



Note

Does ice float in Titan's lakes and seas?

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ABSTRACT

We model Titan's lakes and seas as methane–ethane–nitrogen systems and model the buoyancy of solids in these systems assuming thermodynamic equilibrium. We find that ice will float in methane-rich lakes for all temperatures below the freezing point of pure methane and that ice will also float in ethane-rich seas provided the ice has an air porosity of greater than 5% by volume.

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1. Introduction

The Cassini RADAR instrument has detected standing liquid in both the north and south polar regions of Titan's surface (Stofan et al., 2007; Lunine et al., 2009). The presence of liquid ethane in the south polar Ontario Lacus was confirmed using Cassini's Visual Infrared and Mapping Spectrometer (VIMS) instrument (Brown et al., 2008). Furthermore, the Huygens probe which landed near Titan's equator, is believed to have landed in a dry lake bed, based on geomorphological characteristics of the surrounding surface (Tomasko et al., 2005). The discovery of hydrocarbon lakes and seas makes Titan the only body in the Solar System, aside from the Earth, known to have liquid on its surface. While only liquid ethane has been confirmed on Titan's surface, the lakes and seas may also be composed of significant amounts of methane and propane (Cordier et al., 2009). Methane and ethane both have triple points near to the temperatures and pressures observed at the surface of Titan and may exist in all three phases at the surface (Cordier et al., 2009); propane's triple point is well below the minimum surface temperature on Titan.

The fact that water ice floats in water is an important aspect of Earth's hydrological cycle and may have been significant to the preservation of life on Earth during times of near-global ice cover. Until now however the fate of solids formed from the freezing of Titan's lakes and seas has not been studied quantitatively, though many qualitative statements are found in the literature that the ice will always sink. The range of parameters that lead to floating ice is of particular interest and may be relevant to the future exploration of Titan (Stofan et al., 2007). Roe and Grundy (2012) recently studied the buoyancy of ice in the methane–nitrogen system and their results provide a good check in the limit of a pure methane–nitrogen lake. From the results of thermodynamic calculations (cf. Cordier et al., 2009), however, ethane is present or even dominates the composition of lakes and seas that are in equilibrium with Titan's atmosphere; therefore it is important to include ethane in models of these systems. In this note we show that for model lakes and seas composed of methane–ethane–nitrogen mixtures, lakes and seas on Titan can have ice that floats. Ice will float in mixed methane–ethane lakes on the methane-rich side of the binary phase diagram, for all temperatures below the freezing point of pure methane. Ice will also float in ethane-rich lakes provided the ice has an air porosity of greater than 5% by volume.

2. Model lake and lake ice

2.1. Composition of the lake and ice

Ethane-rich seas will contain methane and propane as secondary components (Cordier et al., 2009). However, given the importance of nitrogen in Titan's atmosphere (95% N₂ by mole fraction (Fulchignoni et al., 2005)), it may be present in amounts of several percent up to 20% in the lakes and seas depending on the methane mole fraction (Lunine et al., 1983). Unfortunately, we have not been able to find published experimental data for an ethane–methane–propane–nitrogen system at the temperatures of interest. In fact, the literature appears to contain no data for any ternary combination of the above three compounds at relevant temperatures. Thus to construct our model lake we use thermodynamic data for a methane–ethane binary mixture as well as data about the dissolution of nitrogen in methane and ethane separately. We model the lakes on Titan as methane–ethane–nitrogen mixtures and ignore the small influence of propane in the system.

Surface temperatures in the high latitudes have only modest seasonal swings. Jennings et al. (2009) found from observations of Titan's surface brightness with the Cassini Composite Infrared Spectrometer that in late northern winter the temperature near the northern and southern poles is approximately 91 and 92 K respectively. Cassini radio occultations measure near-surface temperatures near the summer southern pole to be approximately 93 K (Schinder et al., 2012). Schneider et al. (2012), using a general circulation model, predict winter lows near the poles between 90–91 K, and summer highs of 91–92 K. However, the lake energy balance model of Tokano (2009) predicts somewhat larger excursions ranging from just at or below 90 K in winter to 94 K in summer. Our conclusions are the same regarding the propensity of the solid to float whether we take the full range of seasonal temperature swings (90–94 K) or a narrower range (91–93 K).

