On the chemical composition of Titan's dry lakebed evaporites

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ABSTRACT

Titan, the main satellite of Saturn, has an active cycle of methane in its troposphere. Among other evidence for a mechanism of evaporation at work on the ground, dry lakebeds have been discovered. Recent *Cassini* infrared observations of these empty lakes have revealed a surface composition poor in water ice compared to that of the surrounding terrains—suggesting the existence of organic evaporites deposits. The chemical composition of these possible evaporites is unknown. In this paper, we study evaporite composition using a model that treats both organic solids dissolution and solvent evaporation. Our results suggest the possibility of large abundances of butane and acetylene in the lake evaporites. However, due to uncertainties of the employed theory, these determinations have to be confirmed by laboratory experiments.

1. Introduction

For a long time the existence of liquid hydrocarbons at the surface of Titan has been suspected (Sagan and Dermott, 1982; Lunine et al., 1983; Lunine, 1993a,b). The dark features observed by Stofan et al. (2007) in the north polar region were the first confirmed lakes or seas of hydrocarbons. Subsequently, other evidence for the RADAR-dark areas' lacustrine nature was found in the RADAR and IR ranges, to the extent that the existence of lakes/seas is now rather well established. In fact, the number of detected manifestations (e.g. Turtle et al., 2011a,b) of an active tropospheric methane hydrologic cycle is increasing. The lakes are expected to take part in this cycle, providing methane and/or ethane to the atmosphere through evaporation processes.

In past years, the signature of lake evaporation has been actively researched. Already, Stofan et al. (2007) noticed features showing margins similar to those of established lakes but having a RADAR surface backscatter similar to the surrounding terrain, suggesting the occurrence of an evaporation process in the recent past. Barnes et al. (2009) performed a detailed study of shoreline features of Ontario Lacus, the largest southern latitude lake. These authors interpreted the 5-μm bright annulus around Ontario Lacus as a dry, low-water ice content zone, possibly corresponding to a deposit of fine-grained organic condensates. These patterns, created by the shoreline recession, could have been caused by an evaporation episode. In their study of the same system, Wall et al. (2010) reported evidences for active shoreline processes. Although evidence for short-term changes in the extent of Ontario Lacus has been put forward (Turtle et al., 2011b), a subsequent reanalysis came to the conclusion that there is no indication of lake extent changes in the *Cassini* dataset (Cornet et al., 2012). Hayes et al. (2011) noticed that some observed dry lakebeds in Titan's arctic appear to be brighter than their exteriors in both nadir and off-nadir observations, which suggests compositional differences. However Hayes et al. (2011) were not able to exclude the possibility of an infiltration of liquids into a subsurface hydrologic system. Barnes et al. (2011a) used a sample of several lakes and lakebeds located in a region south of the Ligeia Mare. They obtained a strong correlation between RADAR-empty lakes and 5-μm-bright unit interpreted as low-water ice content areas.

As mentioned by Barnes et al. (2011a) these observed dry lake floors cannot be made only of sediments, indeed a pure sedimentary origin of these deposits would produce lakebed showing a 5-μm-brightness similar to that of their surrounding zones. One possible explanation proposed by Barnes et al. (2011a) consists of evaporation of the solvent (here a mixture of methane and ethane) yielding to the saturation of the dissolved solutes. The top layer of the resulting evaporites is being observed now in dry lakebeds if this idea is correct. This paper is devoted to an exploration of the evaporite scenario on the theoretical side. We have developed a model allowing for the computation of the chemical composition of such evaporites.

This paper is organized as follows. In Section 2, we outline our model for calculating chemical composition of putative evaporite deposits in dry lakebeds. Section 3 is devoted to evaporite

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Table 1

Solids assumed to be dissolved in the lake and some of their properties. The Hildebrand's solubity parameter δ has to be compared to the value for methane and ethane at the same temperature (i.e. 90 K), which are respectively 1.52×10^4 $(J\,m^{-3})^{1/2}$ and 2.19×10^4 $(J\,m^{-3})^{1/2}$. For comparison purposes, for H_2O $\delta \sim 5 \times 10^4$ $(J\,m^{-3})^{1/2}$.

