

# Composition of Titan's dry lakebeds: what can be inferred from the solubility theory

Cordier<sup>1</sup>, D., Barnes<sup>2</sup>, J. W. and Ferreira<sup>3</sup>, A.G.M.



Contact: [daniel.cordier@obs-besancon.fr](mailto:daniel.cordier@obs-besancon.fr)

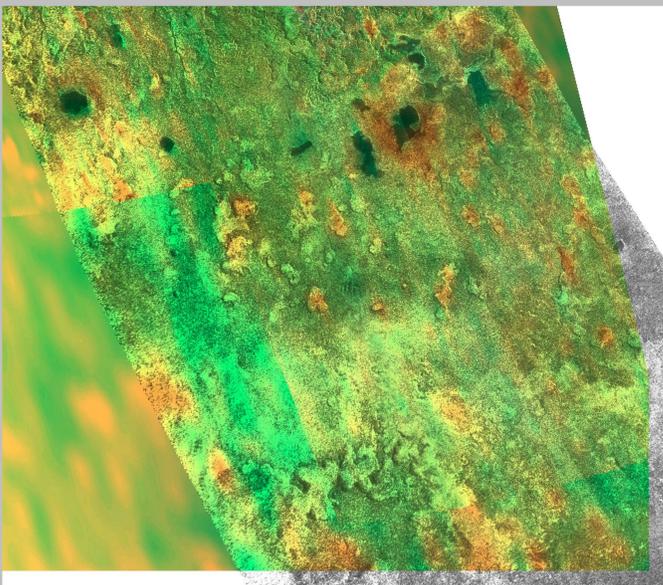


<sup>1</sup> Institut UTINAM, CNRS, UMR 6213, Université de Franche-Comté, 41bis, avenue de l'Observatoire, 25 000 Besançon, France  
<sup>2</sup> Department of Physics, University of Idaho, Engineering-Physics Building, Moscow, ID 83844, USA  
<sup>3</sup> Departamento de Engenharia Química, Universidade de Coimbra, Coimbra 3030-290, Portugal

**ABSTRACT** Titan, the main satellite of Saturn, seems to have an active cycle of methane in its troposphere. Among other evidences of a mechanism of evaporation at work on the ground, **dry lakebeds have been discovered**. Recently, 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 work, we propose a study of evaporites composition using a model of organic solids dissolution and of the solvent evaporation. Our results suggest the **possibility of large abundances of butane and acetylene in the lake evaporites**. But, due to uncertainties of the employed theory, these determinations have to be confirmed by laboratory experiments.

**I- Introduction** Since the eighties, the existence of liquid hydrocarbons at the surface of Titan has been suspected (see for instance Sagan & Dermott, 1982). Thanks to the Cassini orbiter RADAR system, dark patterns were observed in the north polar region of the main satellite of Saturn (Stofan *et al.*, 2007). These features, presented a very low reflectivity in the RADAR wave lengths domain and a morphology similar to Earth's lakes one. Consequently, they have been interpreted as hydrocarbon lakes, this interpretation has been reinforced by the observation of a specular reflection of sunlight through the 5- $\mu$ m window (Stephan *et al.*, 2010). Such lakes have also been detected in the south hemisphere polar area (Turtle *et al.*, 2009), but they show a smaller surface coverage. Already, during the first RADAR lakes detection, the presence of features that look like dry lakebeds have been noticed. A strong correlation between RADAR dry lakebeds and surface patches bright at 5- $\mu$ m has been found by Barnes *et al.* (2011). This brightness associated to high reflectivity in the 2.8- $\mu$ m window relative to the 2.7- $\mu$ m window, seems to be characteristic of very low water ice abundance relative to the rest of Titan (Barnes *et al.* 2009, Barnes *et al.* 2011). The neighbouring terrains having a different aspect in infrared VIMS observations. In summary, all of this suggests the formation of an evaporitic layer of organic matter in the Titan's liquid empty lakebeds.

