The Structure and Dynamics of the $\text{NaOH}_{(\text{aq})}$:Gibbsite Interface

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Abstract

Gibbsite ($\gamma\text{-Al}(\text{OH})_3$) is one of the primary mineral structures containing Al, and its interfacial chemistry in $\text{NaOH}_{(\text{aq})}$ solutions is relevant to the industrial processing of aluminum, including metal production and the disposition of Al-containing wastes. To date, little is known about the structure, speciation, and dynamic behavior of gibbsite interfaces with $\text{NaOH}_{(\text{aq})}$ —particularly as a function of ionic strength. Yet this is critical in order to understand interfacial reactivity, including dissolution mechanisms and rates that underpin industrial Al processing. This work reports equilibrium molecular dynamics simulations of the $\gamma\text{-Al}(\text{OH})_3\text{:NaOH}_{(\text{aq})}$ interface, revealing the sorption behavior and speciation of ions from 0.5 – 10 M [NaOH]. As inner-sphere complexes, Na^+ primarily coordinates to the side of the gibbsite hexagonal cavities, while OH^- accepts hydrogen-bonding from the surface -OH groups. The mobility of inner-sphere Na^+ and OH^- ions is obviously reduced due to the strong surface affinity. At high [NaOH], ion pairing that is observed in the bulk solution is partially disrupted upon sorption to the gibbsite surface by the individual ion-surface interactions. We anticipate that surface ion-pairing is a key element of the dissolution mechanism and that its modulation (by considering concentration and different ion combinations) may be used to tune gibbsite interfacial chemistry.

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1) Introduction

Gibbsite ($\gamma\text{-Al(OH)}_3$) is one of the most abundant aluminum hydroxide polymorphs in supergene environments [1]. It consists of octahedral Al-atoms coordinated by three hydroxyl O-atoms each above and below the Al sheet [2, 3] that form hexagonal cavities in the basal plane (001) (Figure 1); its basal surface is terminated by doubly coordinated hydroxyls, while the (100) and (110) edge surfaces consist of a mix of singly and doubly coordinated hydroxyl groups and OH_2 groups [4, 5]. The dissolution of gibbsite from bauxite ores (which contain gibbsite) followed by its re-precipitation in concentrated $\text{NaOH}_{(\text{aq})}$ are the two critical steps of the Bayer process for aluminum and alumina production [6-8]. The caustic chemistry of gibbsite is relevant to other industrial settings, for example to the treatment and disposal of highly radioactive wastes such as those at the Hanford nuclear reservation. Therein, tank sludge, primarily composed of gibbsite and boehmite is leached by highly concentrated NaOH solutions [9].

The nature of the sorption of Na^+ and OH^- on gibbsite surfaces has not been studied, with prior work focusing upon the development of a macroscopic or mesoscopic understanding of gibbsite dissolution by $\text{NaOH}_{(\text{aq})}$ [7, 10-17]. Dissolution of the basal surface of gibbsite occurs via the formation of etch pits due to defects (dislocation, impurities), as observed by atomic force microscopy at basic [18] and acidic [19] pH. Gibbsite dissolution mechanisms have been studied in pure water [20], but the gibbsite dissolution rate increases (linearly) with NaOH activity [11], which implies that hydroxide perturbs the mechanism – perhaps due the stronger nucleophilic character of OH^- compared to H_2O [21]. The availability of these ions to participate

within interfacial reactivity could be intrinsically dependent upon their surface speciation and adsorption characteristics. Here we present the results from molecular dynamics (MD) simulation that have comprehensively investigated the concentration-dependent interfacial organization, speciation, and diffusive behavior of Na^+ , OH^- and $\text{Na}^+\cdot\text{OH}^-$ ion pairs on the basal surface (001)

Figure 1. Top: Illustration of hexagonal cavities in the basal plane (001) of gibbsite. Bottom: Simulation setup of an aqueous NaOH solution confined in a gibbsite slit pore formed between two basal surfaces. The O atoms of gibbsite are shown in red, Al in pink, H atoms of gibbsite in white, O atoms of water in red, H atoms of water in white, Na^+ in green, O atom of OH^- in magenta, H atom of OH^- in cyan. The shaded areas represent the inner-sphere (IS) and outer-sphere (OS) adsorption regions, respectively.

of gibbsite (from 0.5 M to 10 M). As inner-sphere complexes, Na^+ primarily adsorbs to the side of the gibbsite hexagonal cavities, while OH^- accepts hydrogen-bonding from the surface hydroxyls. The ion mobility along the perpendicular direction is greatly inhibited due to the strong surface adsorption interaction and the mobility of NaOH ions in the inner-sphere region is clearly reduced.

