

Physical Properties of Ammonia-Rich Ice: Application to Titan

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Abstract. We report simple measurements of the physical properties of frozen aqueous solutions of NH_3 down to 80 K. These measurements are relevant for the geophysics of icy satellites and Titan in particular. We find that the thermal conductivity of NH_3 -rich (~ 10 -30%) water ice is 1 - $2 \text{ Wm}^{-1}\text{K}^{-1}$, or 2 - 3 times lower than that of pure water ice. We find evidence for significant microwave absorptivity in NH_3 -rich ice - even at 100K - and that the electrical properties are very strongly temperature-dependent. At around 100K the Young's Modulus for NH_3 -free and NH_3 -rich ice appears to be about the same, while at 160K the NH_3 -rich ice is 10x more compliant.

1. Introduction

Saturn's giant moon Titan has a thick nitrogen atmosphere whose origin begs question. The leading hypothesis [Owen,2000] is that in the cold protoSaturnian nebula significant amounts ($\sim 15\%$) of NH_3 were incorporated [Lewis, 1972]. Some of this NH_3 was photolyzed into the N_2 we see today, but large amounts may remain as a contaminant in the icy crust. In particular, cryovolcanic flows are likely to be composed of the peritectic 176K melt, containing about 30% NH_3 by weight.

To date the rheology of NH_3 -rich ices [Durham et al, 1998] and ice slurries [Kargel et al., 1991] has been studied. The crystallization behavior has been explored by [Van Kasteren, 1971] and [Yarger et al, 1993]. [Lorenz, 1998] found that the relative permittivity of NH_3 -rich ice is rather higher than pure ice (4.5 vs 3.1). In anticipation of results from the Cassini mission which is to arrive in the Saturnian system in 2004, we report preliminary measurements of other physical properties of NH_3 -rich ice, namely thermal conductivity, microwave absorptivity and mechanical strength. All three properties differ quite markedly from those of pure water ice.

2. Sample Preparation

Samples were prepared simply by freezing NH_3 solution (determined by titration to be 16% by weight), diluted with tap water if appropriate, in polyethylene containers immersed in liquid nitrogen. No procedures were followed in these rudimentary experiments to near-melt and re-chill samples to create single crystals. However, erupted cryovolcanic melt is likely to be simply chilled in a similar way, so we believe even these crude experiments have relevance for real planetary surfaces.

3. Thermal Conductivity Measurements

[Kargel, 1990] - see also [Ross and Kargel, 1998] - reported preliminary measurements of the thermal conductivity k of frozen NH_3 solutions at 135K . Pellets of ice were stacked in an insulated cylinder between other pellets of known thermal conductivity such that a known heat flow passes through the sample. The interface temperatures allow the conductivity to be estimated. He found that k for NH_3 -doped ice decreased linearly (as far as could be determined with 4 measurements) as NH_3 concentration was increased, from about $4.5 \text{ Wm}^{-1}\text{K}^{-1}$ at 0% to about $1 \text{ Wm}^{-1}\text{K}^{-1}$ at 30% .

We made preliminary measurements using a differentiated line heat source technique [Shandera and Lorenz,2000] where a nichrome wire was heated by a current after being frozen in place 2 - 4mm from a thermocouple. The results from this technique agreed with those of Kargel, although with large scatter (around 30%) owing to slight movement of the thermocouple during warming and cooling of the sample.

A transient hot wire technique avoided this problem. At the suggestion of K. Seiferlin (pers. comm., 2000) we used a very fine (28 AWG) enamelled copper wire ('magnet wire') as both heater and thermometer. Driven by a constant 1.2 A current, the voltage across a 30cm length of wire changes by about $5\text{mV}/\text{K}$, and has a power per unit length q of $0.43 \text{ W}/\text{m}$.

A plot of temperature against $\log(\text{time})$ e.g. Fig.1 yields (after a starting transient due to the switch and current regulator) a straight line, whose slope is $q/4\pi k$. The technique works best for weak thermal conductors (since the temperature changes more rapidly) and calibrated well with corn oil, glycerol and water ($k=0.18, 0.34$ and $0.59 \text{ Wm}^{-1}\text{K}^{-1}$ respectively).

