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A Pinch of Salt Is All It Takes: Chemistry at the Frozen Water Surface

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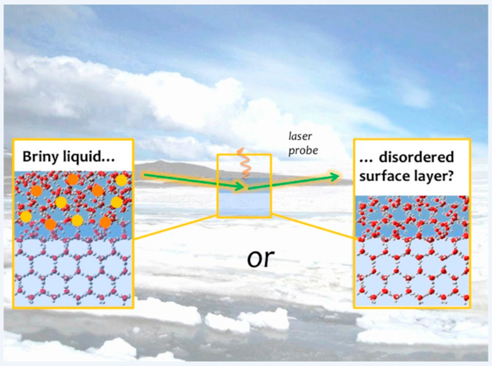

CONSPECTUS: Chemical interactions at the air–ice interface are of great importance to local atmospheric chemistry but also to the concentrations of pollutants deposited onto natural snow and ice. However, the study of such processes has been hampered by the lack of general, surface-specific probes. Even seemingly basic chemical properties, such as the local concentration of chemical compounds, or the pH at the interface, have required the application of assumptions about solute distributions in frozen media. The measurements that have been reported have tended for the most part to focus on entire ice or snow samples, rather than strictly the frozen interface with the atmosphere.

We have used glancing-angle laser spectroscopy to interrogate the air–ice interface; this has yielded several insights into the chemical interactions there. The linear fluorescence and Raman spectra thus measured have the advantage of easy interpretability; careful experimentation can limit their probe depth to that which is relevant to atmospheric heterogeneous processes.

We have used these techniques to show that the environment at the interface between air and freshwater ice surfaces is distinct from that at the interface between air and liquid water. Acids such as HCl that adsorb to ice surfaces from the gas phase result in significantly different pH responses than those at liquid water surfaces. Further, the solvation of aromatic species is suppressed at freshwater ice surfaces compared with that at liquid water surfaces, leading to extensive self-association of aromatics at ice surfaces. Photolysis kinetics of these species are much faster than at liquid water surfaces; this can sometimes (but not always) be explained by red shifts in the absorption spectra of self-associated aromatics increasing the extent to which solar radiation is absorbed.

The environment presented by frozen saltwater surfaces, in contrast, appears to be reasonably well-described by liquid water. The extent of hydrogen bonding and the solvation of adsorbed species are similar at liquid water surfaces and at frozen saltwater surfaces. Adsorbed acids and bases evoke similar pH responses at frozen saltwater ice surfaces and liquid water surfaces, and photochemical kinetics of at least some aromatic compounds at frozen saltwater ice surfaces are well-described by kinetics in liquid water.

These differences are not observed in experiments that interrogate the entire ice sample (i.e., that do not distinguish between processes occurring in liquid regions within bulk ice and those at the air–ice interface). Our work has shown that in general, the chemistry occurring at salty frozen interfaces is well described as being cold aqueous chemistry, whereas that seen at the pure ice interface is not. These findings have significant implications for heterogeneous atmospheric processes in ice-covered environments.

1. THE IMPORTANCE OF THE AIR–ICE INTERFACE

Chemical processes taking place at the air interface with ice and snow are of importance to the overlying atmosphere and have attracted growing attention in the past decade. The exchange of trace chemicals between snow and ice and the atmosphere is important to establishing atmospheric concentrations of these species, both in urban areas impacted by anthropogenic activities and in pristine environments such as Greenland and the Antarctic. For example, these exchange processes are ultimately responsible for driving observed ozone- and mercury-depleting events in the Arctic boundary layer and for controlling the local oxidative capacity above snowpacks via NOx and VOC emission and uptake and are implicated in the fates of persistent (and other) organic pollutants in the Arctic.[1−3]

To understand and predict chemical reactivity in ice and snow environments, one must understand where in such media these reactions take place. Although processes important to atmospheric exchange are expected to occur at the interface with the atmosphere, it is very difficult to perform direct measurements of reactions taking place at such interfaces. The expected presence of a liquid-like region at the borders of ice crystals, including the air interface but also grain boundaries and liquid inclusions within the ice crystal (vide infra), makes it a convenient assumption that chemistry takes place as though in a true liquid environment. Indeed, experiments that aim to probe chemical reactions within snowpacks have indicated that

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liquid phase kinetics are often appropriate to use in modeling snow and ice chemistry.[4−9]

Our work has focused on understanding chemical processes taking place at the air−frozen aqueous interface. We have developed laser spectroscopic probes and used them to interrogate many aspects of the chemistry that takes place there. This Account will describe some of this work and support our conclusion that frozen water surfaces display very different chemical natures depending on whether the aqueous substrate is composed of freshwater or contains enough salt for the frozen system to be well represented by a multicomponent phase diagram.

