Investigating the Role of Ion Specificity on Water Structure and Hydrophobic Collapse

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The presence of various salts in aqueous solution influences processes ranging from enzyme turnover rates and protein folding to colloidal assembly and macromolecular precipitation. The ordering of the anions with respect to their influence on a particular physical property generally follows a recurrent trend. The trend, known as the Hofmeister series, has been known since the late nineteenth century. The series is as follows:

$$CO_3^{2-} > SO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > Cl^- > NO_3^- > Br^- > I^- > ClO_4^- > SCN^-$$

The underlying mechanism of this phenomenon has remained unclear for over one hundred years. Two competing hypotheses have been put forth. One involves the relative influence of the anions on bulk water structure, while newer theories claim that dispersion effects and specific interactions with macromolecules are more important. Using a combination of vibrational sum frequency spectroscopy, microfluidic technologies, and light scattering techniques we have been able to test these theories in a variety of interfacial and colloidal systems. The results clearly indicate that direct anion/macromolecular interactions play a key role. On the other hand, indirect effects on water structure are not necessarily of paramount importance.