Supplementary Information

Concentration Dependent Interfacial Chemistry of the $NaOH_{(aq)}$:Gibbsite Interface

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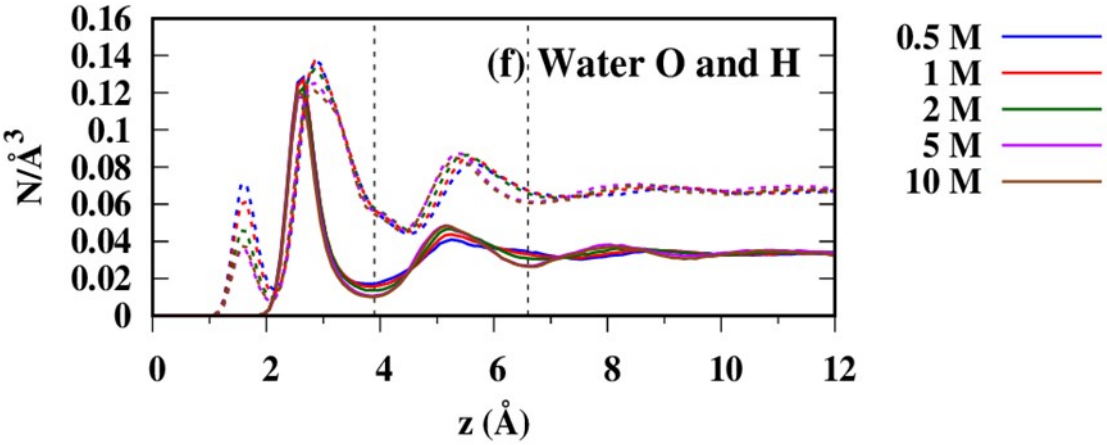
1) Supplementary Information for Computational Methods

Table S1. Composition of the bulk aqueous solutions simulated in this work and corresponding densities and concentrations (molalities (b) in mol/kg, molarities in mol/L, mole fractions(x), density (d) in kg/L) at 300 K and 1 atm.

N(NaOH)	$N(H_2O)$	x(NaOH)	b_{NaOH}	$d_{exp.}$	d_{MD}	$[NaOH]_{exp}$	$[NaOH]_{FF}$
23	2520	0.0091	0.507	1.019	1.023	0.50	0.50
45	2510	0.0179	0.995	1.039	1.054	1.00	1.01
90	2490	0.0361	2.006	1.077	1.098	2.00	2.04
226	2470	0.0915	5.079	1.180	1.182	5.00	5.01
454	2330	0.1948	10.816	1.325	1.338	10.00	10.10

2) *Supplementary Information for Results and Discussion*

Figure S1. Number density profiles of water O (solid) and H (dashed). The vertical dashed lines indicate the boundaries between the first water layer and the second water layer (3.9 Å), and between the second water layer and the rest of the solution (6.6 Å)



