

Water exchange rates and reaction pathways on Mg^{2+}

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Molecular dynamics (MD) simulations are utilized extensively in investigations of geochemical reactions. However, reconciling experimental and simulation derived rates remains a significant challenge, especially as reaction frequencies approach the microsecond regime. Rare events simulation methods facilitate the calculation of rate constants on such timescales, but sampling can be complicated by the presence of multiple coexisting reaction pathways.

In this study, the pathways and kinetics of water exchange on Mg^{2+} were investigated in the canonical ensemble (NVT) using direct MD simulations, the reactive flux method (RF), and a novel forward flux sampling procedure (FFS). Several established Mg-H₂O potential models were initially evaluated at 373K using direct simulations. This analysis showed that the experimental rate [1] was best reproduced by the Li and Merz 12-6-4 potentials for SPC/E and TIP4P water [2]. At 373K, the FFS-derived rates compared well with the direct simulation results, while the RF-derived rates were consistently 1-2 orders of magnitude slower. However, at 298K, the FFS and RF methods produced comparable results. An examination of the FFS and RF trajectories suggested that the two methods sample the cis and trans exchange pathways in different proportions.

[1] Bleuzen et al. (1997) *Magn. Reson. Chem.* 35, 765–773.

[2] Li and Merz (2014) *J. Chem. Theory Comput.* 10, 289–297.