The temperature–composition phase diagram for methane–ethane mixtures at temperatures near the solid–liquid equilibrium, as experimentally determined by Moran (1959),¹ is presented in Fig. 1. The system is a eutectic system with a minimum freezing point at $T = 72.2$ K, $X_m = 0.675$. All compositions with a methane mole fraction greater than that at the eutectic point will be referred to as *methane-rich* and all compositions with less methane than the eutectic composition will be referred to as *ethane-rich*. From both the ethane and methane rich sides of the phase diagram,

¹ To the extent of the authors knowledge, this is the only experimentally determined phase diagram for methane–ethane systems in this temperature regime.

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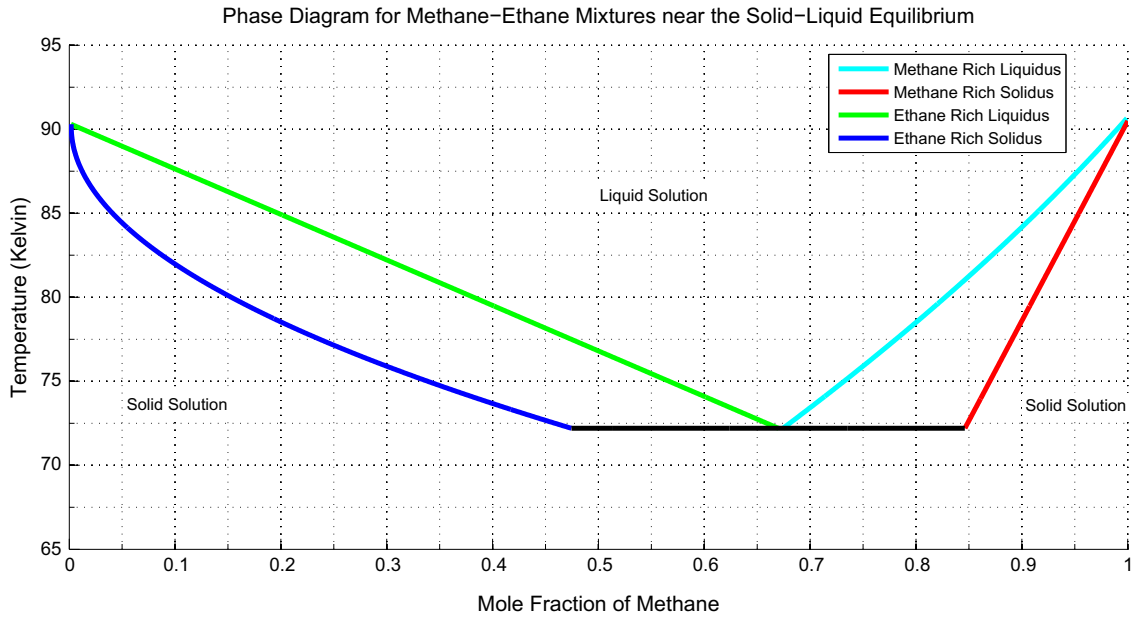


Fig. 1. Methane–ethane phase diagram. Credit: Moran (1959).

two curves intersect the eutectic point. The higher temperature curves are referred to as the *liquidus curves* and the lower temperature curves as the *solidus curves*. For temperatures and compositions that plot above the liquidus curves and the eutectic point, systems in equilibrium will be in the liquid phase. Methane and ethane liquids are completely miscible in the sense that for all compositions, the system forms a single liquid phase rather than multiple liquid phases of varied composition. For temperatures and compositions that plot below the solidus curves and the eutectic point, systems in equilibrium will be in the solid phase. The miscibility of the solid phases below the eutectic point is not presented in the phase diagram, however Moran (1959) comments that all the systems investigated formed solid solutions, though the deviation from ideal solid solution behavior was considerable. It will be assumed that for temperatures above the eutectic point (i.e. the temperatures pertinent for Titan’s surface) the solids are completely miscible. Finally, in the two remaining regions that are bounded by liquidus and solidus curves, both the liquid and solid phases are stable when the system is at equilibrium.

Consider for example a system that is between the ethane-rich liquidus and solidus curves. For a particular temperature of the system, the compositions of the liquid and solid phases will be given by the intersection of the constant temperature horizontal line with the ethane-rich liquidus and solidus lines respectively. For example, a system at equilibrium with a temperature of 78 K and a total methane mole fraction of 0.3 ($X_m^t = 0.3$) will have a liquid phase with $X_m^l = 0.455$ and a solid phase with $X_m^s = 0.21$. The relative abundance of the two phases is given by the lever rule (e.g. Rosenberg, 1977)

$$\frac{\text{moles of liquid}}{\text{moles of solid}} = \frac{|X_m^s - X_m^t|}{|X_m^l - X_m^t|} \quad (1)$$

For the example system above

$$\frac{\text{moles of liquid}}{\text{moles of solid}} = 0.6. \quad (2)$$

To have floating ice (i.e. a situation where both the solid and liquid phases are present when the system is in equilibrium) Titan’s lakes must be in one of the two regions of phase space that are between a liquidus and solidus curve.

