

PARTIAL DISSOCIATION OF CLATHRATE HYDRATES IN PRESENCE OF AMMONIA UNDER CRYOGENIC CONDITIONS. M. Choukroun¹, T. Vu¹, E. Gloesener¹, A. Ibourichene², W. Smythe¹, M. Barmatz¹, R. Hodys¹. ¹Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr., MS 79-24. ²Ecole Normale Supérieure Paris. (E-mail: Mathieu.choukroun@jpl.nasa.gov).

Introduction: The likely presence of clathrate hydrates on Titan has long been inferred from cosmochemical, thermal, and thermodynamic models (e.g. [1,2]). As gas-laden icy structures (up to 15 % molar), they may be internal reservoirs of methane and other atmospheric gases, and their dissociation during cryovolcanic activity or their involvement in substitution processes could be main contributors to the replenishment of Titan's atmospheric methane [3,4]. However, the controversial nature of the few cryovolcanic features tentatively detected on Titan by the Cassini spacecraft questions our current understanding of the modalities of outgassing processes.

Specifically, the paucity of experimental data on the stability of clathrate hydrates in the presence of ammonia (likely source of Titan's atmospheric nitrogen) and the lack of a fundamental understanding of how such inhibitors affect the phase behavior of clathrate hydrates are severe limitations for our ability to approach the modalities of outgassing on Titan.

Methods: We are conducting an experimental study in the ternary systems $\text{H}_2\text{O}-\text{CH}_4-\text{NH}_3$ and $\text{H}_2\text{O}-\text{THF}-\text{NH}_3$. Phase diagrams of the former are constructed under pressures up to 100 bars using a high-pressure cryogenic calorimeter, while the latter is investigated at atmospheric pressure using a liquid nitrogen cooled cryostage coupled to a microscope and a Raman spectrometer.

High-pressure calorimeter: This consists of a Setaram BT2.15 Calvet calorimeter equipped with 100 bar cells and cooled by liquid nitrogen. A custom gas handling system has been developed, and preliminary measurements obtained on pure gases and on clathrates in the $\text{H}_2\text{O}-\text{CH}_4$ system validate this method.

1-bar optical cryostage with Raman: This consists of a Linkam LTS 350 cryostage, cooled by liquid nitrogen, that is coupled to a Horiba Jobin-Yvon LabRam HR, equipped with a 532 nm solid-state and a 633 nm He-Ne lasers, and two gratings, to achieve a spectral resolution of 0.4 cm^{-1} (high resolution grating) to 1 cm^{-1} (low resolution broadband grating).

Results: The main results [5] are: 1/ the dissociation proceeds incongruently, similarly to the incongruent melting of water ice in the $\text{H}_2\text{O}-\text{NH}_3$ system, and 2/ the effect of ammonia on the stability of clathrates in the $\text{H}_2\text{O}-\text{NH}_3-\text{THF}$ system is the same as its effect on water ice in the $\text{H}_2\text{O}-\text{NH}_3$ system.

Partial dissociation process: Figure 1 shows microscopic images of THF clathrate hydrates in a 10 wt% $\text{NH}_3-\text{H}_2\text{O}$ solution. The solution was deliberately supersaturated in THF with respect to the guest-host stoichiometry of structure II clathrates, in order to prevent the formation of water ice below 0°C , which would preclude the observation of THF clathrates (denser than the solution). The images obtained on this sample, as well as all other samples studied with NH_3 concentrations ranging from 0 to 25 wt% with respect to H_2O , clearly show that dissociation of the THF clathrates started around -70°C . Continuous "melting" of the clathrates is observed upon warming, all the way to a point of total dissociation, equivalent to a liquidus. This unambiguously indicates an incongruent melting / partial dissociation process in THF clathrates when NH_3 is present in the system.

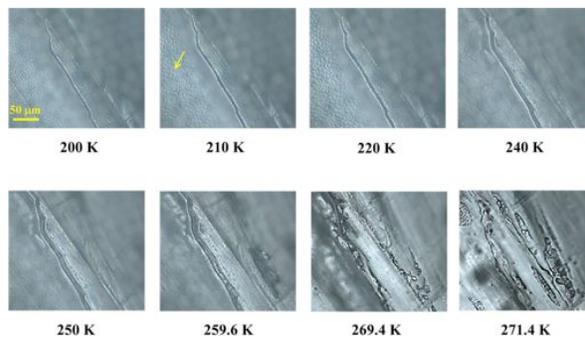


Figure 1. Microscope images at 10X~ magnification for THF clathrate in a 5 wt % (with respect to water) solution of NH_3 . Note the partial melting of the clathrate as the temperature increases. The arrow in the photo at 210 K highlights changes in texture of the smaller crystals on the left.

The partial dissociation process described above is further substantiated by comparing sample textures obtained at the same temperature for different ammonia concentration, see Figure 2. At very low concentrations (1.9%) and low temperature (220 K), the subautomorph texture of THF clathrate crystals is easily observed. At higher concentrations, of 10 then 13.7%, the extent of partial dissociation becomes more and more visible, as the fraction of liquid increases and the crystalline structure is less obvious. At 22.4% NH_3 concentration, only a few remaining crystals bathing in liquid can be seen, because the temperature is very close to the point where all THF clathrates disappeared for that NH_3 concentration (231 K).

