Experimental Correlation Between Interfacial Water Structure and Mineral Reactivity

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Ⓢ *Supporting Information*

ABSTRACT: We present an experimental demonstration of the effect of solvent structure on the interfacial reactivity of the silica/water interface using in situ vibrational Sum-frequency Generation (vSFG) spectroscopy. The response of the molecular arrangement of the interfacial solvent to the presence of cations is pH dependent with the highest sensitivity at neutral pH, relevant to geochemical and biological environments. The pH-dependent changes in vSFG spectra are in excellent correlation with the enhancement of quartz dissolution in salt water, which was hypothesized by Dove et al. to be due to changes of the interfacial solvent structure at the silica surface. vSFG provides mechanistic insights into silica dissolution and sheds light on the role of ions in altering interfacial solvent ordering, which has implications in fields ranging from protein—water interactions to oil recovery.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis
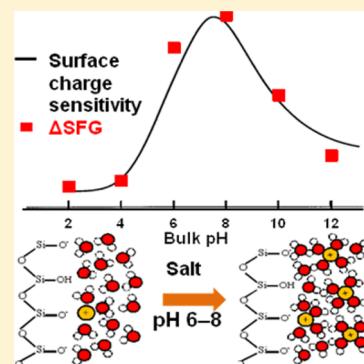
Understanding the structure and dynamics of aqueous interfaces and what makes them unique from bulk media remains an area of fundamental importance.[1−3] In particular, ions at aqueous interfaces play critical roles in biology,[4,5] physics,[6] and geology,[7] with many known commercial applications.[8] Since chemical interactions in bulk liquids are sensitive to the local molecular arrangement of the solvent,[9] it is reasonable to expect that interfacial solvent structure could also influence liquid/solid interface reactivity. While some reports suggest that the reactivity of the aqueous/solid interface, for example, depends on the orientation of interfacial water molecules,[10,11] the exact role of ions and their effect on interfacial water structure and surface reactivity remains elusive. In this report, we present experimental evidence for the influence of interfacial water structure induced by salt on interfacial silica reactivity, which has geochemical,[12,13] biological,[11] and industrial implications.[14,15]

The interplay of salt and pH strongly affects the dissolution of quartz and amorphous silica, which is important for alkaline flooding in enhanced oil recovery,[14] maintenance of concrete roads and bridges,[16] and silicate cycling of marine biogenic silica.[17] Addition of alkali salts to aqueous solutions increases the dissolution rate of quartz, with a greater enhancement at near-neutral bulk pH.[18] Moreover, the dissolution rate is more sensitive to the identity of the cation at near-neutral pH than at high pH.[18,19] Although the surfaces of quartz and amorphous silica have different long-range structural order, their points of zero charge (PZCs) are fairly close, and their dissolution behaviors show similar trends.[13,18] Thus, the interfacial

characteristics at quartz/water and amorphous silica/water interfaces should be qualitatively the same.

In an effort to elucidate the dissolution mechanism of quartz and to explain the cation-specific effects observed at near-neutral pH, Dove developed an empirical rate expression that relates dissolution rate (reactivity) to the fraction of negatively charged surface SiO⁻ groups.[20] The enhancement in the dissolution rate with bulk cation concentration was attributed to the sensitivity of charged surface SiO⁻ groups to the cations. This "surface charge sensitivity" (SCS), and hence the change in quartz dissolution rate, with salt concentration was found to be maximum at the pH of neat water ∼6−8 (this pH regime will be referred to as "near-neutral pH" throughout the document).[20] Subsequently, Dove et al. hypothesized that cations indirectly enhance dissolution by modifying rates of solvent exchange or orientation at the mineral-solution interface and accelerating the frequency of Si−O bond rupture.[18] The observation that cations modify the solvent behavior most at near-neutral pH has critical environmental and biological implications, since many naturally occurring silica and other mineral oxides are in contact with aqueous environments in this pH regime.

