

## 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  $\gamma_{X^-}$ . 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  $\gamma_{X^-}$  in environmental aqueous media.

### Introduction

Few phenomena are more ubiquitous, or have been more investigated, than those induced by the dissimilar propensities of anions for aqueous interfaces.<sup>1–4</sup> Fundamental biochemical, technological, and environmental processes are driven by the selective affinities of the various anions for the interfaces involved. They are labeled “Hofmeister effects” (HE) after observations made 118 years ago.<sup>5,6</sup> Explanations abound. They range from those based on continuum,<sup>7–13</sup> or heuristic molecular models,<sup>14</sup> to non-primitive molecular dynamic simulations.<sup>15–18</sup> However, “HE remain a mystery after more than 100 years”,<sup>10</sup> “perhaps the only thing certain about HE is that we do not understand the physical basis for the process”,<sup>19</sup> “simulations that confirm intuitions should be considered tautological”.<sup>11</sup>

Hofmeister correctly linked anion propensities for the boundaries between water and less polar media with the “water withdrawing power” of anions, an unquantified property at the time.<sup>20</sup> It has been recently argued, however, that anion polarizability is the most important factor determining HE at air/electrolyte solution interfaces.<sup>18,21,22</sup> This argument rests on molecular dynamic (MD) calculations showing that anions accumulate in the outermost layer after their polarizabilities are turned on, and on similarly interpreted surface-sensitive experiments.<sup>23</sup> Thus, it has been alleged that halide anion propensities are proportional to their polarizabilities.<sup>24</sup> Notice that the mostly negative surface potentials measured over electrolyte solutions ~50 years ago require that anions lie closer than cations to the interface.<sup>25–27</sup>

The affinities of the heavier halide anions for aerosol interfaces play important roles in atmospheric chemistry.<sup>2,28–36</sup>

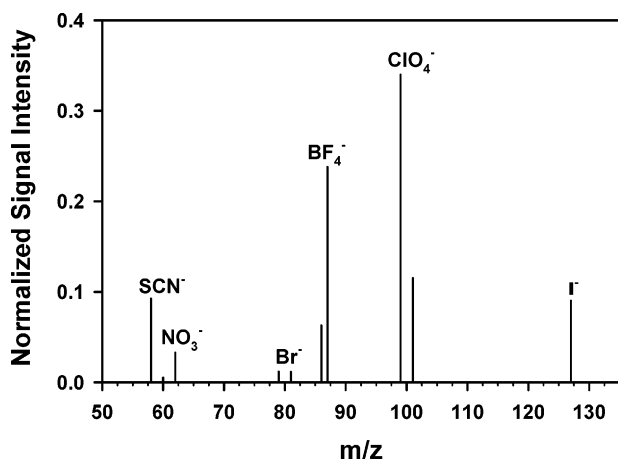
The same tendencies likely underlie the fact that the saline aerosol (up to  $\sim 10^4$  Tg/yr) incessantly released by the oceans is highly (10 to  $10^4$  times) enriched in bromide and iodide.<sup>32,37</sup> Considering that these huge enrichment factors cannot be accounted for by the modest differential  $\text{Cl}^-/\text{Br}^-/\text{I}^-$  concentration gradients predicted for the interfacial region, we decided to reinvestigate the mechanism of anion fractionation during the aerosolization of electrolyte solutions.<sup>33,38–43</sup> In this letter we report the simultaneous detection of  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{I}^-$ ,  $\text{SCN}^-$ ,  $\text{BF}_4^-$ , and  $\text{ClO}_4^-$  at the aerial interface of submillimolar aqueous senary solutions via electrospray ionization mass spectrometry,<sup>40,44–48</sup> in the presence or absence of surfactants and urea.<sup>31,49–55</sup> The results are analyzed in terms of fundamental concepts and new information.

