MAPPING CHANGES IN THE METHANE-ETHANE SYSTEM WHEN ADDING NITROGEN AT TITAN SURFACE CONDITIONS.

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Introduction: From 2004 to 2017, the Cassini spacecraft explored the Saturn system and provided an in depth look at its largest moon, Titan. During the mission, the RADAR (RAdio Detection And Ranging) instrument detected lakes and seas on Titan's polar regions. [1-2]. Since Titan's surface temperatures range from 89-95 K and the surface pressure is ~1.47 bar [3], water is not the liquid in the lakes and seas, but rather it is a combination of methane (CH_4), ethane (C_2H_6), and dissolved nitrogen (N_2) [1]. In particular, recent analysis of RADAR data estimates mixing ratios of 69% methane, 15% ethane, and 16% nitrogen in the north polar lakes and seas [4].

Recent work in the Astrophysical Materials Laboratory mapped the methane-ethane phase diagram at low temperatures and pressures using Raman spectroscopy [5]. The work completed on the binary system shows the eutectic point to be at 71.15±0.65 K and at a composition of around 64.4±1.8% methane and 35.6±1.8% ethane, which is an approximate temperature depression of 19 K compared to the freezing points of the pure species. We also found that supercooling occurs at the liquidus on the ethane-rich side and a supercooling-like effect takes place at the solidus on the methane-rich side. It is suspected that both effects are due to the ethane solid I-III transition (skipping solid II at low pressures when cooling) and could have implications for the lakes and seas. Specifically, [6] report that the solid I-III transition is quite exothermic, which could result in heat being released into the surrounding environment when the transition occurs.

With the completion of the methane-ethane work, we now aim to identify the temperature at which ice first appears when nitrogen is added to the system at 1.45 bar as compared to that of the binary system. A previous study by [7] examined the dissolution of nitrogen into methane-ethane mixtures and demonstrated that nitrogen has a higher tendency of dissolving into the hydrocarbon mixture when it is introduced into methane-rich mixtures at lower temperatures and higher pressures. The work conducted in the Astro Mat Lab builds on this by focusing on changes in the phase transitions caused by the introduction of nitrogen.

Along with the experiments by [7], [8] also shows strong temperature and composition dependencies on the dissolution of nitrogen into methane-ethane mixtures. This significantly affects the liquids' densities and since estimates show the northern lakes to be methane-rich, it could lead to lake turnover and/or stratification.

We also see an added complexity to the ternary system with the presence of two liquids at certain pressures and temperatures. Modeling completed by [9] and lab work by [10] show that this two-liquid system is composed of an ethane-rich top layer and a methane- and nitrogen-rich bottom layer. Mostly, the two-liquid system appears to favor temperatures and pressures that could be found at the bottom of the seas, but this may still have repercussions for the surface since it could encourage nitrogen bubble formation and further promote lake turnover and/or stratification.

This is all to say that the methane-ethane-nitrogen system found on Titan is complex and lends itself to additional investigation beyond what has already been conducted in the past. The ongoing experiments in the Astro Mat Lab look at the ternary system from a different angle, namely in identifying how nitrogen affects the binary system, as opposed to looking at all three in the scope of a ternary system. We use the [7] dissolution rates as a guide for introducing nitrogen into the methane-ethane system, with the intent of providing clarification on potential processes occurring in the lakes at Titan surface conditions.

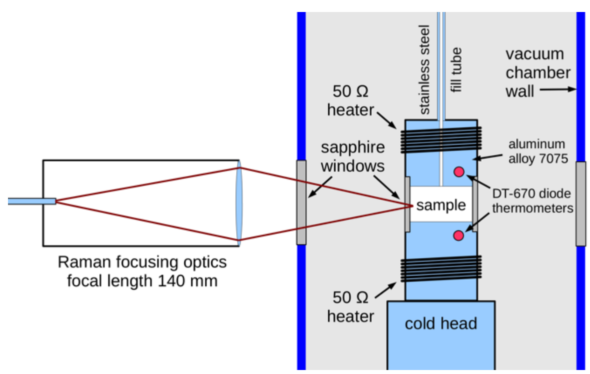

Figure 1. Schematic of cell with Raman optics.

Experimental Procedure: The system (Figure 1) is located in the Astrophysical Materials Laboratory at Northern Arizona University [5, 10-12]. The set-up is cooled by closed-cycle helium refrigerators and consists of a vacuum chamber that is connected to gas cylinders and a mixing chamber through a series of stainless-steel manifolds. The sample cell is enclosed in the vacuum chamber and is 15 mm in diameter and 5 mm in width.