Species	Precipitation rate molecules $(m^{-2}\,s^{-1})$	$\delta\,10^4$ $(J\,m^{-3})^{1/2}$	Melting temperature (K)	Enthalpy of melting $(kJ\,mol^{-1})$
HCN	1.3×10^8[a]	2.99	260.0	8.406
C_4H_{10}	5.4×10^7[a]	1.91	136.0	4.661
C_2H_2	5.1×10^7[a]	2.28	192.4	4.105
CH_3CN	4.4×10^6[a]	2.92	229.3	6.887
CO_2	1.3×10^6[a]	1.98	216.6	9.020
C_6H_6	1.0×10^6[b]	2.48	279.1	9.300

[a] Lavvas et al. (2008a,b).
[b] Vuitton et al. (2008).

composition computations, and we discuss our results and conclude in Section 4.

2. Model description

We consider a portion of a Titan lake of uniform depth h that has a free surface of area S in contact with the atmosphere. For the sake of simplicity, methane, ethane and nitrogen are considered to be the only volatile compounds; they form a ternary mixture which will be our solvent. The presence of H_2, Ar and CO is neglected as they have low abundances in the atmosphere and as a consequence in the solution; C_3H_8 and C_4H_8 are also not taken into account because C_2H_6 seems to be much more abundant and their behaviors should not be very different than that of ethane. In addition to the solvent chemistry itself, we considered species in the solid state under Titan's surface thermodynamic conditions that may dissolve in the solvent. In the following, for short, we will simply call these compounds "dissolved solids" or "solutes": they include all the species, except those belonging to the solvent (i.e., methane, ethane and nitrogen). These supposed dissolved species are ultimately the products of the complex photochemistry taking place in the upper Titan atmosphere. In this work, we used the same list of solid compounds as in previous papers (Cordier et al., 2009, 2010, 2012 hereafter respectively C09, C10 and C12. Note that Cordier et al. (2013) is an erratum of Cordier et al. (2009).) These species appear to be among the main products found by photochemical 1D-models of Lavvas et al. (2008a,b) and Vuitton et al. (2008); the list is displayed in Table 1. This list differs from the list of species detected by CIRS[1] (i.e., CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_8, CH_3C_2H, C_4H_2, C_6H_6, HCN, HC_3N, C_2N_2, CO, CO_2 and H_2O, see Vinatier et al., 2010) as CIRS observations relate to Titan's stratosphere and do not imply that these species reach the thermodynamic conditions of their precipitation to the ground. In addition, some species (for instance C_4H_3, C_4H_4, C_4H_5; see Table 5 of Lavvas et al., 2008a) are included in models while they are not yet observed by Cassini instruments. Thanks to their melting temperatures ranging between 136.0 K (C_4H_{10}) and 279.1 K (C_6H_6), all these molecules are in solid state under the Titan's surface conditions ($T \sim 90$ K in the region of lakes; Jennings et al., 2009). Although it has still to be confirmed by laboratory experiments, the materials listed in Table 1 are theoretically predicted to be soluble in a mixture of methane and ethane. Indeed, the Hildebrand's solubility parameters δ's for these solids (see Poling et al., 2007; Ahuja, 2009) are close to the ethane value (see Table 1). We implement a numerical calculation for the dynamic composition evolution of liquid mixtures using discrete timesteps. At each time t, the saturation mole fraction $X_{i,sat}$ of each dissolved solid species i is computed via

$$\ln \Gamma_i X_{i,\mathrm{sat}} = -\frac{\Delta H_{i,\mathrm{m}}}{RT_{i,\mathrm{m}}}\left(\frac{T_{i,\mathrm{m}}}{T} - 1\right) \tag{1}$$