### Experimental Section

An electrospray ionization mass spectrometer (HP-1100 MSD) with an atmospheric pressure ionization interface of orthogonal geometry was used in this study. Electrolyte solutions ( $50 \mu\text{L min}^{-1}$ ) were pumped into the spraying chamber through a grounded stainless steel needle injector ( $100 \mu\text{m}$  bore). Continuous flow conditions minimize contamination by spurious tensioactive species, which often compromise static experiments. Instrumental parameters (drying gas flow,  $10 \text{ L min}^{-1}$ ; drying gas temperature,  $250^\circ\text{C}$ ; nebulizer pressure, 35 psi; collector capillary voltage, 1.5 kV; fragmentor voltage, 80 V) were chosen to optimize mass signals with minimal ion fragmentation. Mass spectra were acquired at preset  $m/z$  values: 58 and 60 ( $^{32,34}\text{SCN}^-$ ), 62 ( $\text{NO}_3^-$ ), 79 and 81 ( $\text{Br}^-$ ), 86 and 87 ( $^{10,11}\text{BF}_4^-$ ), 99 and 101 ( $^{35,37}\text{ClO}_4^-$ ), and 127 ( $\text{I}^-$ ). Reported data are the average of at least duplicate experiments.

Pure (98% purity or higher) NaBr, NaI,  $\text{NaNO}_3$ ,  $\text{NaClO}_4$ ,  $\text{NaBF}_4$ , and NaSCN (EM science or Sigma-Aldrich), Triton

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**Figure 1.** ESI-MS of a 100  $\mu\text{M}$  aqueous solution of the sodium salts of each of the following anions:  $\text{SCN}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{BF}_4^-$ ,  $\text{ClO}_4^-$ , and  $\text{I}^-$ , at pH 6.5. Ion signal intensities normalized to the total ion intensity:  $\sum I_i = 1$ .  $I_{\text{SCN}^-} = 0.097$ ,  $I_{\text{NO}_3^-} = 0.033$ ,  $I_{\text{Br}^-} = 0.023$ ,  $I_{\text{BF}_4^-} = 0.301$ ,  $I_{\text{ClO}_4^-} = 0.455$ ,  $I_{\text{I}^-} = 0.090$ .

X-114, and cetyltrimethyl ammonium chloride (CTAC, Sigma-Aldrich), sodium dodecylsulfate (SDS, Bio-Rad) and urea (Mallinckrodt) were used as received. Equimolar senary solutions were prepared in MilliQ water or  $\text{D}_2\text{O}$  (Cambridge Isotopes) with and without surfactants or urea. The use of senary solutions substantially reduces experimental dispersion and the possible effect of potential impurities on present measurements. The pH of senary solutions, initially at 6.5, was adjusted by addition of 1 mM NaOH or HCl at constant ionic strength and measured with a calibrated pH meter.

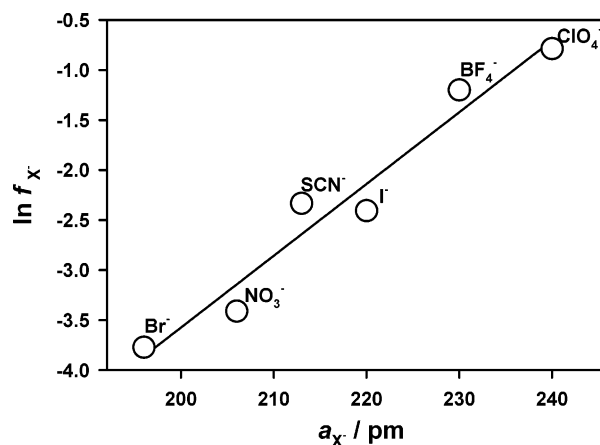
## Results and Discussion

Figure 1 shows a negative ion mass spectrum of electro-sprayed salt solutions. From this information, normalized anion affinities,  $f_{X^-}$ , were calculated from the sum of ion counts,  $I_{m/z}$ , for the isotopic variants of each anionic species [e.g., ( $I_{58} + I_{60}$ ) for  $\text{SCN}^-$ , etc.] and the total ion count:

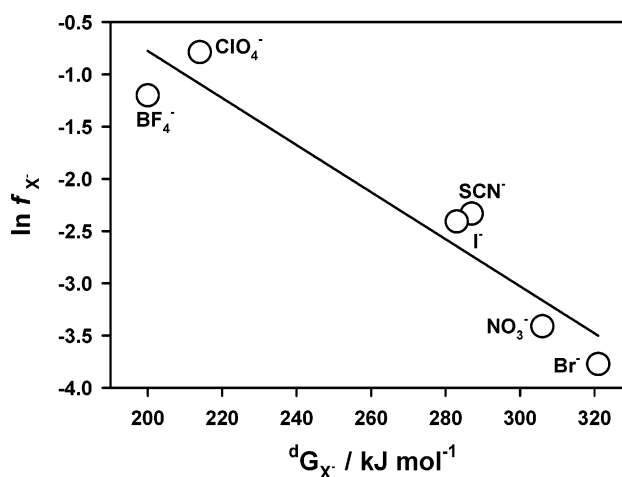
$$f_{X^-} = \left[ \sum_{X^-} I_{m/z} \right] / \sum I_{m/z} \quad (1)$$

