

# Supporting information: Cation Hydration in Supercritical NaOH and HCl Aqueous Solutions

Christoph J. Sahle,<sup>\*,†</sup> Johannes Niskanen,<sup>‡</sup> Christian Schmidt,<sup>¶</sup> Johannes Stefanski,<sup>§</sup> Keith Gilmore,<sup>†</sup> Yury Forov,<sup>||</sup> Sandro Jahn,<sup>§</sup> Max Wilke,<sup>⊥</sup> and Christian Sternemann<sup>||</sup>

*European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France., Helmholtz Zentrum Berlin für Materialien und Energie, Institute for Methods and Instrumentation for Synchrotron Radiation Research, Albert-Einstein-Str. 15, 12489 Berlin, Germany, Deutsches GeoForschungsZentrum GFZ, Section 4.3, Telegrafenberg, 14473 Potsdam, Germany., Institute of Geology and Mineralogy, University of Cologne, Zùlpicher Strasse 49b, 50674 Köln, Germany., Fakultät Physik/DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany., and Institute of Earth and Environmental Science-Earth Science, Universität Potsdam, 14476 Potsdam, Germany.*

E-mail: christoph.sahle@esrf.fr

## Supporting Information Available:

Fig. 1 shows a comparison of oxygen K-edge spectra of differently concentrated NaOH(aq). The differences between the two concentrations are relatively minor and, most importantly, the overall trends are reproduced by the theoretical model calculations. Due to the slightly higher statistical accuracy of the spectra taken of the 13 m solution, we use these data in the main text. Fig. 2 shows a comparison of spectra also shown in Fig. 2 for each temperature in order to directly compare the influence of the

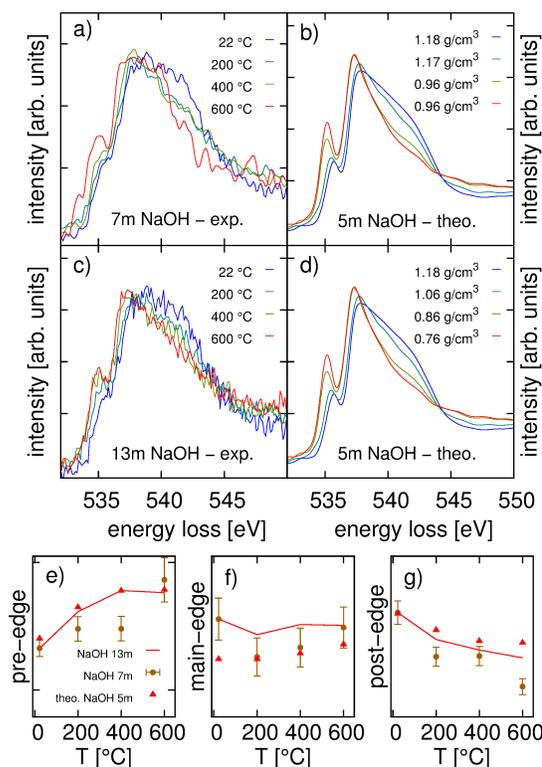


Figure 1: Experimental oxygen K-edge spectra from 7 m and 13 m aqueous NaOH solutions compared with spectra calculated from AIMD simulation data at 5 m concentration.

<sup>\*</sup>To whom correspondence should be addressed

<sup>†</sup>European Synchrotron Radiation Facility, 71 Avenue des Martyrs, 38000 Grenoble, France.

<sup>‡</sup>Helmholtz Zentrum Berlin für Materialien und Energie, Institute for Methods and Instrumentation for Synchrotron Radiation Research, Albert-Einstein-Str. 15, 12489 Berlin, Germany

<sup>¶</sup>Deutsches GeoForschungsZentrum GFZ, Section 4.3, Telegrafenberg, 14473 Potsdam, Germany.

<sup>§</sup>Institute of Geology and Mineralogy, University of Cologne, Zùlpicher Strasse 49b, 50674 Köln, Germany.

<sup>||</sup>Fakultät Physik/DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany.

<sup>⊥</sup>Institute of Earth and Environmental Science-Earth Science, Universität Potsdam, 14476 Potsdam, Germany.

electrolytes on the shape of the oxygen K-edge. All spectra of the HCl solution show decreased pre- and main-edge intensities, whereas up to 400 °C the post-edge is slightly enhanced when compared to the spectra of pure water. The spectra of the NaOH solution are noticeably blue-shifted and the spectra recorded in the supercritical regime show smaller pre-edge intensity and considerably enhanced post-edge features in comparison to neat water. All relative trends are reproduced by the simulations, also shown in Fig. 2. Oxygen-oxygen and

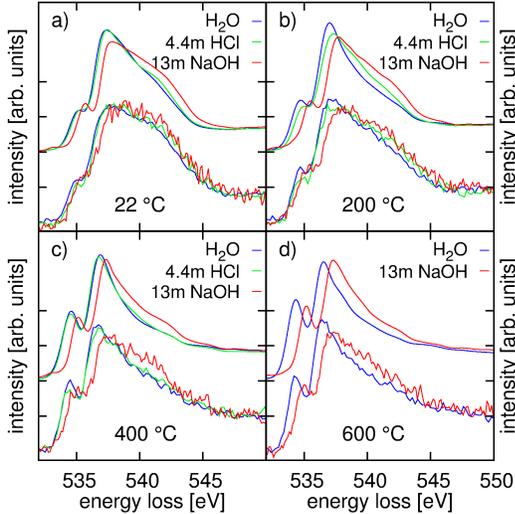


Figure 2: Comparison of experimental and computational results for the different systems (blue lines for H<sub>2</sub>O, green lines for aqueous HCl, and red solid lines for aqueous NaOH) (a)-(d).