We have used vibrational sum-frequency generation (vSFG) spectroscopy to determine the fundamental role of the interfacial solvent arrangement in silica/water interface reactivity, as hypothesized by Dove et al.[18,20] In the dipole
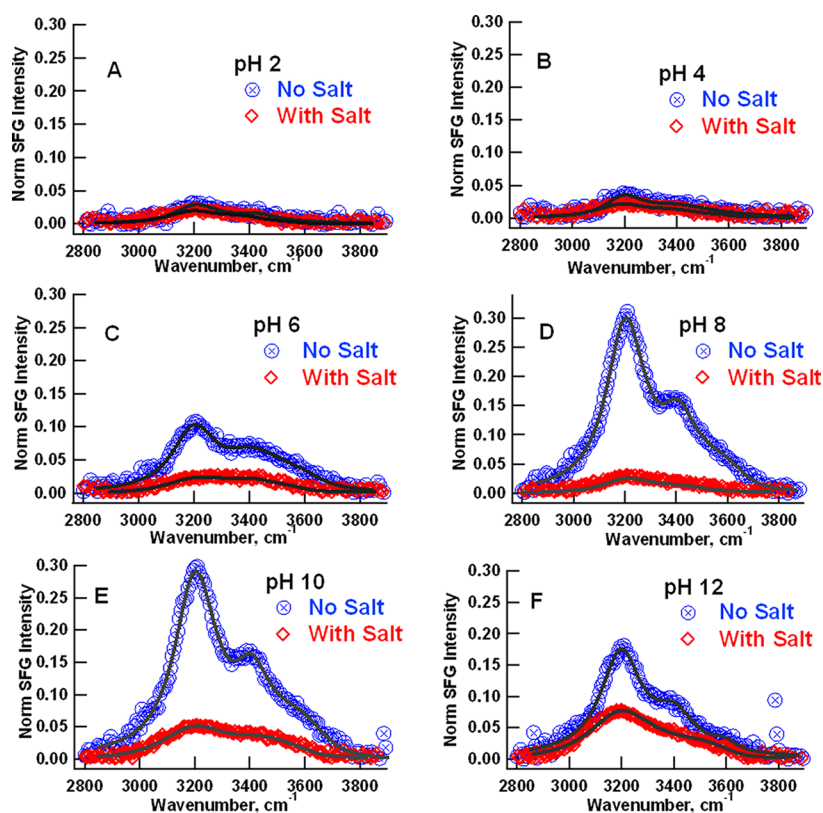
Figure 1. (A−F) vSFG spectra of the silica/water interface in the absence (blue) and in the presence of 0.1 M NaCl (red) at (A) pH = 2, (B) pH = 4, (C) pH = 6, (D) pH = 8, (E) pH = 10, and (F) pH =12. Black solid lines are fits to data using equation S1, described in the Supporting Information.

approximation, vSFG is prohibited in centrosymmetric materials, e.g., bulk aqueous and amorphous silica, but allowed at noncentrosymmetric interfaces, making vSFG spectroscopy an intrinsically in situ probe of changes in water molecular arrangement at the mineral/water interface .[21,22] In addition, when there is a uniaxial perturbation, e.g., a surface electric field, the nominally centrosymmetric bulk can contribute via a third-order response or $\chi^{(3)}$ term.[23−25] The role of $\chi^{(3)}$ is considered in the discussion below. vSFG reveals that the highest perturbation to interfacial water arrangement due to salt occurs at near-neutral pH, and closely follows the predictions of the SCS model. These results demonstrate the influence of microscopic interfacial solvent (water) structure on macroscopic surface processes such as silica dissolution.