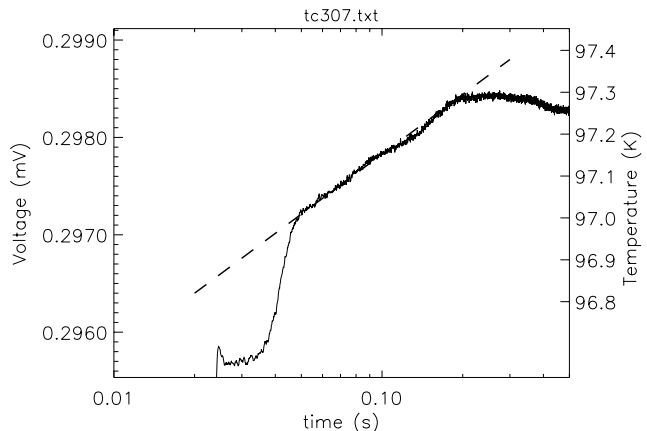


Figure 1. Thermal conductivity measurement : voltage across thermometer/heater wire is shown against $\log(\text{time})$ - right scale indicates corresponding temperature change. Linear fit determines thermal conductivity.

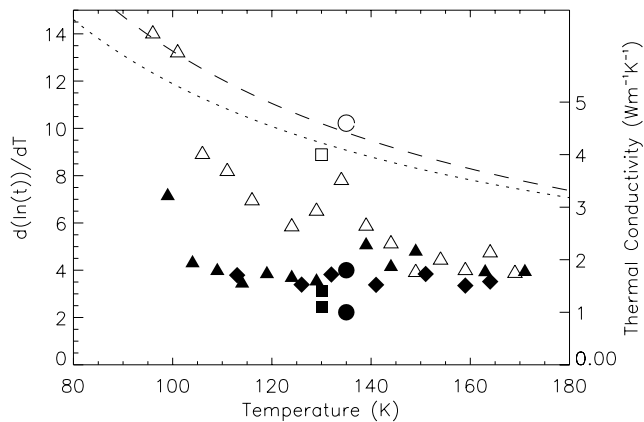


Figure 2. Thermal Conductivity measurements for pure water ice (open symbols), and 16% NH_3 (filled symbols). Hot wire results are shown as triangles, diamonds are NH_3 -rich samples after warming and refreezing - presumably crystalline, rather than glassy. Circles are differentiated line source [Shandera and Lorenz, 2000] and squares are 30% from [Kargel, 1992]. Lines are literature ice values ($488.2/T + 0.47$: dotted, and $597/T$ dashed).

Fig.2 shows the results - the NH_3 -rich samples have a thermal conductivity around half that of pure ice. The technique seems to read a little low for pure ice (which is quite conductive at these temperatures) and a factor of 3 between that and NH_3 -rich ice may be more likely - as indicated by our initial results and those of Kargel. Another source of error [Ross and Kargel, 1998] may be poor contact between the ice and wire owing to thermal contraction - a confining pressure may mitigate this problem.

We did not characterize the phases (H_2O , $\text{NH}_3\cdot\text{H}_2\text{O}$, $\text{NH}_3\cdot 2\text{H}_2\text{O}$ etc.) that were present, nor could we determine whether they were glassy (although such amorphous phases tend to have much lower k than we observe [Ross and Kargel, 1998]. Titration showed the sample to be slightly heterogeneous (varying by about 1/5 of the mean concentration on 0.5cm scales).

4. Dielectric Measurements

We measured the microwave absorptivity of NH_3 -doped ice calorimetrically, recording the temperature rise in a calibrated microwave oven with a ballast load, as described in [Lorenz, 1999]. The first set of results, using only weakly-doped ice at dry-ice temperatures is shown in Figure 3 - the loss tangent relates to NH_3 concentration - see also [Arias *et al.*, 1965]. Thin films of liquid (as in sea ice) may be partly responsible.

We applied the same method to liquid-nitrogen chilled samples of higher NH_3 concentration [Shandera and Lorenz, 2000]. The method is much more difficult at these low temperatures, since heat leak from the warm room is significant compared with the microwave heating. However, loss tangents of about 0.02 were determined, compared with values about 100x less for pure water ice. At these low temperatures below the eutectic, intrinsic absorption in the ice matrix, rather than due to intergranular films of liquid, may be responsible. The high loss tangent may play a role in Titan's unusual radar albedo [Lorenz, 1999].

