EXPERIMENTAL STUDY OF THE EFFECTS OF FREEZING ON LIQUID HYDROCARBONS ON THE SURFACE OF TITAN. K. Farnsworth[1], Z. McMahon[1], D. Laxton[1], V. Chevrier[1], J. Soderblom[2]. [1]University of Arkansas, Center for Space and Planetary Sciences FELD 202, University of Arkansas, Fayetteville, AR 72701. (kkfarnsw@email.uark.edu).[2]Massachusetts Institute of Technology, Department of Earth, Atmospheric and Planetary Sciences, 77 Massachusetts Ave, Cambridge, MA 02139-4307.

Introduction: Besides Earth, Titan is the only known planetary body with a thick nitrogen (N_2) atmosphere, and stable liquids on its surface. Titan's nitrogen atmosphere and smaller atmospheric constituent, methane (CH_4), allows the body to have a methane hydrologic cycle [1] and the minor presence of ethane (C_2H_6), through methane photolysis [2]. These processes create stable mixture lakes of methane and ethane on Titan's surface [2]. These lakes are possible due to the triple point (~91 K) of methane and ethane falling very close to Titan temperatures. This means ethane and methane ice could also be a strong possibility if Titan becomes slightly colder.

In this preliminary analysis, new experimental data acquired from freezing ethane and methane-ethane mixtures are presented. This study focuses on the freezing process of ethane, as well as the dynamics of methane-ethane mixtures involving the dissolution of nitrogen. This analysis studies the relationship between liquid methane, liquid ethane, nitrogen gas, and temperature. The outcome of this study will help understand the possible thermodynamic processes occurring on Titan's surface regarding ethane and ethane-methane mixtures.

Methods: The experiments were conducted at the University of Arkansas in a Titan surface simulation chamber [5]. This chamber retains temperature of ~94K and pressure of 1.5 bar using liquid nitrogen and nitrogen gas, respectively. The sample is condensed to liquid phase directly from a gaseous phase and is expelled onto a petri dish connected to a hanging electronic balance. Once the liquid has accumulated on the petri dish, the temperature is lowered to -185ºC to induce freezing. The mass and temperature is continuously recorded for the duration of the experiment.

Results/Discussion: The first section of this preliminary study analyzes the freezing points of pure methane and ethane at 1.5 bar of nitrogen. Under these conditions, ethane has an average experimental freezing point of -185.55ºC with a 2% error at 1.5 bar. Figures 1, 2, and 3 represent example elements of a freezing point experiment that validates freezing. These include temperature data (Fig. 1), visual images (Fig. 2) and spectral analysis (Fig. 3). Methane on the other hand, will not freeze below -187ºC in this chamber.

Methane and ethane have previously been studied at 1 bar, with known freezing points both near -183ºC. According to the data presented in this study, ethane follows this trend of -185.55ºC at 1.5 bar. On the other hand, methane does not freeze near the same temperature as ethane, due to nitrogen dissolution lowering its freezing point. (Note: Nitrogen dissolution described in greater detail in references 3, 4, and 6). Therefore, ethane is able to freeze near Titan conditions, but methane does not.

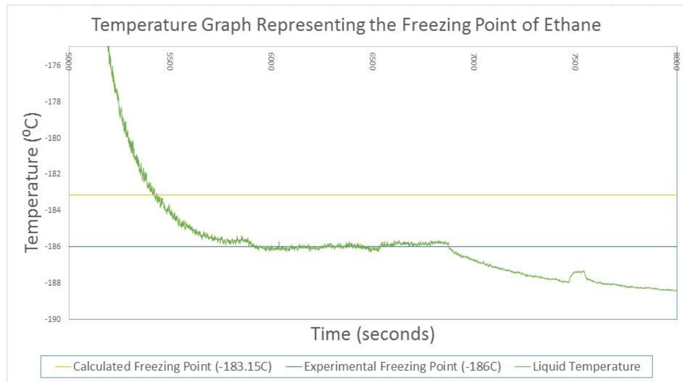

Figure 1: Temperature graph representing -186 ºC as the freezing point of ethane at 1.5 bar. (Note: The calculated temperature is computed for ethane freezing at 1 bar).

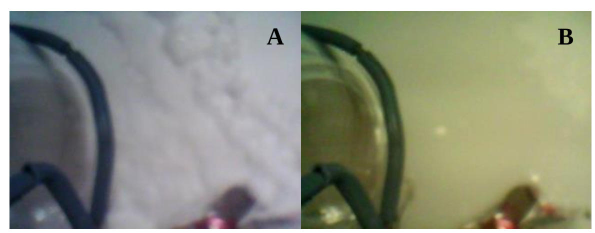

Figure 2: Images of ethane in a frozen state (**A**) and liquid state (**B**).

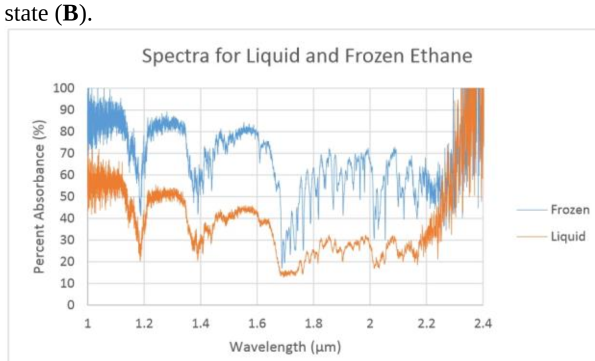

Figure 3: Spectra representing frozen and liquid ethane. The shift in percent absorbance indicates freezing has occurred.