oxygen-hydrogen radial distribution functions (RDF) for pure water (data taken from<sup>1</sup>), aqueous NaOH, and aqueous HCl at different temperatures and pressures are shown in Figs. 3 and 4. Fig. 3 shows them as temperature series for each of the three solutions separately, whereas Fig. 4 shows a comparison of the RDFs of the different solutions for each temperature point. In all cases, the first solvation shell shifts to higher distances with increasing temperature (see left column in Fig. 3), as expected because of the lower densities at higher temperatures. However, the O-O RDF shows considerable contraction upon solvation of both HCl and NaOH throughout the probed ( $p, T$ ) range when compared to neat water (see Fig. 4). This is in line

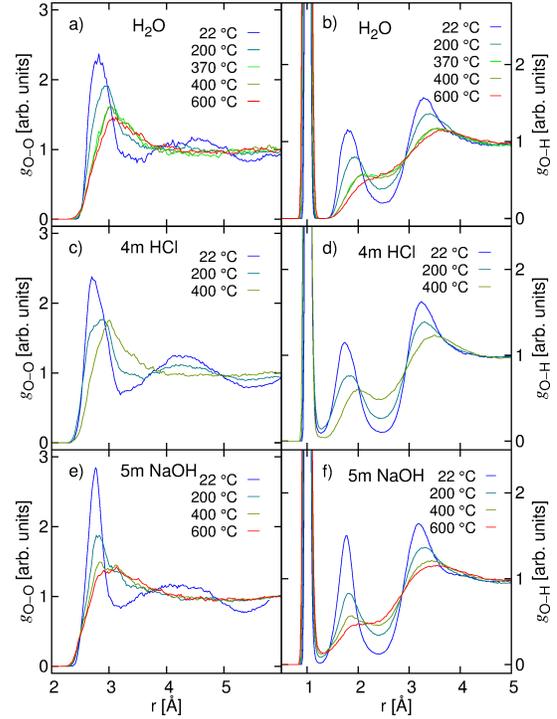


Figure 3: Comparison of the oxygen-oxygen and oxygen-hydrogen RDFs extracted from the molecular dynamics simulations.

with our interpretation based on the oxygen K-edge fingerprints that addition of HCl and NaOH stabilize the water structure at higher  $T$ . Consistent with our earlier observation, the RDFs of the NaOH solution always peak at shorter distances compared to those of HCl. The O-O RDFs of the NaOH solution exhibit a considerable sharpening at lower  $T$ . This general behavior has been observed earlier and has been described as ion solvation having a similar effect as the application of pressure.<sup>2-4</sup> All O-H RDFs of HCl(aq) and NaOH(aq) show the first solvation shell at closer distances  $r$  than in neat water (right column of Figs. 3 and 4). At 22 °C the NaOH O-H RDF also shows a narrower and higher peak, as a sign of higher local order around the hydroxide anions. However, this higher local order comes along with a smaller number of overall water-water H-bonds at ambient temperature for NaOH(aq) (compare Fig. 3 c)). The O-H RDFs underline the increased hydrogen bonding observed at higher temperatures: the first and second peaks both

remain at shorter distances in the solutions of NaOH and HCl compared to neat water, which is in line with our experimental observation of an increased hydrogen bonding and tetrahedral-order signatures in the oxygen K-edge spectra.

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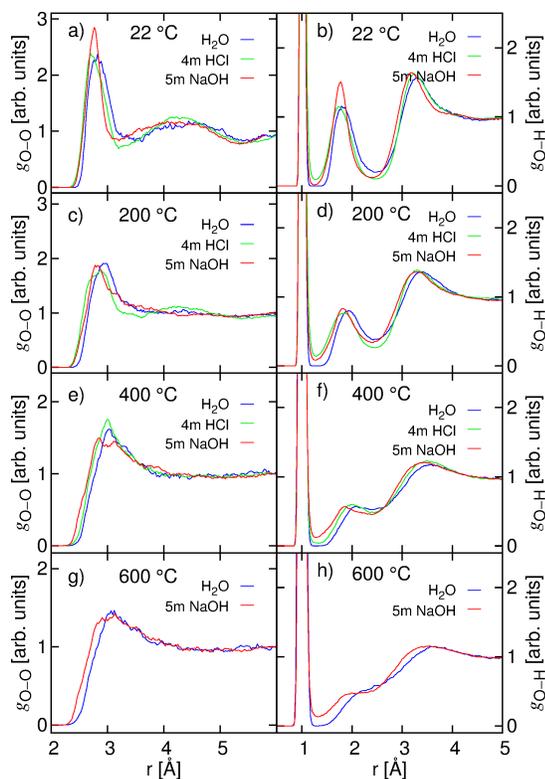


Figure 4: Comparison of the RDFs of the different solutions for each sampled temperature and pressure.

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## References

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