Adding Propane to the Methane–Ethane–Nitrogen System at Titan-like Conditions. A.E. Engle[*,1,2], J. Hanley[2,1], C.L. Thieberger[1,2], W.M. Grundy[2,1], S.C. Tegler[1], G.E. Lindberg[1], S.P. Tan[3], S.M. Raposa[1,2], J.K. Steckloff[3,4]. [*]Correspondence: aee98@nau.edu, [1]Northern Arizona University (Flagstaff, AZ), [2]Lowell Observatory (Flagstaff, AZ), [3]Planetary Science Institute (Tucson, AZ), [4]University of Texas at Austin (Austin, TX).

Introduction:

Titan, Saturn's largest moon, is shrouded in a thick nitrogen-rich (N_2) atmosphere that supports ongoing methane (CH_4) photochemistry, with two of the principal hydrocarbon products being ethane (C_2H_6) and propane (C_3H_8) [1]. Its polar surfaces host stable bodies of liquid, with methane, ethane, and dissolved atmospheric nitrogen making up the bulk of their compositions. It is suspected there could be a range of 0.8–8.5% propane [2–4] that resides in them as well, finding its way to the lakes either by falling directly into them or being transported by fluvial processes.

So far, experimental efforts that relate to Titan's surficial liquids have focused on binary [5,7] and ternary [8,9] combinations of methane, ethane, propane, and nitrogen, with modeling being the primary mechanism for probing the four species as one system [2–4]. The Astrophysical Materials Laboratory at Northern Arizona University has initiated a study that investigates the changes in freezing point temperatures and physical properties of the methane–ethane–nitrogen system when 0–10% propane is added.

The overarching goal of the current experiments is to provide a deeper understanding of the coupled chemical-dynamical behavior of Titan's lakes. The results may aid in identifying scenarios in which ice could form alongside the surface liquid.

Experimental Protocol:

The work leading up to this study involved recording the changes in freezing point temperatures of the methane–ethane binary system when nitrogen was added at a 1.5 bar vapor pressure (Engle et al., *in prep*). The ternary system will be written as methane–ethane +nitrogen in this text, given that nitrogen was added after the alkane liquid had been deposited into the cell.

The present work with propane follows the same protocol as the methane–ethane +nitrogen experiments (Fig. 1). 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 rains down and 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 ternary results. Images, timelapse videos, and Raman spectra are also collected.

As temperature decreases, nitrogen dissolves more readily into methane–ethane mixtures [9]. 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.

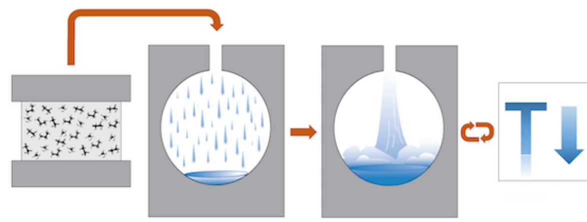

Figure 1. *Depiction of steps in experimental protocol. 1) The alkane mixture is created in the gas phase, 2) the mixture is released into the cell where it then condenses into a liquid, 3) nitrogen is injected and is used to maintain a 1.5 bar vapor pressure, 4) the temperature in the cell is lowered, 5) steps 3 and 4 are repeated until ice forms or the cell overfills.*

Results:

The current experiments focus on the addition of 5% and 10% propane to the methane–ethane +nitrogen system, starting with ethane-rich mixtures. Although Titan's major lakes are estimated to be methane-rich (even the southern Ontario Lacus has an estimated 51% methane content [10]), the starting alkane mixing ratios have been selected due to methane-rich samples reaching their bubble points at lower temperatures at 1.5 bar; at this point, the vapor phase disappears from the phase equilibrium and a constant vapor pressure cannot be sustained.

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.

Preliminary 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 at and preceding 10% methane +5% propane on Figure 3 generally form ice starting at the bottom of the cell and move upward, eventually permeate the liquid. Conversely, the 15% and 20% methane +5% propane compositions first form a second liquid and shortly afterward form ice at the meniscus (Figure 4). While there is interest in investigating the presence of two liquids, it is outside the scope of the present study and will not be discussed.