To include nitrogen in the liquid phase we use the prediction of Lunine and Stevenson (1985) for the solubility of nitrogen in liquid methane–ethane mixtures at the temperatures relevant to Titan’s surface. In their work, Lunine and Stevenson assumed that nitrogen obeys Henry’s law in the methane and ethane liquids separately and that the Henry’s law constant for methane–ethane mixtures behaves ideally. In calculating the molar fraction of nitrogen in the liquid we use their Henry’s constant for a total (essentially, nitrogen) pressure at Titan’s surface of approximately 1.5 bar (Niemann et al., 2005). Unfortunately, to our knowledge, no similar estimate for the solubility of nitrogen in solid methane–ethane mixtures has been published for the temperatures relevant to Titan’s surface. The solubility of nitrogen in pure solid methane has however been determined (Omar et al., 1962) and we use this solubility to estimate the amount of nitrogen dissolved in the methane-rich solids. The solubility of nitrogen in pure solid ethane is unknown and thus we ignore dissolved nitrogen in the ethane-rich solids. This is reasonable since we know from the cases of the liquid mixture and pure solid methane that only a very small (few percent) amount

of nitrogen will be dissolved. Furthermore we expect that the difference in chemical structure between N_2 and C_2H_6 will lead to a significant substitution energy necessary to substitute nitrogen for ethane in the crystal structure. Thus the amount of nitrogen dissolved in solid ethane is expected to be less than the amount of nitrogen dissolved in liquid ethane as is the case for methane. Lastly, since we expect any N_2 molecule dissolved in the solid ethane to simply substitute for a C_2H_6 molecule and the atomic masses of these two molecules are very similar (28 amu to 30 amu) we expect the dissolved nitrogen to only minimally affect the density.

2.2. Density of the lake and ice

To have floating ice it is not only necessary that both the liquid and solid phases are present at equilibrium but also that the liquid phase is denser than the solid phase. Fortunately, in his experiments Moran (1959) also measured the density of the liquid methane–ethane mixtures. For six systems of a particular composition, Moran (1959) measured the density of the liquid phase at various temperatures and fit the density to straight lines of the form

$$\rho_{m-e}^l = E \cdot T + F, \quad (3)$$

where ρ_{m-e}^l is the density of the liquid phase, T is the temperature of the system, and E and F are constants. We determined the functional dependence of these constants on composition, yielding a density (in g/mL) of the liquid methane–ethane mixture as a function of both temperature and composition:

$$\rho_{m-e}^l = \frac{-0.1868 \cdot X_m^l - 1.0098}{1000} \cdot T - 0.1766 \cdot X_m^l + 0.7562. \quad (4)$$

To determine the density of nitrogen in the liquid phase at these temperatures a curve was fit to the data for the saturation density of liquid nitrogen in the CRC Handbook of Chemistry and Physics (Lide, 2012). The density of the liquid phase is then

$$\rho^l = \frac{\rho_{m-e}^l + \rho_n^l \cdot X_n}{1 + X_n}, \quad (5)$$

where the $1 + X_n$ term in the denominator normalizes the liquid to have a total mole fraction of unity.

Moran (1959) did not measure the density of the solid methane–ethane mixtures and no such measurements are published in the scientific literature. Bol’shutkin et al. (1971) however determined the density of pure solid methane for 22 different temperatures, ranging from 11 to 70 K. Using these data the density of solid methane (in g/mL) as a function of temperature was determined to be

$$\rho_m^s = -5.121 \times 10^{-4} \cdot T + 0.5312. \quad (6)$$

Similarly, Klimenko et al. (2008) measured the density of pure solid ethane for 21 different temperatures ranging from 5 to 89.5 K. From these data the density of solid ethane (in g/mL) as a function of temperature was determined to be

$$\rho_e^s = -88.3301 \left(\frac{T}{1000}\right)^3 + 6.3244 \left(\frac{T}{1000}\right)^2 - 0.2590 \left(\frac{T}{1000}\right) + 0.7421. \quad (7)$$

