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The fate of ethane in Titan's hydrocarbon lakes and seas

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ABSTRACT

Ethane is expected to be the dominant photochemical product on Titan's surface and, in the absence of a process that sequesters it from exposed surface reservoirs, a major constituent of its lakes and seas. Absorption of Cassini's 2.2 cm radar by Ligeia Mare however suggests that this north polar sea is dominated by methane. In order to explain this apparent ethane deficiency, we explore the possibility that Ligeia Mare is the visible part of an alkanofer that interacted with an underlying clathrate layer and investigate the influence of this interaction on an assumed initial ethane–methane mixture in the liquid phase. We find that progressive liquid entrapment in clathrate allows the surface liquid reservoir to become methane-dominated for any initial ethane mole fraction below 0.75. If interactions between alkanofers and clathrates are common on Titan, this should lead to the emergence of many methane-dominated seas or lakes.

1. Introduction

Titan has a thick atmosphere dominated by nitrogen and methane. The dense orange-brown smog hiding the satellite's surface is produced by photochemical reactions of methane, nitrogen, and their dissociation products with solar ultraviolet, which lead primarily to the formation of ethane and heavier hydrocarbons (Lavvas et al., 2008a,b). Ethane and propane are expected to accumulate in the surface liquids and thus to be important constituents of liquid bodies that are in equilibrium with the atmosphere (Cordier et al., 2009, 2013; Tan et al., 2013). This classical picture, derived from Titan's photochemistry models, contrasts with the indirect measurements of the composition of Ligeia Mare obtained via radar absorption, suggesting that this sea is dominated by methane (Mastrogiuseppe et al., 2014; Mitchell et al., 2015). There is thus a discrepancy between the measured ethane/methane ratio and the expectation from otherwise well-tested photochemical schemes for Titan's atmospheric methane.

On the other hand, the temperature and atmospheric pressure conditions prevailing at Titan's ground level permit clathrate formation when liquid hydrocarbons enter in contact with the exposed water ice (Mousis and Schmitt, 2008). Assuming a high porosity for Titan's upper crust, clathrates with hydrocarbon guest species are stable and expected to occur down to several kilometers from the surface (Mousis and Schmitt, 2008; Choukroun and Sotin, 2012). These clathrates may contain a significant fraction of the ethane and propane generated in Titan's atmosphere over the Solar System's lifetime (Mousis and Schmitt, 2008). Also, under some circumstances, the lakes and seas present on Titan (Stofan et al., 2007; Mastrogiuseppe et al., 2014) can interact with underlying clathrate layers and, as a result, present compositions different from those expected from atmosphere–sea equilibrium (Mousis et al., 2014). In particular, if the basins containing liquids are in contact with the icy crust of Titan, their compositions may be altered by interactions with clathrate reservoirs that progressively form if the liquid mixtures diffuse throughout preexisting porous icy layers (Mousis et al., 2014).

The model proposed by Mousis et al. (2014) predicted that, if Titan's lakes interacted with clathrate reservoirs, they could become dominated by ethane and/or propane and be extremely impoverished in methane. This conclusion was based on an initial lake composition equal to that from the model of Cordier et al. (2009, 2013). However, several recent studies point toward very different compositions of the lakes and seas, which depend on the particular thermodynamic approach (Glein and Shock, 2013; Tan et al., 2013, 2015; Luspay-Kuti et al., 2015). The initial lake composition is a key parameter because it determines the amounts of the different species that become entrapped in clathrate and thus the ultimate composition of the lakes and seas.

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Here, we utilize the model proposed by Mousis et al. (2014) to investigate the range of initial compositions of Titan's Ligeia Mare that could be consistent with the recent measurements that show it to be dominated by methane (Mastrogiuseppe et al., 2014; Mitchell et al., 2015). We demonstrate that a sea will become methane-dominated for any initial ethane mole fraction below 0.75 if it interacted with an underlying clathrate layer that progressively formed from the entrapment of methane and ethane.

2. Model description

Our liquid reservoir is considered as a mixture of methane and ethane, and its equilibration is assumed faster with clathrate than with the atmosphere. This implies that the considered hydrocarbon lake or sea is the only visible part of a larger alkanofer that is in contact with the icy porous crust. We follow the approach proposed by Mousis et al. (2014), who consider an isolated system composed of a clathrate reservoir that progressively forms and replaces the crustal material with time and a well-mixed liquid reservoir that correspondingly empties due to the net transfer of molecules to the clathrate reservoir. We use the numerical procedure defined in Mousis et al. (2014) with the intent to determine the mole fractions of each species present in the liquid reservoir and trapped in the forming clathrate reservoir. These mole fractions depend on the species initial fractions (before volatile migration) in the liquid and clathrate. Our computations start from a predefined composition of the liquid reservoir. They use an iterative process for which the number of moles in the liquid phase being trapped in clathrates between each iteration is equal to 10^{-4} the total number of moles available. The numerical procedure utilized to calculate at each step the relative abundances of guest species incorporated in clathrates is based on a statistical mechanics model that relates their macroscopic thermodynamic properties to the molecular structures and interaction energies (van der Waals and Platteeuw, 1959; Lunine and Stevenson, 1985; Sloan and Koh, 2008; Mousis et al., 2014).

