

Modeling on Multiple Scales Establishes the Atomistic Details of Ion-Solvent and Ion-Ion Interactions in Experimental, PT-Dependent NMR Chemical Shifts of Aqueous Alkali Fluorides

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NMR experiments show that the shielding of ^{19}F nuclei in aqueous alkali fluoride solutions depends on temperature, pressure, and concentration. We use multiscale modeling to quantify the role of ion-solvent and ion-ion interactions. Molecular dynamics simulations with fixed-charge and polarizable force fields are used to explore the atomistic details of how ion-ion and ion-solvent interactions change with external parameters and concentration. Qualitative agreement between force fields is found for changes in the ion-ion potential of mean force and solvation structure; thus, robust molecular parameters for explaining the experimental trends are revealed. These molecular parameters are refined through quantum chemical calculations of NMR shielding tensors in a cluster-continuum framework. Contributions from direct and indirect interactions are further dissected to both validate the level of theory and to clarify the shielding effects of counter ions and solvent in different regions of the condensed phase.