THE STABILITY OF TRACE SPECIES IN THE LIQUIDS OF TITAN.

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Introduction: Titan is the only other known planetary body in our Solar System that has stable bodies of liquids on its surface. The lakes and seas of Titan are composed primarily of methane (CH_4) and/or ethane (C_2H_6), with the concentration of dissolved nitrogen (N_2) from the atmosphere dependent on the ratio of methane to ethane, the temperature, and pressure.

Propane (C_3H_8) is formed photochemically in the upper atmosphere of Titan, and its primary loss from the atmosphere is due to condensation at the tropopause [1]. The freezing point of propane is 85.5 K, meaning that it is liquid on the surface of Titan, like methane and ethane. Mixing methane and ethane can lower the freezing point beyond that of either pure species [2] due to the presence of a eutectic; the same is true for mixtures of methane-propane and ethane-propane [3]. Recently, we have shown that the addition of dissolved nitrogen at 1.5 bar will change the freezing profile of methane-ethane mixtures as well [4]. We will explore how the addition of trace species such as propane, ethylene and acetylene affect these mixtures through both experiments and modeling.

Methodology: Northern Arizona University (NAU) hosts one of a handful of laboratories around the world devoted to studies of astrophysical ices and liquids [2,4]. In it, volatiles are condensed within an enclosed cell (Fig 1). Cooling is provided by closed-cycle helium refrigerators, within vacuum chambers for insulation. Cryogenic samples are studied via various analytical techniques including visible and infrared transmission spectroscopy, Raman spectroscopy (Fig 1), and photography (e.g. Fig 3).

We are interested in the stability of the system. That includes identifying phase changes (e.g. freezing points, dissolution/exsolution) as well as measuring the composition of the system under Titan surface conditions and before/after any phase changes. We are especially interested in determining the freezing points of the system, identifying which, if any, species freeze, and building phase diagrams that include possible liquid-liquid-vapor equilibrium (LLVE).

The work with propane follows the same protocol as prior methane–ethane +nitrogen experiments [4]. The process starts with creating an alkane mixture in the gas phase in a 0.5 L mixing volume. Then, the methane–ethane–propane sample is inserted into the cell—cooled to 95 K—where it condenses into liquid. Once the alkane mixture has settled, gaseous nitrogen is injected into the cell and is used to maintain a constant 1.5 bar vapor pressure throughout the duration of the experiment. The final step is to incrementally lower the temperature in the cell, with 30 minutes between each step, until ice forms. The freezing point temperatures are then recorded and compared to the methane-ethane +nitrogen ternary results. Images, timelapse videos, and Raman spectra are also collected.

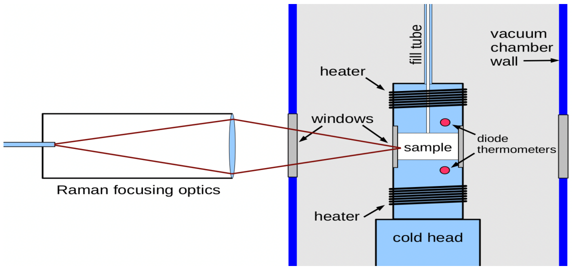

Fig 1. *Schematic of the sample cell and raman optics.*

As temperature decreases, nitrogen dissolves more readily into methane–ethane mixtures [5]. This means more of it must be added to the sample as the experiment progresses to maintain the constant vapor pressure. While this causes the liquid concentration of the samples to change as the experiment progresses, the total relative alkane ratio remains the same.

Experimental Results: Freezing point temperatures are mapped on a pseudo binary phase diagram (Fig 2), with comparisons being based on $CH_4/(CH_4+C_2H_6)$ ratios and nitrogen concentrations extending beyond the two-dimensional plot. Although the propane results are plotted in the context of $CH_4/(CH_4+C_2H_6)$ concentration, the true alkane mixing ratios are not those presented in the diagram. For example, the hydrocarbon mixture plotted on the diagram as 5% methane–95% ethane +10% propane is actually 4.5% methane–85.5% ethane–10% propane when prepared as a sample. Continuing with the example above, the compositions noted here will be generally formatted as 5% methane +10% propane. This format is meant to illustrate the direct comparison of the ternary system to the samples with added propane when reading the pseudo binary phase diagram.

