observations are against a strong hydronium adsorption at the oil–water interfaces. The electrophoretic mobility curve measured with the addition of NaCl in the emulsions at pH ~ 6 was also plotted in Fig. 3. It can be noticed that the decrease of the electrophoretic mobility with salt addition followed the same trend as that observed in HCl addition with only a small deviation. This control experiment also confirmed that hydronium ions don't have specific affinity at the hexadecane–water interface.

Fig. 3 shows that the absolute value of the electrophoretic mobility reached a maximum at pH 11 and decreased at even higher pH values. This observation was also consistent with our SHG measurements. Fig. 4 shows the electric field of the SHG signal from the hexadecane–water interface with alkali addition measured at the total internal reflection geometry with square sample cells. The blue curve in Fig. 4 follows the same trend as that in our previously reported data measured with cylindrical cells with only a small deviation.¹¹ As we discussed before,⁹ the data presented here are more accurate in principle, although this deviation wouldn't affect the interpretation of the data we presented.¹¹ It was also shown that the SHG field decreased monotonously to ~80% of its original value while NaCl was added into the water phase.⁹ This also supports the conclusion that the OH^- concentration was enhanced at the oil–water interface.

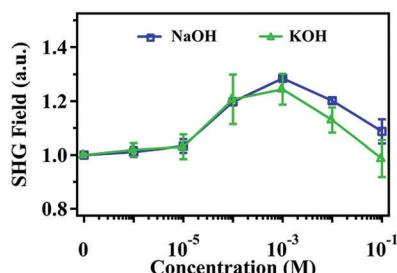


Fig. 4 Normalized SHG fields from the hexadecane–water interface as a function of the concentration of NaOH or KOH.

The decrease of the SHG fields at the high NaOH or KOH concentration ranges shown in Fig. 4, and the decrease of the electrophoretic mobility value shown in Fig. 3 from pH 11 to 13, also come from the enhanced screening effect with increased ionic strength. As a matter of fact, addition of NaCl into the water phase containing 1 mM NaOH or KOH caused a similar decrease in SHG intensities as that caused by further alkali addition, as shown in Fig. 5. It can be noticed that after the addition of 0.1 M NaCl to the pH 11 solution, the SHG fields from the hexadecane–water interface is close to that upon addition of 0.1 M NaOH or KOH. This observation indicated that the adsorption of hydroxide ions at the interface had been almost saturated at an alkali concentration of \sim 1 mM. Beyond this concentration, the addition of NaOH, KOH or NaCl brought out a similar effect on the electric potential of the interface. The fact that the adsorption of hydroxide ions was nearly saturated at a relatively low concentration supports the strong specific affinity of hydroxide ions at the oil–water interface. The adsorption free energy of hydroxide ions at the hexadecane–water interface can be deduced from the SHG measurements to be -8.3 ± 0.2 kcal mol $^{-1}$, based on the Langmuir fitting detailed in our previous report⁹ and briefly described in the ESI.[†]

It needs to be noted that in the Langmuir fitting, the lateral interaction between the adsorbed ions, *i.e.*, the electric repulsion, was not considered. In principle, the Frumkin–Fowler–Guggenheim (FFG) equation^{42,43} which takes lateral interaction during the adsorption process into account, is more accurate in the analyses of interfacial adsorption of charged species. However, normally

the FFG equation has to be solved numerically.⁴³ As detailed in the ESI,[†] we have applied an approximate treatment with FFG fitting and found that the adsorption free energy only varied slightly from the value obtained by the Langmuir fitting, though the repulsive interaction between the adsorbed hydroxide ions at the oil–water interfaces was confirmed. Also it needs to be noted that the obtained adsorption free energy reveals the tendency of the hydroxide ions towards the negatively charged hexadecane–water interface instead of a neutral oil–water interface. The effect of interface charge on further adsorption of molecules with the same or opposite charges has been systematically discussed in the literature.⁴⁴

