

Water hydrogen bond structure near highly charged interfaces is not like ice

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Supporting information

1. Experimental condition

The optical configuration and Fourier transform analysis of HD-VSFG have been described elsewhere.¹ Briefly, a part of the output from a regenerative amplifier (Spectra Physics, SpitfireProXP; ~3.5 W, 1 kHz) was used for excitation of a commercial optical parametric amplifier and a difference frequency generator (Spectra Physics, TOPAS C & DFG1) to generate broadband IR (ω_2 , center wavelength: 2800 nm, bandwidth: ~500 cm^{-1}). The rest of the regenerative amplifier output was made pass through a narrow band filter (CVI, center wavelength: 795 nm, bandwidth: 1.5 nm (24 cm^{-1})) and was used as the visible (ω_1) light for the HD-VSFG measurement. The ω_1 and ω_2 beams were spatially and temporally overlapped on a sample surface with incident angles of 44 and 59 degree, respectively, to generate the SF at $\omega_1 + \omega_2$. The ω_1 , ω_2 , and SF beams reflected by the sample surface were refocused by a concave mirror onto a GaAs(110) surface to generate another SF that acted as a local oscillator (LO). The SF pulse from the sample passed through a 1-mm thick silica plate located in between the sample and the concave mirror, which delayed the SF pulse relative to the ω_1 and ω_2 pulses by 1.7 ps. This delay generated the time difference between the SF pulse from the sample and that from the GaAs. The two SF beams were introduced together into a polychromator and then detected by CCD. In the polychromator, the two SF pulses were stretched in time and interfered to generate an interference fringe in the frequency domain. A typical CCD exposure time was 1 min and each spectrum presented in this paper is an average of ~20 measurements. The SF, ω_1 , and ω_2 beams were *s*-, *s*-, and *p*- polarized, respectively, (*ssp* polarization combination) in the present study. All spectra were normalized to the quartz spectrum.

Sodium dodecylsulfate (SDS) (Aldrich) and cetyltrimethyl-ammonium bromide (CTAB) (Wako) were used as received. The surfactants and NaCl (Wako) were dissolved in purified water (Millipore, 18.2 M Ω cm resistivity). Deuterium oxide (NMR grade, 99.9 %) was purchased from Wako. For isotopic dilution experiments, H₂O (*x*) and D₂O (1-*x*) were mixed to obtain the mixture of H₂O: HOD: D₂O = x^2 : 2*x*(1-*x*): (1-*x*)²,

assuming the equivalent H/D substitution. The bulk IR absorption spectra were measured using a commercial FTIR (Shimadzu, IRPrestige-21) with a thin layer liquid sample sandwiched by two calcium fluoride windows without a spacer. The IR spectrum of HOD with saturated NaCl was arbitrarily scaled in Figure 1, because the IR pass length was not precisely controlled. The saturation concentration of NaCl is near 6 M.

2. The real part and squared $\chi^{(2)}$ spectra

Figure S1 shows the real part of $\chi^{(2)}$ ($\text{Re}\chi^{(2)}$, black), $\text{Im}\chi^{(2)}$ (red) and absolute square ($|\chi^{(2)}|^2$) (blue line) spectra of the air/HOD solution interfaces containing 0.5 mM SDS in the mixture of H_2O : HOD: D_2O = 2.2: 25.5: 72.3. Figure S2 shows $\text{Re}\chi^{(2)}$ (black), $\text{Im}\chi^{(2)}$ (red) and $|\chi^{(2)}|^2$ (blue line) spectra of the air/HOD solution interfaces containing 0.1 mM CTAB. The spectral shape of the $|\chi^{(2)}|^2$ spectrum (Fig. S2, blue) is similar to that of the reported homodyne VSG spectrum of positively charged lipid/water interface in the OD stretch region.² The peak positions of $|\chi^{(2)}|^2$ spectra in Fig. S1 and S2 largely differ from those of the corresponding $\text{Im}\chi^{(2)}$ spectra. This is due to the interference between the OH resonance ($\chi^{(2)}_{\text{OH}}$) and nonresonant contribution ($\chi^{(2)}_{\text{NR}}$). The former changes the sign at oppositely charged interfaces but the latter is negative in both cases.

