FREEZING POINTS OF METHANE-ETHANE-NITROGEN MIXTURES UNDER TITAN SURFACE PRESSURE.
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Introduction: Titan is the only body in the Solar System, besides Earth, with a dense atmosphere and stable surface liquids [1]. Titan's atmosphere is predominantly nitrogen, with several percent methane, which enables a methane hydrologic cycle [2] and the production of ethane via methane photolysis [3]. Titan's polar surface temperature (~91K [4]) permits liquid methane and ethane to be stable lakes on the surface [3] and is within a few degrees the ethane's freezing point (~90K), which allows the possibility of short time scales of stable ethane ice. This may be achieved when local temperatures drop below the mean regional temperature, such as in ponds that undergo evaporative freezing.

This study aims to discover the conditions in which ethane-nitrogen and ethane-methane-nitrogen mixtures freeze under Titan surface pressure by experimentally investigating the mixture's freezing point, including the role of dissolved atmospheric nitrogen. We aim to determine the freezing processes plausible on Titan's surface and to further our understanding of Titan's geologic and atmospheric processes.

Methods: Experiments were conducted in the University of Arkansas' Titan surface simulation chamber [5], where hydrocarbon ponds are analyzed at conditions relevant to Titan's surface (83–91 K; 1.5 bar nitrogen atmosphere). This chamber maintains temperature and pressure using liquid and gaseous nitrogen, respectively. The sample gas is condensed into liquid phase before delivery to a sample dish, which is suspended from an electronic balance. After the desired sample mixture is poured into the sample dish, the temperature is lowered (down to ~ 83K) to induce freezing. Freezing is verified by visual phase change (Fig. 1), liquid temperature profile (Fig. 2), and Fourier-Transform Infrared Spectroscopy (FTIR) (Fig. 3). Mass and temperature are continuously recorded for the duration of the experiment.

Results/Discussion: We find that when ethane-nitrogen mixtures freeze, a nearly constant temperature is maintained, indicative of the freezing point of a single component (Fig. 2 Top). As we increase the concentration of methane in our mixtures, however, the temperature profile becomes less defined and is best fit with a fourth order polynomial that indicates a lower freezing temperature (Fig. 2 Bottom: 28 methane mol%). Occasionally, in methane-ethane-nitrogen mixtures, we observe two plateau regions, one near ethane's freezing point and another, less defined, at cooler temperatures. The first plateau region is associated with ethane freezing out on the edges of the sample (observed visually), while the second plateau is likely related to the freezing of the methane-ethane in the center of the sample.

For the pure end members, we find ethane-nitrogen has a freezing point of 90.5K (Fig. 2, 4), just above the freezing temperature of pure ethane (90.15K). We are unable to freeze the methane-nitrogen mixture as our liquid nitrogen cooling system can only lower the sample temperature to 83.5K, well above the ~63K freezing temperature of a methane-nitrogen mixture [6]. The freezing point depression in the methane component results from the significant dissolution of nitrogen into methane [7–10].

In methane-ethane-nitrogen mixtures, the freezing point remains near 90K until ~30 mol% methane (relative to the total hydrocarbon abundance). As the methane concentration increases, the freezing point significantly decreases. At 58 mol%, the sample remains liquid down to the limit of our experimental setup (83.5K, see Fig. 4), indicating that the freezing temperature of this liquid is lower than 83.5K. This abrupt change in freezing temperature between ~40 and 60% methane mol% is consistent with recent modeling [10] and laboratory work [7,9], which shows that the amount of nitrogen dissolved in methane depends strongly on the ratio of methane to ethane and the temperature of the liquid.

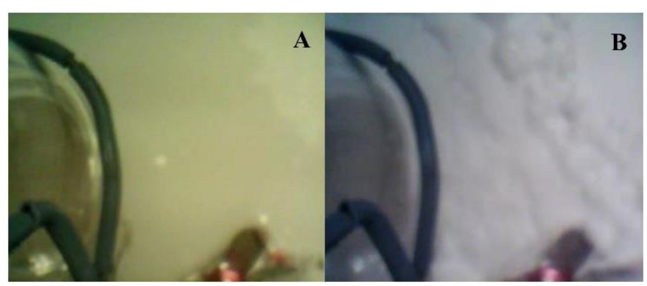

Figure 1: Arial image of ethane from the test chamber. (**A**) Liquid ethane. (**B**) Solid ethane. Yellow-green color is due to endoscope quality, not phase change.