2) Computational methods

Simulation Model. The structural model of the gibbsite interface is illustrated in Figure 1 and consists of a $4 \times 6 \times 2$ supercell created from the monoclinic gibbsite unit cell of dimensions $a = 8.68 \text{ \AA}$, $b = 5.08 \text{ \AA}$, and $c = 9.74 \text{ \AA}$, with $\alpha = \gamma = 90^\circ$, and $\beta = 94.54^\circ$ and where the unit cell was cleaved along the (001) plane to form a gibbsite slab of dimensions $34.7 \times 30.4 \times 38.8 \text{ \AA}^3$. Two such mineral slabs were put in contact with an aqueous NaOH solution to form a slit pore. Five different NaOH concentrations examined: 0.5, 1.0, 2.0, 5.0, and 10 M (molecular compositions and densities presented in Table S1). The surface oxygens of the basal surface were all singly protonated even at 10 M NaOH ($\text{pH} = 15$), as the predicted pK_a from first-principles molecular simulations is 22 [22]. To examine and compare the effect of the interface upon ion-pairing, simulations of bulk NaOH solutions at the same concentrations were also performed.

Force Field Implementation and Benchmarking. The ClayFF potential [23] was employed to describe the gibbsite mineral interactions. An Al-O-H bending term [25] was used along with an harmonic O-H bond term and the flexible water SPC model [26] to describe water.

87 The original harmonic O-H bond term was modified by selecting $r_0(\text{O-H}) = 0.9572 \text{ \AA}$ instead of
88 $r_0(\text{O-H}) = 1.0 \text{ \AA}$, resulting in virtually identical surface/water hydrogen-bonding properties
89 compared to the Morse O-H bond term by Greathouse et al. [24]. The Na^+ Lennard-Jones
90 parameters were taken from Joung *et al.* [27] and the OH^- parameters from Weiner *et al.* [28].
91 The Lorentz–Berthelot mixing rules were applied for the Lennard-Jones interactions of unlike
92 particles. The particle-particle particle-mesh (PPPM) method [35] was employed to compute the
93 long-range electrostatic interaction with a tolerance of 10^{-5} . Combined with the flexible SPC
94 model, the Na^+ model predicts the experimentally observed water O-atom coordination number
95 (CN) of $\text{Na}^+\dots\text{O}_w$ to be 5.8 in pure water [29]. The predicted hydroxide model $\text{HO}^-\dots\text{H}_w$
96 coordination number of 5.8 is an overestimation relative to the experimental value of 4.1 [30],
97 however this is a common feature of 2-site point charge models [31]. Although explicit
98 polarization can improve the OH^- coordination number [32,33] they do not necessarily improve
99 the general NaOH solution structure obtained from X-ray or neutron scattering [34] and they are
100 further incompatible with the nonpolarizable ClayFF model of gibbsite. The nonpolarizable
101 model by Ufimtsev et al. [31] could have been employed, however it is computationally
102 impractical because of the large number of sites involved, and further it is only tailored for water
103 solvation without consideration of ion pairing. The electrostatic continuum correction was
104 subsequently examined to as a means to improve the OH^- CN. Test calculations indicated that
105 although the $\text{H}_2\text{O}\dots\text{OH}^-$ binding energies in the gas phase and $\text{HO}^-\dots\text{H}_w$ coordination numbers
106 in solution were improved by scaling the charges by 75%, a significant underestimation of both
107 the $\text{Na}^+\cdot\text{OH}^-$ ion pairing energy and ion-surface interactions in the gas phase being was predicted

that could not be recovered by a modification of the Lennard-Jones terms. Given these observations, the original nonpolarizable OH⁻ potential was employed. Interestingly, a comparison of a set of DFT surface energies with those from ClayFF has a RMS error of only 3.83 kcal/mol, which indicates that this potential will provide a reasonable description of the interfacial interactions between Na⁺, OH⁻ and the gibbsite surface (see Supplementary Information and Figure S1).