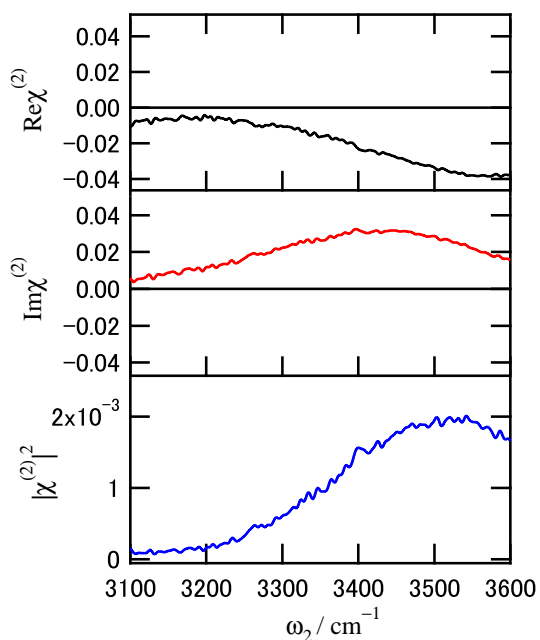


Figure S1. $\text{Re}\chi^{(2)}$ (black), $\text{Im}\chi^{(2)}$ (red) and $|\chi^{(2)}|^2$ (blue line) spectra of the air/HOD solution interface containing 0.5 mM SDS.

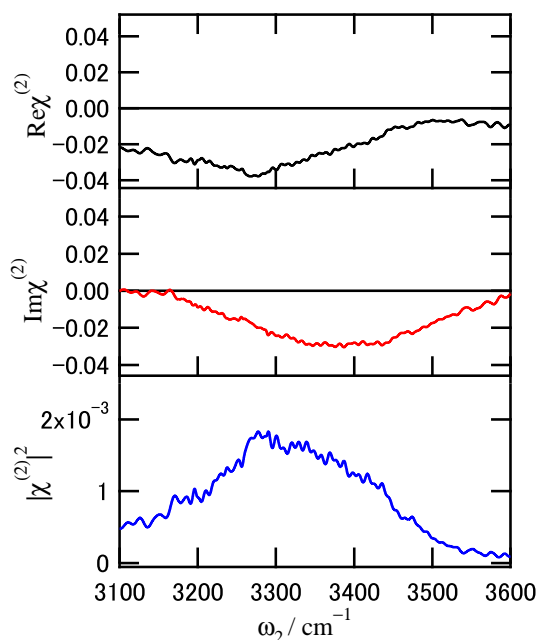


Figure S2. $\text{Re}\chi^{(2)}$ (black), $\text{Im}\chi^{(2)}$ (red) and $|\chi^{(2)}|^2$ (blue line) spectra of the air/HOD solution interface containing 0.1 mM CTAB.

3. Gouy-Chapman theory of the electric double layer

The charge density (σ) of SDS is estimated to be $13 \mu\text{C}/\text{cm}^2$ at 0.5 mM SDS³ and that of CTAB is $14 \mu\text{C}/\text{cm}^2$ at 0.1 mM CTAB.⁴ The decay of electronic potential along the distance from the interface ($\phi(x)$) in the Gouy-Chapman layer is given by solving Poisson-Boltzmann equation for a symmetric electrolyte ($M^{+z} X^{-z}$, in which the magnitude of the charge on the ions (z) are the same) as follows,⁵

$$\phi(x) = \frac{4kT}{ze} \tanh^{-1} \left\{ \tanh \left(\frac{ze\phi_0}{4kT} \right) \exp(-\kappa x) \right\}, \quad (1a)$$

$$\kappa = \left(\frac{2N_A c_0 z^2 e^2}{\epsilon \epsilon_0 kT} \right)^{1/2}, \quad (1b)$$

$$\phi_0 = \frac{2kT}{ze} \sinh^{-1} \left\{ \frac{\sigma}{(8kT \epsilon \epsilon_0 N_A c_0)^{1/2}} \right\} \quad (1c),$$

with the Boltzmann constant (k), absolute temperature (T), elementary charge (e), dielectric constant of water (ϵ), permittivity of free space (ϵ_0), Avogadro number (N_A), and concentration of each ion in the bulk (c_0). Using (1c), the surface potential ϕ_0 is estimated to be -235 mV at the given SDS concentration (0.5 mM) and the charge density. $1/\kappa$ is known as the Debye length and is 14 nm at 0.5 mM bulk concentration. The counter ion concentration at x , ($c(x)$), is given by the Boltzmann distribution:⁶

$$c(x) = c_0 \exp \left[-\frac{ze}{kT} \phi(x) \right] \quad (2).$$

The calculated depth profile of ϕ and $c(x)$ at $c_0 = 0.5 \text{ mM}$ are shown in Figure S3 and S4. The x at which the ϕ becomes $1 / 2.718$ of ϕ_0 is $\sim 5 \text{ nm}$. This is the value usually referred to as the thickness of EDL. If we assume the probing depth is in the order of EDL thickness, the averaged counter ion concentration in this region is

