Direct Observation of Segregation of Sodium and Chloride Ions at an Ice Surface

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Distribution of electrolyte ions near the surface of water or ice is a subject of interest in both fundamental chemistry and atmospheric chemistry of sea-salt aerosols and ice particles. The ion distribution at the surface of these particles may affect their reaction with ozone and organic species in the troposphere and the generation of reactive halogen species.[1, 2] In early studies, the surface of aqueous solutions containing simple electrolytes such as alkali halides was thought to be deficient of ions, as inferred from the surface tension of solutions.[3] Molecular dynamics (MD) simulations have been widely employed since the 1990s to study the molecular details of solvation and segregation of atomic ions in water clusters.[4–8] MD calculations[6–8] predict that the large and polarizable anions are more readily available at the surface than the small nonpolarizable cations, in both water slab models[6] and clusters of finite sizes.[6, 7, 9] Photoelectron spectroscopic studies[10] of anionic water clusters in the gas phase support the surface residence of the larger halide anions by comparing the ionization energies with calculations. Further studies of the anionic clusters \[X(H_2O)_{1–5}, X=\text{F, Cl, Br and I}\] using vibrational spectroscopy[11–13] indicate that the larger halides (Cl\(^–\), Br\(^–\) and I\(^–\)) are solvated at the surface of water clusters. The spectra from clusters with the larger halides reveal a hydrogen-bonding network of water molecules, which supports surface solvation of anions, whereas the spectra from the F\(^–\)-containing clusters lack such hydrogen-bonding features.[12b, 13]

A limited number of experimental studies were performed to investigate the ion distribution at the surface of real aqueous solutions, and basically none at ice surfaces. Morgner and co-workers[14] measured He(I) photoelectron spectra from the surface of concentrated aqueous solutions of CsF and observed that the salt concentration is strongly depleted in the surface region. MD simulations from the same group[15] explain the phenomena by the circumstance that the ions near the surface mostly keep their first solvation shell intact. Using X-ray photoelectron spectroscopy and scanning electron microscopy, Ghosal et al.[16] observed selective segregation of Br\(^–\) ions to the surface of a NaCl crystal, which was slightly doped with Br\(^–\) ions, under conditions of relative humidity, where the condensed water films caused partial dissolution of the crystal surface. Their results provide the first experimental evidence for preferential segregation of large halide anions to the surface of mixed alkali halides. More recently, vibrational sum frequency generation spectroscopy for sodium halide solutions[17]

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showed that the hydrogen-bonding network of water molecules in the surface region is weakened for NaBr and NaI aqueous solutions, suggesting higher concentrations of Br$^-$ and I$^-$ in the surface region relative to the bulk. Despite the long attention, direct experimental verification of the ion distribution at the water surface remained unfulfilled, due to the difficulties inherent in probing the highly disordered surface region of water, which has thickness of a few water molecules at most.

Herein, we report observations on the segregation process of Na$^+$ and Cl$^-$ ions present at the surface of amorphous ice films for temperatures of 105–140 K. The concentrations of Na$^+$ and Cl$^-$ ions at the surface are measured as a function of temperature to reveal their vertical distributions. Owing to the low mobility of ions on ice films, the measurements provide a unique opportunity to take a snapshot of the segregation process of solvated ions.

Details for low-energy sputtering (LES) and Cs$^+$ reactive ion scattering (RIS) experiments have been described previously.$^{[19]}$ Briefly, in the ultrahigh vacuum (UHV) chamber with a base pressure of 1.0 × 10$^{-10}$ Torr, a Cs$^+$ beam with an incident energy of 10–35 eV and a current density of 2–3 nA cm$^{-2}$ was scattered at the sample surface to be analyzed. The beam incidence and the detector angles were both 45$^\circ$ with respect to the surface normal. A quadrupole mass spectrometer (QMS; ABB Extrel) measured both positive and negative ions emitted from the surface with its ionizer filament switched off. The emitted ions were composed of reflected Cs$^+$ primaries, RIS products which are the association products of Cs$^+$ with neutral molecules at the surface, and LES ions which are the pre-existing ions ejected from the surface by the Cs$^+$ impact. The mechanisms of RIS and LES processes on thin ice films are explained in refs. [19b, 20].