It has been reported that the negative charges at the oil–water interface may come from impurities: carboxylic acids in the oil phase.^{14,45} It was shown that deprotonation of the carboxylic acids at the mM concentration level in the commercially available hexadecane sample contributed to the negative potential at oil–water interfaces.^{14,45} However, with experiments performed in our lab, the adsorption of hydroxide ions instead of carboxylic acids at the interface was supported by the following evidence: first, the hexadecane used in our experiments was purified by basic alumina columns six times. It was shown that SHG is sensitive to oleic acids in the hexadecane at the μ M concentration level. However, no observable change in the SHG field can be induced by the addition of less purified hexadecane (purified five times) into the oil phase in our experiments.^{4,9,11} This observation demonstrated that with the purification process used in our lab, the acidic impurities in the hexadecane had been reduced to the sub- μ M level, rather than the mM level detected in the sample used in previous reports.^{14,45} Second, the electric charge density at the surface of oil droplets in the hexadecane–water emulsions can be estimated by the measured electrophoretic mobility and zeta potential based on the Graham equation, which was believed to be applicable at low and moderate electrolyte concentrations.¹⁶ The estimated maximum surface charged density (at pH 13) was 0.14 ± 0.01 e nm $^{-2}$. Assuming it is caused by the carboxylic acids in oil, a concentration of \sim 5.8 mM is required. This value is well beyond the detection limit of our SHG analyses, which is at the micromolar level.^{9,11} One may argue that this value deduced from the electrophoretic mobility measurements is not very accurate. However, the large concentration gap between the millimolar and micromolar levels, and the fact that the electrophoretic mobility measurement may underestimate the number of the interfacial negative ions because of the existence of counter ions, make this evidence supportive of our judgement. Third, by mixing the prepared emulsions with NaOH solutions at pH values around 10.5 and measuring the pH values of the mixtures, we estimated the number of adsorbed hydroxide ions at the oil–water interfaces. As detailed in the ESI,[†] the obtained surface density of hydroxide ions was 0.14 ± 0.01 e nm $^{-2}$, which is smaller but at the same level as the value obtained by J. K. Beattie *et al.*¹⁷ Overall, these experimental pieces of evidence support the adsorption of hydroxide ions rather than deprotonation of carboxylic acids at the interface, or the charge transfer scenario⁴⁶ which cannot explain the pH measurements. Recent reports on the adsorption of hydroxide ions at other water–hydrophobic interfaces such as the Teflon–water interface

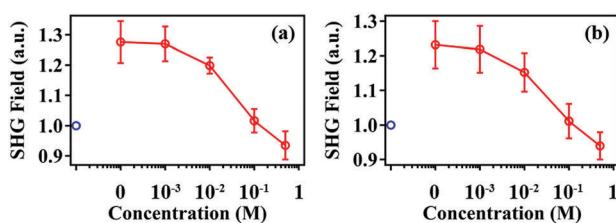


Fig. 5 Change of the SHG fields from the hexadecane–water interface with increasing NaCl concentration in aqueous phase containing (a) 1 mM NaOH; (b) 1 mM KOH. The first point in each curve is the original SHG field from the pure hexadecane/water interface, while the rest are measured after the addition of NaOH or KOH. All data points are normalized to the first point.

and the gas–water interface also support specific hydroxide adsorption at the hydrophobic–water interface rather than an impurity effect, since no oil was involved in these studies.^{47–49}

One can notice that the debate on the adsorption or depletion of hydroxide and hydronium ions at the air–water interface has not ended yet.^{48–50} Several previous reports have summarized the varied conclusions on the enrichment/depletion of the hydronium and hydroxide ions at hydrophobic–water interfaces with both experimental and theoretical approaches.^{11,12,51,52} Besides concern about the purity of the oil phase as we have discussed above, there are also other disagreements raised in the literature. For example, it has been argued that the electrophoretic mobility of the oil droplet (or gas bubble) can originate from preferentially oriented molecules or surface roughness instead of actual electric charge at the surface.^{53–56} It was also suggested that the negative charge at the oil–water interface can be induced by the charge transfer effect across the slip plane in the electrophoretic experiments.^{46,57} These discussions are focused on the data obtained from electrophoretic experiments only, with the results from SHG,^{11,51} SFG-VS,^{27,58,59} X-ray photoemission spectroscopy,⁶⁰ electrospray ionization mass spectroscopy⁴⁸ performed at air–water or oil–water interfaces unaccounted for, even though the conclusions from these experimental approaches also varied.¹²

Taking the studies with second order nonlinear spectroscopic techniques for example, C. S. Tian *et al.* reported the resonance characteristics of the hydronium and hydroxide ions at the vapor–water interface and suggested the surface adsorption of these species in the solutions of HCl, HI and NaOH, respectively.⁵⁸ Later, Imamura *et al.* reported MD simulation for the same interfaces and calculated the SFG-VS spectra.⁵⁹ They have shown that although Na^+ is slightly more buried than OH^- , none of them are surface enriched. However, the slight charge separation induces a change in the orientational order of interfacial water molecules,⁵⁹ which can contribute to the second order nonlinear susceptibility of the interface and can be detected by SFG-VS and SHG. With resonant SHG, P. B. Peterson and R. J. Saykally probed the surface of HI and NaOH solutions. They revealed that I^- and H^+ are enriched at the surface while OH^- , in contrast, is repelled or at most weakly enhanced at the surface.^{51,61} They also summarized molecular-scale studies that demonstrate the absence of OH^- at the hydrophobic–water interface, which are in conflict with macroscopic bubble experiments. The oil–water interface, such as the d_{34} –hexadecane–D₂O interface was also probed with SFG-VS by J. S. Samson *et al.* who found no spectra of the OD⁻ within the detection limit,⁴⁶ implying an absence of OD⁻ species around the oil–water interface.