Simulation and Equilibration Protocol. All simulations were performed using LAMMPS [36] with a time step of 1 fs. The volume of the aqueous phase was first equilibrated using the *NPT* ensemble according to the equations of Shinoda *et al.* [37]. at 300 K and 1 atm along the *z*-axis, resulting in a slit pore of length ~ 70 Å along this dimension. Within this stage of the equilibration, the integrity of the mineral slab was preserved by constraining the velocity of its Al- and O-atoms to zero, which still allowed fluctuations of the volume of the aqueous phase. In the subsequent *NVT* run, two 1 ns-long temperature cycles from 300 K to 500 K and back were performed. At the final temperature of 300 K the mineral slab constraint was released; during this phase, the Na⁺-O(OH⁻), and for the interfacial systems the O(mineral)-O(OH⁻) and O(mineral)-Na⁺ radial distribution functions (RDFs), were monitored and the system was considered equilibrated when they reached convergence (after 30 - 40 ns). A final 1 ns equilibration of the density was done in the *NPT* ensemble at 300 K. All the properties of the system were computed based on a subsequent 40 ns production phase in the *NVT* ensemble.

Umbrella Sampling. Umbrella sampling was employed to investigate the free energy profiles of the ion adsorption. Either Na⁺ or OH⁻ was placed in the aqueous phase without the presence

any other ion, and the collective variable was defined as the z -coordinate of the ion relative to the surface formed by the outermost mineral O-atoms. Umbrella sampling windows were separated by 0.1 Å with $k = 125$ kcal/mol/Å² for $1 \text{ Å} < z < 6 \text{ Å}$ and 0.2 Å with $k = 30$ kcal/mol/Å² for $6 \text{ Å} < z < 11 \text{ Å}$, and the collective variable was collected over 100 ps. The inclusion of other ions would have necessitated 10's of ns of ensemble averaging for the 75 umbrella sampling windows and been computationally prohibitive. To prevent the Na⁺ from jumping between the side and the center of the cavity, the distance between the ion and the line orthogonal to the surface and passing through the site was constrained to zero. However, the force constant of the restraint $k = 1$ kcal/mol/Å², was significantly smaller than the restraint of the biasing collective variable, ensuring that this secondary, lateral restraint had a negligible influence on the potential of mean force (PMF).

3) Results and Discussion

Adsorption Characteristics. We first consider the general adsorption characteristics of NaOH_(aq) moving from the bulk solution to the surface of gibbsite, as shown in Figure 2 via the number density profiles for Na⁺, OH⁻ and the contact ion pairs between Na⁺ and OH⁻, abbreviated Na⁺·OH⁻ in the following. The value of the z -coordinate of the outermost layer of O-atoms on both surfaces was defined as 0, and the density profiles averaged over the two surfaces of the mineral slab. Inner-sphere (IS) and outer-sphere (OS) sorbed ions were defined based on their z -coordinate as the first and second distinct layers of ions from $z = 0 \text{ Å}$, respectively. The inner-sphere layer is defined as $z < 3.3 \text{ Å}$ and the outer-sphere layer corresponds to $3.3 < z < 5.3 \text{ Å}$. The distribution of Na⁺ within the IS layer consists of three peaks at 1.4 Å, 1.8 Å and 2.3 Å

that correspond to different adsorption sites (*vide infra*). The distribution of OH^- within the IS layer consists of one peak at 2.6 Å. The $\text{Na}^+\cdot\text{OH}^-$ ion pairs—whose position was defined by the center of the Na-O axis—are mostly located within the IS layer at a distance of 2.2 Å. The water O_w and H_w number density profiles are shown in Figure S2. The most prominent effect therein is the decrease of the height of the first H_w peak ($z < 2$ Å) associated with $\text{OH}(\text{water})\cdots\text{O}(\text{gibbsite OH})$ hydrogen bonding, presumably caused by hindrance due to the increased number of Na^+ coordinated to the surface O-atoms.

