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Titan's lakes chemical composition: Sources of uncertainties and variability

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ABSTRACT

Between 2004 and 2007 the instruments of the Cassini spacecraft, orbiting within the Saturn system, discovered dark patches in the polar regions of Titan. These features are interpreted as hydrocarbon lakes and seas with ethane and methane identified as the main compounds. In this context, we have developed a lake–atmosphere equilibrium model allowing the determination of the chemical composition of these liquid areas present on Titan. The model is based on uncertain thermodynamic data and precipitation rates of organic species predicted to be present in the lakes and seas that are subject to spatial and temporal variations. Here we explore and discuss the influence of these uncertainties and variations. The errors and uncertainties relevant to thermodynamic data are simulated via Monte Carlo simulations. Global circulation models (GCM) are also employed in order to investigate the possibility of chemical asymmetry between the south and the north poles, due to differences in precipitation rates. We find that mole fractions of compounds in the liquid phase have a high sensitivity to thermodynamic data used as inputs, in particular molar volumes and enthalpies of vaporization. When we combine all considered uncertainties, the ranges of obtained mole fractions are rather large (up to ~8500%) but the distributions of values are narrow. The relative standard deviations remain between 10% and ~300% depending on the compound considered. Compared to other sources of uncertainties and variability, deviation caused by surface pressure variations are clearly negligible, remaining of the order of a few percent up to ~20%. Moreover, no significant difference is found between the composition of lakes located in north and south poles. Because the theory of regular solutions employed here is sensitive to thermodynamic data and is not suitable for polar molecules such as HCN and CH_3CN, our work strongly underlines the need for experimental simulations and the improvement of Titan's atmospheric models.

1. Introduction

The surface of Saturn's haze-shrouded moon Titan had long been proposed to be at least partly hidden by oceans or seas, on the basis of the stability of liquid methane and ethane at the surface (Flasar, 1983; Lunine et al., 1983; Lorenz et al., 2003). The presence of a global ocean on Titan was excluded from ground-based radar observations in the mid 1990s (Muhleman et al., 1995). In mid 2006, dark, lake-like features of a range of sizes were detected at Titan's north polar region by the Cassini RADAR (Stofan et al., 2007). The chemical composition of these lakes remains, however, poorly determined. Spectra of the southern hemisphere lake Ontario Lacus have been obtained by the visual and infrared mapping spectrometer (VIMS) aboard Cassini but the only species that has been firmly identified is C_2H_6 (Brown et al., 2008). The difficulty in determining the composition of the lakes is essentially due to the presence of a large atmospheric fraction of CH_4 that impedes this molecule's identification in the liquid phase present on the surface, irrespective of the value of its mole fraction. However, methane is indirectly inferred in Ontario Lacus by the secular decline of the lake extent over the Titan summer

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(Hayes et al., 2010) and the observation of troposphere clouds, which must be methane, coincident with surface darkening over the southern pole during the summer (Turtle et al., 2007). 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 their chemical composition is to develop and utilize a thermodynamic model based on theoretical calculations and laboratory data. Several models investigating the influence of photochemistry and the atmospheric composition on the chemical composition of putative hydrocarbon oceans or seas 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). These models suggested that the liquid phase existing on Titan contains a mixture made from C_2H_6, CH_4 and N_2, and a large number of dissolved minor species.

On the other hand, the Cassini–Huygens measurements have improved our knowledge of the structure and composition of Titan's atmosphere. 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, and Table 1). Moreover, near-surface brightness temperatures and corresponding estimates for physical temperatures in the high latitudes at which numerous lakes are found have now been determined (Jennings et al., 2009). These atmospheric and surface conditions have been recently used to recompute the solubilities of the different compounds in the hydrocarbon lakes (Cordier et al., 2009, hereafter C09). The same model has also been employed to explore the possibility of noble gas trapping in the lakes of Titan in order to provide an attempt of explanation of their atmospheric depletion (Cordier et al., 2010).

The assumptions considered by C09 are similar to those made by Dubouloz et al. (1989) (hereafter DUB89): in both cases, lakes are considered as nonideal solutions in thermodynamic equilibrium with the atmosphere. However, neither DUB89 nor C09 have taken into consideration the influence of uncertainties on the data used as inputs in their models. Indeed, some thermodynamic data are measured at much higher temperature and extrapolated down to temperatures relevant to Titan's conditions. Precipitation rates are also supposed to vary with respect to latitude, longitude and time. In this work, we investigate the influence of thermodynamic uncertainties, and in a lesser extent, the geographic influence of the variation of precipitations on the lakes composition. In the latter case, we restrict our study to a supposed north/south poles asymmetry in chemical composition.

