

Electron transfer reactions in solution and at interfaces

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We present a molecular model for ferrous-ferric electron transfer in an aqueous solution and at interfaces that accounts for electronic polarizability and exhibits spontaneous cation hydrolysis, and allows estimation of *pH* dependence. In solution, the model predicts that the diabatic barrier to electron transfer increases with increasing *pH*, due to stabilization of the Fe³⁺ by fluctuations in the number of hydroxide ions in its first coordination sphere, in much the same way as the barrier would increase with increasing dielectric constant in the Marcus theory. As expected, increasing *pH* reduces the potential of mean force between the ferrous and ferric ions in the model system. The magnitudes of the predicted increase in diabatic transfer barrier and the predicted decrease in the potential of mean force nearly cancel each other at the canonical transfer distance of 0.55 nm. Even though hydrolysis is allowed in our calculations, the distribution of reorganization energies has only one maximum and is Gaussian to an excellent approximation, giving a harmonic free energy surface in the reorganization energy $F(\Delta E)$ with a single minimum. Evidently, fluctuations in hydrolysis state can be viewed on a continuum with other solvent contributions to the reorganization energy. There appears to be little justification for thinking of the transfer rate as arising from the contributions of different hydrolysis states.

We have used the same methods to examine electron transfer rates at interfaces. An important question is whether electron-hopping rates would be faster in the bulk or at the interface. On the one hand the enhanced conformational flexibility and coupling with proton hopping may facilitate surface-mediated electron hopping. On the other hand, the proximity of the high dielectric water layer will act to trap the electrons. Our calculations suggest that, at low *pH*, the dielectric contribution dominates and reorganization energies are higher near the interface than in the bulk.

First-principles simulation of solvation structure and deprotonation reactions in very nonideal solutions

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The structure of the water molecules neighboring an M³⁺ ion in an aqueous solution is strongly perturbed leading to a structured second and a weakly structured third solvation shell and increased acidity of the solution. For simple ions, e.g. Al³⁺, standard pseudopotential based first principle molecular dynamics methods can be applied. Simulation results agree well with the measured octahedral structure of the 1st solvation shell of Al³⁺. Less can be determined experimentally about the structure of the 2nd shell. However, the calculated average radius is in good agreement with the measured values. This shell contains roughly 12 water molecules, which are trigonally coordinated to the 1st shell waters. This is also consistent with experimental estimates. The emergence of tetrahedral bulk water coordination as a function of the distance from the ion center occurs in the third shell. While there is no transfer of waters from the first to the 2nd shell, there is picosecond time scale transfer between the 2nd shell and third shell. For high T the transfer of protons in the solvation shells leads to hydrolysis species. For transition metal ions pseudopotential methods are not reliable. For these systems we have implemented an augmented wave method which allows the use of a plane wave basis without the introduction of pseudopotentials. Results for the solvation structure of Fe³⁺ will be presented. As time allows, the local structure of counter ions in the solvation shells will also be discussed.