Halide-mediated behaviour of nitrate at the air-aqueous interface and implications for the liquid layer at the surface of snow and ice

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Introduction

- Nitrate (NO$_3^-$) is found in polar snow and ice through HNO$_3$ deposition and heterogeneous hydrolysis of HNO$_2$(g) and is source of NO$_2$ = NO$_2^+$ + NO(g) and HONO(g)\footnote{Berec, V. J. et al., J. Aerosol Sci., 30, 3777-3792.}
- The liquid-like layer (LLL) at the surface of frozen solutions is a unique reaction environment that is poorly parameterized (e.g., composition, pH, mechanisms): current thermodynamic models over predict the exclusion of NO$_3^-$ at the LLL\footnote{Wein, S. D.; Donaldson, D. J. Phys. Chem. Lett., 2011, 2, 1967-1971.} whereas the exclusion of halides (X = Cl$^-$/Br$^-$) are well described\footnote{Wein, S. D.; et al., J. Phys. Chem., 2010, 114, 1-6.}
- Enhanced production of NO$_2$(g) was observed from illuminated aqueous solutions of NO$_3^-$ and X\footnote{Wingen, L. M., et al. Phys. Chem. Chem. Phys. 2008, 10, 5688-5697.} (1,25)
- The LLL of snow and ice may exhibit properties similar to a liquid; it is important to understand what is happening at the surface of liquid solutions
- How is the distribution of NO$_3^-$ at the air-aqueous interface influenced by X$^-$?

Experimental

- Solutions of NaNO$_3$ were prepared with addition of NaX (X = Cl$^-$/Br$^-$)
- Intensity of NO$_3^-$ stretch, $\nu$(v-NO$_3^-$), was monitored and normalized to water bend, $\nu$(v-H$_2$O), to determine amount of NO$_3^-$ at interface (Fig. 2) and bulk
- Urban snow samples were collected and analysed by ion chromatography

Results – nitrate at the air-aqueous interface

- The relative $\nu$(v-NO$_3^-$) are plotted for constant 0.5 M NO$_3^-$ and increasing halide concentration (0 – 2 M X$^-$) for the bulk and surface measurements; the relative nitrate response is compared to the experimental condition when 0 M X$^-$ is present in solution (Fig. 3)
- The known effect of halides on the water bend\footnote{Richards, N. K. et al., J. Phys. Chem. A, 2011, 115, 5810-5821.} is corrected for to obtain surface NO$_3^-$ amounts
- Nitrate at the surface is enhanced compared to the bulk when Br$^-$ is present, but Cl$^-$ has no effect
- Surface adsorption isotherms for nitrate with constant [X$^-$] concentration (no X$^-$ 0.5 M Br$^-$, and 0.5 M Cl$^-$) are shown in Fig. 4 by plotting the corrected surface $\nu$(v-NO$_3^-$) against bulk NO$_3^-$ concentration
- Single-component NO$_3^-$ has neutral surface propensity but this is changed when NaX are added: NO$_3^-$ is enhanced by Br$^-$ and suppressed by Cl$^-$

Implications for snow and ice chemistry

- Halide-mediated changes in NO$_3^-$ propensity for the air-aqueous interface may impact production of NO$_x$, OH, and O($^3$P) (e.g., if NO$_3^-$ is enhanced at the interface by Br$^-$, it is more available for photochemistry)
- Upon freezing solutions, halides are enriched at the interface and nitrates are also somewhat enriched. Now, what happens when we freeze salty solutions with NO$_3^-$ and Br$^-$?
- Ion concentrations for Toronto snow are shown in Table 1
- Climate change will alter large-scale human activities in the Arctic regions and change the chemical composition of the polar atmosphere, sea ice, and snowpacks
- We anticipate that increasing NO$_x$ emissions will be relevant for chemistry in the Arctic environment

References


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