Relative anion affinities,  $\gamma_{X^-}$ , are defined as multiples of  $f_{\text{Br}^-}$ , the value for the least enriched anion at the interface in the absence of surfactants:  $\gamma_{X^-} = f_{X^-}/f_{\text{Br}^-}$  (Table 1).  $\gamma_{X^-}$ -values measured in  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  are identical within experimental error.

Droplets generated during breakup of the liquid jet issuing from the grounded nozzle are spontaneously charged via microscopic fluctuations. The subsequent, uneven shedding of mass and charge by electro-sprayed droplets forces the anions present at the air/water interface to preferentially carry most of the excess charge into offspring droplets.<sup>56</sup> Individual anions are ultimately ejected into the gas phase via field desorption from negatively charged nanodroplets.<sup>40,45,46,57–63</sup> Therefore, the



**Figure 2.** Symbols: Normalized anion affinities,  $f_{X^-}$ , versus anionic radii,  $a_{X^-}$ , from ref 64. Solid line: linear regression:  $\ln f_{X^-} \propto a_{X^-}$  ( $R^2 = 0.956$ ).



**Figure 3.** Symbols: Normalized anion affinities,  $f_{X^-}$ , versus free energies of anion dehydration,  ${}^dG_{X^-}$ , from ref 64. Solid line: linear regression:  $\ln f_{X^-} \propto {}^dG_{X^-}$  ( $R^2 = 0.910$ ).

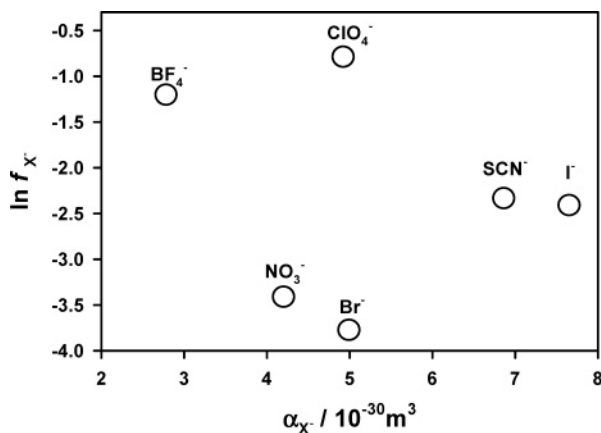
relative anion abundances registered by the mass spectra (Figure 1) reflect the anion distribution of the ensemble of single-ion water clusters ejected from the surface of disintegrating nanodroplets.<sup>57,58</sup> In the orthogonal geometry employed in these experiments the instrument samples the nanodroplets ejected laterally from the electro-sprayed jet. There is conclusive evidence that tensioactive species tend to accumulate in the periphery of the conical mist created ahead of the needle outlet.<sup>48</sup> Considering that the relative anion signals obtained by spraying solutions doped with 10  $\mu\text{M}$  SDS (anionic) or CTAC (cationic) surfactants are identical within experimental error, we conclude that the basic mechanism of anion enrichment does not involve ion–ion interactions.

Figures 2, 3, and 4 show semilogarithmic plots of  $f_{X^-}$  as a function of the aqueous anionic radius,  $a_{X^-}$ , free energy of