The normalized vSFG spectra of the OH stretch region at the silica/water interface, as presented in Figure 1, show two broad regions at ∼3200 cm^{-1} and 3400 cm^{-1}, commonly attributed to contributions from strongly and weakly hydrogen bonded water, respectively.[26,27] While some argue that these two features do not belong to two types of water species,[28] recent theoretical studies have shown that contributions from strongly hydrogen-bonded and weakly hydrogen-bonded distributions of water will indeed appear at ∼3200 cm^{-1} and 3300−3500 cm^{-1}, respectively.[29] There is also a weak shoulder at ∼3600 cm^{-1} which may be attributed to the asymmetric OH stretch or incompletely hydrogen−bonded water molecules.[30] In the "no salt" case, the spectral intensity increases as the pH rises from 2 to 10 due to the growing negative surface charge (Figure 1).[31] However, the spectral intensity decreases from pH 10 to 12 as the effect of increasing ionic strength from 10^{-4} to 10^{-2} M overshadows the simultaneous increase in surface

charge. In the "with salt" case, the ionic strength, determined by the 0.1 M NaCl, remains constant, and the vSFG intensity monotonically rises with pH. At all pHs above 2, addition of 0.1 M NaCl leads to an overall decrease in the vSFG intensity (Figure 1), consistent with previous observations.[25,32,33] The reduction in the vSFG signal (Figure 1) due to salt strongly depends on the pH and hence the extent of silica surface ionization.

The effect of electrolyte on the second-harmonic (SHG) and vSFG signals from the quartz/water interface has been observed previously.[22,23,34] In fact, consistent with our observation, Du et al., who used vSFG to investigate the effect of electrolyte (NaCl) at three bulk pH values, reported a more pronounced change in near-neutral water (pH∼5.7) than in basic water (pH∼12), while their vSFG showed no effect at pH 1.5.[22] The authors discussed two consequences of adding electrolytes: (1) a decrease in spectral intensity, which was attributed to screening of negative surface charge by Na$^+$ ions and (2) a decrease in the relative strength of the peaks at 3200 and 3450 cm^{-1}, which was interpreted as an increase in molecular ordering. However, it is unclear why electrolytes would increase molecular ordering of water at the interface with a simultaneous decrease in the vSFG spectral intensity as observed in many vSFG reports.[22,25,33]

The vSFG signal at a charged interface originates from water molecules in a noncentrosymmetric environment induced by interfacial molecular ordering and/or the surface electric field (E_0). The resonant vSFG intensity consists of two terms:

$$I_{SFG} \propto |\chi^{(2)}E_{vis}E_{IR} + \chi^{(3)}E_{vis}E_{IR} \int_0^\infty E_0 \, dz|^2 \tag{1}$$
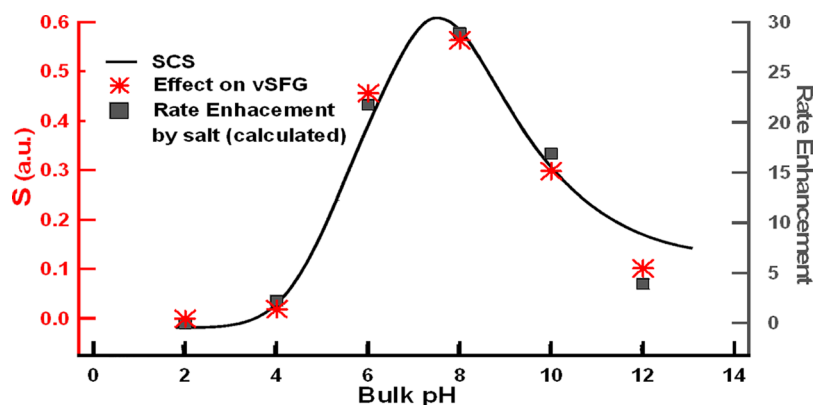
Figure 2. Comparison between the effect of salt on the vSFG response of the silica-water interface and effect of salt on silica dissolution, as a function of pH. Red crosses: salt effect (S) as obtained from eq 2; Black squares: calculated quartz dissolution rate enhancement on adding 0.1 M NaCl salt using the model in ref 1 (Supporting Information); Solid line: "surface charge sensitivity (SCS)" curve; data taken from ref 1.
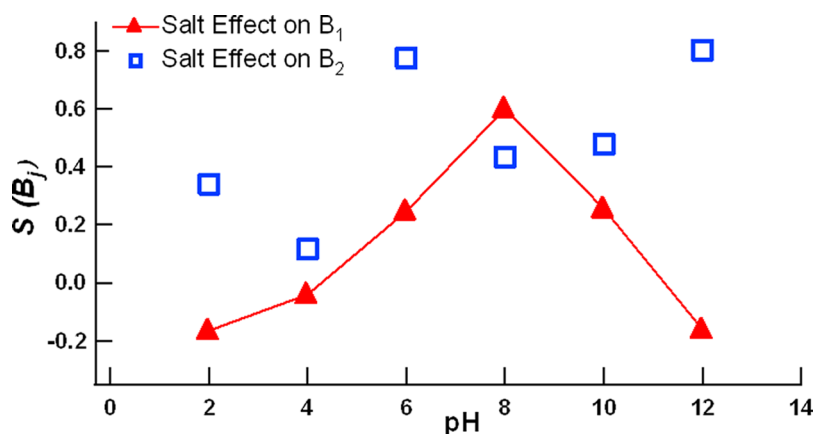