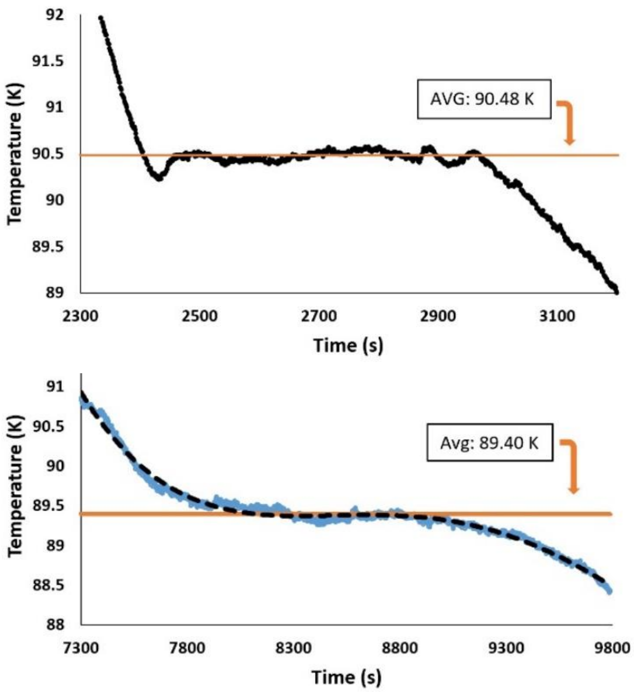

Figure 2: Temperature profiles for 0% methane / 100% ethane (top) and 26% methane / 74% ethane (bottom) experiments. The freezing process is exothermic and thus, the plateau in temperature is indicative of the freezing point. The orange horizontal line shows the average freezing point over the plateau region while the black dotted curve is a polynomial best fit for the temperature profile.

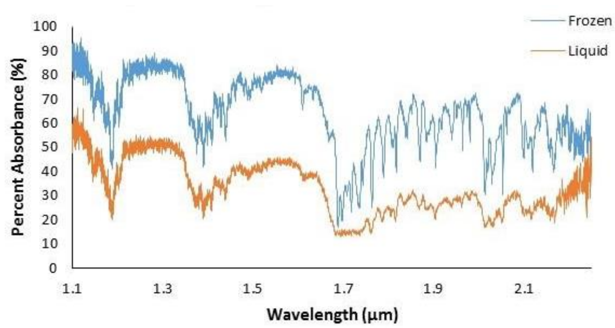

Figure 3: FTIR spectra of liquid (orange) and solid (blue) ethane. The increase in percent absorbance indicates freezing.

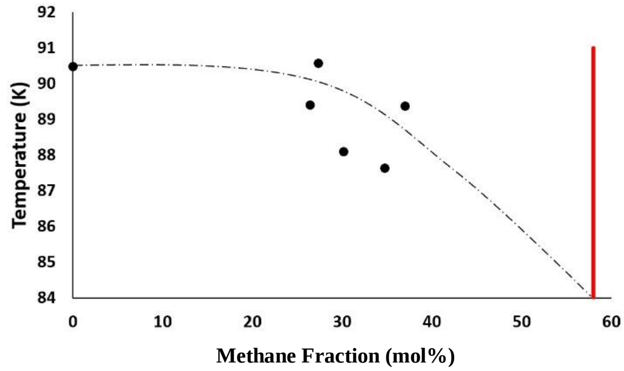

Figure 4: Experimental freezing point as a function of methane mol% in a 1.5 bar nitrogen atmosphere. The mixture remains liquid at a methane concentration of at most 58% (red vertical line), and the dotted curve is an estimate of the liquidous curve.

Summary: This study investigates the freezing point of various liquid methane-ethane mixtures with dissolved atmospheric nitrogen via laboratory experiments. We find that ethane-nitrogen and pure ethane have similar freezing points, however, methane-nitrogen freezes much lower, below 83.5K. Nitrogen dissolution causes freezing point depression of the methane component, and thus plays an important role in the freezing point of the methane-ethane mixtures in a nitrogen atmosphere.

Understanding the mixtures viable to freeze on Titan is important in understanding Titan's hydrologic cycle and geologic processes, as well as have significant implications for Titan's lakes and rain. Additional experiments will improve the solidus curve.

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