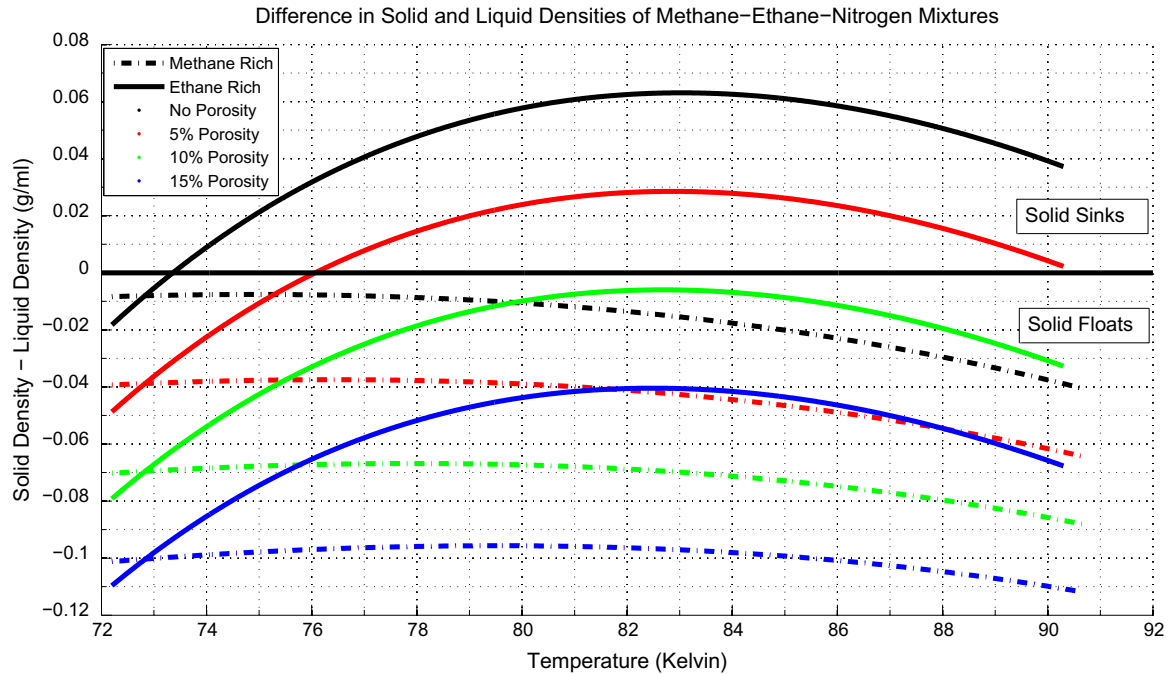


Fig. 2. Density difference between equilibrium solid and liquid phases in methane–ethane–nitrogen system. Ice will float in Titan’s lakes and seas for systems with a negative difference.

The density of solid nitrogen in the temperature regime pertinent to Titan’s surface is unknown. The density of solid nitrogen at 60 K is known to be 0.949 g/mL (Scott, 1976) and we assume this to be the density of solid nitrogen for all temperatures. This is a conservative estimate since we expect the density to decrease with temperature as most substances do and as solid nitrogen does for temperatures below 60 K (Scott, 1976). To estimate the density of the solid phase, ideal behavior is assumed such that the density is given by a compositionally weighted sum of the densities of its components. Thus for example the density of ethane-rich solids is

$$\rho^s = X_m \rho_m^s + (1 - X_m) \rho_e^s, \quad (8)$$

and the density of methane-rich solids is similarly determined with the density of nitrogen as the third component.

2.3. Porosity in the ice

We consider the influence of porosity in the solid phase. Sea ice in oceans on Earth has two types of porosity, brine porosity and air porosity. In our model we only consider the effect of air porosity. The air porosity of sea ice on Earth is quite variable, depending primarily upon the salinity of the ocean water from which it formed and the number of freeze–thaw cycles the ice has experienced but also on a number of other factors. The number of freeze–thaw cycles is important because thawing and refreezing of the ice tends to convert brine porosity to air porosity. Since the influence of brine porosity is not considered in this analysis, the air porosity of first year sea ice that has not experienced a freeze–thaw cycle (and thus not converted its brine porosity to air porosity) is the most relevant. First year sea ice on Earth generally has an air porosity of approximately 0–10% by volume (Nakawo, 1983; Kovacs, 1996; Zyryanov, 2012). It is also worth noting that glaciers on Earth which form from an entirely different mechanism than sea ice also tend to have air porosity and the porosity in the Greenland ice cap also varies from approximately 0% to 10% by volume (Schwander et al., 1993). By analogy to water ice on Earth it will be assumed that the porosity of the solid phase in the case of Titan’s lakes is somewhere between 0% and 15% by volume.