2. STRUCTURE OF AIR−ICE INTERFACES

Even at temperatures well below freezing, there exists a molecular-level disordered region at the ice interface with air that is not predicted by the Gibbs phase rule.[10] The existence of such a "premelting layer" on ice has been confirmed by several techniques such as atomic force microscopy, ellipsometry, and sum-frequency generation (SFG) spectroscopy.[2,11−21] Although studied for several decades, the important properties of this layer (e.g., the temperature dependence of its thickness, the temperature of onset, molecular orientation, density, viscosity) are still not well characterized or understood, with results that often depend on the method used to probe the interface.[2] Despite this incomplete understanding, it is clear that the surface of ice and snow represents a different environment from the bulk, frozen, underlying sample.

Because water molecules at the air−ice interface are more dynamic and disordered than those in the bulk ice matrix (i.e., more "liquid-like"), the disordered region at the ice surface is frequently referred to as the "quasi-liquid layer" (QLL). The notion that a "liquid-like" region exists at the air−ice interface has provided the rationale for using aqueous phase chemistry to interpret ice/snow chemistry. However, there is growing consensus that the disordered surface region has properties that are distinct from liquid water[2,3] and indeed may consist of different phases itself.[22] Therefore, other terms such as "disordered interface" (DI) are gaining popularity.[3,10]

In the presence of soluble salts at temperatures between the freezing point of water and the solution eutectic temperature, two phases coexist. For dilute salt solutions, these are a pure ice phase and a liquid brine phase. If the amount of brine (governed by the total salt concentration in the system) is large enough, the liquid phase may wet the ice−air interface. Because this is a true liquid phase, unlike the DI described above, the saltwater ice−air interface (designated hereafter as the SWI−air interface) may exhibit very different properties from those shown by freshwater ices (designated hereafter as FWI), described above. While the FWI−air interface is "wetted" by the DI,[10] which may not be appropriately described as a true liquid, the SWI−air interface *is* likely covered by a thermodynamically predicted brine, which is a true liquid. Brine may be located in the ice interior as well (at grain boundaries, triple junctions, or trapped liquid pockets). The location of the brine, as well as its abundance, will have important consequences for chemistry occurring at the air−ice interface.

3. PROBING THE AIR−ICE INTERFACE

Our work has mainly used glancing-angle laser-induced fluorescence (LIF) and glancing-angle laser Raman spectroscopies to probe the air−ice interface. The glancing-angle LIF approach was first described for water surfaces by Mmereki and Donaldson[23] and the glancing-angle Raman approach by Kahan et al.[24] In brief, fluorescence or Raman scattering is induced at the sample surface by a linearly polarized laser beam that impinges the surface at a very shallow, glancing angle (>87° from the surface normal). Unlike methods such as surface second-harmonic or sum-frequency generation, neither of the glancing-angle approaches is restricted to probing interfacial species. The surface region sensitivity of the technique relies on the fact that at such high angles of incidence, the majority of the input radiation is reflected at the interface and so interacts only with the uppermost layers of the substrate.[24] In the case of glancing-angle LIF, we achieve additional surface sensitivity through the use of surface-active fluorescent probe molecules.

To test the depth of probing, we have conducted many different experiments, on both liquid and solid water surfaces. Using fluorescence, we have measured adsorption isotherms of anthracene, pyrene, harmine, and acridine at the air−water interface and noted significant changes in adsorption, reactivity, and spectral properties in the presence of monolayer and submonolayer quantities of soluble surfactants (e.g., octanol).[23,25−30] This suggests a probe depth for such strongly surface-active molecules of perhaps tens of water layers.[23,26] At the air−ice interface, we assume a similar probe depth.

The much lower sensitivity of Raman scattering requires higher concentrations of probe species (except for water, the solvent) and probably probes a thicker layer than fluorescence. The dependence of the glancing-angle Raman intensity on bulk solute concentration for both DMSO and nitrate anion clearly differ from the corresponding bulk intensity dependences; the DMSO adsorption isotherm tracks that extracted from surface tension measurements.[31] This suggests that the glancing-angle Raman probe interrogates depths similar to those explored using surface tension techniques, perhaps tens to hundreds of water layers.

4. THE CHEMICAL NATURE OF THE INTERFACE

4.1. The Pure Ice Surface

Glancing-angle Raman spectra acquired at the air−liquid interface show an OH-stretching signature indicative of reduced hydrogen bonding there.[24] Figure 1 shows spectra of the OH-stretching band in bulk liquid water, at a liquid water surface, in bulk ice, and at an ice surface.[24] The relative intensity of the shoulder at ∼3200 cm^{-1} to the peak at ∼3450 cm^{-1} gives information on the relative extent of hydrogen bonding in the local environment.[24] The high shoulder-to-peak ratios seen in the bulk water and ice spectra indicate significant hydrogen bonding, while the low ratio at the liquid water surface indicates less extensive hydrogen bonding. The extent of hydrogen bonding we infer from the ice surface spectrum falls between that for bulk liquid water and that at a liquid water surface.