Figure 2. Concentration profiles (averaged over both interfaces within the simulation) of Na^+ , OH^- , $\text{Na}^+\cdot\text{OH}^-$ ion pairs (a) - (e), and (f) the number density profiles of water O_w (solid) and H_w (dashed). The vertical dashed lines indicate the boundaries between inner sphere (IS) and outer-sphere (OS) regions (at 3.3 Å) and between the OS and the rest of the solution (at 5.3 Å). Ion-paired species are identified as the cation having at least one contact with the anion, or *vice versa* and where the coordinates of the $\text{Na}^+\cdot\text{OH}^-$ ion pair are chosen as the center of the Na-O axis.

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167 From 0.5 M to 2 M the surface coverages of Na^+ and OH^- continuously increase, and
168 saturation is reached 5 M with a coverage of $\sim 7 - 8$ ions/ nm^2 . Interesting comparisons can be
169 made to a similar study of $\text{NaCl}_{(\text{aq})}$ sorption by Ho *et al.* [5] at the same concentrations. Although
170 this work reports a surface coverage of Na^+ and OH^- at 1 M that is greater than 2, in the case of
171 Na^+ and Cl^- from $\text{NaCl}_{(\text{aq})}$ surface coverage values of 0.4 and 0.7 ions/ nm^2 were observed,
172 respectively. At 2 M $\text{NaCl}_{(\text{aq})}$, 1.1 Na^+/nm^2 were observed to be sorbed to the basal surface of
173 gibbsite as compared to our 4 Na^+/nm^2 from 2 M $\text{NaOH}_{(\text{aq})}$. Excluding the possible effects of box
174 size, the force field, and the equilibration procedure, which are likely minor, these data indicate a
175 smaller affinity of Cl^- for the surface than OH^- . This concomitantly results in less Na^+ adsorbed
176 as a result of to charge compensation. Ho *et al.* found even smaller adsorption values for Ca^{2+} (in
177 $\text{CaCl}_{2(\text{aq})}$) and Ba^{2+} (in $\text{BaCl}_{2(\text{aq})}$) ions, where 0.8 - 0.9 ions/ nm^2 were sorbed from 2 M electrolyte
178 solutions. The surface coverage of Na^+ in the IS layer is systematically larger than that of the OS
179 layer, in agreement with observations regarding $\text{NaCl}_{(\text{aq})}$ on the gibbsite basal surface. However,
180 the IS/OS ratio for Na^+ decreases with increasing concentration. Very different trends are
181 observed for OH^- sorption, as similar amounts of anions are found in the IS and the OS layers
182 irrespective of $[\text{NaOH}]$. The lower degree of adsorption of OH^- (as indicated by the density in
183 the z -axis) in the IS layer compared to Na^+ indicates a cumulatively weaker interaction of OH^-
184 with the hydroxyls caused by hydrogen-bonding and coulombic forces than the coulombic forces
185 of Na^+ with the surface O-atoms. At higher concentrations, the balance between Na^+ and OH^- in
186 the inner sphere tends to equalizes as a result of saturation being reached. With these results, the

187 total amounts of cations and anions at the interface (IS and OS) are essentially the same. Finally,
 188 water surface coverage is very modestly affected by ion sorption, with a decrease in surface
 189 coverage of only 1 H₂O/nm² between 0.5 M and 10 M in the first layer, virtually no change in
 190 the second layer (Figure 3). This is simply explained by the increase in total density with
 191 increasing concentration.

192 **Figure 3.** Surface adsorption coverage for inner-sphere (IS) and outer-sphere (OS) Na⁺ and
 193 OH⁻ ions as well as 1st water layer (W_{L1}) and 2nd layer (W_{L2}) as a function of ion concentration.
 194 The value indicated for the water surface coverage is relative to its value at 0.5 M; the absolute values at
 195 0.5 M are 9.32 and 8.75 per nm² for W_{L1} and W_{L2}, respectively.