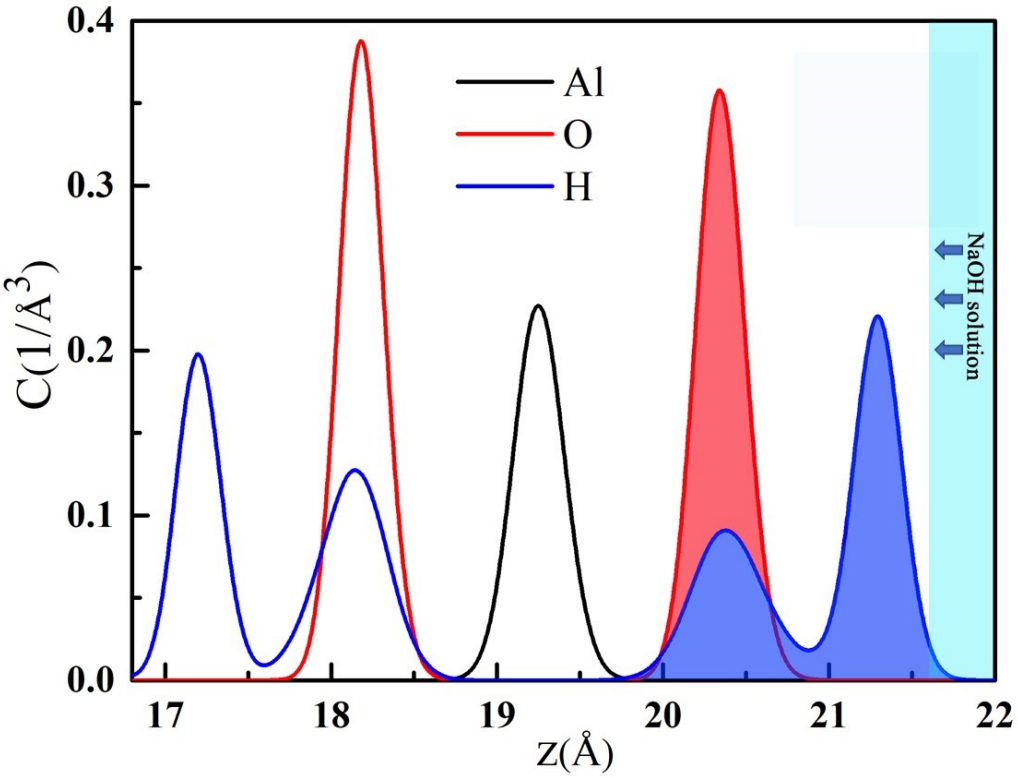


Figure S2. Density profile of one of the two outermost layers of the gibbsite slab. The distribution of the *z* coordinate of the outermost O and H atoms are shaded.

As shown in Figure S2, we can clearly see that there are two orientations for the surface hydroxyl groups. They are either roughly parallel to the surface (where the O and H distributions overlap at *z*~20.4 Å) or out of the plane formed by the surface (*z*(H) distribution centered at *z*~21.3 Å). Integration of the first and second *z*(H) distributions at and *z*=21.3 Å indicates 58% of the hydroxyl groups are oriented out of the basal plane i.e. point towards the solution (42% are parallel to the plane).

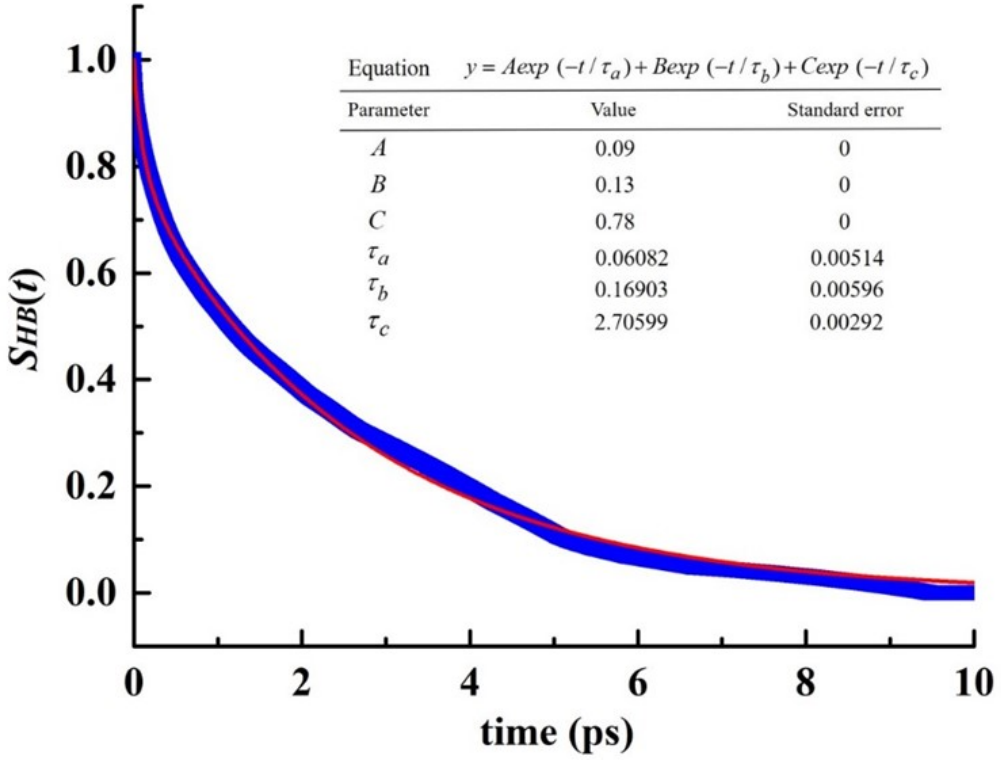


Figure S3. The comparison of the simulated $S_{HB}(t)$ of the OH^--surface HBs with the model obtained from a fit for the 0.5 M NaOH solution system

