Analysis of Hydration Structures in Inorganic Salt Solutions using Molecular Dynamics and Molecular Orbital Methods

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Water treatment membranes have traditionally been understood using the molecular sieving principle. However, recent experiments using liquid-crystal polymer membranes have shown that $MgSO_4$ exhibits higher permeability than NaCl, suggesting that ion-selective transport is significantly influenced by the stability of the hydrogen bonds surrounding the ions [1]. X-ray Emission Spectroscopy (XES) further indicated a high structural similarity between the water within the membrane and $MgSO_4$ hydration water; however, the precise nature of these hydration structures remains unclear. This study aims to clarify how ions modify water networks using Molecular Dynamics (MD) simulations and theoretical XES calculations.

MD simulations were performed using GROMACS for NaCl and $MgSO_4$ solutions up to the saturation concentrations. The systems were equilibrated for 2 ns using NVT and NPT ensembles, followed by hydrogen-bond analysis [2] to investigate the water orientation and structural deviations from pure water within each ion's hydration sphere. Furthermore, theoretical XES spectra were calculated for 20-molecule clusters sampled from the MD trajectories, specifically focusing on 1M/4M concentrations and the first hydration spheres of each ion.

Hydrogen bond analysis revealed that the structural modifications were most prominent in the first hydration sphere [2]. For cations, Mg^{2+} showed a significantly higher proportion of hydrogen-donating water molecules than Na^+. As confirmed by the radial distribution functions, the divalent nature of Mg^{2+} results in shorter ion-water distances, which sterically hinders water molecules from acting as hydrogen acceptors. Theoretical XES results showed that increasing the salt concentration broadens the $1b_1'$ peak and increases its intensity, reflecting ion-induced structural distortions in the water network. In NaCl solutions, the $1b_1'$ intensity was higher in the first hydration sphere than that in the bulk. This enhancement is likely due to the formation of linear hydrogen bonds associated with fast dynamics [3], a trend that is more pronounced for Cl^- than for Na^+. While the cations showed little difference between the two salts, the $1b_1'/1b_1''$ relative intensities for the anions shifted significantly. This suggests that SO_4^{2-}interacts with water via slower dynamics than Cl-because of its larger size and greater ion-water distance.

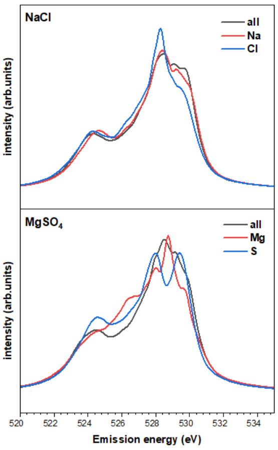

FIGURE 1. XES spectra of NaCl (upper) and MgSO4 (lower) aqueous solutions

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