Figure 4. Contact ion pairing as a function of concentration, where $N(\text{Na}^+ \cdot \text{OH}^-)$ is the total number of contacts between Na^+ and OH^- . (a) The number of ion pairs normalized by the number of Na^+ in the bulk $\text{NaOH}_{(\text{aq})}$ model and gibbsite/ $\text{NaOH}_{(\text{aq})}$. Note that the “interface” values reflect only the ion pairs and Na^+ in the IS and OS. (b) The number of ion pairs in different inner-sphere and outer-sphere regions, normalized by the total number of Na^+ . In this case the X-Y notation reflects ion-pairing between an ion in the X layer and an ion in the Y layer with X, Y indicating IS, OS, or B – where IS = inner-sphere; OS = outer-sphere; B = rest of the solution ($z > 5.3 \text{ \AA}$).

As indicated from Figure 4a, between 0.5 and 2 M NaOH the overall $\text{Na}^+ \cdot \text{OH}^-$ ion-pairing is slightly increased at the gibbsite surface relative to bulk $\text{NaOH}_{(\text{aq})}$ simulations, suggesting that the surface facilitates ion pairing at moderate concentrations. In contrast, under higher [NaOH] ion pairing is strongly reduced at the solid/liquid interface where the IS and OS layers are saturated (Figure 3, 5 and 10 M). Across the concentration range, there is competition amongst the inter-particle interactions associated with adsorption of individual ions vs. ion-pairing. Figure 4b shows the number of contact ion pairs between an ion in the IS and an ion of opposite charge either in the IS (IS-IS) or in the OS (IS-OS), divided by the total number of Na^+ in the solution. This increases up to 2 M NaOH, then decreases with higher concentrations, indicating that ion saturation at the surface causes an energetic penalty for ion-pair interactions of sorbed species.

Ion Adsorption Sites.

The planar (xy) density distributions were then examined to elucidate the adsorption sites of Na^+ and OH^- . Figure 5 depicts the preferential adsorption sites along the xy plane for inner-sphere adsorbed Na^+ and OH^- . Two adsorption sites are observed for Na^+ (Figure 5a): #1 above the center of a hexagonal cavity formed by the Al-atoms and coordinating with three surface O-atoms; #2 above the Al-atoms and coordinated by three surface O-atoms. The ratio between the number of IS Na^+ and the number of hexagonal cavities is 76% at saturation. For OH^- , the surface adsorption site is primarily located near the surface H-atoms belonging to the surface hydroxyls that point toward the solution (Figure 6b) through a hydrogen bond (HB) interaction. Figure 5c shows the planar density distributions of H_2O in the 5 M $\text{NaOH}_{(\text{aq})}$. It is clear that most H_2O are distributed on the edge of the hexagonal cavities on the surface (001), just like the inner-sphere bound OH^- . The heterogeneous distribution of sorbed ions and ion-pairs similarly causes uneven H_2O adsorption as compared to the uniform density distributions for a pure H_2O :gibbsite system (Figure 5c, d). Thus, ions that occupy adsorption sites exclude H_2O from those sites within the IS adsorption layer. As expected, as the ionic concentration increases, the surface adsorption layer is covered with more and more ions, in turn excluding H_2O and restricting their adsorption. The anticipated affect this may have upon an estimated surface charge is discussed in the Supplementary Information.

Figure 5. Planar density distributions of the inner-sphere (IS) layer for the 5 M NaOH solution. (a) Na^+ (b) OH^- (c) O_w . (d) Planar density distributions of O_w of the first H_2O layer for the pure water system.

Ion Hydration and Interfacial Hydrogen-Bonding. RDFs were used to characterize the

structure of the ion hydration shells where IS complexation significantly decreases hydration numbers (Figure 6). For the 2 M system, this translates into ion- O_w coordination numbers of 5 - 6 in the bulk and in the outer-sphere region (Figure 6c, d, e) and 2 - 3 when ions are bound as inner-sphere complexes.

Figure 6. RDFs between ions and water molecule O-atoms (O_w) within the 2 M NaOH solution when the ions exist as (a) inner-sphere and (b) outer-sphere complexes, or when they are in the bulk (c). The corresponding configuration snapshots are presented in (d), where the immediately surrounding H_2O are indicated with ion-water distances reported for reference.

