

HO⁻ (aq) Structure and Mobility

D. Asthagiri^{C, S}

Group T-12 MS-B268, Los Alamos National Laboratory, Los Alamos, NM, U.S.A.

L.R. Pratt

MS-B268, Group T-12, Los Alamos National Laboratory, Los Alamos, NM, U.S.A.

J.D. Kress

MS-B268 Group T-12, Los Alamos National Laboratory, Los Alamos, NM, U.S.A.

M.A. Gomez

Department of Chemistry, Vassar College, Poughkeepsie, NY, U.S.A.

The hydroxide anion plays an essential role in many chemical and biochemical reactions. But questions of its hydration state and transport in water are currently controversial. Here we address this situation using the quasi-chemical theory of solutions. The simplest such approach suggests that HO[H₂O]₃⁻ is the most probable species at infinite dilution in aqueous solution under standard conditions, followed by the HO[H₂O]₂⁻ and HO[H₂O]⁻ forms which are close together in stability. In contrast to recent proposals, HO[H₂O]₄⁻ is not more stable than HO[H₂O]₃⁻. Ab initio molecular dynamics results presented here support the predominance of the tri-hydrated form, but that the population distribution is broad and sensitive to solution conditions. On the basis of these results, the mobility of hydroxide appears to be simply that of a proton hole. This contrasts with recent proposals invoking the interconversion of a stable 'trap' structure HO[H₂O]₄⁻ to HO[H₂O]₃⁻ as the rate determining step in the transport process.