The existence of more extensive water−water hydrogen bonding at the air−ice interface than at the liquid water surface implies that different hydrogen-bonded solvation environments exist at the two surfaces. For solutes that are only poorly solvated, the smaller availability of "free" water at the frozen surface can lead to a change in the solvation preference, from full hydration to self-association. We suggest that aromatic species interact less favorably with ice surfaces than with liquid water surfaces because of the lack of "free" OH bonds on ice.[32]

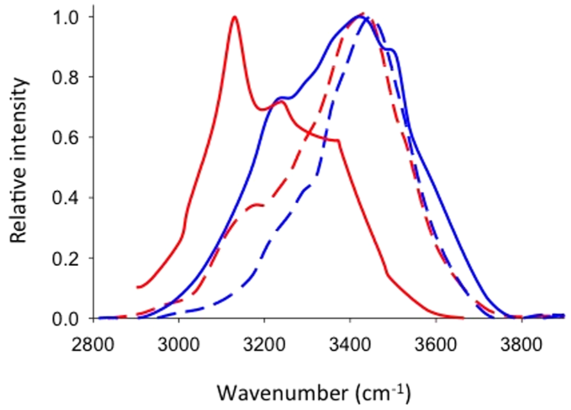

Figure 1. Intensity-normalized Raman spectra of the OH-stretching region of room temperature bulk water (solid blue trace), the air—water interface (dashed blue trace), bulk ice at −20 °C (solid red trace), and the air—ice interface at −15 °C (dashed red trace). Reproduced from ref 24 with permission. Copyright 2007 American Chemical Society.

Self-association of small aromatics is seen readily on the frozen surface, even at (prefreezing) bulk concentrations that show no such effects at the liquid water surface.[33−35] Figure 2a shows emission spectra of naphthalene in aqueous solution and at an ice surface, and Figure 2b shows excitation spectra of benzene in aqueous solution and at an air−ice interface. Clear differences are observed in the two environments. The spectra observed at air−ice interfaces, for naphthalene and benzene, as well as for other PAHs such as phenanthrene and anthracene, resemble spectra of crystalline PAHs. This general observation is seen not only for aromatic species frozen from solution but also when the aromatic is introduced to ice surfaces from the gas phase, even at surface loadings below 10% of a monolayer.[33,34,36]

Although some of the self-association may be a consequence of a concentration enhancement at the interface due to exclusion of solutes during freezing, a molecular dynamics (MD) study supports the hypothesis that interactions between aromatics and supercooled liquid water are more energetically favorable than those between the aromatic and ice at the same temperature. Specifically, naphthalene molecules at ice and at supercooled water surfaces at the same temperature interact less favorably with ice surfaces than with water surfaces; this leads to the formation of naphthalene−naphthalene complexes at ice surfaces, which stabilize the naphthalene−ice interaction significantly.[32] Other recent MD and Monte Carlo (see especially Figure 7 of ref 38) simulations also imply such behavior at the FWI−air interface even at submonolayer coverages, further supporting the spectroscopic results.[37−39]

4.2. The Frozen Salt Water Interface

The situation seems different for the air interface with frozen salt solutions, however. As discussed above, at temperatures above the eutectic point for the specific salt solution, thermodynamics predicts a two-phase system: frozen water and a liquid brine whose concentration is determined by the temperature and whose relative amount is governed by the system composition. Glancing-angle Raman spectra of the water OH-stretching band acquired at the SWI−air interface show differences from those measured at the FWI−air interface.[24] As shown in Figure 3, freezing a 0.01 mol L^{-1} NaCl solution to 258 K leads to a reduction in the relative intensity of the ∼3200 cm^{-1} shoulder, suggesting a less hydrogen-bonded, more liquid surface-like environment at the SWI surface compared with the FWI surface, consistent with the formation of a true liquid brine at the air−ice interface.

