



## Experimental anion affinities for the air/water interface

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Anion affinities,  $\gamma_{X^-}$ , for the aerial interface of aqueous ( $\text{Br}^- + \text{NO}_3^- + \text{I}^- + \text{SCN}^- + \text{BF}_4^- + \text{ClO}_4^-$ ) solutions are determined by electrospray ionization mass spectrometry. The composition of the ions ejected from the surface of fissioning nanodroplets shows that  $\gamma_{X^-}$  increase (decrease) exponentially with anionic radii,  $a_{X^-}$  (dehydration free energies,  $^dG_{X^-}$ ), and selectively respond to the presence of surfactants.  $\text{BF}_4^-$ , the least hydrated and polarizable anion of the set, has one of the largest  $\gamma_{X^-}$  values. Non-ionic surfactants decrease  $\gamma_{\text{I}^-}$  and  $\gamma_{\text{SCN}^-}$  but increase  $\gamma_{\text{BF}_4^-}$ . Cetyltrimethyl ammonium markedly enhances the  $\gamma_{X^-}$  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 document  $X^-$ . 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,  $\ln(\gamma_{X^-}) \propto -(^dG_{X^-})$ , 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 document  $X^-$  in environmental aqueous media.