Figure 3. Comparison of the effect of salt on strongly (B_1) and weakly hydrogen bonded (B_2) water. $S(B_j) = (B_{jnosalt} - B_{jsalt})/B_{jnosalt}$. Open blue squares: effect of salt on the 3200 cm^{-1} feature; Red triangles: effect of salt on the 3400 cm^{-1} feature.

where $\chi^{(2)}$ and $\chi^{(3)}$ are the second- and third-order susceptibilities, respectively.[32] The major part of the resonant contribution to the $\chi^{(2)}$ term comes from anisotropic water, i.e., molecules oriented by the interface. The $\chi^{(3)}$ term reflects water that can be either oriented by, or experiences the polarizing effects of, E_0. In principle, the length scale over which $\chi^{(3)}$ contributes is determined by the Debye length. Under conditions of high surface charge and low ionic strength, the interfacial potential is high, and the Debye length extends many layers into bulk water, which can make the $\chi^{(3)}$ contribution non-negligible.[30,32] For the silica/water interface, it was shown that $\chi^{(3)}$ contribution to vSFG starts to decrease at ionic strengths of 0.1 M and higher.[25,32] While the significance of the $\chi^{(3)}$ term or bulk-like response to the observed vSFG intensity is still a subject of debate,[25,35] there is no doubt that the SFG intensity depends on the structural properties of water in the interfacial region and the magnitude of the nonlinear optical response. At constant ionic strength, the vSFG signal grows with pH because of a greater ordering of interfacial water due to the rising interfacial electric field, and/or an increased contribution of molecules within the Debye length via a $\chi^{(3)}$ contribution.[23,26] At constant pH, the vSFG signal decreases with increasing ionic strength.[25,33] This may be a result of the shrinking Debye length and/or the decreasing interfacial potential.[25,36] In addition, the cations accumulating near the negatively charged surface perturb the interfacial water ordering. Irrespective of the precise mechanism, the presence

of salt in aqueous systems at charged interfaces reduces the nonlinear optical response, reflecting reduced solvent ordering.

The vSFG intensity, specifically the amplitudes associated with strongly (B_1) and weakly (B_2) hydrogen-bonded water contributions ($\sim$3200 cm^{-1} and 3400 cm^{-1}, respectively) obtained from the fits using equation S1 (Supporting Information), reflects the ordering of interfacial water. A quantitative analysis of the effect of salt on interfacial water structure is provided by comparing the total vSFG spectral amplitudes for the "no salt" case, $(B_1 + B_2)_{nosalt}$, and the "with salt" case, $(B_1 + B_2)_{salt}$. Specifically, the normalized difference between the two cases provides a measure of the extent to which salt alters the interfacial water structure, i.e., the "salt effect (S)", given by eq 2.

$$S = \frac{(B_1 + B_2)_{nosalt} - (B_1 + B_2)_{salt}}{(B_1 + B_2)_{nosalt}} \quad (2)$$