Discussion:

The current Titan surface conditions of 89–95 K and ~1.5 bar do not cater to ice formation on top of the lakes, but there are other potential scenarios that could promote it. In particular, modeling carried out by Rafkin & Soto (2020) [11] suggest there could be appreciable cooling of the lakes and freezing occurring in shallow mixed lakes, deep lakes with a shallow mixed layer, low atmospheric humidity, and in the case of a non-zero background wind.

There is also interest in determining the existence of a snowball or "slushball" state in Titan's climate history [12, 13]. According to these studies, the surface temperature may drop to as low at 82 K through depletion of methane in the atmosphere, leading to a lowering of the greenhouse effect. While this cooler temperature could have consequences for ice formation on Titan's surface, more studies will need to be conducted to estimate how much propane could be created with a lower concentration of atmospheric methane, as well as how impactful that amount of produced propane would be on the system. Despite this uncertainty, the experiments currently being conducted may encourage further discussion on this topic.

Future Work:

Although the preliminary results have already proven to be intriguing, there is still much to be done and more information to uncover. The first step will be to complete the experiments that focus on how 5% and 10% propane addition impacts the freezing point temperatures of the methane–ethane +nitrogen system. Next, emphasis will be placed on mapping freezing point temperatures involving 3% and 7% propane addition. Comparisons in nitrogen dissolution between the ternary and quaternary systems will also begin in the near future. These experiments will ideally capture trends in phase behavior, physical properties, and changes in nitrogen concentration.

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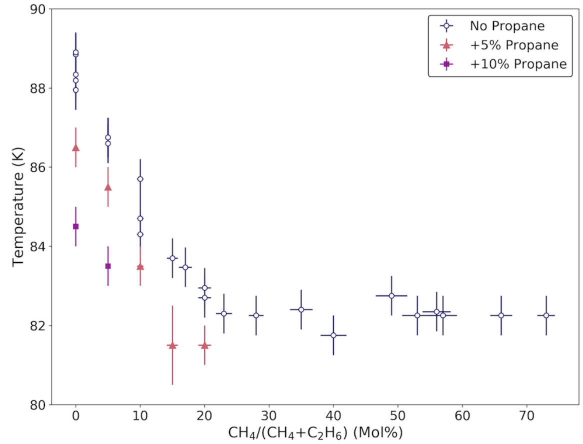

Figure 2. *Comparisons of results from the methane–ethane +nitrogen experiments to those of 5% and 10% propane addition.*

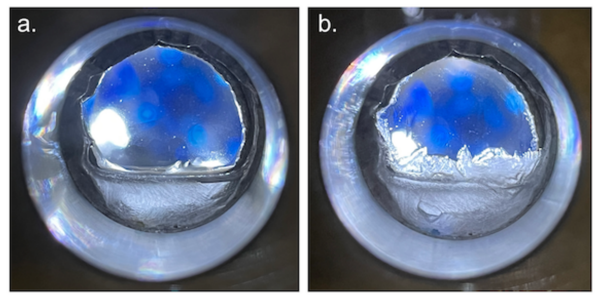

Figure 3. *Ice formation at 5% methane +5% propane. The transition from a) to b) depicts ice first forming at the bottom of the cell and then gradually moving upward.*

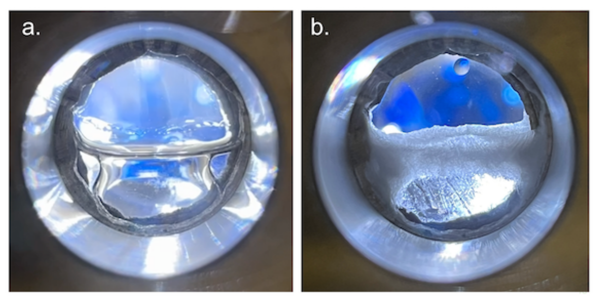

Figure 4. *Ice formation at 15% methane +5% propane. A second liquid forms first, followed by ice, which forms at the meniscus as opposed to the bottom of the cell.*

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