In this approach, the fractional occupancy of a guest molecule K for a given type q (q = small or large; see Sloan and Koh, 2008) of cage is written as

$$y_{K,q} = \frac{C_{K,q} f_K}{1 + \sum_J C_{J,q} f_J}, \tag{1}$$

where the sum in the denominator includes all the species which are present in the liquid phase (here methane and ethane). $C_{K,q}$ is the Langmuir constant of species K in the cage of type q, and f_K the fugacity of species K in the mixture. Using the Redlich–Kwong equation of state (Redlich and Kwong, 1949) in the case of a mixture dominated either by methane or ethane, we find that its coefficient of fugacity ϕ converges towards 1 at Titan's surface conditions, implying that f_K converges towards P_K, namely the vapor pressure of species K.

We consider the liquid hydrocarbon mixture as an ideal solution and the value f_K of each species K can then be calculated via the Raoult's law, which states

$$f_K \simeq P_K = x_K^{lake} \times P_K^*, \tag{2}$$

with P_K^* the vapor pressure of pure component K in the liquid, defined via the Antoine equation given in Mousis et al. (2014) and x_K^{lake} the mole fraction of pure component K in the liquid.

The Langmuir constant, which depends on the strength of the interaction between each guest species and each type of cage, is determined by integrating the molecular potential within the cavity as

$$C_{K,q} = \frac{4\pi}{k_B T} \int_0^{R_c} \exp\left(-\frac{w_{K,q}(r)}{k_B T}\right) r^2 dr, \tag{3}$$

where R_c represents the radius of the cavity assumed to be spherical, k_B the Boltzmann constant, and $w_{K,q}(r)$ is the spherically averaged Kihara potential representing the interactions between the guest molecules K and the H_2O molecules forming the surrounding cage q. In our formalism, $w(r)$ is written for a spherical guest molecule (McKoy and Sinanoğlu, 1963):

$$w(r) = 2z\epsilon \left[\frac{\sigma^{12}}{R_c^{11} r} \left(\delta^{10}(r) + \frac{a}{R_c} \delta^{11}(r) \right) - \frac{\sigma^6}{R_c^5 r} \left(\delta^4(r) + \frac{a}{R_c} \delta^5(r) \right) \right], \tag{4}$$

with

$$\delta^N(r) = \frac{1}{N} \left[\left(1 - \frac{r}{R_c} - \frac{a}{R_c} \right)^{-N} - \left(1 + \frac{r}{R_c} - \frac{a}{R_c} \right)^{-N} \right]. \tag{5}$$

In Eq. (4), z is the coordination number of the cell. Its value, taken from Sloan and Koh (2008), depends on the clathrate structure (I or II) and on the type of the cage (small or large). The Kihara parameters a, σ and ϵ for the molecule–water interactions are also derived from Sloan and Koh (2008).

Finally, the mole fraction x_K^{clat} of a guest molecule K in a clathrate can be calculated with respect to the whole set of species considered in the system as

$$x_K^{clat} = \frac{b_s y_{K,s} + b_\ell y_{K,\ell}}{b_s \sum_J y_{J,s} + b_\ell \sum_J y_{J,\ell}}, \tag{6}$$

where b_s and b_l are the number of small and large cages per unit cell respectively, for the clathrate structure under consideration, and with $\sum_K x_K^{clat} = 1$. Values of R_c, z, b_s and b_l are taken from Sloan and Koh (2008). All the computations performed here are based on the assumption that only structure I clathrates form at equilibrium from a mixture of methane and ethane, as suggested by experiments (Takeya et al., 2003).

3. Results

Fig. 1 represents the evolution of the mole fractions of species present in the liquid reservoir and its associated clathrate as a function of the progressive liquid entrapment. Our calculations have been conducted at a surface temperature of 91 K and the starting mole fractions of methane and ethane have been set to 0.7 and 0.3 in the liquid reservoir, respectively. These mole fractions are close to the values found in the lake–atmosphere model of Tan et al. (2013). The mole fraction of ethane in the liquid significantly decreases with progressive entrapment of the liquid reservoir, forcing this reservoir to become methane-pure when more than ~half (in mole fraction) of the initial reservoir has been trapped in clathrates. In this case, the mole fraction of ethane is below 5% in the liquid phase when more than ~40% of the initial liquid reservoir is trapped in clathrate. The significant sink of ethane in the liquid phase results from its more efficient trapping in clathrate compared to methane, as illustrated by Fig. 1 at low mole fractions of entrapped liquid. As the liquid reservoir becomes ethane depleted, progressive liquid entrapment occurs primarily for methane molecules and the mole fraction of methane in the clathrate increases. At the end of the liquid reservoir enclathration, the mole fractions of trapped methane and ethane converge towards their starting values in the liquid.

Fig. 2 displays the starting mole fractions of ethane in the liquid phase and corresponding fractions of the remaining liquid reservoir that give methane mole fractions of 0.90, 0.95 and 0.99. Our computations have been performed at a surface temperature of 91 K but a temperature difference of a few K would have not affected the results. The figure shows that ethane can be severely