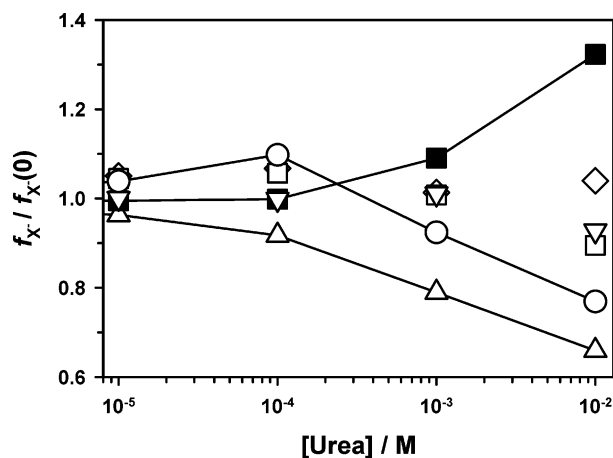
**TABLE 1: Interfacial Affinities and Molecular Properties of Anions**

anion $X^-$	normalized affinities <sup>a</sup> $f_{X^-}$ <sup>b</sup>	relative affinities <sup>a</sup> $\gamma_{X^-}$ <sup>b</sup>	radii <sup>c</sup> $a_{X^-}$ ( $10^{-12}$ m)	dehydration free energies <sup>c</sup> ${}^dG_{X^-}$ ( $\text{kJ mol}^{-1}$ )	polarizabilities <sup>c</sup> $\alpha_{X^-}$ ( $10^{-30}$ m <sup>3</sup> )
$\text{Br}^-$	0.023	1.00	196	321	4.99
$\text{NO}_3^-$	0.033	1.40	206 <sup>d</sup>	306	4.20
$\text{I}^-$	0.090	3.85	220	283	7.65
$\text{SCN}^-$	0.098	4.17	213	287	6.86
$\text{BF}_4^-$	0.301	12.86	230	200	2.78
$\text{ClO}_4^-$	0.455	19.45	240	214	4.92

<sup>a</sup> See text for definition. <sup>b</sup> This work. <sup>c</sup> Reference 64. <sup>d</sup> Equatorial radius.



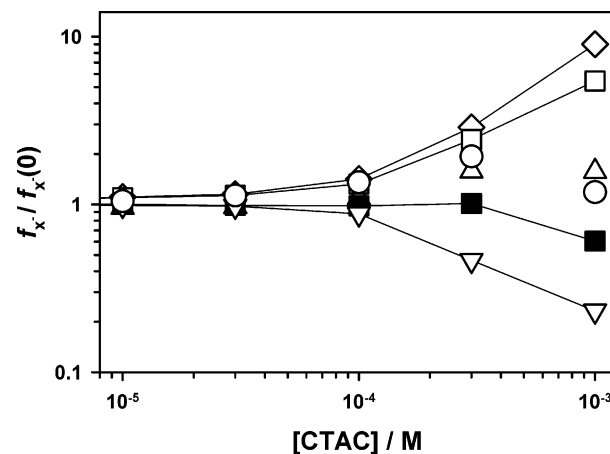
**Figure 4.** Normalized anion affinities,  $f_X^-$ , versus anion polarizabilities,  $\alpha_X^-$ , from ref 64.



**Figure 5.** Symbols: Ratios of normalized anion affinities,  $f_X^-/f_X(0)$ , as function of urea concentration. ■ ( $\text{BF}_4^-$ ); ◇ ( $\text{NO}_3^-$ ); ▽ ( $\text{ClO}_4^-$ ); □ ( $\text{Br}^-$ ); ○ ( $\text{I}^-$ ); △ ( $\text{SCN}^-$ ).  $[\text{X}_i^-] = 0.1 \text{ mM}$ .

dehydration  $^dG_X^-$ , and polarizability  $\alpha_X^-$ , respectively.<sup>64</sup> It is apparent that anion affinities for the air/water interface are strongly correlated with anionic radii,  $\ln f_X^- \propto a_X^-$  ( $R^2 = 0.96$ ), and free energies of dehydration,  $\ln f_X^- \propto ^dG_X^-$  ( $R^2 = 0.91$ ), in full accord with Hofmeister's analysis<sup>20</sup> and Monte Carlo calculations.<sup>15,65</sup> However, there is no discernible correlation between  $f_X^-$  and anion polarizabilities  $\alpha_X^-$  (Figure 4).<sup>3,7,18,21,66,67</sup> Tetrahedral  $\text{BF}_4^-$ , which has the smallest dehydration free energy of this set of anions but is  $\sim 2.75$  times less polarizable than iodide (Table 1), provides a fair test of the relative importance of anion polarizability vs anion dehydration energy in the mechanism of interfacial enrichment. Although the reported anion affinities depend to a certain extent on instrumental settings, these correlations are robust:  $f_X^-$  measured at 3 kV capillary voltage still increase exponentially with  $a_X^-$  and  $f_X^-$  measured in the 10  $\mu\text{M}$  to 10 mM concentration range are identical within experimental error.

