

Supporting Information

Effect of electrolyte on XAS, XRS, XES, and PES

Faubel et al. measured the O(1s) X-ray photoelectron spectrum of liquid water using Mg X α radiation (1253.6 eV) and estimated the binding energy (538 eV) and the shift from the gas phase value (1.9 eV), although they did not show the spectrum [S1]. They found that the gas–liquid shift was independent of the alkali halide added and that it was identical to the value reported by Lundholm et al. [S2] for a highly cooled aqueous solution of 3.8 M LiCl. Faubel et al. could obtain a reproducible X-ray photoelectron spectrum only by adding salts to suppress the streaming potential caused by electrokinetic charging; therefore, the value given above was obtained from salt solutions. Photoelectron spectroscopy (PES) of aqueous salt solutions has been performed in more detail by Winter and coworkers [S3–S5] at photon energies of 90–100 eV. PES is highly sensitive to the surface due to the short electron attenuation length (EAL) (see next section). The concentrations were 2–12 M (mostly 2–3 M), which are one or two orders of magnitude higher than our case (0.14 M). Even at such high concentrations, they did not observe any noticeable changes in the spectral features of water at a resolution of 0.1 eV, which agrees with earlier observations by Faubel et al. [S1]. In ref. [S5], they described the photoelectron spectra of aqueous NaCl (3 M) and NaOH (2 M) solutions as being “nearly identical with the corresponding water spectrum”. The effect of salt on hydrogen bonding in liquid water has been investigated by several workers using X-ray absorption spectroscopy (XAS) and X-ray Raman spectroscopy (XRS) [S6–S8]. These studies found that the addition of NaI, NaBr, and NaCl to water enhances the absorption intensities of the pre-edge and the main edge, whereas it reduces the post-edge intensity. However, noticeable changes in the spectra were observed only for high salt concentrations (> 1 M). Naslund et al. stated that “neither strongly nor weakly hydrated ions affect significantly the average number of hydrogen bonds in the bulk liquid as probed with XAS/XRS” [S9]. Again, the NaCl concentration used in our study is an order of magnitude lower than those used in XAS [S6–S8].

Guo et al. [S7] reported X-ray emission spectroscopy of aqueous solutions of NaCl, MgCl₂, and AlCl₃ (1 M). Their spectra of these solutions and of pure water exhibited a single-peaked narrow band of $1b_1 \rightarrow 1a_1$ at $h\nu = 534.5$ eV, which became

broad bands at $h\nu = 570$ eV. The broadness of the band in the latter case is essentially the same as the band splitting observed by Tokushima et al. [S9], although the low-resolution (0.4 eV) measurements by Guo et al. made it difficult to resolve the splitting of the band. This result clearly indicates that the mysterious split of the $1b_1 \rightarrow 1a_1$ band in liquid water is essentially the same as that in aqueous salt solutions.

The electron attenuation length in PES and surface activity of ions

The EAL is defined as the distance at which the electron flux is reduced by a factor of $1/e$. It is rather difficult to evaluate the EAL for liquid water, but it is estimated to be about 2 nm (3 nm) at a kinetic energy of 100 eV (500 eV) [S10]. Jungwirth and Tobias calculated depth profiles for the $[Na^+]$ and $[Cl^-]$ concentrations in aqueous NaCl solution [S11]. Their profiles are almost flat, unlike that of NaI, for instance. Furthermore, electrical bilayers of alkali metal ions and halogen ions exist within ca. 1 nm from the liquid surface, whereas the EAL (3 nm at 500 eV) is over 2–3 times greater than this distance.

OH dangling bonds at the surface

The influence of the electrolyte on hydrogen bonding at the air–liquid interfacial region of aqueous salt solutions has been investigated by vibrational sum frequency generation spectroscopy [S12, S13]. It was found that the infrared spectrum in the OH stretching region is least affected by aqueous NaCl solution of various aqueous alkali halide solutions. These studies were performed using 1–2 M solutions. Thus, we believe that the OH hydrogen bonding structures at the surface will not be noticeably affected by the presence of 0.14 M NaCl in solution. Again, the EAL of PES is much larger than the depth of a single monolayer of surface molecules. We do not anticipate that dangling OH bonds at the surface affect PES at photoelectron kinetic energies of over 500 eV.

References

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