To determine the HB lifetimes (τ_S^{HB}), the $S_{HB}(t)$ curves have been fitted by three weighed exponentials (with a total weight of unity, *i.e.*, $A + B + C = 1$), which is expressed as

$$S_{HB}(t) = Aexp(-t/\tau_a) + Bexp(-t/\tau_b) + Cexp(-t/\tau_c)$$

where A, B, and C are tunable parameters, while τ_a, τ_b, and τ_c are the characteristic time constants. All the fitted parameters are listed in Table 2 and a typical fitting result is given in Figure S4. According to the fitted parameters, the HB lifetime τ_S^{HB} can be calculated as, $\tau_S^{HB} = A\tau_a + B\tau_b + C\tau_c$. All calculated τ_S^{HB} values are listed in Tables S2 and S3.

Table S2. The fitting parameters and the average lifetime τ_S^{HB} of water-surface hydrogen bonds

$S_{HB}(t)$	A	B	C	τ_a	τ_b	τ_c	τ_s^{HB}(ps)
0.5 M	0.55	0.36	0.09	0.64	0.06	3.51	0.66
1 M	0.54	0.34	0.12	0.80	0.07	3.44	0.86
2 M	0.32	0.49	0.19	0.06	0.68	3.01	0.92
5 M	0.45	0.27	0.28	1.01	0.07	6.18	2.20
10 M	0.43	0.33	0.24	0.77	0.07	6.33	1.87

Table S3 · The fitting parameters and the average lifetime τ_S^{HB} of OH^--surface hydrogen bonds

$S_{HB}(t)$	A	B	C	τ_a	τ_b	τ_c	τ_S^{HB}(ps)
0.5 M	0.09	0.13	0.78	0.06	0.17	2.71	2.14
1 M	0.15	0.15	0.70	1.80	0.13	18.74	13.41
2 M	0.25	0.13	0.62	1.02	0.08	19.74	12.50
5 M	0.21	0.08	0.71	1.04	0.04	28.61	20.53
10 M	0.22	0.08	0.70	0.94	0.03	26.85	19.01

Surface Charge Caused by Adsorption. Figure S4a presents the interfacial charge density distributions, which include the Na^+, OH^- ions and the water molecules on the gibbsite surface. We further calculated the interfacial electrostatic potential of gibbsite/water due to NaOH adsorption. The electrostatic potential $\Psi(z)$ is related to the interfacial charge density $\rho(z)$ via the Poisson equation[55]:

$$\frac{d^2\Psi(z)}{dz^2} = -\frac{\rho(z)}{\varepsilon_0} \quad (1)$$

where $\varepsilon_0 = 8.85 \times 10^{-12}$ C/m·V is the vacuum dielectric permittivity. Herein, the electrostatic potential is computed by integrating Equation (3) twice. Figure 9b shows the simulated $\Psi(z)$ near the gibbsite surface along the z axis. The positive charge density for $z < 2.4$ Å corresponds to the Na^+ of the IS layer and H_w, while the negative charge density and electrostatic potential for 2.4 Å $< z <$ 3.3 Å is due to the adsorbed OH^- ions and O_w. With an increase in the NaOH concentrations, the interfacial charge density below 3.2 Å becomes more asymmetric, with an increase in the negative charge density for 2.4 Å $< z <$ 3.3 Å compared to the relatively constant positive charge density

across the concentration range in the first area ($z < 2.4$ Å). This is due to the increase in the ratio between the IS OH^- and the IS Na^+ (Figure 5).