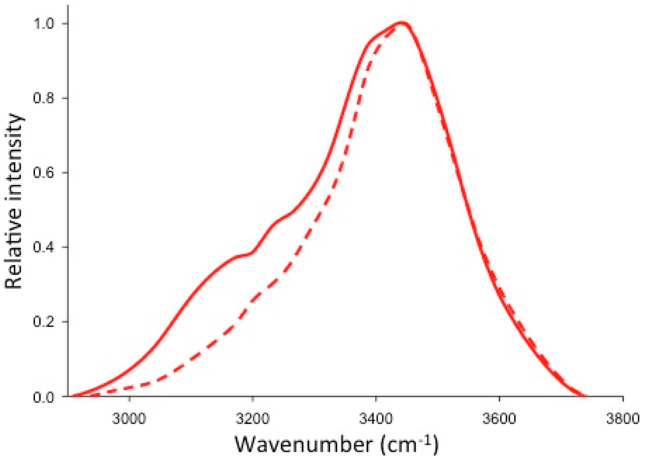

Figure 3. Intensity-normalized Raman spectra of the OH-stretching region at the surfaces of pure ice (solid trace) and a frozen 0.01 mol L^{-1} NaCl solution (dashed trace), both at −15 °C. Reproduced from ref 24 with permission. Copyright 2007 American Chemical Society.

Further evidence for a difference in surface properties between FWI and SWI is provided by differences in the fluorescence quenching of harmine. This compound serves as a

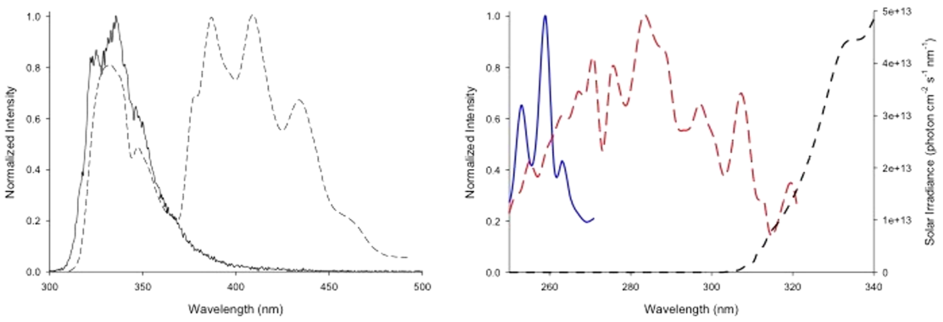

Figure 2. (a) Intensity-normalized naphthalene fluorescence spectra at the water surface (solid line) and on ice (dashed line). Reproduced from ref 33 with permission. Copyright 2007 American Chemical Society. (b) Excitation spectra of benzene in aqueous solution (blue trace) and the surface of a frozen benzene solution (red trace). The black trace is the average solar irradiance at earth's surface for Toronto in midwinter at noon (right axis). Taken from ref 34 with permission. Copyright 2010 American Chemical Society.

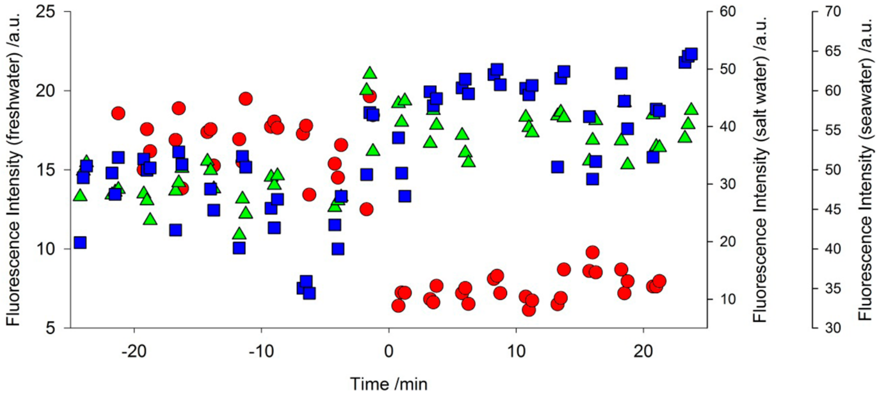

Figure 4. Harmine fluorescence intensity (in arbitrary units) measured at 430 nm following excitation at 320 nm plotted as a function of time relative to the freezing of a freshwater sample (red circles, left axis), salt water sample (green triangles, inner right axis), and artificial seawater sample (blue squares, outer right axis). Reproduced from ref 40 with permission. Copyright 2012 European Geosciences Union.

convenient probe molecule because its fluorescence is not strongly quenched in the presence of halide anions. Figure 4 shows that upon freezing fresh water solutions of harmine its absolute fluorescence intensity at the FWI−air interface decreases significantly, indicating that it experiences a different local environment than at the liquid surface. By contrast, when saltwater solutions are frozen, no change in the fluorescence quenching is observed at the SWI−air interface.[40] This implies that harmine's local environment remains unchanged at the frozen salt solution surface from what it experienced at the liquid interface. Such an inferred liquid-like environment at the frozen saltwater surface is consistent with an excluded brine being present there, as outlined above. The presence of such a true liquid at the interface would reasonably be expected to have significant effects on chemistry that takes place there.