Results suggest that even small quantities of propane depress the freezing points of the ternary system. Notable differences have also been seen in the ice formation. The freezing points ≥82 K form ice starting at the bottom of the cell and move upward, eventually permeating the liquid. Conversely, the

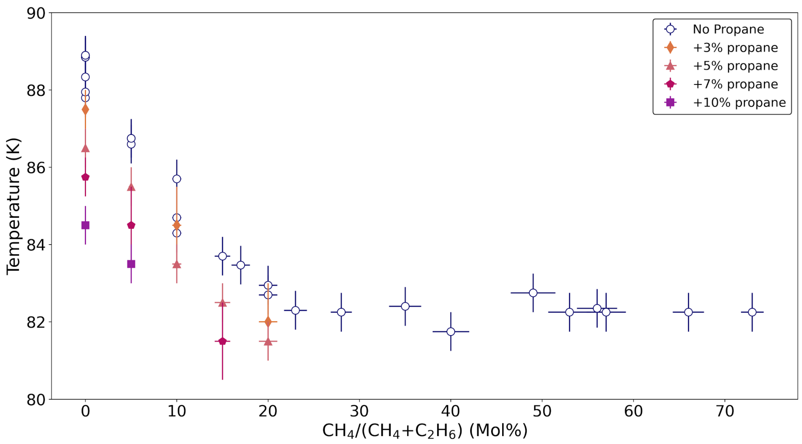

Figure 2. Plot of freezing temperature for methane-ethane +1.5 bar nitrogen (no propane) compared to the addition of 3, 5, 7, or 10% propane.

freezing points below 82 K first form a second liquid and shortly afterward form ice at the meniscus (Fig 3).

As nitrogen entered the cell, it dissolved into the hydrocarbon mixture and formed a second liquid. This second liquid initially formed at the meniscus, growing until it connected with the bottom of the cell to form the layer seen at the bottom left of Figure 3. We have started an investigation into the two-liquid formation with propane added to methane-ethane +nitrogen. This will allow us to understand the phase diagram as well as the solubility of propane and nitrogen in methane-ethane mixtures at Titan conditions.

Numerical Simulations: We examined a homogeneous N_2:CH_4:C_2H_6:C_3H_8 liquid system to understand the breakdown of ideality. In these simulations, real effects are quantified by calculating the binding free energy between each pair of molecules. We found that the binding free energies of N_2 to CH_4, C_2H_6, and C_3H_8 are -0.86, -0.60, and -0.35 kJ/mol, respectively. This is typically compared with the thermal energy k_BT, which is 0.83 kJ/mol at 100 K, to estimate the 'stickiness' of two molecules. When the magnitude of the thermal energy is greater than the binding free energy, the molecules have the kinetic energy to separate. This reveals that increasing alkane length results in a decrease in binding strength between N_2 and each of the alkanes, which suggests a molecular explanation for the phase behavior observed in the experiments of these systems at lower temperatures.

Discussion: Our observations of propane mixtures revealed some behaviors that diverge from the behavior of pure propane. The second liquids that form in the systems with propane seem to have a large difference in surface tension compared to the other liquid, and thus form highly curved interfaces.

When nitrogen is dissolved in binary mixtures of propane-methane and ethane-methane, a second liquid may appear, one liquid is richer in N2 and the other is richer in alkane. The appearance of the second liquid, thus the three-phase LLVE upon nitrogen injection to these binary systems could be detected by repeating these experiments with different mixing ratios of propane-methane-ethane while measuring the total amount of nitrogen that enters the cell. For further analysis, the phase diagrams at conditions where the second liquids were observed will be used. They are calculated using CRYOCHEM 2.0 [6].

Conclusions and Future Work: Pure propane should not freeze on the surface of Titan. However, we see propane ice form under certain conditions that might be possible on Titan (Fig 3, right). We also see that the liquid-liquid system can form with the addition of propane (Fig 3, left). We are beginning experiments and models with acetylene and ethylene and will measure solubility and any phase changes that occur. We continue to explore the effects of propane on methane, ethane and nitrogen, both individually and additively, and constrain the conditions under which interesting phenomena occur.

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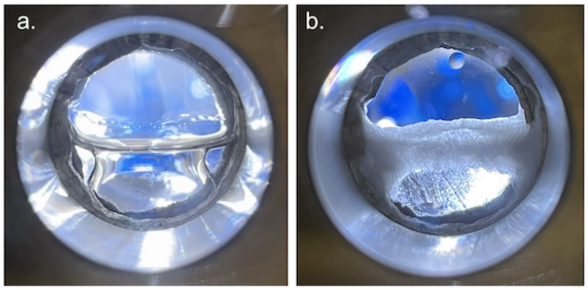

Figure 3. Ice formation at 15% methane +5% propane at 1.5 bars. A second liquid forms first, followed by ice, which forms at the meniscus as opposed to the bottom of the cell.