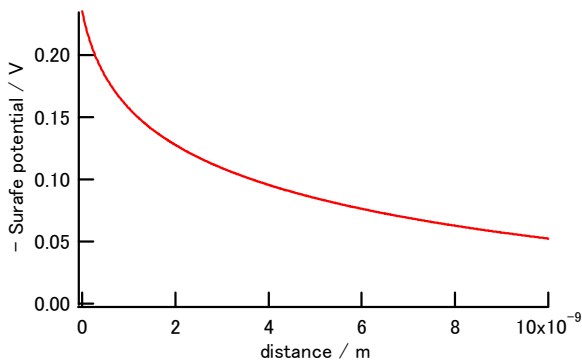


Figure S3. The potential profile calculated from GC theory using $\sigma = 13 \mu\text{C}/\text{cm}^2$ and $c_0=0.5 \text{ mM}$.

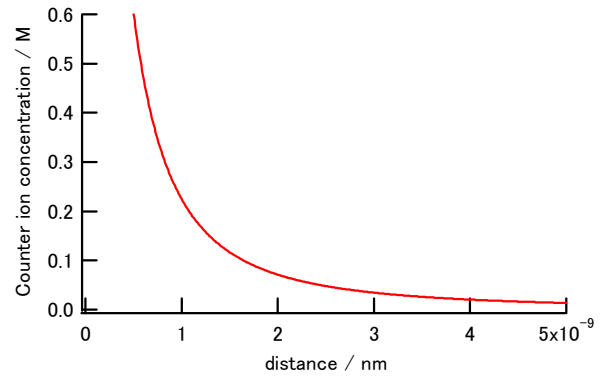


Figure S4. The counter ion concentration profile calculated from GC theory using $\phi_0 = -0.235 \text{ V}$ and $c_0=0.5 \text{ mM}$.

estimated to be 0.27 M. Figure S4 shows the plot of the counter ion concentration versus distance calculated from equation (2), which decays in a few nm thickness. The maximum concentration at the interface is ca. 0.5 M, assuming the smallest distance between sulfate head group and sodium ion to be 0.6 nm. This shows that the ion concentration in EDL at maximum is lower by at least an order of magnitude than that of the saturated NaCl solution, for which the blue-shift of the OH stretch band was observed in the FTIR spectrum.

4. Estimation of the ion concentration at interface with excess salt

The charge density (σ) of SDS is saturated at 0.5 mM SDS concentration in the presence of excess salt (e.g. 0.5 M NaCl), and it has been reported to be $\sigma = 2.6 e / \text{nm}^2$.⁷ With GC theory, the thickness of EDL at 0.5 M NaCl solution is calculated to be 0.4 nm. The interfacial ion density is estimated by dividing the surface density of the head group and counter ion by the EDL thickness, which yields 10.8 M ($= 2.6 \times 10^{16} \text{ dm}^{-2} / 0.4 \times 10^{-8} \text{ dm} / 6 \times 10^{23} \text{ mol}^{-1}$). Note that this value is considered to be the maximum limit. In the Helmholtz-Stern (HS) model, the HS layer is assumed to consist of the surface charge and the counter ion which locates at a constant distance. We assume that the distance is the sum of a hemisphere of the sulfate head group, one sphere of water molecule and hemisphere of sodium ion. The crystallographic radii of sulfate and sodium are 0.23 and 0.12 nm, respectively.⁸ The diameter of water is 0.28 nm. In this simplest model, the sum of these values (0.63 nm) is taken as a HS layer thickness. With this value, the interfacial ion density is estimated to be 6.85 M ($= 2.6 \times 10^{16} \text{ dm}^{-2} / 0.63 \times 10^{-8} \text{ dm} / 6 \times 10^{23} \text{ mol}^{-1}$) as written in the main text.

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