Electronic Supplementary Material (ESI) for Soft Matter.
This journal is © The Royal Society of Chemistry 2017

Supplementary Material of

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

Wei Gan,*[*,a,b] Wei Wu,[b,c,d] Fangyuan Yang,[b,c] Deping Hu,[c,e] Hui Fang,[b,c,†] Zhenggang Lan*[*,e] and Qunhui Yuan*[*,f]

[a] School of Sciences, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China.

[b] Laboratory of Environmental Science and Technology, Xinjiang Technical Institute of Physics & Chemistry; Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi 830011, China.

[c] University of Chinese Academy of Sciences, Beijing 100049, China.

[d] College of Chemistry and Chemical Engineering, Xinjiang Normal University, Urumqi, 830054, China.

[e] Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao, Shandong 266101, China.

[f] Department of Material Science and Engineering, Harbin Institute of Technology (Shenzhen), Shenzhen 518055, China.

† Present address: Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, United States.

* Corresponding author. Email: ganwei@hit.edu.cn, lanzg@qibebt.ac.cn, yuanqunhui@hit.edu.cn

I: Estimating the adsorption density of hydroxide ions at the hexadecane-water interface with *p*H measurements

II: Calculating the adsorption free energy of hydroxide ions at the interface by analyzing the second harmonic generation signal

III: Approximate treatment with Frumkin-Fowler-Guggenheim equation

I: Estimating the adsorption density of hydroxide ions at the hexadecane-water interface with *p*H measurements

The adsorption density of hydroxide ions at the surface of oil droplets in hexadecane-water emulsions was estimated by measuring the pH values of the emulsions after an addition of NaOH solution. In these experiments deionized water that had been boiled and cooled under N_2 atmosphere was used. The measurements were carried out under an Ar_2 atmosphere in a glove box, which can eliminate the influence of CO_2 in air. The prepared emulsions (without diluting, oil/water = 1/50 in volume, *p*H = 5.5 ± 0.5) or water (*p*H = 6.5 ± 0.5) were mixed with equal amount of NaOH solutions (*p*H ~10.5), respectively. The *p*H values of the mixtures were measured and listed in Table S1. The difference between columns II and III originated from the adsorption of hydroxide ions at the interfaces. So it was used to calculate the adsorption density of the hydroxide ions, as listed in column V.

Table S1 The *p*H values of the NaOH solutions (I) and the NaOH solutions that were mixed with emulsions/water (II/III). The average diameter of the oil droplets in the emulsions (IV) and the calculated hydroxide ion densities at the oil-water interfaces (V).

I	II	III	IV	V
pH (NaOH)	pH (I + emulsion)	pH (I + water)	diameter (nm)	OH^- density (e/nm^2)
10.45±0.02	9.90±0.04	10.14±0.02	250±9	0.15±0.04
10.60±0.03	10.10±0.04	10.27±0.02	233±18	0.14±0.04
10.64±0.02	10.03±0.03	10.23±0.01	230±23	0.14±0.03

II: Calculating the adsorption free energy of hydroxide ions at the interface by analyzing the second harmonic generation signal