Surfactants significantly affect  $f_X^-$ . All surfactants depress the total anion count at concentrations below their critical micellar concentrations.<sup>68,69</sup> Since nonionic surfactants do not displace anions from the interface at these concentrations (a weak attraction might be even expected) this finding suggests that surfactants compete with anions in decreasing surface energy. Urea (Figure 5), a water structure-breaker,<sup>52</sup> and Triton X-114 (Supporting Information), a non-ionic polyether amphiphile, comparably, slightly, but selectively influence  $f_X^-$ . The interfacial layer becomes more populated by the least hydrated  $\text{BF}_4^-$  at the expense of the more polarizable  $\text{I}^-$  and  $\text{SCN}^-$  anions upon



**Figure 6.** Symbols: Ratios of normalized anion affinities,  $f_X^-/f_X(0)$ , as function of cetyltrimethyl ammonium chloride (CTAC) concentration. ■ ( $\text{BF}_4^-$ ); ◇ ( $\text{NO}_3^-$ ); ▽ ( $\text{ClO}_4^-$ ); □ ( $\text{Br}^-$ ); ○ ( $\text{I}^-$ ); △ ( $\text{SCN}^-$ ).  $[\text{X}_i^-] = 0.1 \text{ mM}$ .

addition of urea or Triton X-114. The devaluation of the comparative advantage of  $\text{I}^-$  and  $\text{SCN}^-$  over  $\text{BF}_4^-$  ( $\text{BF}_4^-$ , having the smallest  $^dG_X^-$ , is indeed underrepresented at the interface, cf. Figure 3) further suggests that the more polarizable anions are somewhat more efficient in stabilizing the interfacial layer.<sup>70,71</sup>

While the anionic dodecylsulfate indiscriminately repels all anions from the interface (Supporting Information), as expected from electrostatics,  $f_X^-$  are quite sensitive to the cationic amphiphile cetyltrimethyl ammonium (Figure 6).<sup>72,73</sup> The smallest (and least enriched in the absence of additives) anions,  $\text{NO}_3^-$  and  $\text{Br}^-$ , are specifically enhanced several-fold. As a result, the  $f_X^-$  measured in the presence of 1 mM CTAC no longer correlate with anion radii or dehydration free energies. Positive head-groups seem to attract the smaller anions into closer contact and induce significant changes in their orientation and solvation at the interface.<sup>74</sup> It is well known that ion charges and radii both affect ion distributions near interfaces.<sup>75</sup> We also found that  $\gamma_{\text{NO}_3^-}$  increases 2.3 times, while most  $\gamma_X^-$  remain constant as the pH of the bulk solutions is lowered from 8.2 to 3.0. The onset of  $\gamma_{\text{NO}_3^-}$  increases at pH  $\sim 4.0$  suggests that the interface becomes positively charged under acidic conditions.<sup>4</sup> In this context, it is relevant to point out that the marine aerosol generated during bubble bursting at the ocean surface consists of positively charged droplets.<sup>39,76</sup>

Much of the current literature focuses on the width of the interfacial region.<sup>77</sup> However, since even surface-sensitive spectroscopies collect signals from interfacial slabs of  $\delta \sim 1.0 \text{ nm}$  thicknesses,<sup>23</sup> the fine-grained interfacial concentration profiles obtained by MD calculations, if they were consequential, represent an authentic challenge.<sup>18</sup> Anions are effectively enriched in the layers probed in our experiments because the combined  $\text{ClO}_4^-$  ( $m/z = 99$  and  $101$ ) signals are only 2.5 times smaller than the  $m/z = 265$  signal of the SDS surfactant in 10  $\mu\text{M}$  equimolar solutions. Assuming that SDS is bound to a  $\delta \sim 0.3 \text{ nm}$  outermost layer, we tentatively infer that the sampled  $\text{ClO}_4^-$  ions are sampled from  $\delta \sim 1.0 \text{ nm}$  interfacial sections, which are smaller than the estimated  $\sim 2.5 \text{ nm}$  radii of fissioning droplets.<sup>57,58</sup> On the other hand, surface tension measurements involve integral concentration profiles. The possibility that different interactions dominate at various depths, i.e., that the results obtained by different techniques could not be comparable, cannot be dismissed at this time.<sup>23</sup>