As addition to these studies with varied observations, the increased non-resonant SHG intensity from the hexadecane–water interface in the presence of HCl and NaOH can provide new information to this discussion. As we pointed out before, the orientation of water molecules at the hexadecane–water interface is mostly with the hydrogen atoms pointing to the oil phase,^{9,11} and the increased SHG intensity upon addition of NaOH and KOH, as well as the fact that non-resonant SHG can be used to reveal the interfacial potential by the

“water indicator”,^{11,24–27} revealed that hydroxide ions preferentially adsorbed at the hexadecane–water interface, which is consistent with the electrophoretic measurements. Here the varied SHG emission from the hexadecane–water interface was considered to be mainly contributed from the reoriented water molecules instead of hexadecane molecules because the latter have much a smaller dipole moment and are supposed to be less influenced by the interfacial potential. Also, it is worth noting that with the hydrogen atoms pointing towards the hydrophobic phase, most of the OH groups tend to donate a hydrogen bond by corrugation of the interface as suggested by J. S. Samson *et al.*⁴⁶

At the same time, we have to admit that we cannot exclude the possibility that K⁺ and Na⁺ also are enriched at the hexadecane–water interface, but with less density or located farther from the interface, as suggested by Imamura *et al.* for the air–water interface.⁵⁹ For the HCl case, we also cannot exclude the possibility that H⁺ and Cl⁻ are both enriched at the interface so that interfacial water molecules are not significantly affected by the uneven distribution of net electric charges. It has been pointed out that the formation of contact ion pairs alters the interfacial behavior of the undissociated acid, the ions and the ion pairs.⁶² However, the experiments presented in this work clearly show a much higher tendency for the hydroxide ions to attach to the oil–water interface compared with other ions, including the hydronium ions.

It is also worth noting that with the pH value of the hexadecane–water emulsion decreased to 1, the emulsion becomes very unstable and hinders the electrophoretic measurement. This observation implies that the zeta potential and the electric charge at the oil–water interface are close to zero at pH 1. Fig. 2 shows that with the addition of 0.1 M HCl or HNO₃ in the water phase, the electric field of the SHG emission from the hexadecane–water interface is around ~70% of the original value that was measured from the interface between hexadecane and pure water. This finding indicates that the electric field of the nonlinear signal from the hexadecane–water interface with no interfacial electric charge/potential, *i.e.*, E_0 is around 70% while E_{induced} varies with the electric charge/potential at the interface. This ratio is also consistent with our previous observation.³⁹

The obtained adsorption free energy of the hydroxide ions at the oil–water interface is smaller than that of long chain surfactants containing much larger hydrophobic moieties that was reported in our recent work.⁹ It is also relatively lower than the reported OH⁻ adsorption free energy at the water–OTS interface.²⁷ Still, the reason for such a strong specific affinity to the oil–water interface for hydroxide ions but not for hydronium ions is not clear. It has been shown that hydroxide and hydronium ions behave like amphiphilic surfactants near a hydrocarbon surface.²⁰ Several previous studies^{63–66} suggested that the first solvation shell of the solvated hydronium or hydroxide ion contains three water molecules, giving a cluster with hydrogen atoms pointing outside (see ESI†). Y. Crespo and A. Hassanali reported 4 or 5-water coordinated hydroxide ions and suggested the formation of amphiphilic clusters which prefer to be a buried or a surface state, depending on their

specific molecular structures.⁶⁷ However, we believe that more needs to be done in order to get a straightforward explanation for strongly hydrophobic hydroxide ions in the aqueous phase.

Conclusions

In summary, it was revealed that hydronium ions don't have a specific affinity to an oil–water interface although strong hydroxide ion adsorption at the interface was consolidated. The observed adsorption of hydronium ions at the hexadecane–water interface was caused by the negative potential at the interface rather than their specific affinity to the interface. Though, one may notice that based on the many theoretical and experimental studies reported so far, the actual behavior of hydroxide and hydronium ions at the oil–water interface and the mechanism behind it still awaits further work.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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