The gibbsite basal surface features intralayer hydrogen-bonding between hydroxyl groups in the basal plane and out of the basal plane [38]. Hydroxyl groups also form HBs with adsorbed H_2O (both as HB donors and acceptors) and OH^- (only donated). The evolution of the average number of HBs as a function of concentration is represented in Figure 7b. The corresponding HB autocorrelation function [39] is defined as

$$S_{HB}(t) = \frac{\langle h(t)h(0) \rangle}{\langle h(0)h(0) \rangle} \quad (1)$$

260 where $h(t) = 1$ if the tagged water pair maintains a HB from time 0 to time t ; otherwise, $h(t) = 0$.
 261 Figures S4a and S4b present the $S_{HB}(t)$ curves for the electrolyte-surface HBs and OH^- -surface
 262 HBs as a function of NaOH concentration, while the HB lifetimes τ_s^{HB} determined from a
 263 triexponential fit of $S_{HB}(t)$ are presented in Figure 7b. The fitted parameters are listed in Tables
 264 S2 and S3 and a typical fitting result is provided in Figure S4c. Notably, as the concentration and
 265 the number of adsorbed OH^- increases, more surface -OH groups donate HBs to OH^- , with an
 266 increase in $N(\text{HB})$ from ~ 0 (0.5 M) up to 0.12 (5 and 10M, Figure 7a) In other words, the site
 267 occupancy at saturation is 24% for OH^- and only half of the gibbsite hydroxyl groups are out-of-
 268 plane (meaning they point towards the solution). Overall, this is accompanied by a decrease in
 269 the number of hydrogen bonds between the surface and adsorbed H_2O . More precisely, a
 270 decrease in the number of accepted HBs from H_2O by the surface -OH from 0.28 to 0.15 is
 271 observed, but perhaps surprisingly there is no sensible change in the HBs donated to H_2O .
 272 Interestingly, the magnitude of the change in $N(\text{HB})$ between the surface and OH^- between 0.5 M
 273 and 10 M NaOH (0.12) is very similar when compared to the change in $N(\text{HB})$ surface and
 274 adsorbed H_2O ($0.28 - 0.15 = 0.13$). This seems to contradict the fact that the within this
 275 concentration range the surface coverage of inner-sphere sorbed OH^- increases (by $2.9 \text{ OH}^-/\text{nm}^2$)
 276 far more than the sorbed H_2O decreases (by $-1.1 \text{ H}_2\text{O}/\text{nm}^2$ as shown in Figure 3). This apparent
 277 discrepancy is likely related to ion-pairing with Na^+ , specifically OH^- could be in the IS region
 278 without being directly attached to the surface as a result of ion-pairing to Na^+ that are themselves

280 coordinated to surface O-atoms. The increase in the number of surface-hydroxide HBs is
 281 accompanied by a strong increase in their lifetime from ~ 2 to ~ 20 ps (Figure 7b), a feature that is
 282 related to a strengthening of the network of interactions that include hydrogen bonding, ion-
 283 dipole, and ion-ion interactions. In contrast, the increase in the lifetime of HBs between the
 284 surface and sorbed H_2O is much more modest, from 0.5 to 2 ps. This indicates that water
 285 diffusion is not considerably slowed down by the creation of the network of interactions that
 286 involve sorbed OH^- and Na^+ .