5. EXCLUSION OF SOLUTES DURING FREEZING

The work outlined in the previous section strongly suggests that the FWI−air and SWI−air interfaces are chemically quite different and thus could exhibit different chemical effects. Here we discuss work that addresses our understanding of how a concentrated brine layer is formed via exclusion of salts from freezing solutions.

Direct evidence for freezing-induced exclusion of inorganic salts to the air−ice interface comes from the observation of an interfacial concentration increase following freezing of the solution. We used glancing-angle Raman to study the exclusion of nitrate anions to the air−ice interface during freezing.[41] As illustrated in Figure 5, at the solution concentration used for this study, nitrate is not easily detectable at the air−water interface, but it is quite apparent at the frozen solution surface. We infer that the nitrate anion is excluded to the air−ice interface during freezing. Comparison of the Raman intensity of the excluded nitrate to that measured at the liquid water interface[41] reveals that the effective concentration of the excluded anion is much lower than that predicted using an equilibrium thermodynamic approach[42] and is independent of temperature.

The low measured surface concentration suggests that nitrate prefers to remain in liquid pockets or other interfacial regions within the bulk; the reason for this is not clear. Domine et al. also address several shortcomings of bulk thermodynamic approaches (such as those presented in refs 42 and 43) to predicting concentrations at the air interface of frozen water systems, particularly the lack of surface energy terms in their formulations.[10] Clearly, more work is required to understand how properties of ions (charge, size, polarizability, water surface activity) influence their exclusion to the air−ice interface during freezing. Additionally, further work is required to understand whether and how this exclusion may be influenced by the presence of other solutes, both organic and inorganic.

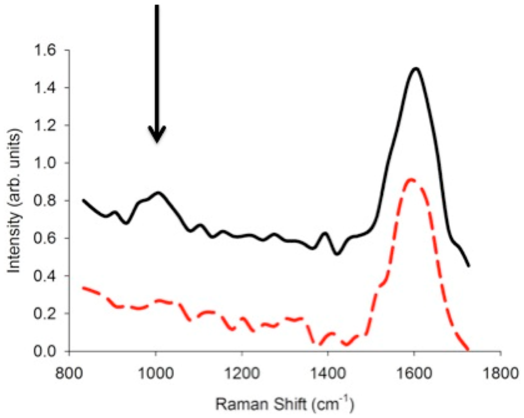

Figure 5. Glancing-angle Raman spectra acquired at the surface of a dilute $Mg(NO_3)_2(aq)$ sample at room temperature (dashed line) and after freezing to 268 K (solid line). The nitrate symmetric stretch feature near 1000 cm^{-1} is indicated with an arrow. Adapted from ref 41 with permission. Copyright 2011 American Chemical Society.

6. DEPOSITION OF GAS PHASE ACIDS AND BASES

Although uptake of gas phase acids by ice has been the subject of considerable investigation,[44,45] such studies have concentrated on the loss of acid from the gas phase only. We studied pH changes taking place at the air−ice interface using glancing-angle LIF in conjunction with the surface-active, pH-sensitive fluorescent dyes acridine and harmine.[40,46] For acridine ($pK_a \approx 4.5$), the ratio of intensities at 430 and 470 nm (henceforward the 430/470 ratio) in the emission spectrum is related to the relative proportion of the neutral and protonated forms, respectively, and hence the local pH.[28] A similar approach is used for harmine ($pK_a \approx 7.7$), although in this case the ratio of intensities at 290 and 320 nm (the 290/320 ratio) in its excitation spectrum is used.

Figure 6a shows the acridine 430/470 ratio measured at the FWI−air interface plotted as a function of prefreezing pH. Freezing a solution initially containing HCl or HNO_3 leaves the

