Probing the liquid-like surface of frozen salt solutions via infrared spectroscopy

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Motivation

- Snow and ice in marine environments affect the local atmosphere
- Frozen water solutions have a liquid-like layer
- Understanding morphology, dynamics, and reactivity of this layer is crucial to modeling

Experiment: ATR – IR Spectroscopy

- Cold attenuated total reflection infrared spectroscopy
- The IR beam is attenuated via the exponentially decaying evanescent wave
- The penetration depth d_p is defined as the depth where the electric field falls to $1/e$

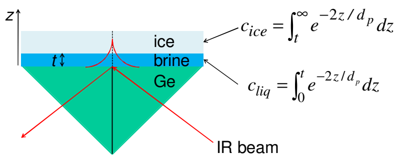


Fig 1. Cartoon of the ATR experiment showing an ice film with an interfacial brine layer on the Ge crystal. The depth of the brine layer is t. The fractions of brine and ice are scaled exponentially relative to d_p.

Modeling ATR Spectra

- Fresnel equations for internal reflection
- Complex indices of refraction for ice (235 K) and water (273 K)
- A combination of the reflectance due to the liquid and solid:

$$R = c_{liq}R_{liq} + c_{ice}R_{ice}$$

- This model does not account for liquid at grain boundaries or in inclusions

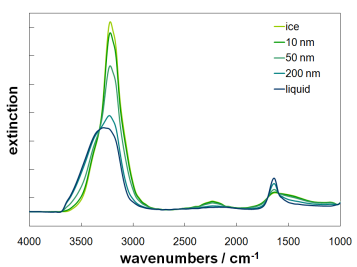


Fig 2. Modeled reflection spectra ranging from pure ice to pure liquid with various liquid layer thicknesses.

- OH stretch at ~3300 cm^{-1} shows an isobestic point
- OH bend at ~1700 cm^{-1} shows two isobestic points
- As t increases, the ice character of the spectra decreases
- This behavior is also seen in experimental spectra

Liquid-Like Layer Thickness as a Function of Temperature

- Aqueous solutions of NaCl were frozen at -18°C
- Spectra were taken as the film was warmed
- Films equilibrated ~ 10 min at each temperature
- Spectra show a mixture of liquid and solid with an isobestic point
- The fraction of ice, c_{ice}, was calculated from the spectra
- The thickness, t, was calculated from the equation shown in Figure 1.

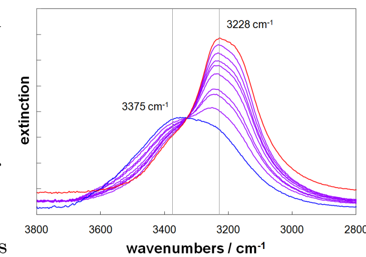


Fig 3. OH stretch region of the spectrum for solid 0.01 M NaCl films from -18 to -2°C (purple), ice (-17°C, red), and liquid 0.01 M NaCl (-1.8°C, blue).

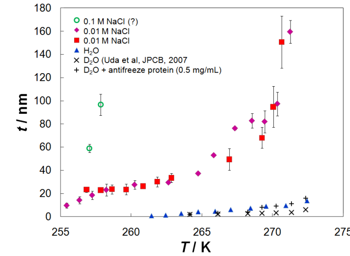


Fig 4. Liquid layer thickness, determined by isobestic analysis of the OH (OD) stretch, as a function of temperature and [NaCl]. Error bars are the standard deviation for values calculated at two wavelengths.

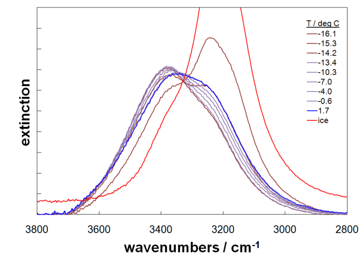


Fig 5. The spectra of solid 0.1 M NaCl films show more complex behavior with two distinct isobestic points.

Brine Layer Thickness as a Function of Concentration

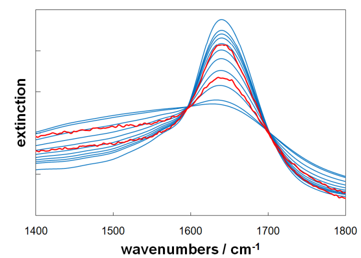


Fig 6. Comparison of spectra of frozen 0.01 M KBr (red) to modeled water/ice spectra (blue) at about -8°C.

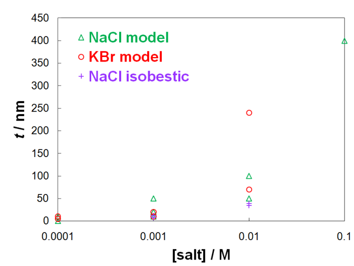
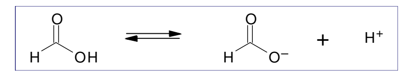


Fig 7. Brine layer thickness, determined by comparison to the OH bend of modeled spectra and isobestic analysis of the OH stretch, as a function of salt concentration at about -8°C.

- Brine layer thickness was estimated by comparison of experimental spectra to model spectra of varying t
- Experimental spectra varied in intensity
- The blue lines in Figure 6 are for 10 nm $\leq t \leq$ 400 nm
- Thickness increases with salt concentration, as expected
- In most cases, 1 M and 0.1 M frozen salt solutions were indistinguishable from liquid water
- This method may overestimate thickness due to differences in the index of refraction of NaCl solutions

Measuring the Acidity of the Interface



- Most calculations assume complete ion exclusion upon freezing
- In ATR-IR, peak height is linear with respect to concentration
- Changes in concentration at the interface upon freezing can thus be quantified with ATR-IR
- Small organic acids show changes in spectra with changes in pH
- Changes in acidity upon freezing at the interface can also be quantified with ATR-IR

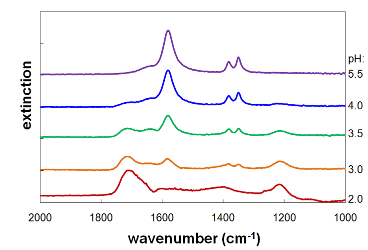


Fig 8. Spectra of aqueous formic acid at 25°C, showing the change from the basic form (pH = 5.5) to the acidic form (pH = 2.0). Spectra have been offset for clarity and the contribution from water has been subtracted.

Conclusions and Future Work

- ATR-IR is a reliable way to measure and observe liquid interfaces on frozen aqueous films
- The brine layer is ~10 to 160 nm thick between 255 to 271 K for 0.01 M NaCl
- Future experiments will explore changes in acidity and concentration upon freezing of aqueous solutions

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