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Ions in water: Lessons from the Hofmeister series. Kim D. Collins, Center of Marine Biotechnology and Molecular Biology Center, University of Maryland Biotechnology Institute, 725 W.Lombard, Baltimore, MD 21201, collinsi@umbi.umd.edu

The Hofmeister series arises from the surface charge density of ions. Arguing from (a) the striking systematic dependence of the heats of solution of the simple alkali halides on the water affinity of the individual ions; (b) the dependence of the solubilities of the alkali halides on ion size; (c) the fact that Cl^- competes with DNA for positively charged binding proteins but glutamate does not; and (d) the fact that basic proteins are crystallized most effectively by chaotropic anions; we conclude that contact ion pairs are formed by oppositely charged ions of matching water affinities, while oppositely charged ions with differing water affinities stay apart. We call this The Law of Matching Water Affinities, and it gives rise to biological structure. For example, the tendency of monovalent cations to form contact ion pairs with the carboxylate decreases linearly with their mismatch in water affinities as measured by the Jones-Dole viscosity B coefficient [$\text{Na}^+ > \text{K}^+ > \text{Li}^+, \text{Cs}^+$]; recent molecular dynamics simulations by others confirms the greater tendency of Na^+ as compared to K^+ to form a contact ion pair with the carboxylate. The role of the ion pumps of the cell is to create a mismatch between the water affinities of the intracellular small cations (such as K^+) and the major intracellular anions (carboxylates and phosphates). This keeps the charged groups of macromolecules free of counterions, increasing the macromolecular net charge and thus solubility while leaving their charged groups available for use as binding determinants.