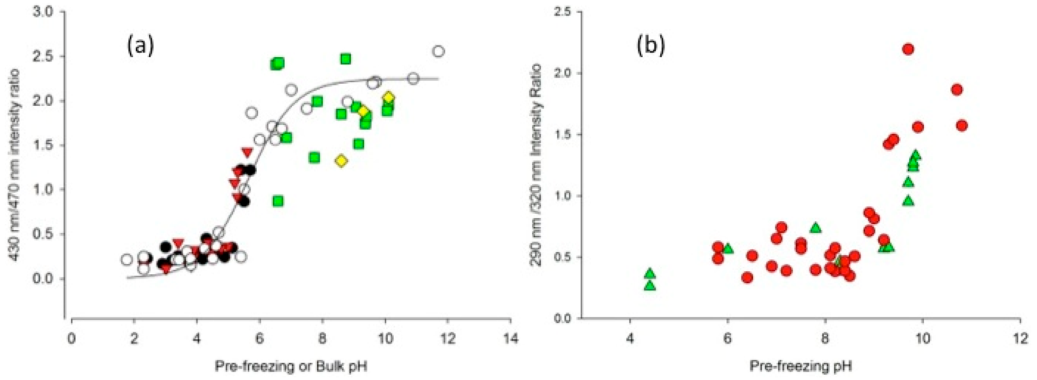

Figure 6. Fluorescent indicator intensity ratios as a function of prefreezing pH. (a) Acridine 430/470 intensity ratios. The liquid surface results are shown as open circles. At the frozen surface (solid symbols), samples had prefreezing pH adjusted with HNO_3 (red triangles), HCl (black circles), or NaOH (green squares) Reproduced from ref 46 with permission. Copyright 2012 American Chemical Society. (b) Harmine 290/320 intensity ratio at the frozen freshwater surface (red circles) and at the frozen salt water (0.5 M NaCl) surface (green triangles). Reproduced from ref 40 with permission. Copyright 2012 European Geosciences Union.

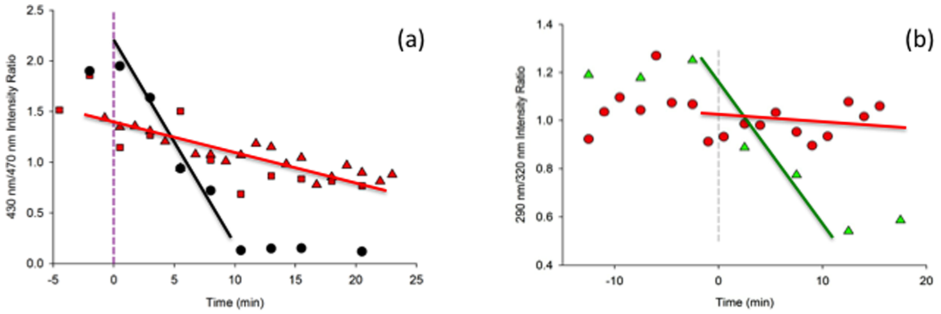

Figure 7. (a) Acridine 430/470 intensity ratio as a function of time following introduction of HCl(g) (at t = 0) above the liquid surface (black circles) and the frozen surface (two trials shown in red). Adapted from ref 46 with permission. Copyright 2012 American Chemical Society. (b) Harmine 290/320 intensity ratio measured at the frozen freshwater surface (red circles) and at the frozen salt water (0.5 M NaCl) surface (green triangles) as a function of time following introduction of HCl(g) (at t = 0). Adapted from ref 40 with permission. Copyright 2012 European Geosciences Union.