In Section 2 we detail our lake–atmosphere equilibrium model. Section 3 is dedicated to the study of the influence of uncertainties on thermodynamic data (vapor pressures, molar volumes, enthalpies of vaporization and parameters of interaction) on the resulting lakes composition. In Section 4, simulations are conducted with the use of precipitation rates derived from a version of the IPSL[1] two-dimensional climate model of Titan's atmosphere (Crespin et al., 2008) and allow comparison between chemical composition of south pole and north pole lakes. Section 5 is devoted to discussion and conclusions.

Table 1
Assumed composition of Titan's atmosphere at the ground level.

Atmosphere	Mole fraction	Determination
H_2	9.8×10^{-4}	Huygens GCMS[a]
CH_4	0.0492	Huygens GCMS[b]
CO	4.70×10^{-5}	Cassini CIRS[c]
^{40}Ar	4.32×10^{-5}	Huygens GCMS[b]
N_2	0.95	C09[d]
C_2H_6	1.49×10^{-5}	C09[d]

[a] Owen and Niemann (2009).

[b] Niemann et al. (2005).

[c] De Kok et al. (2007).

[d] N_2 and C_2H_6 abundances have been calculated by C09 and correspond to a ground temperature of 93.65 K. In Monte Carlo simulations presented here, the mole fractions of N_2 and C_2H_6 are varying (see text).

2. Description of the lake–atmosphere equilibrium model

Our model is based on regular solution theory and thermodynamic equilibrium is assumed between the liquid and the atmosphere. This equilibrium, which is expressed by the equality of chemical potentials, can be written as follows (Eq. (1) of DUB89):

$$Y_k P = \Gamma_k X_k P_{vp,k}, \tag{1}$$

where P is the total pressure at Titan's surface, Y_k and X_k respectively the mole fractions of the k compound in the atmosphere and in the liquid, and $P_{vp,k}$ its vapor pressure. The activity coefficient Γ_k (dimensionless) of the k compound is given by (frame of the regular solution theory—see Poling et al., 2007)

$$RT \ln \Gamma_k = V_{m,k} \sum_i \sum_j (A_{ik} - A_{ij}) \Phi_i \Phi_j, \tag{2}$$

where

$$A_{ij} = (\delta_i - \delta_j)^2 + 2 l_{ij} \delta_i \delta_j \tag{3}$$

and

$$\Phi_i = X_i V_{m,i} \Big/ \sum_j X_j V_{m,j}. \tag{4}$$

δ_i ($(\mathrm{J\,m^{-3}})^{1/2}$) is the Hildebrand's solubility parameter of the ith compound. The value of this parameter is given by

$$\delta_i = \sqrt{\frac{\Delta H_{v,i} - RT}{V_{m,i}}}, \tag{5}$$

where $\Delta H_{v,i}$ ($\mathrm{J\,mol^{-1}}$) is the enthalpy of vaporization and $V_{m,i}$ ($\mathrm{m^3\,mol^{-1}}$) the molar volume. A δ_i represents a measure of the molecular cohesion energy of the pure component i. It depends on the nature and the *strength* of intermolecular forces (hydrogen bond, etc.) between molecules of the same species. In general, two components i and j with δ_i and δ_j presenting close values, have a high solubility. Beside this, the l_{ij}'s parameters represent the effects of interactions between molecules of different species. These l_{ij}'s are empirically determined and are generally poorly known. The situation $\forall i,j$: $\delta_i = \delta_j$ and $l_{ij} = 0$ corresponds to all activity coefficient equal to one, in other words this is an ideal solution in which all intermolecular forces are negligible.

Our model also allows us to estimate the mole fraction of each solid precipitate that is dissolved in the lakes of Titan. To this end, we calculate the *saturation* mole fraction[2] $X_{i,sat}$ of the compound i, which is given by (Eq. (7) of DUB89)

$$\ln(\Gamma_i X_{i,sat}) = (\Delta H_m / R T_m)(1 - T_m / T), \tag{6}$$

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

1. The unknown X_i's and Y_i's are computed via the Newton–Raphson method.

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[1] Institut Pierre-Simon Laplace.

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