Methane and ethane are mixed first as room temperature gases. The sample cell is cooled to 95 K and the gas mixture is then released into the cell via a fill tube at the top. The mixture rains down into the cell, which additionally aids in creating a homogeneous sample. The hydrocarbon mixture is then allowed to settle for approximately 10 minutes before continuing with the experiment.

For the work presented here, the system was further cooled to 85 K, at which time the sample was pressurized to 1.45 bar by introducing nitrogen into the cell. The hydrocarbon mixing ratios chosen were methane:ethane molar concentrations of 20:80, 50:50, and 80:20. Due to nitrogen dissolution rates, more of it has to be added to the sample with increasing methane concentration and decreasing temperature. While this does change the overall composition of the sample as the experiment progresses, the hydrocarbon ratio remains the same and is tracked on the pseudo binary phase diagram as such (Figure 2).

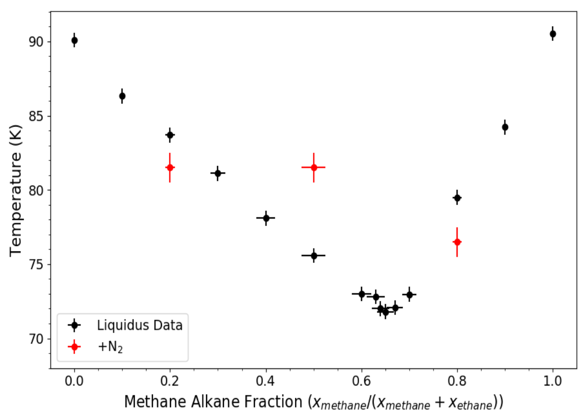

Figure 2. Comparison of temperatures for the methane-ethane liquidus curve (black dots) to the temperatures of the first appearance of ice when nitrogen is added to the system (red dots).

Initial experiments were carried out to narrow down the temperature range at which the first ice forms. This consisted of going down in temperature in increments of 5 K with 20 minutes in between each step. The second run constrained the temperature range further by going down in steps of 1 K between the 5 K window located in the first run. Raman spectra and temperature measurements were taken throughout the cooling sequence and a vertical spectroscopic scan of the cell was collected once the first ice formed. While the first ice was identified through visual inspection, the spectra collected during the experiments will be used to track changing compositions throughout the cell in addition to what compositions preferentially freeze first.

Preliminary Results: As shown in Figure 2, the 20:80 and 80:20 hydrocarbon mixing ratios demonstrate a temperature depression of the first ice formation when nitrogen is introduced into the system, whereas the first ice for the 50:50 mixture is raised. This result may indicate that the addition of nitrogen will not necessarily shift the first ice temperature in a consistent direction.

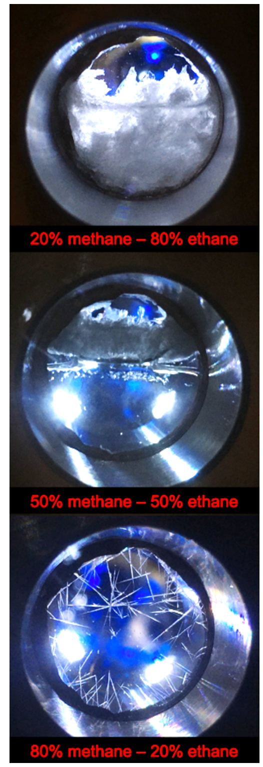

Figure 3. Images of samples directly after the appearance of the first ice.

However, initial CRYO-CHEM 2.0 [13] models suggest that the first ice temperature for the 20:80 ratio should appear at a higher temperature than the recorded 81.5 K. This could be attributed to the tendency of ethane to supercool. Currently, we have only allowed the samples to settle for 20 minutes in between each temperature step; for the ethane-rich species, we may need to allow for longer equilibration times to get a more accurate temperature reading of the first appearance of ice.

Future Work: Going forward, we will expand on how nitrogen affects the temperature at which the first ice forms in the methane-ethane system. This will be followed by determining the temperature at which the last liquid is present. After exploring the methane-ethane-nitrogen system, we will add propane, ethylene, and acetylene in small quantities to further simulate the potential compositions of Titan's lakes and seas.

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