The substrate was a Ru single crystal with a (0001) face, and its temperature could be varied in the range of 90–1500 K. Ice films were deposited on a clean Ru(0001) surface at 130 K by backfilling the chamber with D$_2$O vapor at a pressure of 1.0 × 10$^{-8}$ Torr—a condition that normally produced nonporous, amorphous films.$^{[21]}$ D$_2$O (Aldrich, 99.96% purity, melting point = 1038 K) was degassed by freeze-vacuum-thaw cycles before introduced into the chamber. The ice films were prepared to a thickness of a few water molecules at most. The ice films were deposited on a clean Ru(0001) surface at 130 K by backfilling the chamber with D$_2$O vapor at a pressure of 1.0 × 10$^{-8}$ Torr—a condition that normally produced nonporous, amorphous films.$^{[21]}$

Figure 1 shows LES spectra obtained from a D$_2$O ice film, on which NaCl was adsorbed at 120 K to a coverage of 0.8 monolayers (ML). The Cs$^+$ beam energy was 35 eV. The ice film was four bilayers (BLs) thick and prepared by condensing D$_2$O vapor on Ru(0001) at 130 K. The spectra were obtained 2 min after the NaCl exposure. 1.0:0.63:0.16. The negative ion spectrum in Figure 1b shows Cl$^-$ ions (m/z = 35 and 37 amu/charge) as the only major peak. Its monohydrated signal (ClD$_2$O$^-$) constituted less than 4% of the Cl$^-$ intensity and was almost invisible in the displayed scale. All these peaks seen at such low energy were attributed to emission of pre-existing ions at the surface, produced by spontaneous dissociation of NaCl to Na$^+$ and Cl$^-$ and hydration of these ions. This interpretation is based on the LES threshold measurements.$^{[22]}$ Cs$^+$ beams with energies below 40 eV do not produce significant Na$^+$ and Cl$^-$ intensities by collisional dissociation of NaCl. Collisional ionization of water molecules does not occur either at such energies.$^{[19b, d]}$ Another feature noticeable in the spectra is that Na$^+$ ions have higher propensity for being ejected as hydrated cluster ions than Cl$^-$ ions. The observation must be related to the stronger binding energy of Na$^+$ ions to water molecules (105 kJ mol$^{-1}$) than that of Cl$^-$ (61 kJ mol$^{-1}$).$^{[24]}$ In addition, if Na$^+$ ions preferentially migrate from the surface to the interior of the film, Na$^+$ ions can be more efficiently solvated and be ejected in hydrated forms.

Figure 2 shows RIS spectra obtained from the NaCl-adsorbed ice films. Note that RIS detects neutral species at a surface, whereas LES detects ions.$^{[16]}$ Therefore, RIS and LES investigations are complimentary with each other, the former identifying the neutral molecular states of electrolytes on the surface and the latter analyzing the ionized dissociated states. The sample of Figure 2a was prepared just as that of Figure 1, by exposing NaCl vapor on a D$_2$O film with a thickness of four BLs. The spectrum shows RIS products at m/z = 153, 173, 191 and 193 amu/charge, in addition to the reflected Cs$^+$ primaries at m/z = 133 amu/charge. The peaks at m/z = 153, 173 and 193 amu/charge were Cs(D$_2$O)$^{m+}$ (n = 1–3), representing the
pickup of D₂O molecule(s) by the Cs⁺ projectile. The peaks at m/z = 191 and 193 amu/charge were attributed to CsNaCl⁺. Possibly they are produced from NaCl that remained undissociated at the surface. The CsNaCl⁺ intensity was about 2% of the CsD₂O⁺ intensity, indicating that the undissociated portion of NaCl was quite small.

