First principles simulation of aluminium solvation in aqueous solutions

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The behaviour of ions in aqueous solutions plays a critical role in Earth processes such as precious metal transport, mineral deposition, metasomatism, etc. Recently considerable progress has been made in the development of thermodynamic models even for systems that display complex chemistry (Felmy, 1986; Moller, 1988). Direct comparison of predictions to field observations has shown remarkable agreement. These models were for high-density liquid systems near room temperature for which we have adequate phenomenological theories and a substantial database (Weare, 1987). For systems that are less well studied experimentally or for PT conditions which are poorly understood (essentially all conditions for polar fluids above the critical point) the situation is far less satisfactory.

Efforts to provide information about fluid behaviour by direct simulation using molecular dynamics methods (MD) have recently been reported (Chialvo, et. al., 1996). In the usual MD simulations for ionic solutions the interactions between the species are approximated by equations of the schematic form

$$U = U_{\text{w-w}} + U_{\text{ion-w}} + U_{\text{ion-ion}} \qquad (1)$$

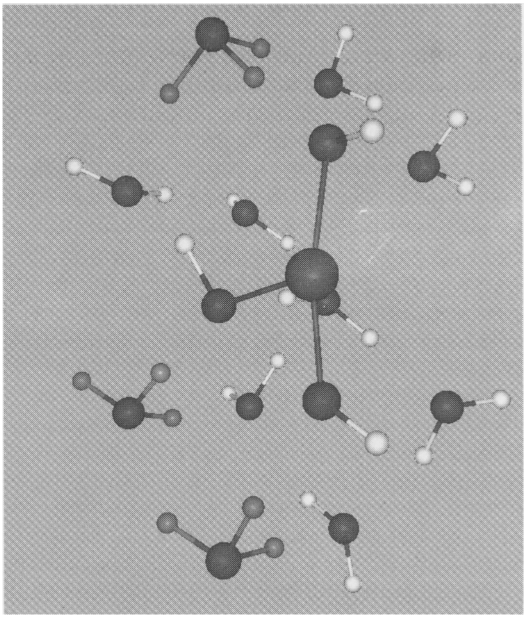
where $U_{\text{w-w}}$ represents water-water interactions and is taken to be one of several well established interaction potentials. The ion-water and ion-ion potentials are based on Lennard-Jones and Coulomb interactions, which must be parameterized from experimental data. The form for the potential, Eq. (1), is adequate for systems with low ionic charge such as Na^+, Cl^- etc. However, highly charged solutes such as Al^{3+} interact strongly with the molecules in their close vicinity (the solvation shell) via reactions such as

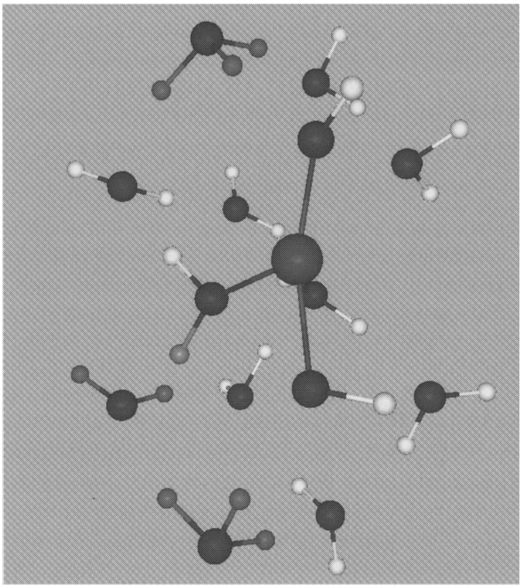
$$AL^{3+} + nH_2O \rightarrow AL(OH)_n^{(3-n)+} \qquad (2)$$

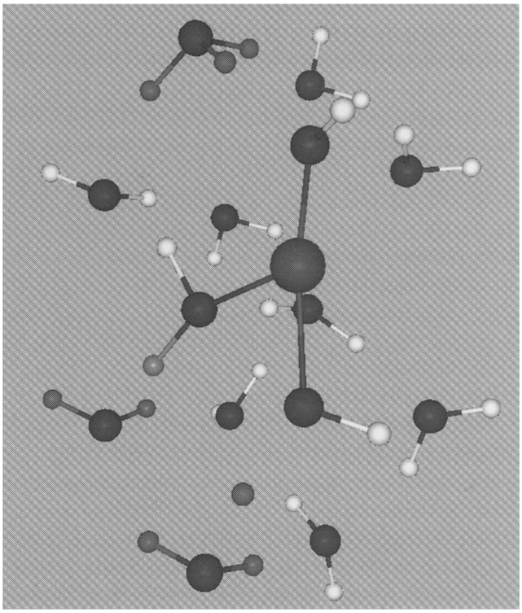
For chemical changes such as these the simple form represented by Eq. (1) cannot represent the redistribution of species. For example none of the well-parameterized water-water potentials allow bond breaking necessary for reaction, Eq. (2).

Here we report results of molecular dynamics simulations of the behaviour of Al^{3+} in water clusters based on the first principles calculation of the interactions in the system. In this approach, no assumptions about the interparticle interactions need to be made. Forces on the ions are calculated directly from a very fast solution to the electronic Schr'dinger equation within the local density approximation. A new solution is recalculated at each step in the simulation. In order to produce a sufficiently fast solution, the Coulomb potentials between the atom centres and the electrons are replaced by pseudopotentials. The wavefunctions are expanded in a plane wave basis and the solutions propagated in time by a Car-Parrinello algorithm (1985). In this report only cluster calculations are presented because calculations for bulk water are still not feasible with a first principles method.

Snapshots of the simulations are shown in the adjoining figures. These figures illustrate the extensive







reaction of the Al^{3+} ion (large sphere) in the solvation region. The shaded green and yellow atoms in the figure represent protons associated with the hydronium species, H_30^+. Three of these protons have been released in the hydrolysis of Al^{3+} to form $Al(OH)_3$. The snapshots are selected to illustrate that the species in the solvation region are highly fluxtional. For example, in the top figure the protons released in the reaction are all associated with water molecules, whereas in the middle figure the yellow proton has migrated to the Al species. In the lower figure a second proton has left the hydronium species. The snapshots represented in these figures are separated in real time by about 0.1 picosecond. We have done similar calculations for Na^+ ions solvated in water. As expected in this case there is no reaction. The Na^+ ion is solvated by roughly four intact water molecules with their negative oxygen atoms pointing toward the positive ion.

References

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