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Experimental Anion Affinities for the Air/Water Interface

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The affinities of the heavier halide anions for aerosol interfaces play important roles in atmospheric chemistry by affecting not only heterogeneous reaction rates but also fractionation of ions during sea-salt aerosol formation. This study revisits the mechanism of anion fractionation during aerosolization of electrolyte solutions. Anion affinities, γ_{X-}, for the aerial interface of aqueous (Br^- + NO_3^- + I^- + SCN^- + BF_4^- + ClO_4^-) solutions are determined by electrospray ionization mass spectrometry. The composition of the ions ejected from the surface of fissioning nanodroplets shows that γ_{X-} increase (decrease) exponentially with anionic radii, a_{X-}(dehydration free energies, ${}^dG_{X-}$), and selectively respond to the presence of surfactants. BF_4^-, the least hydrated and polarizable anion of the set, has one of the largest γ_{X-} values. Non-ionic surfactants decrease γ_{I-} and γ_{SCN-} but increase γ_{BF4-}. Cetyltrimethyl ammonium markedly enhances the γ_{X-} of smaller anions. A similar but weaker effect is observed upon lowering the pH of the bulk solutions from 8.2 to 3.0. Dodecyl sulfate has a negligible effect on γ_{X-}. Considering that (i) universal many-body electrodynamic interactions will progressively stabilize the interfacial layer as its dielectric permittivity falls relative to that of the bulk solution and (ii) water permittivity is uniformly depressed by increasing concentrations of these anions, we infer that the observed Hofmeister correlation, ln γ_{X-} $\propto$ - ${}^dG_{X-}$, is consistent with the optimal depression of the permittivity of the drier interfacial layer by the least hydrated ions. Interfacial ion-ion interactions can significantly influence γ_{X-} in environmental aqueous media.