The porous volume in the ice will be occupied by the air at Titan’s surface which is 95% nitrogen and 5% methane. The Huygens probe that landed on Titan’s surface in 2005 measured a surface air density of 5.3446×10^{-3} g/mL (Fulchignoni, 2006). The total density of the solid phase is given by

$$\rho^{\text{solid}} = \frac{V^s \rho^s + V^{\text{porous space}} \rho^{\text{porous space}}}{V^{\text{total}}}, \quad (9)$$

but since $V^{\text{total}} = V^s + V^{\text{porous space}}$

$$\rho^{\text{solid}} = (1 - \phi) \rho^s + \phi \rho^{\text{porous space}}, \quad (10)$$

where ϕ is the fraction of the total volume that is porous.

3. Results

The density difference between the equilibrium solid and liquid phases is plotted in Fig. 2. Both methane and ethane rich systems that have temperatures and compositions that plot between their respective liquidus and solidus curves are included in the figure. For an ethane-rich system at a particular temperature, the equilibrium solid and liquid phases have the composition of the ethane-rich solidus and liquidus curves respectively for that particular temperature. The composition of methane-rich systems is similarly determined. Floating ice corresponds to a negative density difference in the figure. Solids in methane-rich systems are less dense than the coexisting liquid regardless of the air porosity and thus would float. For temperatures near the upper limit investigated (those most relevant to present surface conditions on Titan (Jennings et al., 2009; Schinder et al., 2012), solids in ethane-rich systems require air porosities of greater than approximately 5% in order to float. In the limit of a pure methane–nitrogen system (methane-rich system at 90.7 K), the nitrogen mole fraction in our model lake and ice is approximately 0.23 and 0 respectively and ice will float for this system. This is in agreement with the results of Roe and Grundy (2012) where the ice is pure methane and floats for all liquid nitrogen mole fractions greater than approximately 0.15. We also note that a recent experiment (Luna et al., 2012) found that at 14 K, the density of solid methane–nitrogen mixtures is less than the density calculated when ideal behavior is assumed (mixture density is given by the compositionally weighted sum of the densities of its components). Thus the density of methane-rich solids may be less than we calculate, which will act to enhance the tendency of the solids to float.

4. Discussion and conclusions

For a fairly robust range of parameters, ice formed from the winter freeze-over of Titan’s high latitude lakes and seas would float on the coexisting hydrocarbon liquid. Methane-rich lakes will have floating ice for all temperatures below the freezing point of methane (90.7 K) even if the ice does not have any air porosity. The model for methane-rich lakes includes the effect of dissolved nitrogen in both the lake and ice assuming the density behaves ideally. The seas, if ethane-rich, will have floating ice only if the ice forms with a porosity (in which the pores are filled with air that is almost all nitrogen) of greater than approximately 5% by volume, which is plausible based on terrestrial analogs (Nakawo, 1983; Kovacs, 1996; Zyryanov, 2012; Schwander et al., 1993). If upon freezing, Titan’s seas are able to incorporate a reasonable air-filled porosity into the ice phase, the ice will float in the lakes. Interestingly, in the case of ethane-rich seas, if the ice forms with an air-filled porosity of between 5% and 10%, the ice will initially float but if the temperature drops by just a few Kelvin the ice will sink. This sensitive dependence of the behavior of the ice on the temperature could lead to some interesting effects. For example, if the surface temperature of the sea oscillates about the point where the solid and

liquid have equal density the lake could actually form both ice that floats and sinks. In transitioning from winter to summer a lake could have both ice at its bottom and its surface: Cassini observations of northern hemisphere lakes and seas in the coming few years may see changes in surface reflectivity as spring progresses, in which the liquid surface becomes more and then less reflective as ice rises to the surface and then melts.

Finally, it is possible that some of the differences in radar reflectivities seen by Cassini from lake to lake during the winter (Hayes et al., 2008) might indicate variability in ice cover due in part to variations in the methane mole fraction. Such variation could indicate some of the smaller lakes are not purely rain-fed, but access crustal methane sources. In those cases the formation of floating ice will result in higher reflectivities than lakes with purely liquid surfaces, providing an alternative explanation for the appearance of the so-called “granular” lakes (Hayes et al., 2008). A test of this model will be to observe such lakes as spring progresses in the northern hemisphere; if ice is the cause of the increased reflectivity, the granular lakes should darken in radar images taken now relative to those obtained during the depths of Titan’s northern winter.

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