The second part of the study involves the relationship between liquid methane, liquid ethane, nitrogen gas, and temperature. A mixture experiment was conducted with 92.5% methane and 7.5% ethane. The temperature of the mixture was lowered to -185°C to induce freezing of ethane and then raised to -169°C. During this transition, bubbles began forming rapidly where the mixture visually appeared to be in a liquid state, and in another area larger bubbles moved under an ice layer (Fig. 4). Since methane, ethane, and nitrogen have boiling temperatures of -161°C, -89°C, -195°C respectively at 1 bar, nitrogen has the highest probability of creating the bubbles. Since nitrogen is approximately 2 orders of magnitude more soluble in methane at 100 K and 1 bar than ethane, [6] and methane does not freeze near -185°C due to nitrogen dissolution [3,4], nitrogen must be degassing out of the methane under a frozen layer of ethane. The nitrogen was not directly detected, nor is it possible to analyze the bubble contents at this time, but nitrogen is very likely to have caused this phenomenon.

This hypothesis is supported by the spectra presented in Figure 5. In the mixture spectra before the bubbles were observed, methane was only slightly detected around 1.7 µm, but not fully represented at 1.2 µm and 1.4 µm (Fig. 5A). Once the chamber was warm enough for ethane to become a liquid, methane was strongly detected and the absorbance percentage increased, resembling a normal methane-ethane mixture spectra (compare figure 5C and 5D). There was also only a small percentage of ethane present in the mixture, which explains the presence of an ice layer that did not cover the entire sample liquid.

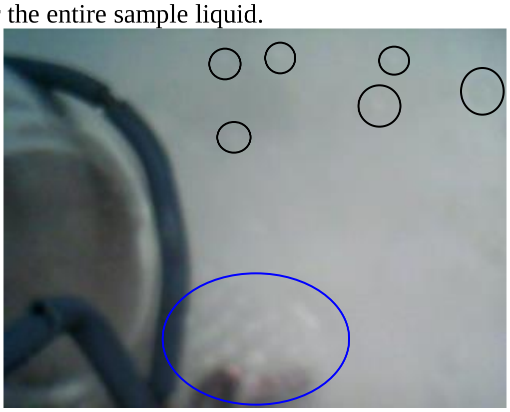

Figure 4: An image of the nitrogen bubbles. The lower center is a cluster of bubbles (blue circle), while the top right are larger bubbles moving under an ice layer (black circles).

These findings indicate that changes of ethane / methane ratios can easily result in nitrogen degassing. This study proposes that the freezing of ethane induces a change of the activity of nitrogen in the liquid resulting in exsolutions of N_2 gas. This should have significant implications for Titan especially if phenomena like evaporative freezing occur. More experiments will be conducted to solidify the freezing point of ethane at 1.5 bar, and to determine the homogeneity of the mixture, as well as the occurrence parameters of the bubbles.

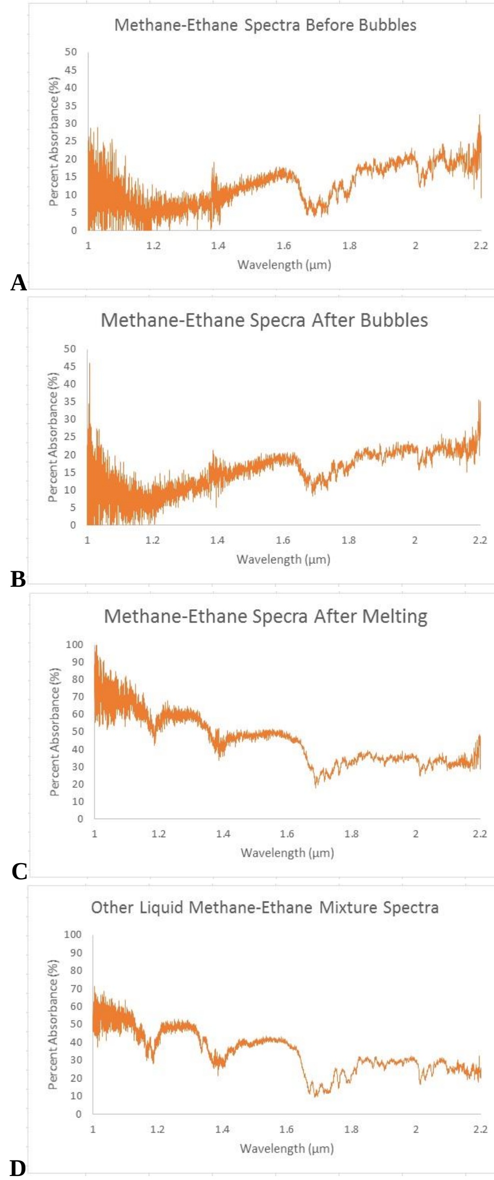

Figure 5: A-C shows spectra at different intervals in the methane-ethane mixture experiment where nitrogen bubbles occurred. **D** is included for comparison between the bubble experiment and a regular mixture experiment.

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References: [1] Lunine J.. and Atreya S. K. (2008) *Nature Geosci.*, *1*, 335. [2] Wilson E. H. and Atreya S. K. (2004) *JGR 109:*E06002 [3] Luspay-Kuti A. et al. (2012) *GRL 39*, L23203. [4] Luspay-Kuti A. et al. (2014) *EPSL 410*, 75-83 [5] Wasiak F. C. et al. (2013) *ASR 51*, 1213-1220 [6] Battino R. et al. (1984) *J. Phys. Chem. Ref. Data 13*, 563.