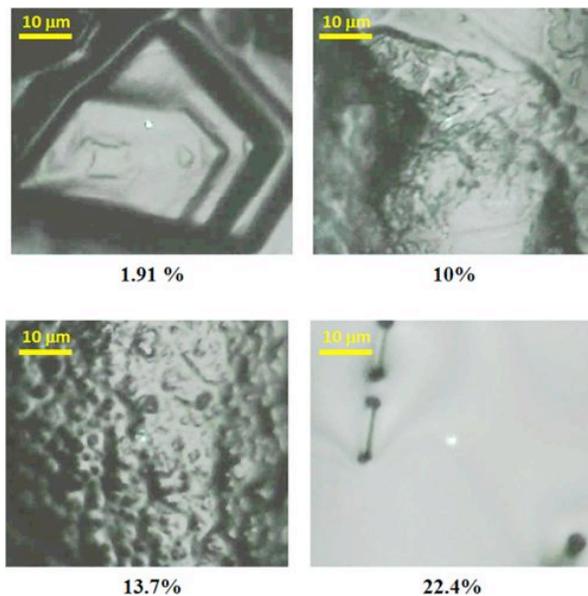


Figure 2. Sample textures observed in the $\text{H}_2\text{O}-\text{NH}_3-\text{THF}$ system at 220 K for various ammonia concentrations.

Phase diagram comparisons: Figure 3 shows the phase boundaries in the $\text{H}_2\text{O}-\text{NH}_3$ (literature interpolation) and $\text{H}_2\text{O}-\text{NH}_3-\text{THF}$ (new data and interpolation) systems at 1-bar. The NH_3 concentration is expressed in weight fraction relative to H_2O to allow for a direct comparison. At 0 wt% NH_3 , the observed dissociation temperature for THF clathrates was 4.7 °C, a value consistent with the literature [e.g., 6]. The partial dissociation curve of the clathrates follow almost exactly the liquidus of ice Ih. Regardless of the NH_3 concentration, THF clathrates always start to show evidence for dissociation at -70 °C, which we interpret to be an upper bound for that of a THF clathrate eutectic point. Indeed, the determination of apparition of the first drop of liquid via optical methods is not the most reliable, and the actual temperature may be a few degrees lower. Preliminary experiments have been conducted at 1-bar with the Setaram BT2.15 calorimeter in order to refine this initial estimate, and suggest the eutectic temperature may be closer to 198-200 K. Further experiments are needed to fully constrain the eutectic temperature.

These results strongly suggest that the effect of ammonia on THF clathrates is the same as on ice I_h . This would imply that clathrate inhibition by NH_3 operates in the same way as incongruent melting of ice: by modifying the activity of water in the liquid phase.

Implications: The results obtained on THF clathrates in $\text{H}_2\text{O}-\text{NH}_3-\text{THF}$ indicate that clathrates in pres-

ence of inhibitors undergo a partial dissociation process analogous to the incongruent melting of ice, with a eutectic point and a liquidus-like partial dissociation curve. Also, in the case of THF at least, ammonia seems to have the same effect of clathrates as on water ice. This suggests that, on icy moons such as Titan where clathrates are likely involved in methane outgassing, the presence of even minute amounts of inhibitors might be sufficient to trigger some partial dissociation and perhaps some outgassing into the atmosphere. Further work is needed to ascertain this behavior and verify that it applies to other clathrate-formers such as methane as well.

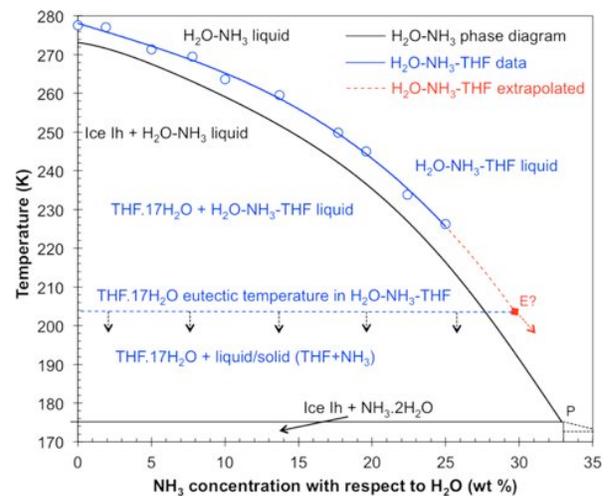


Figure 3. Phase diagrams in the $\text{H}_2\text{O}-\text{NH}_3$ (black) and $\text{H}_2\text{O}-\text{NH}_3-\text{THF}$ (blue) systems. Both phase diagrams use for x-axis the NH_3 concentration relative to water only; the THF concentration is omitted so a direct comparison is meaningful. The “E?” indicates the extrapolated location of a THF clathrate eutectic inferred from our data.

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References: [1] Lunine J.I. and Stevenson D.J. (1987) *Icarus* 61, 70-77. [2] Tobie G. et al. (2006), *Nature* 440, 61-64. [3] Lunine J.I. et al. (2009) In: Titan from Cassini-Huygens, U. Arizona Press, 35-59. Choukroun M. and Sotin C. (2012) *Geophys. Res. Lett.* 39, L04201. [4] Choukroun M. et al. (2010) *Icarus*, 205, 581-593. [5] Vu T. et al. (2014) *J. Phys. Chem. B* 118, 13371-13377. [6] Sloan E. D. (1998), *Ed: Marcel Dekker, N.Y.*