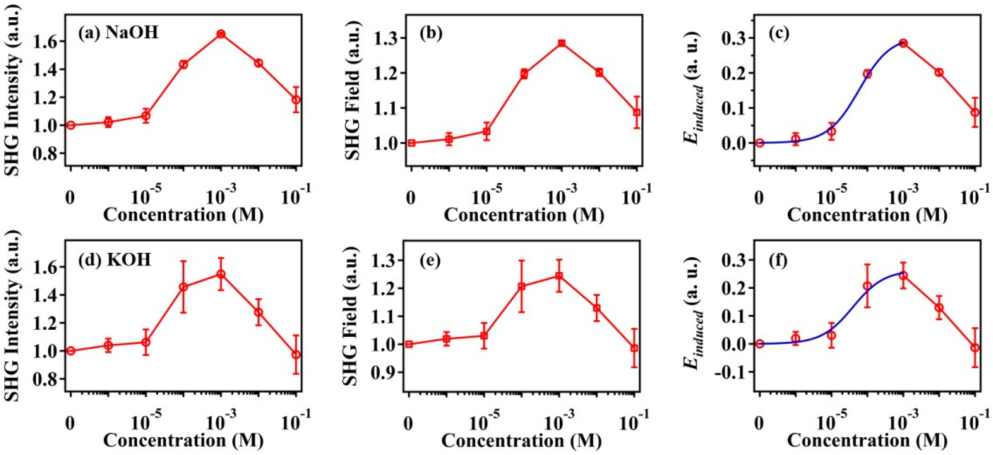

Figure S1 Normalized SHG signals from the hexadecane-water interface at varied base concentrations shown in Figure 3 of the main text (a, d), the SHG fields (b, e) and $E_{induced}$ (c, f) at varied alkali concentrations. The smooth blue curves in (c) and (f) are the fitting with the Langmuir model.

The procedure and the reasoning for estimating the adsorption free energies of hydroxide ions at interfaces have been described in our recent work.[1] Briefly, from the measured SHG field at varied bulk OH^- concentration, the changed SHG field induced by OH^- adsorption ($E_{induced}$) can be deduced, as shown in Figure S1 (c, f). Assuming $E_{induced}$ is proportional to the surface OH^- coverage (θ), the adsorption free energy (ΔG) of hydroxide ions at the hexadecane-water interface can be obtained by fitting the low concentration part of the curves with the Langmuir equation: $\theta = (1 + 55.5 / KC)^{-1}$. Here K is the equilibrium constant that can be correlated with ΔG by $\Delta G = -RT \ln K$. The fitting in Figure S1 (c,f) led to adsorption free energy of hydroxide ions as -8.3±0.2 kcal/mol.

III: **Approximate treatment with Frumkin-Fowler-Guggenheim equation**

In the Frumkin-Fowler-Guggenheim (FFG) equation[2,3] $\frac{\theta}{1-\theta}\exp(-2a\theta) = K_{ads}[\mathrm{A}]$, parameter a is the interaction efficiency that reflects the interaction between adsorbates at the interface. If $a = 0$, FFG equation is reduced to Langmuir equation. $a > 0$ indicates attraction between adsorbates while $a < 0$ indicates repulsion. Parameter θ indicates the surface coverage, K_{ads} is the adsorption equilibrium constant and [A] is the bulk concentration of the adsorbates.[3]

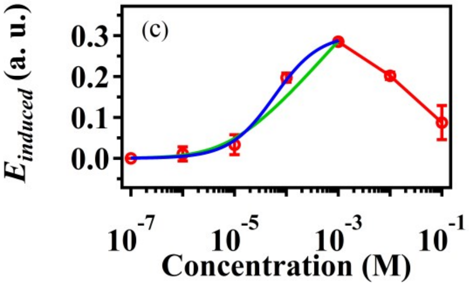

Figure S2 Approximated fitting with data shown in Figure S1 c and FFG equation (green curve).

Since an analytical solution of $\theta = f([\mathrm{A}])$ from the FFG equation is hard to be obtained, we used following approximation to simplify the FFG fitting. In this treatment the x (bulk concentration) and y (surface coverage) were inversed in the fitting with function of $[\mathrm{A}]=\frac{1}{K_{ads}}\frac{\theta}{1-\theta}\exp(-2a\theta)$. The fitting result is plotted as green in Figure S2 with parameter a as -2.4 and the adsorption free energy as -8.1±0.1 kcal/mol. This approximate treatment confirms the electric repulsion between the adsorbed hydroxide ions at the interface. It also shows that Langmuir fitting leads to a reasonable estimation on the adsorption free energy of hydroxide ions.

References:

1 W. Wu, H. Fang, F. Y. Yang, S. Chen, L., X. F. Zhu, Q. H. Yuan and W. Gan, *J. Phys. Chem. C* 2016, **120**, 6515-6523

2 H. A. Al-Abadleh, A. L. Mifflin, M. J. Musorrafiti and F. M. Geiger, *J. Phys. Chem. B* 2005, **109**, 16852-16859.

3 W. Stumm and J. J. Morgan *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*; Wiley-Interscience: New York, 1995.