In Figure 2b, an ice film was prepared, only to a thickness of one BL, in order to examine the possible influence of the Ru substrate on the NaCl dissociation. The CsNaCl⁺ intensity slightly increased compared to that in Figure 2a, but the increase was not drastic. The observation suggested that an ice film with a thickness of one BL was sufficient to ionize the major portion of NaCl on the surface. A new peak was seen at m/z = 174 amu/charge, which was assigned as CsNaOD⁺ (the pickup of sodium hydroxide). This peak was not due to NaH₂O⁺, because the spectrum did not show its major isotope signal, CsNaD₂O⁺. We interpreted that NaOD species resulted from the reaction between D₂O and Na atoms, the latter being formed by neutralization of Na⁺ at the Ru surface of low water coverage. It is suggested that D₂O might partially dissociate to OD and D on Ru(0001). However, the absent CsOD⁺ signal (m/z = 151 amu/charge) in Figure 2 showed that the population of surface OD species was negligible, and the CsNaOD⁺ signal could not originate from this species. The Cs(D₂O)ₓ⁺ peaks in Figure 2b were accompanied by shoulder peaks at masses lower by 1 amu, indicating that the surface was covered by a small amount of HDO formed possibly by H/D exchange reactions between D₂O and H₂O impurities from the residual gas. When Figures 2a and 2b were compared, the substrate-originating peaks such as CsNaOD⁺ and Cs(HDO)ₓ⁺ were almost absent from Figure 2a, indicating that the substrate effects were negligible on ice films with a thickness of four BLs.

An important feature of the RIS and LES techniques is their shallow probing depth. RIS has an effective probing depth of one BL for water molecules on ice films when the incident Cs⁺ energy is below 25 eV. In LES experiments on ice films, a water overlayer with a thickness of one BL effectively blocks the emission of Na⁺ ions and their hydrated clusters from the surface. The sensitivity of LES to the outermost surface layer is considered to be due to the inherent nature of ion sputtering. MD simulations indicate that for sputtering of Cu single crystals by 600-eV Ar⁺ beams, 90–95% of the sputtered atoms originate from the first layer of the surface, even though the Ar⁺ impact induces significant movement of deeper layer atoms. Sputtering at lower energy (<100 eV) further reduces the emission of subsurface particles. These effects seem to be responsible for the observed first-layer sensitivity of LES on ice films, though quantitative comparison of the sputtering depth based on energy scaling may not be feasible for the metal and ice surfaces.

In Figure 3a, populations of Na⁺ and Cl⁻ ions at the surface of ice films were measured as a function of temperature in a range from 100–140 K. The LES intensity of the sodium ion in Figure 3a represents a summation of all intensities of Na⁺ ions and its hydrated species; the same applies for the chlorid ion. For each measurement at a different temperature a freshly prepared film was used to avoid contamination and ion segregation, possibly induced by a prolonged beam exposure. The sodium ion intensity gradually decreased with increasing tem-
perature, whereas the chloride ion intensity remained almost at the same level. The result indicated that Na\(^+\) ions move from the surface to the interior of the film at elevated temperatures. Thermal desorption of Na\(^+\) ions or NaCl did not occur at these temperatures, as we checked the amount of NaCl left on the Ru substrate after evaporation of the ice films. The constant Cl\(^-\) ion intensity revealed that Cl\(^-\) ions stayed at the surface without inward migration.