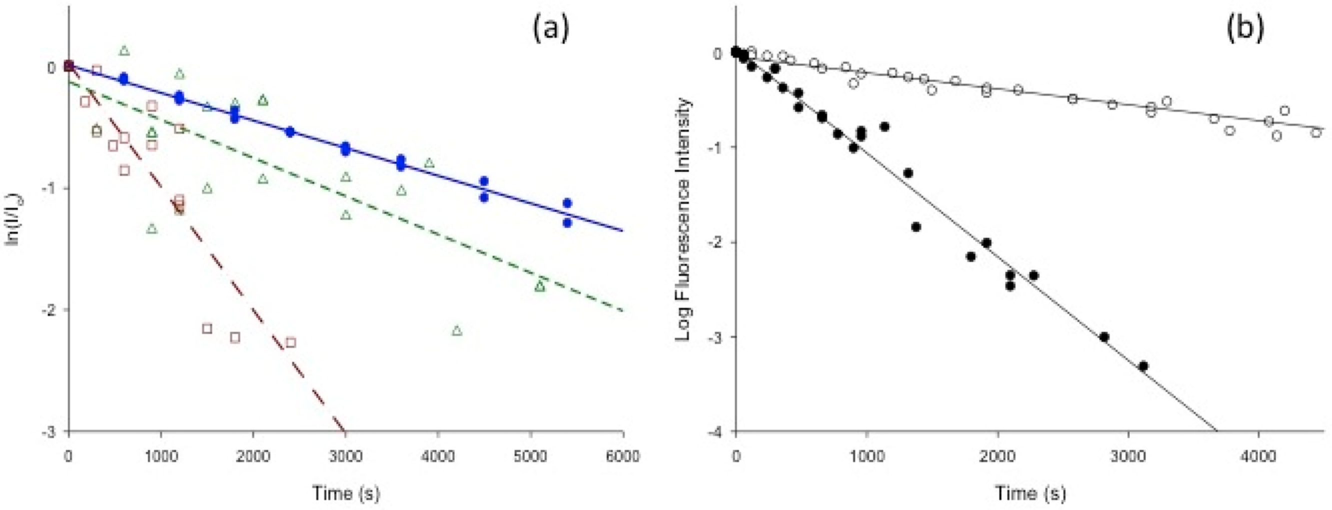

Figure 8. (a) Decay profiles for anthracene photolysis in room-temperature aqueous solution (blue circles), in ice cubes (green triangles), and in ice granules (brown squares). The straight lines are linear fits to the data, and indicate first-order decay. Taken from ref 49 with permission. Copyright 2010 American Chemical Society. (b) Photolytic loss of anthracene at the water surface (hollow circles); and at the ice surface (filled circles). Reproduced from ref 33 with permission. Copyright 2007 American Chemical Society.

pH of the DI largely unchanged with respect to that measured at the corresponding liquid surface. Furthermore, as illustrated in Figure 6b, the harmine 290/320 intensity ratios observed at the FWI and SWI surfaces are essentially identical, indicating that there is no difference in the exclusion of hydronium or hydroxide to the air−frozen water interface when salty vs freshwater solutions are frozen.[40] We note that because we cannot limit the probe depth to the uppermost one or two water layers, the present results do not directly address the issue of whether these layers experience a change in their pH with respect to the bulk.

This suggests that the surface and bulk pHs of frozen fresh or salt water may be treated as identical. However, deposition of gas phase HCl or NH_3 to these surfaces shows a strong dependence on the nature of the interface. Figure 7a shows that the pH at the FWI−air interface, as inferred from the acridine 430/470 ratio, decreases very slowly upon addition of HCl(g), in contrast to what is seen at the liquid water surface.[46] The same result is obtained using the harmine 290/320 ratio.[40] Melting the sample and measuring the bulk pH reveals that the sample does indeed take up the acid, achieving a bulk pH < 3. Refreezing the melted sample gives the expected result, that is, the low pH measured at the liquid surface is also seen in the refrozen sample.[46] We conclude that freezing and deposition processes have different impacts on pH at the air−ice interface and that the FWI−air interface does not behave as if it were an air−water interface. The difference in this case may be related to the different hydrogen bonding environments in the two surface regions, as discussed above. It is interesting to note that changing the hydrogen bonding structure of liquid solutions may also strongly affect the surface interactions and uptake of gas phase HCl.[47]

This result stands in strong contrast to what is seen at a frozen salt water sample, shown in Figure 7b. Deposition of HCl(g) to the surface of a frozen 0.5 M NaCl(aq) solution leads to a decrease in surface pH, as inferred from the harmine 290/320 ratio; this decrease is consistent with the final bulk pH. That is, the SWI surface behaves very differently from the FWI surface, as if were covered by a "true" liquid, consistent with the presence of an excluded brine. Additional experiments in which NH_3(g) is deposited to the frozen salt water surface give the same result.[40]

7. PHOTOCHEMICAL REACTIONS AT FROZEN INTERFACES

It had long been assumed that photolysis of aromatic compounds in snow and ice matrices is well described by aqueous-phase kinetics. However, our work has shown that photolysis rates measured at the FWI surface are considerably faster than those seen in aqueous solution or within the ice matrix,[33,44] whereas those measured at SWI−air interfaces match the aqueous result.[48]

Figure 8 displays anthracene photolysis kinetics. Figure 8a shows concentration vs time plots for photolysis of this compound frozen within an ice matrix composed of solid (2 cm)^3 ice cubes, the result when the ice cube is crushed into granules—increasing the surface-to-volume by about 4.5 times—and in liquid solution. Photolysis in ice cubes occurs at a similar rate as in liquid water, while photolysis in the crushed ice granules is much faster.[49] Figure 8b shows the loss of anthracene at FWI−air and air−water interfaces during exposure to actinic radiation, measured using glancing-angle fluorescence.[33] Photolysis is much more rapid at the FWI−air interface than in liquid water or at the air−water interface. Similar rate enhancements versus the aqueous result are observed for benzene, naphthalene, and harmine at the FWI surface.[33,34,48] These results, in conjunction with the surface-to-volume dependence, provide strong evidence that photolysis of these aromatic compounds at FWI surfaces is significantly more rapid than that seen either within the ice matrix or in aqueous solution.

