

Nuclear Magnetic Resonance Spectroscopy Experiments and Multiscale Modeling Give Insights into Ion-Solvent Interactions and Ion Pairing in Simple Aqueous Salt Solutions

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After more than a century of investigating ion-solvent interactions and ion pairing in aqueous solution, this topic still attracts intense interest. This is perhaps unsurprising because almost all important biological, along with many chemical and technological processes, take place in aqueous solution. Furthermore, the nature of ion-solvent interactions and ion pairing in aqueous electrolyte solutions is both complex and subtle. Therefore, much remains to be learned about the behavior of ions in aqueous solution.

In this talk, temperature and molality changes are used to probe the balance of ion-solvent interactions and ion pairing in aqueous fluoride-based salt solutions. A divide and conquer approach is pursued, whereby experimental characterization of the free ion (FI) state then allows unambiguous interrogation of ion pairing. Low uncertainty Nuclear Magnetic Resonance (NMR) spectroscopy experiments clearly show that cations (⁷Li, ²³Na, ⁸⁷Rb, and ¹³³Cs) and ¹⁹F nuclei become significantly shielded as temperature increases for the FI state. As molality increases, the resonance frequencies are further changed by ion pairing or remain unchanged depending on the nuclei being analyzed. The same strategy is applied using multiscale models that combine molecular dynamics simulations with quantum chemistry calculations. Good agreement between theoretical and experimental shielding trends is achieved for both temperature and molality. Distant-dependent chemical shielding calculations establish that the sensitivity of NMR spectroscopy extends from the generally accepted contact ion pair (CIP) region out to the single solvent-separated ion pair (SIP) region.