Figure 3b presents the relative abundance of sodium and chloride ions at the surface, which was converted from the results of Figure 3a according to Equation (1):

\[
l_{\text{rel}}(\text{Na}) = \frac{C_s(\text{Na})}{(C_s(\text{Na}) + C_s(\text{Cl}^-))}
\]

Here, \(l_{\text{rel}}(\text{Na})\) is the relative abundance of Na\(^+\) ions, and \(C_s(\text{Na})\) is the surface concentration of sodium ions corresponding to \(2\text{Na}(\text{D}_2\text{O})_m^+\) \((m \geq 0)\). Calculations of the surface concentrations from the LES intensities required knowledge of the relative LES yields for Na\(^+\) and Cl\(^-\) ions on ice films. For this, we calibrated the Na\(^+\) and Cl\(^-\) intensities from the ice films against those from an NaCl-deposited Ru(0001) surface at which Na\(^+\) and Cl\(^-\) existed in equal amounts. Through the calibration procedure, we obtained \(l_{\text{rel}}(\text{Na}) = 0.55 \pm 0.05\) and \(l_{\text{rel}}(\text{Cl}^-) = 0.45 \pm 0.05\) on ice films at 105 K. These values agreed with the Na\(^+\)/Cl\(^-\) ratio of 1:1 expected in the absence of ion segregation at the ice surfaces at sufficiently low temperatures. Indeed, the measured Na\(^+\)/Cl\(^-\) ratio remained almost constant with little deviation from 1:1 over the temperature range of 105–115 K, supporting that Na\(^+\) and Cl\(^-\) ions stayed frozen at the surface at these temperatures. Subsurface migration of Na\(^+\) ions became significant only at temperatures > 120 K, and its strong dependence on temperature indicated that the migration process was thermally activated. At 140 K, more than 90% of the Na\(^+\) ions appeared to migrate into the subsurface region.

The Na\(^+\) and Cl\(^-\) distribution measured at an ice surface can ultimately be related to that at a liquid water surface. The thermodynamic state of amorphous ice is mostly at extrapolation from liquid water. Water molecules near the ice surface are somewhat mobile; they can undergo self-diffusion and assist movement of ions in higher temperature regions as those studied herein.\(^{[18]}\) In this respect, much resemblance can be expected thermodynamically for the ion segregation processes occurring at an ice surface and a liquid water surface. Kinetically, however, ion mobility is extremely slow near the ice surface compared to that in liquid water.\(^{[16,18]}\) Owing to the very slow motion of ions near the ice surface, the observed ion distribution represents a snapshot of ion segregation in progress. The ice film offers a unique opportunity to monitor the kinetics of ion segregation which would be too fast in liquid water to be measured in real time.

The inward migration of Na\(^+\) ions agrees with the results from MD simulations for aqueous solutions and water clusters containing sodium halides,\(^{[4–8]}\) which predict that Na\(^+\) ions are practically absent from the water surface at 300 K.\(^{[6,8]}\) In the present experiments, more than 90% of the Na\(^+\) ions were transported from the surface to the sublayer within 2 min at 140 K. It appeared that the ion segregation almost reached a thermodynamic equilibrium at this temperature. Both theory\(^{[6–9]}\) and experiment on water clusters\(^{[10–11]}\) indicate that larger halide anions (Br\(^-\) and I\(^-\) ions) reside at the surface of clusters, whereas the F\(^-\) anion prefers the interior residence. The propensity for surface solvation of Cl\(^-\) ions has been somewhat controversial in theoretical calculations,\(^{[4–9]}\) but there seems to be agreement for the surface residence of Cl\(^-\) ions at least in spectroscopic studies of anionic clusters.\(^{[11–12]}\) The present study supports the surface residence of Cl\(^-\) ions by showing that Cl\(^-\) ions stays in the first layer of the ice surface even when 90% of Na\(^+\) moves inward at 140 K.

In conclusion, besides demonstrating that most of the adsorbed NaCl molecules dissociate to Na\(^+\) and Cl\(^-\) ions on ice films, the RIS and LES studies provide evidence for thermally activated migration of Na\(^+\) ions from the surface to the interior of ice films, and for the surface residence of Cl\(^-\) ions. The present study stands for the first direct observation of the ion segregation process driven by water solvation. Thermodynamic aspects of our results are expected to be extendible to a liquid water surface.

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