A physically meaningful interpretation of interfacial anion affinities should be based on an energy balance between opposing effects, rather than on simply correlating affinities with specific ion properties. Since anions *are* polarizable, the finding that some anions become enriched at the interface after their polarizabilities are included in MD calculations strictly shows that a deficiency has been corrected, not that anion enrichments should correlate with anion polarizabilities. While it is easy to envision that water density decreases smoothly toward the interface, the factors that determine the concentration profiles of cations and anions in the boundary layer are not immediately apparent. The sizable dehydration free energies of most ions, in conjunction with lower water density at the interface, will pull them into the bulk.<sup>9,15,65</sup> Image charge repulsion will enhance this tendency. This drive would be ultimately balanced by the entropy losses associated with ion confinement into a reduced volume. Hence, large dehydration free energies conspire against significant interfacial ion excesses. The preferential stabilization of the more polarizable anions in the strong electric field at the interface would, in principle, contribute to mitigate the adverse energy balance. Figure 4 shows, however, that this contribution is at best minor. Clearly, the major interactions that draw anions toward the interface and offset their aversion for this drier medium remain to be identified. Notice that if these were the only interactions involved, the solution bulk would be separated from air by a more dilute layer.

The thermodynamic stability of a contiguous three-layer array cannot be exclusively analyzed in terms of localized ion–water interactions. Macroscopic phases in contact are mutually stabilized via collective dispersive interactions arising from density and orientation fluctuations over the entire system.<sup>78–80</sup> By properly accounting for the global, many-body electrodynamic interactions among three contiguous phases it is possible to infer that the central layer is stabilized when its overall (i.e., dispersive and orientational) polarizability lies between those of air and the bulk solution.<sup>78,79</sup> This powerful criterion shifts the focus from ion polarizabilities to ion effects on the polarizability of water as a macroscopic medium. The broad temporal scales of many-body interactions in dielectric water are presumably better captured by Monte Carlo than by molecular dynamic calculations. The large difference between the dielectric permittivities of water and air, due to the unique properties of water as a hydrogen-bonded solvent, tends to amplify the effects of perturbations to water dynamics. Since electrolytes, as a rule, decrease the dielectric permittivity of water,<sup>81–84</sup> aqueous layers separating electrolyte solutions from air are expected to be stabilized by excess ion concentrations. Anions largely achieve this effect in the bulk by shortening the range and slowing down water dipolar correlations. From this perspective the rival factors controlling ion affinities for the air/water interface are: (i) ion dehydration energies and (ii) nonlocal stabilization energies resulting from the depression of interfacial water permittivity by local ion excesses.<sup>9</sup>

Since the concentration dependences of the static permittivities and relaxation times of water in NaBr, NaI, NaNO<sub>3</sub>, NaClO<sub>4</sub>, and NaSCN solutions are nearly independent of the nature of the anion,<sup>85,86</sup> anion affinities largely reflect differences in dehydration free energies. Considering that the dehydration energies of anions are considerably smaller than those of cations, this analysis naturally accounts for negative (relative to the bulk) surface potentials.<sup>26,27</sup> The Jones–Ray effect,<sup>87</sup> i.e., the lower surface tensions of dilute aqueous electrolyte solutions, also follows from this analysis and the Gibbs isotherm. This view readily allows for variations of anion affinities when air is

replaced by other media, such as hydrophobic membranes, proteins, etc.<sup>1,11,20</sup> If for no other reason, anions, particularly in the ~1 M model solutions used in MD simulations, *must* be polarizable to relay (rather than shielding) electrodynamic interactions over the entire molecular ensemble.

Summing up, the Hofmeister series of anion affinities for the air/water interface is paradoxically realized by the nonspecific effect of anions on the dielectric properties of interfacial water. Under realistic environmental conditions surfactants may decisively affect anion affinities. The huge anion enrichments found in the finest marine aerosol likely result from the amplification of relative anion affinities in successive droplet fission events.<sup>39,47</sup> Further work is underway.

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**Supporting Information Available:** Ratios of normalized anion affinities,  $f_X^-/f_X^-(0)$ , as function of Triton X-114 (Figure 7), and sodium dodecylsulfate (Figure 8) concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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