The sensitivity of the salt effect (S) to the bulk pH follows the trend predicted by the SCS model (Figure 2).[20] To further elucidate the strong correlation between the pH-dependent perturbation of interfacial water structure on addition of salt and the pH-dependent enhancement of silica dissolution rate by salt, the relative increase in dissolution rate on addition of 0.1 M NaCl was calculated at each pH using the empirical rate equation developed by Dove,[22] (Supporting Information) and overlain on our vSFG data (Figure 2). At near-neutral pH 6–8,
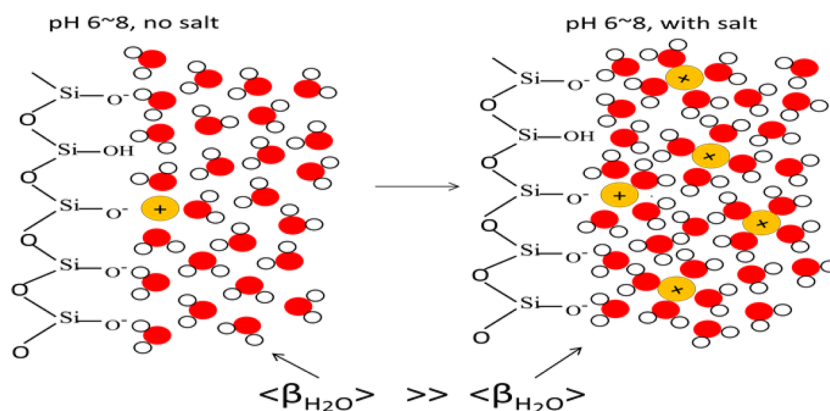
Figure 4. Cartoon depicting decrease in ordering of interfacial water at near-neutral bulk pH on addition of NaCl.

where the silica surface is partially ionized to SiO^-, there is a sharp increase in S indicating that salt perturbs the interfacial ordering most at this pH regime. This perturbation starts to decrease at pH > 8. At pH ~12 the silica surface is highly ionized and the addition of salt has a diminished influence on the vSFG response.

To understand the effect of salt on the different hydrogen bonding environments, the relative changes in the vSFG amplitudes of the 3200 cm^{-1} and 3400 cm^{-1} features are compared (Figure 3). While salt does not significantly modify the amplitude of the weakly hydrogen bonded water feature with pH, salt has an effect on the strongly hydrogen bonded water (B_1) which follows the "surface charge sensitivity" trend, showing a maximum at pH 8. This is in agreement with previous observations, albeit performed at a single pH, that the 3200 cm^{-1} feature experiences larger perturbation with increasing ionic strength.[33] We speculate that the overall salt effect on the vSFG signal comes mainly from the response of water molecules in strongly hydrogen bonded environments.

The salt effect on the vSFG response is a consequence of the modifications induced in water ordering due to the opposing effects of increasing surface charge and ionic strength. One could argue that the changes in vSFG intensity observed upon addition of salt at each pH are simply a result of the reduction in the Debye length and the decrease in the number of water layers contributing to the detected signal. If this were the case, then the loss in vSFG intensity should be proportional to the reduction in the Debye length. However, the effect of salt, reflected in S (Figure 2), on the vSFG signal is different at pH 6 and pH 8, even though the extent of Debye length shrinking is the same. A similar observation holds for pH 4 and pH 10, although at these two pH conditions the silica surface charge and hence surface potential are significantly distinct. This suggests that the change in the vSFG on addition of salt is not due to the screening effect of counterions (Na^+) alone. Rather, it reflects a decrease in the overall ordering, i.e., $\chi^{(2)}$, caused by the presence of salt cations in the interfacial water layer (Figure 4).

