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COMPOSITION OF THE LAKES OF TITAN

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Abstract. Hundreds of radar-dark patches interpreted as lakes have been discovered in the north and south polar regions of Titan. We have estimated the composition of these lakes by using the direct abundance measurements from the Gas Chromatograph Mass Spectrometer (GCMS) aboard the Huygens probe and recent photochemical models based on the vertical temperature profile derived by the Huygens Atmospheric Structure Instrument (HASI). Thermodynamic equilibrium is assumed between the atmosphere and the lakes, which are also considered as nonideal solutions. We find that the main constituents of the lakes are ethane (C_2H_6) ($\sim$ 76–79%), propane (C_3H_8) ($\sim$ 7–8%), methane (CH_4) ($\sim$ 5–10%), hydrogen cyanide (HCN) ($\sim$ 2–3%), butene (C_4H_8) ($\sim$ 1%), butane (C_4H_{10}) ($\sim$ 1%) and acetylene (C_2H_2) ($\sim$ 1%). The calculated composition of lakes is then substantially different from what has been expected from models elaborated prior to the exploration of Titan by the Cassini-Huygens spacecraft.

1 Introduction

The surface of Saturn's haze-shrouded moon Titan had long been proposed to have oceans or seas, on the basis of the stability of liquid methane and ethane at the ground level (Flasar 1983; Lunine et al. 1983; Lorenz et al. 2003). Ground-based radar observations ruled out the presence of a global ocean in the 1990s (Muhleman et al. 1995), but the presence of isolated lakes was not precluded (Campbell et al. 2003). A large, dark, lake-like feature subsequently named Ontario Lacus was detected at Titan's south polar region by the Cassini ISS system in 2005 (McEwen et al. 2005) and hundreds of radar dark features with a variety of properties consistent with liquid-filled lakes were found in the northern hemisphere by the Cassini RADAR system (Stofan et al. 2007).

The chemical composition of the lakes of Titan is still not well determined. Good quality spectral data of the Ontario Lacus have been obtained by the Visual and Infrared Mapping Spectrometer (VIMS) aboard Cassini but the only species that seems firmly identified is C_2H_6 (Brown et al. 2008); the atmosphere contains so much CH_4 that it is very difficult to detect the surface liquid phase of this molecule even if it is dominant in the lakes. Because the detection of other compounds in the lakes of Titan remains challenging in the absence of in situ measurements, the only way to get a good estimate of the chemical composition of these lakes is to elaborate a thermodynamic model based on theoretical calculations and laboratory data. Several models, that investigate the influence of photochemistry and the atmospheric composition on the chemical composition of liquids formed on the surface of Titan, have been elaborated in the pre-Cassini years (Lunine et al. 1983; Dubouloz et al. 1989; McKay et al. 1993; Tokano 2005). Based on atmospheric observations these models assumed surface bodies of liquid on Titan to contain a mixture of C_2H_6, CH_4 and N_2 and a large number of dissolved minor species.

However, Cassini-Huygens measurements have improved our knowledge of the structure and composition of Titan's atmosphere, requiring the solubilities to be recomputed under actual Titan conditions. In particular, the Gas Chromatograph Mass Spectrometer (GCMS) aboard Huygens and the Cassini Composite Infrared Spectrometer (CIRS) provided new atmospheric mole fraction data (see Niemann et al. 2005). Moreover, near-surface brightness temperatures at the high latitudes where the lakes exist have now been determined (Jennings

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et al. 2009). Here, we propose a model that takes into account these recent advances and thus provides the most up-to-date chemical composition of Titan's lakes as a function of their location on the satellite's surface. Our model considers the same assumptions as those made by Dubouloz et al. (1989) (hereafter D89) when they calculated the composition of the hypothetical ocean proposed to exist on Titan in the years prior the Cassini-Huygens exploration. The lakes are then considered as nonideal solutions in thermodynamic equilibrium with the atmosphere.

2 The model of lake-atmosphere equilibrium

Our model is based on the regular solution theory and the thermodynamic equilibrium is assumed between the liquid and the atmosphere. This thermodynamic equilibrium, which is expressed by the equality of chemical potentials, can be written (Eq. 1 of D89):

$$Y_i\, P = \Gamma_i\, X_i\, P_{vp,i}, \tag{2.1}$$

where P is the total Titan's surface pressure, Y_i and X_i are respectively the mole fractions of the i compound in the atmosphere and the liquid, $P_{vp,i}$ its vapor pressure, and Γ_i its activity coefficient in the liquid given by Eq. 2 of D89. Because the system of involved equations is non-linear, it is solved with the use of the Newton Raphson's method.

Our model also allows us to estimate the fractions of solid precipitates that can be dissolved in the lakes of Titan. To this end, we calculate the *saturation* mole fraction $X_{i,sat}$[1] of the i compound, which is given by (Eq. 7 of D89):

$$\ln(\Gamma_i\, X_{i,sat}) = (\Delta H_m/RT_m)(1 - T_m/T), \tag{2.2}$$

where T_m is the component's melting temperature and ΔH_m its enthalpy of fusion. Our calculation procedure is then conducted as follows:

1. The unknown X_i's and Y_i's are computed via the Newton-Raphson method.
2. Once the X_i's have been determined, the $X_{i,sat}$'s are in turn calculated and compared to the X_i's for each species. If for compound i we get $X_{i,sat} < X_i$, then we fix $X_i = X_{i,sat}$.
3. We get new values of X_i's and $X_{i,sat}$'s via the resolution of the nonlinear system.
4. The iterations are continued until we get a difference between $X_{i,sat}$ and X_i lower than 10^{-6}, value for which the numerical inaccuracy is clearly negligible compared to other sources of uncertainties.