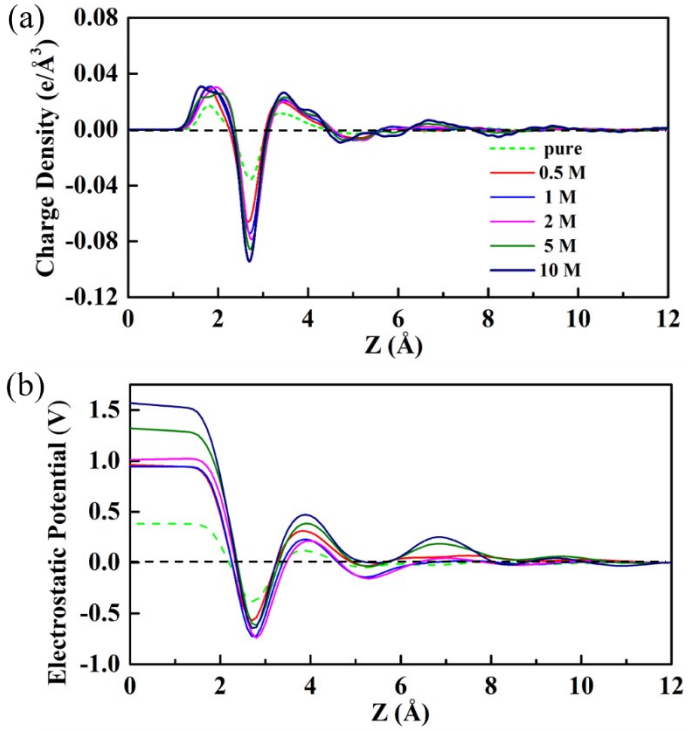


Figure S4. (a) Interfacial charge density profiles due to the adsorption of NaOH and water as a function of distance from the gibbsite surface at different NaOH concentrations. (b) Simulated electrostatic potential as a function of distance from the gibbsite surface.

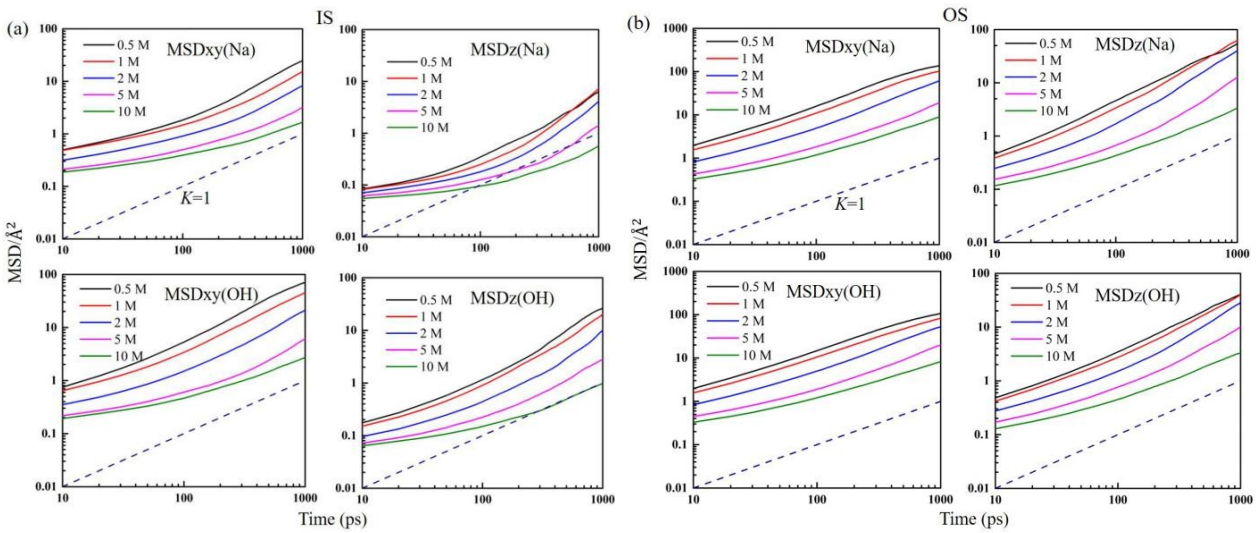


Figure S5. *MSD*s in log−log scale for ions in the interface region (IS(a) and OS(b)) in all concentrations.

Table S4. The self-diffusion coefficients ($10^5 \cdot D_s/cm^2 \cdot s^{-1}$) of Na^+ and OH^- in IS and OS

concentration	ion	IS-xy	IS-z	OS-xy	OS-z
0.5 M	Na	0.074	0.046	0.22	0.31
	OH	0.16	0.15	0.18	0.19
1 M	Na	0.048	0.058	0.19	0.41
	OH	0.12	0.14	0.17	0.25
2 M	Na	0.025	0.034	0.16	0.26
	OH	0.063	0.086	0.13	0.19
5 M	Na	0.0092	0.0098	0.056	0.091
	OH	0.021	0.016	0.055	0.065
10 M	Na	0.0035	0.0034	0.022	0.017
	OH	0.0061	0.0047	0.015	0.019