We should caution that these measurements are not entirely satisfactory, and absorption cell measurements with good temperature control would be most desirable. It may be that our measurements are affected by temperature gradients in the sample. We made simple loss measurements using ices frozen in the parallel plate capacitor [Lorenz, 1999] with an LCR meter, figure 4, and find that the conductivity increases dramatically with temperature, even several 10s of K below the eutectic.

5. Mechanical Measurements

The Young's Modulus E of a material may be estimated from the force on a spherical indenter. We measured this with a small pendulum apparatus, with a piezoelectric accelerometer mounted on a 12.7mm ball bearing at the end of a short arm which could be dropped onto the sample from a fixed end stop. This apparatus is related to that used to calibrate impulse force sensors.

The accelerometer reading was recorded at 30 kHz by the datalogger and the peak height of the signal was measured. The force pulse is approximately sinusoidal [Goldsmith, 1953] and its height scales as $E^{2/5}$. The results are plotted in fig.5 - it is clear that at around 150K, 26K below the melting point, the NH_3 -rich material is 10-20 times softer than pure ice. At around 100K, the Young's moduli are about the same. We were not, with this apparatus, able to measure higher moduli (e.g. that for Lead should be around 20 GPa) because the least stiff element in the measurement chain (and therefore that which determines the peak deceleration) at these high hardness levels becomes the epoxy resin used to affix the ball bearing, rather than the sample itself. However, a crude fit to the pure ice data extrapolates to about 10 GPa at 0K, in good agreement with the value determined from speed of sound measurements on ice [Proctor, 1966]. It appears from the data that the NH_3 -rich samples have a much steeper strength/temperature slope, and it may indeed be that NH_3 -rich ice is stiffer at 50K : however, when modulus is plotted against (T/T_m) where T_m is the melting point, the NH_3 -rich data plot more or less over the pure ice data.

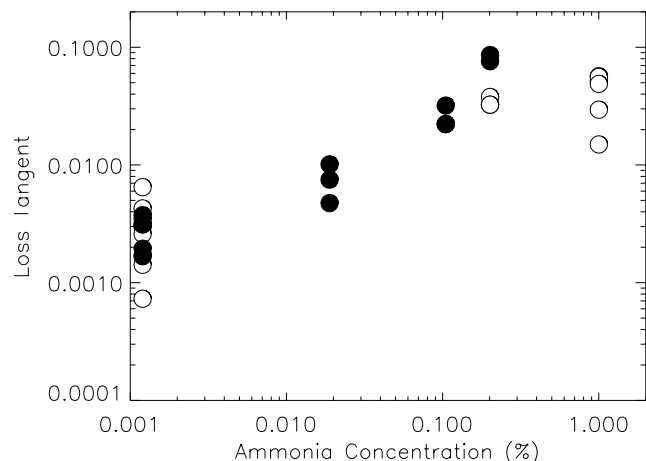


Figure 3. Loss tangent measured in microwave oven with weakly-doped ice at dry-ice temperatures. Loss varies with NH_3 concentration to the power of 0.5-1. Filled symbols 233 to 263 K; open symbols 193 to 233 K.

6. Additional Observations

It was observed, as previously [Lorenz, 1998] that NH_3 -rich ice samples have a clear appearance, while more pure water ice has a milky, crazed appearance (probably due to the exsolution of dissolved air).

Upon warming to close to the 176K melting point, NH_3 rich ices would take on a milky opacity. This is presumably due to the formation of thin leads of melt between ice crystals. It may be that, as for CO_2 ice on Mars and N_2 ice on Triton, the optical texture of ice is a useful diagnostic of its thermal history.

It was noted, usually on the first warming cycle, that the sample would make a loud crack - this did not occur with pure ice or NH_3 -poor samples. This crack is presumably related to the crystallization or recrystallization of NH_3 hydrates : [Yarger et al., 1993] and [Van Kasteren, 1973] have noted this complex crystallization behavior, and the tendency to form a glass.

When samples were drilled to make holes for the insertion of thermometers during the microwave heating experiments, it was noted that the (unchilled) drill bit often seized - becoming frozen in place. This occurred only with the NH_3 -rich samples. It is assumed that the combination of the lower melting point, and the lower thermal conductivity inhibiting the diffusion of heat away from the sample, led to melting of a thin film of sample that subsequently refroze. Sample acquisition systems for future Titan missions [Lorenz, 2000] may need to take effects like this into account.