This relation can be found, for instance, in Section 8s–16 of the textbook by Poling et al. (2007) (hereafter POL07). The physical significance of Eq. (1) is the existence of a thermodynamic equilibrium between the considered precipitated solid i and the liquid solution. The enthalpy of melting is denoted $\Delta H_{i,\mathrm{m}}$, whereas T and $T_{i,\mathrm{m}}$ are respectively the current temperature of the lake and the melting temperature of molecule i; R is the constant of ideal gases and Γ_i is the activity coefficient. Although Eq. (1) has previously been used in several published works (Dubouloz et al., 1989, hereafter D89, and also C09, C10 and C12), we recall that it is approximate and its validity will be discussed in Section 4.

As the thermodynamic computations in the frame of the regular solution theory are uncertain (see C12) due to the lack of knowledge of thermodynamic data, we have distinguished two cases: the approximation of the ideal solution for which all the Γ_i's are equal to unity, and the non-ideal regular solution. In the case of an ideal solution, the molecules of the same species and those of different species interact with same intensity. For a non-ideal solution model, the Γ_i's are computed in the frame of regular solution theory (see D89, C09, POL07) in which the intermolecular interactions of involved species are such that the resulting entropy of mixing is equal to that of an ideal solution with the same composition: zero excess entropy, with the volume of mixing at zero. However in contrast with ideal solutions, regular solutions have mixing enthalpy with nonzero values. The regular-solution theory provides a good and useful semiquantitative representation of real behavior for solution containing nonpolar components as is the case of the mixtures under study in this work and the results based on this theory are in general considerably improved over those calculated by Raoult's law. In the context of the mixtures studied here it is expected that even though results may not possess extreme accuracy they are also hardly ever very bad, providing a valuable guide for future work. We emphasize that the Γ_i's are functions of X_i's, a fact which leads to numerical complications. The temperature T of the liquid remains unchanged during the whole evaporation process. Note, by the way, that for the temperatures relevant (see Table 1 for melting temperatures values) in our context, the right-hand side of Eq. (1) is negative, leading to mole fractions lower than the unity, at least in the case of an ideal solution.

The equilibrium solid-solution written as Eq. (1) must be complemented by the Principle of Matter Conservation. If we denote the total number of moles of all species at time t in the liquid by $N(t)$; at time $t + dt$, one can write for a lake with surface area S

$$N(t + dt) = N(t) - F_{CH_4} \times S \times dt - F_{C_2H_6} \times S \times dt - F_{N_2} \times S$$
$$\times\, dt - \sum_{i,\mathrm{sat},t+dt}\left(X_i(t)\,N(t) - X_{i,\mathrm{sat}}^{\mathrm{ideal}}N(t+dt)\right) \tag{2}$$

where F_{CH_4}, $F_{C_2H_6}$ and F_{N_2} are the assumed respective evaporation rates (in mole $m^{-2}\,s^{-1}$) of CH_4, C_2H_6 and N_2. The terms containing the F_i's represent the evaporation while the sum, which refers to species reaching the saturation at $t + dt$, corresponds to matter that precipitates and deposits on the lake floor.

The number of mole of species i available in the volume $S \times H$ of lake, at time t, is denoted by $n_i(t)$. Thus we arrive at the simple relation $n_i(t) = X_i N(t)$. Our algorithm consists of several steps. For the first one, we compute $N^{(0)}(t + dt)$. This is an estimation of the total number of moles (in volume $S \times H$ of lake) remaining after the time step dt during which only evaporation of methane, ethane and nitrogen is taken into account:

$$N^{(0)}(t + dt) = N(t) - (F_{CH_4} + F_{C_2H_6} + F_{N_2}) \times S \times dt. \tag{3}$$

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[1] Composite Infrared Spectrometer, an instrument onboard the Cassini spacecraft.