The situation is quite different at the SWI−air interface. Figure 9 shows the photolysis rate constants of harmine in aqueous solution and at frozen surfaces as a function of prefreezing NaX concentrations. In solution, the photolysis kinetics are independent of NaCl concentration. As mentioned above, harmine photolyzes more rapidly at the FWI surface than in aqueous solution. However, as NaCl concentrations increase, photolysis at the frozen surface slows, until it eventually levels off. The rate constant measured in this plateau region is the same as that measured in aqueous solution.[48] This observation is again consistent with our understanding that the SWI interface presents a very different (and more liquid-like) environment than that obtained at the FWI surface. Additionally, it provides a dramatic indication of the sensitivity of the surface kinetics to the chemical properties of the local environment. By performing the experiment at a lower temperature or by replacing NaCl with NaBr in solution, we are able to explore different regions of the salt−water phase diagram, giving rise to different amounts of brine and hence different photolysis rates.[48]

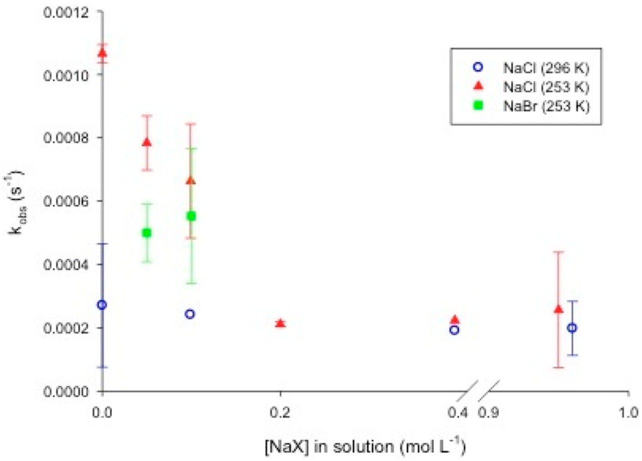

Figure 9. Rate constants for harmine photolysis as a function of salt concentration in aqueous solution at room temperature, at the surface of frozen aqueous NaCl solutions, and at the surface of frozen aqueous NaBr solutions. Taken from ref 48 with permission. Copyright 2010 European Geosciences Union.

As noted in section 4, aromatics tend to self-associate at the FWI−air interface. In some cases, shifts in the absorption spectrum due to such self-association at ice surfaces can explain the enhanced photolysis rates there. Figure 2b shows excitation spectra of benzene in dilute aqueous solution and at the surface of a frozen dilute aqueous solution. At the FWI−air interface, self-association causes the absorption spectrum to shift to longer wavelengths where there is significant actinic radiation. Such a spectral shift is most probably responsible for the enhanced photolysis rate for benzene at the frozen interface.[34] However, this is not the case for all aromatics: the photolysis kinetics of anthracene are enhanced on ice, yet they display the wavelength dependence expected for the monomeric absorption spectrum.[33] Likewise harmine displays faster photolysis kinetics at FWI surfaces, but its excitation spectrum there does not extend to longer wavelengths than that of the monomer.[48] Temperature also does not significantly influence the photolysis kinetics of aromatic compounds.[33]

8. SUMMARY AND OUTLOOK

In the foregoing, we have outlined some of our results on chemical interactions at air−frozen aqueous interfaces. A few clear conclusions, as well as several unanswered questions, arise from these findings. First, it seems fairly well established that freezing halide salts gives rise to a liquid brine present at the air interface and that chemical interactions at such interfaces are well described by those taking place in a true liquid (high ionic strength) environment. It is possible to "tune" the importance of such brine-surface chemistry by altering solution properties to vary the amount of brine present. Other salts (at least nitrate) and organic compounds of weak solubility are also excluded to the air interface during freezing of their aqueous solutions; however it is not clear to what extent these processes agree with current (thermodynamic) models.

It is also clear that the air−ice interface of freshwater systems presents a very different chemical environment from both that of the frozen salty surface and that of liquid water. These differences are manifested in the self-association of weakly soluble organics, their photolysis kinetics, and the behavior of deposited acids at such interfaces. Although we do not know the reason(s) for these differences, it does appear to be established that the molecular arrangement and bonding properties of the water molecules present there are quite different from those pertaining to the liquid surface. Exploring these differences will require a concerted experimental and theoretical effort that is just now beginning to appear feasible.

Apart from its fundamental interest, understanding processes at the interface between air and frozen water is of importance to our ability to model and predict atmospheric and condensed phase chemistry in regions where snow and ice are present. Our findings have some real implications for the kinds and relative importance of chemical processes in such environments. For example, the photolysis lifetimes of pollutants such as PAHs might be quite different in regions covered with freshwater and saltwater ice, and the lower-than-predicted exclusion of nitrate to the air interface changes our understanding of its presence there and thus its importance in photochemical oxidative cycles. The recent finding that the presence of halide anions influences the concentration of nitrate at liquid water surfaces[50,51] introduces a new set of questions about how interactions among the various solutes that are present in a freezing aqueous sample may play a role in the interfacial chemistry. There is much to do!

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Notes

The authors declare no competing financial interest.

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