The known Y_i's are derived from Niemann et al. (2005). The precipitation rates used here derive from the photochemical models of Lavvas et al. (2008a,b) and Vuitton et al. (2008) and correspond to the main products of CH_4 and N_2 photolysis. These rates allow to express each i compound that precipitates in the form $X_i = \frac{\tau_i}{\tau_{C_2H_6}} \times X_{C_2H_6}$. We also ensure that $\sum_{i=1}^{n} X_i = 1$ and $\sum_{i=1}^{n} Y_i = 1$. The thermodynamic data used in our calculations derive from the NIST database[2] when they are available and the remaining ones have been taken from D89. Note that H_2 is the only compound whose mole fraction in the liquid is not determined with the aforementioned procedure. Instead, we calculate the amount of dissolved H_2 in the liquid via Henry's law (D89).

3 Results

Our calculations have been performed for two different zones of Titan's surface. The first zone corresponds to the vicinity of the landing site of the Huygens probe, where the surface temperature was measured to be 93.65 K (Niemann et al. 2005). The Huygens probe detected drainage-like features and a high surface relative

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[1] The saturation mole fraction of the i compound corresponds to the maximum mole fraction of i in the liquid form. Above this value, the i material in excess remains in solid form.

[2] `http://webbook.nist.gov`

Table 1. Chemical composition of lakes at the poles and the equator.

	Equator (93.65 K)	Poles (90 K)
Main composition (lake mole fraction)		
N_2	2.95×10^{-3}	4.90×10^{-3}
CH_4	5.55×10^{-2}	9.69×10^{-2}
Ar	2.88×10^{-6}	5.01×10^{-6}
CO	2.05×10^{-7}	4.21×10^{-7}
C_2H_6	7.95×10^{-1}	7.64×10^{-1}
C_3H_8	7.71×10^{-2}	7.42×10^{-2}
C_4H_8	1.45×10^{-2}	1.39×10^{-2}
H_2	5.09×10^{-11}	3.99×10^{-11}
Solutes (lake mole fraction)		
HCN	2.89×10^{-2} (s)	2.09×10^{-2} (s)
C_4H_{10}	1.26×10^{-2} (ns)	1.21×10^{-2} (ns)
C_2H_2	1.19×10^{-2} (ns)	1.15×10^{-2} (ns)
C_6H_6	2.34×10^{-3} (ns)	2.25×10^{-3} (ns)
CH_3CN	1.03×10^{-3} (ns)	9.89×10^{-4} (ns)
CO_2	3.04×10^{-4} (ns)	2.92×10^{-4} (ns)

(s): saturated; (ns) non saturated.

humidity, so the presence of liquids cannot be excluded in this area (Tomasko et al. 2005; Niemann et al. 2005). The second zone corresponds to the north pole of Titan where the surface temperature is around ∼ 90 K based on near-surface brightness temperature measurements (Jennings et al. 2009). In both cases, the atmospheric pressure is assumed to be identical and corresponds to that (1.46 bar) measured by Huygens at the ground level (Niemann et al. 2005).

Table 1 gives the mole fractions of the main compounds in lakes formed on the surface of Titan and calculated for the two different zones. It shows that, whatever the considered site, their composition is dominated by C_2H_6, C_3H_8, CH_4, HCN, C_4H_8, C_4H_{10} and C_2H_2. On the other hand, with mole fractions much lower than 1%, N_2, C_6H_6, CH_3CN, CO_2, Ar, CO and H_2 are found to be minor compounds in the lakes.

4 Discussion

Our solubility calculations imply that a number of species produced by methane photolysis and energetic particle chemistry in Titan's upper atmosphere should be readily detectable with a mass spectrometer carried to the surface of a liquid-filled lake by a Huygens-like entry probe (Coustenis et al. 2009). The measured abundances of multiple minor constituents in the lake, coupled to measurements and models of stratospheric abundances and production rates, and direct temperature measurements of the lake surface, will constrain lake properties that are of interest in understanding the methane hydrologic cycle. For example, at the winter pole a seasonally deposited upper-layer of liquid methane might exist on top of a longer-lived ethane-methane liquid reservoir by virtue of methane's lower density and limited vertical mixing in the cold lakes (Stevenson and Potter 1986). Such a transient layer would be bereft of minor components compared with our values thanks to the slow sedimentation rate of the high altitude aerosols compared to the seasonal (meteorological) methane deposition rate; our solubility values provide a means of calculating the extent to which the longer-lived liquid reservoir below has mixed into the methane meteorological layer. (The extreme cold of the tropopause of Titan prevents the hydrocarbon constituents other than methane and possibly ethane from passing directly to the lower atmosphere in the gas phase; thus the lakes must be seeded by stratospheric aerosol sedimentation).

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