287

288 **Figure 7.** (a) Average number of hydrogen bonds $N(\text{HB})$ between different atom pairs, based on
 289 the $\text{H}\cdots\text{O}$ distance. The cutoff (ranging from 2.27 to 2.40 Å) corresponds to the first minimum of
 290 the RDF of the corresponding pair after the first intermolecular peak. Within the notation “g”
 291 denotes the gibbsite (001) surface; “w” denotes H_2O . (b) Average hydrogen bond lifetime τ_s^{HB} .
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294 **Adsorption Energetics.** As shown in the Figure 8, the free energy profiles for ion
295 sorption (obtained from potential of mean force simulations) feature two separated free energy
296 minima, corresponding to the IS and OS adsorption positions in the corresponding density
297 profiles (Figure 2). In Figure 8a, the Na^+ on site #2 (side of the hexagonal cavity) has a smaller
298 energy minimum in IS, which agrees with the density profiles. For Na^+ and OH^- the first PMF
299 minimum (corresponding to IS adsorption) is respectively at 1.9 Å and at 2.7 Å, consistent with
300 the observation that the first adsorption layer of Na^+ is closer to the gibbsite surface (001) than
301 OH^- . In the PMF profiles, the first free energy minimum of the Na^+ on site #2 is approximately
302 2.3 kcal/mol lower in energy than that of the OH^- (-2.0 kcal/mol), demonstrating that Na^+ has a
303 stronger adsorption stability. The PMF in Figure 8a reveals that Na^+ adsorption to the side of the
304 hexagonal cavity consists of three sites that correspond to three minima observed at z -values
305 between 1.9 and 2.4 Å depending on whether Na^+ is directly above the Al-atom or slightly offset.
306 However, the difference in stability and the energy barriers between those sites is less than kT
307 (0.6 kcal/mol) and thus inter-site hops are not rare events and thermodynamic distinction
308 between these sites is not meaningful. Less importantly, for the PMF to site #1, near $z = 2.4$ Å
309 (the third IS minimum) some incursions near the center of the cavity occur due to the weak
310 lateral restraint.

Figure 8. PMF of Na^+ (a) and OH^- (b) adsorbing on the gibbsite (001) surface at 1.0 M. Two surface sites for inner-sphere Na^+ and one for OH^- are shown above the image. The blue and red vertical dashed lines, respectively, indicate the separation between the inner-sphere layer and the outer-sphere layer and the separation between outer-sphere layer and the bulk phase.

We calculated the adsorption equilibrium constants (K) for the NaOH near the gibbsite surface, according to:

$$K = \frac{\int_{r_i^\#}^{r_{i+1}^\#} e^{-\beta W(r)} dr}{\int_{r_{i-1}^\#}^{r_i^\#} e^{-\beta W(r)} dr} \quad (2)$$

with “#” referring to a transition state. We take the leftmost defined reaction coordinate (~ 1.3 - $1.6 \text{ \AA}$) as the left boundary for IS and the right boundary is at $9.1 \text{ \AA}$ for the bulk based upon the transition from the OS region and the bulk shown in Figure 8.

Table 1. Equilibrium constants (K) for the interconversion of Na^+ and OH^- between the inner-sphere (IS) and outer-sphere (OS) states and between the OS and bulk state. Given that adsorption to site #2 is more stable than site #1 by ~ 2 kcal/mol in Figure 8, the corresponding PMF was selected for the calculation of K for Na^+ .

		Na^+	OH^-
IS $\rightarrow$ OS	$K = \frac{[\text{OS}]}{[\text{IS}]}$	0.21	0.34
OS $\rightarrow$ bulk	$K = \frac{[\text{dissolved}]}{[\text{OS}]}$	0.88	0.83

These equilibrium constants are in apparent contradiction with the results from Figure 3, e.g., the IS $\rightarrow$ OS transformation for OH^- corresponds to an equilibrium constant of 0.34, yet the ratio between the OS concentration and the IS concentration at 10 M is 1.22. This is due to the fact that at high concentration, both the adsorption equilibrium and the ion-pairing equilibrium need to be taken into account. However the reported value for the adsorption of Na^+ on gibbsite from dilute $\text{NaNO}_3(\text{aq})$ is $K = 0.4$, which is an intermediate value between that of the IS $\rightarrow$ bulk transformation ($0.21 \times 0.88 = 0.18$) and the OS $\rightarrow$ bulk transformation (0.88) [40].

Dynamic Behavior of Adsorbed Ions. In order to elucidate the dynamic behavior of the Na^+ and OH^- ions within the interfacial region, their in-plane mean square displacement along the xy plane (MSD_{xy}) and the out-of-plane mean square displacement along the z -direction (MSD_z) have been computed. The $MSDs$ are defined as:

$$MSD_{xy} = \langle \Delta x(t)^2 + \Delta y(t)^2 \rangle \propto t^k \quad (3)$$

$$MSD_z = \langle \Delta z(t)^2 \rangle \propto t^k \quad (4)$$

The parameter k is an indicator of the diffusion mode. For Fickian diffusion $k = 1$, while $k = 0.5$ represents a single-file diffusion mode. The intermediate states $k > 1$ and $k < 1$ correspond to

superdiffusion and subdiffusion [41-43] regimes, respectively.

