Modelling the effects of salt solutions on the hydration of calcium ions

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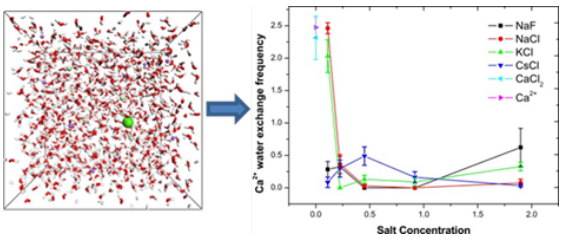
Classical molecular dynamics simulations of several aqueous alkali-halide salt solutions, at different concentrations, have been used to determine the effect of electrolytes on the structure of water and the hydration properties of calcium ions.

Compared with the simulations of Ca^{2+} ions in pure liquid water, the frequency of water exchange in the first hydration shell of calcium, which is a fundamental process in controlling the reactivity of calcium(II) aqua-ions, is drastically reduced in the presence of other electrolytes in solution. The strong stabilization of the hydration shell of Ca^{2+} occurs not only when the halide anions are directly coordinated to calcium, but also when the alkali and halide ions are placed at or outside the second coordination shell of Ca^{2+}. Analysis of the hydrogen-bonded structure of water in the vicinity of the calcium ion also shows that the average number and temporal fluctuations of hydrogen-bonds are also significantly influenced by the specific affinity of alkali and halide ions in solution with the water molecules coordinated to Ca^{2+}. This work shows the importance of solution composition in determining the hydrogen-bonding network and ligand-exchange dynamics around metal ions.



As the kinetics of crystallization of minerals such as calcium carbonate is controlled by de-hydration of the metal ions in solution and at the mineral surface, the information obtained in this study will help in improving our understanding of the mechanism controlling the nucleation of minerals in natural and industrial aqueous environments, which are far from pure water, but rich in electrolytes.