7. Geophysical and Exobiological Implications

The geothermal heat flow on Titan due to radionuclides in Titan's rocky core has been estimated as 4 mWm^{-2} . For a given heat flow, the geothermal gradient depends on the conductivity of the surface material. [Lorenz, 1996] computed that in a pure ice crust the 176K melting isotherm would occur at a depth of around 50 km.

If Titan's crust contains NH_3 , then the geotherm must be steeper, and thus the melting isotherm is met at a rather shallower depth - around 15 km. Perhaps, then, cryovolcanism [Lorenz, 1996] is easier on Titan than previously con-

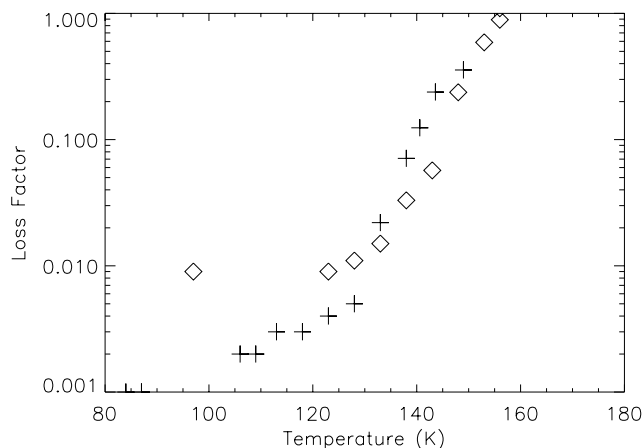


Figure 4. Loss factor (proportional to Loss tangent) for 3% (crosses) and 16% (diamonds) NH_3 doped ice measured with LCR meter at 2kHz. Note the strong temperature dependence.

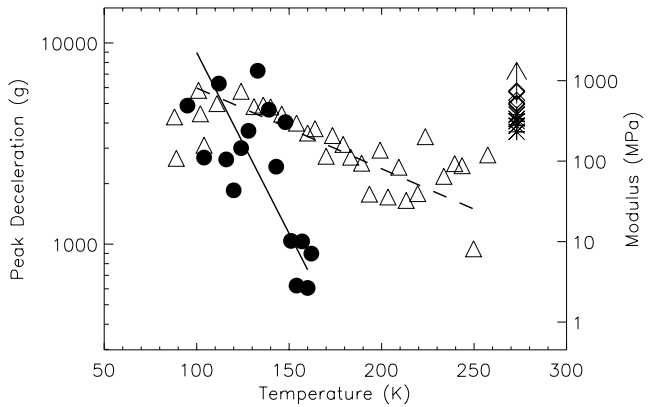


Figure 5. Strength of water ice with 0 (triangles) and 16% NH_3 (filled circles). Left axis is the measured deceleration on a 80g pendulum assembly tipped with a 12.7mm diameter ball bearing, dropped at a speed of 1 m/s onto the sample surface. Estimated relative Modulus (strictly $E/(1-\mu^2)$, where E is the Young's Modulus and μ the Poisson's ratio) is shown on the right axis. Analytic calibration agrees well with the data for Teflon (asterisks : $E=350\text{MPa}$), but data for Lead (20 GPa, diamonds) read a little low (see text) - these should appear above the top of the scale.

sidered: an ascending cryomagma both freezes more slowly and has a shorter distance to travel. The shallowness of the melting isotherm has implications for impact crater morphology, and in particular for the formation of multi-ring impact structures, as studied on Europa [Turtle et al, 1999].

The organic photochemistry in Titan's atmosphere is an evolutionary dead end, since most biomolecules must react in an aqueous environment, for which Titan's surface is too cold. However, [Thompson and Sagan, 1992] noted that atmospheric suppression of plume expansion from impact events would tend to produce significant amounts of (aqueous) impact melt, and that for reasonably large impacts, the melt pools and melt sheets would last for thousands to millions of years. Such prebiotic 'oases' would last longer for NH_3 -rich melt in a given temperature setting due to both the lower freezing point and the low k .

8. Conclusions

Our crude experiments have underscored that the addition of significant amounts of NH_3 dramatically changes the physical properties of ice. Interpretation of the results of the Cassini mission to the Saturnian system must take these different properties into account. Further measurements with higher fidelity than those reported here are encouraged : careful control of the thermal history of samples may be an important factor in controlling physical properties, and should be a key feature of such future experiments, especially given the tendency of frozen ammonia solutions to persist as glasses on laboratory timescales. Another crucial element would be the determination of the ice and hydrate phases present.

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