The simulated MSD_{xy} and MSD_z for both ions at 1 M NaOH within the interfacial IS and OS regions are shown in Figure 9 and those for other concentrations in Figure S5. In general, Na^+ and OH^- ions show identical concentration dependent trends in diffusion behavior. In the IS, the slopes of all the logarithmic MSD curve are nearly 0.5 in the period of 1 – 100 ps. Beyond that, the diffusion of ions exhibits Fickian diffusion ($k \approx 1$). The ion mobility is evaluated using the self-diffusion coefficient D_s with the Einstein relation [44]. We used the $MSDs$ during the 700 ps - 1000 ps to calculate the self-diffusion coefficients (all concentration conditions are listed in Table S4). Unsurprisingly, the self-diffusion coefficients of the NaOH ions in IS and OS are smaller than those of the bulk occurring in the order $IS < OS < bulk$ as a result of the strong surface confining interaction. Further, the in-plane self-diffusion coefficients are larger than the out-of-plane. A drastic decrease of the self-diffusion coefficients for Na^+ (relative to OH^-) is observed for those ions in the inner-sphere layer, and thus Na^+ mobility is more inhibited than OH^- . In addition, the self-diffusion coefficients of Na^+ and OH^- ions in OS are larger than that in IS, which is consistent with the fact that the surface interaction becomes weaker in the OS region. The obviously reduced mobility of NaOH ions in the IS region is in good agreement with their clearly defined surface adsorption sites and the stronger adsorption interaction (see Figure 5 and Figure 8). As shown in Table S4, the self-diffusion coefficients of the Na^+ and OH^- ions in the IS and OS layers become smaller with the increasing concentrations. This can be attributed to the enhancing steric hindrance effect under higher concentration and the noted observed increase in the HB lifetimes. Ion mobility necessitates the ability of other sorbed ions and H_2O to rearrange

on the surface and as the concentration increases ion mobility will increase the number of displacements needed for nearby strongly sorbed ions and the subsequent breakage of intermolecular interactions.

Figure 9. MSDs in log–log scale for ions in the interface region (IS and OS) in the 1 M system. For both Na⁺ and OH[−], the MSDs results include the in-plane MSD along the *xy* plane and the out-of-plane MSD along the *z* direction (the analogous self-diffusion coefficients D_s are presented in the same corresponding color). Dashed lines specifying the plot slopes are provided for comparison.

Conclusions

MD simulations have been employed to investigate the concentration dependent interfacial organization and ion adsorption behavior of $\text{NaOH}_{(\text{aq})}$ on the (001) basal surface of gibbsite. Both Na^+ and OH^- are observed to adsorb primarily as inner-sphere species, with Na^+ residing either within or on the edge of a hexagonal cavity of the surface O-atoms. For OH^- , the surface adsorption sites are located above the gibbsite hydroxyls from which they accept hydrogen bonds. The adsorption capacity of Na^+ and OH^- ions on the gibbsite surface is higher than those for other previously reported for aqueous NaCl , CaCl_2 , or BaCl_2 electrolytes. This behavior could be attributed to the enhanced affinity of OH^- ions with the gibbsite surface (and consequently Na^+ due to ion pairing). Up to 2 M NaOH , the surface is found to enhance ion-pairing within the IS region, however it strongly disrupts the formation of interfacially bound ion pairs above 2 M NaOH . The interfacial diffusion properties of the ions indicate that ion mobility is greatly inhibited in the inner-sphere region, while the motion of ions in the outer-sphere region is more unrestrained due to the weaker surface interaction. The concentration dependent behavior of ion sorption including the modulation of ion-paired species at the surface, in combination with the changes to surface diffusion, provide valuable new insight toward ongoing and future studies of gibbsite dissolution under $\text{NaOH}_{(\text{aq})}$ conditions relevant to Al industrial processing and metal production.

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