At acidic pH, where the surface charge of silica is negligible, the addition of Na^+ ions does not appear to alter the hydrogen-bonding structure of interfacial water (Figure 1). This is due to the lack of a driving force to attract the cations to the neutral surface, thus limiting their perturbing effect on the interfacial region. The dissolution rate at low pH is slow as molecular water, a weak nucleophile, is the primary reactive species responsible for dissolution.[18,20] At pH ~12, the surface charge

density and the bulk Na^+ concentration (10^{-2} M) are large. Many Na^+ ions are already present at the negative silica surface, so that addition of salt causes only small changes in water structure, and thus the vSFG spectrum. In alkaline conditions, it is believed that the hydroxyl ions control the dissolution rate via a faster mechanism involving the adsorption of a proton on the bridging surface oxygen followed by nucleophilic attack of hydroxyl ion on silicon.[18,20]

At pH 6−8, the silica surface has a net negative charge due to some deprotonated SiOH groups and a low Na^+ bulk concentration (10^{-6} M in "no salt"), and the interfacial water region is most prone to disruption by the addition of 0.1 M Na^+. The negatively charged surface attracts the cations and their hydration shells, perturbing the interfacial solvent from its initial salt-free structure (Figure 4), as revealed by the largest changes in vSFG response and S at this pH. One factor influencing the silica surface reactivity is the rate of solvent exchange (k_{ex}), which correlates with dissolution rate of silica for a series of cations and is defined as the frequency at which primary solvation water associated with an ion is exchanged with the surrounding water molecules.[18] In the absence of salt, the only ionic species present near the silica surface is a trace of $H_3SiO_4^-$ from the slow reaction of Si−O surface group with H_2O.[18] On addition of salt the predominant ions near the negative surface are hydrated Na^+, which have a solvent exchange rate that is over 8 orders of magnitude faster than H_4SiO_4, increasing the frequency of Si−O bond breakage.[18] Since the relationship between solvent exchange rate and dissolution rate is not 1:1, the frequency of solvent exchange with cation is not the only mechanism of rate enhancement. It was suggested that, at near-neutral pH, the increase in the rate of reaction between Si−O and water is a consequence of the existence of a higher entropy state of the interfacial system (hydrated quartz surface, interfacial water and hydrated ions together). The attraction of hydrated cations to the negatively charged surface at this pH orients the water at the surface so as to increase the entropy of the system, and hence the pre-exponential term of the reaction rate.[20] This picture of higher disorder induced by cations at near-neutral bulk pH is supported by our vSFG results.

In summary, vSFG spectroscopy reveals that salt influences the molecular arrangement of water at the silica/water interface depending on the bulk pH and hence the surface charge density of silica. The maximum perturbation by salt occurs at near-neutral pH, consistent with Dove's "surface charge sensitivity" and validating the hypothesis that changes in water structure

close to the silica surface directly increase the surface hydrolysis rate. By revealing the in situ structural changes in water on addition of salt as the surface ionization of silica is varied, the vSFG results "connect the dots" between microscopic solvent structure and resulting macroscopic surface reactivity. The fact that maximum variations in interfacial ordering induced by salt are observed at near-neutral bulk pH can have important implications for geochemically and biologically relevant process that occur at this pH regime.

EXPERIMENTAL SECTION

Broadband vSFG spectra of the silica/water interface were acquired by exciting the fundamental OH stretch modes of water (∼3000−3700 cm^{-1}) with tunable broadband IR pulses, and up converting the resultant vibrational polarization with a spatially and temporally overlapped narrowband visible pulse (Supporting Information). Briefly, the silica/water interface was created using a hemicylindrical IR-grade fused silica prism that was pressed against an aqueous solution. First, the vSFG was recorded at six noted pHs of 2, 4, 6, 8, 10, and 12 with "no salt" (in this order), where the solutions were prepared by adding appropriate amounts of NaOH or HCl solutions. Then, the spectra were recorded for the "with salt" pH solutions, prepared by adding required amounts of NaOH and HCl to a 0.1 M NaCl solution. To ensure reproducibility and avoid sample hysteresis, while sequentially going from pH 2 to pH 12, the SFG cell was flushed in situ with deionized water between solutions and before repeating each measurement.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, data analysis, explanation of origin of the vSFG signal, and calculation of the effect of salt on dissolution rate are included in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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