Other observations speak in favor of the existence of evaporation processes from lakes. For instance, evidences for active shoreline processes have been reported (Wall *et al.* 2010, Barnes *et al.* 2009a). On the theoretical side, several authors have developed models that take into account a possible evaporation of lakes (Mitri *et al.* 2007, Tokano 2009). The question of the composition of potential lakebeds evaporites is still widely opened; the present work is dedicated to what can be answered with the help of the solubility models including evaporation of methane and ethane.



**Fig. 1** This figure shows, on Titan, the area south to the north-polar sea Ligea Mare. This is a combined VIMS-RADAR view; the VIMS data are color-mapped with  $R = 5 \mu\text{m}$ ,  $G = 2 \mu\text{m}$ ,  $B = 1.3 \mu\text{m}$ . The zones that appear in orangish/yellowish are interpreted like terrains poor in water ice, suggesting the existence of an organic deposit. The correlation between these zones and the RADAR patterns with the morphology of dry lakebeds is remarkable.

In **Tab. 2**, results relevant for an ideal solution have been gathered. The initial type 1 and 2 mixtures have been considered, both ethane rich ( $\sim 89\%$  of  $\text{C}_2\text{H}_6$  when evaporation starting) with  $\sim 1\%$  of nitrogen to ensure the liquid physical state. While  $X_{\text{liq}}^{\text{ini}}$  quantifies the initial chemical composition of the solution,  $X_{\text{sol}}^{\text{ini}}$  represents the abundances of dissolved solids separated from the solvent (i.e.  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{N}_2$ ), the  $X_{\text{evap}}^{\text{fin}}$ 's are the mole fractions of compounds finally deposited in the evaporites upper layer; the parameter of enrichment  $\Delta$  measures the relative enrichment/empoverishment of a given species in the surface evaporites, compared to the initial composition of solids. As it can be noticed in **Tab. 2**, the only species undergoing an enrichment in the surface evaporites layer, compared to abundances initially taken into account for the dissolved solids, are butane ( $\text{C}_4\text{H}_{10}$ ) and acetylene ( $\text{C}_2\text{H}_2$ ). This behavior can be explained by their high solubilities (i.e. high  $X^{\text{sat}}$ 's). The higher  $X^{\text{sat}}$  is, the more the quantity of dissolved material is. Consequently the saturation occurs later during the evaporation process. If we compare  $X_{\text{evap}}^{\text{fin}}$  obtained for type 1 and type 2 mixtures of solids, we see that evaporite composition obviously depends on the initial abundances of solutes. Our simulation clearly shows, in the frame of our current assumptions, that dissolution in methane/ethane solution, followed by evaporation of the solvent, yields to surface evaporite composition with high abundances of the most soluble species. We stress that identical parameter of the enrichment  $\Delta$  is the consequence of a saturation of solutes that occurs at the very end of the evaporation. Of course, a solvent of a different composition (e.g. a methane rich one) leads strictly to the same result as here we are making the calculations by adopting the ideal solution hypothesis. The results of simulations for which the regular solution  $\Gamma_i$ 's (non-ideal solution) have been gathered in **Tab. 3** and **Tab. 4**, which are respectively devoted to dissolved solids mixture type 1 and type 2. For each of these types, cases of methane rich and poor solvent are considered. As it can be noticed in **Tab. 3** and **Tab. 4**, the general trend remains the same: butane and acetylene, if present in the initial mixture, are the dominant species in the upper evaporite layer. The difference between the results of methane rich and poor are explained by the non-ideality of the solution: in such a situation the molecules undergo interactions, this way solvents with different compositions are not equivalent.

**II- The Model** We consider a lake as a liquid phase with only three volatile compounds: methane, ethane and nitrogen; the roles of argon and carbon monoxide are neglected. The species which are supposed to be dissolved in the methane-ethane mixture are those indicated in Table 1. This inventory comes from photochemical models, these compounds are in solid state under the thermodynamic conditions of the Titan's surface. Methane and ethane evaporate at respective evaporation rates  $F_{\text{CH}_4}$  and  $F_{\text{C}_2\text{H}_6}$  supposed to be known at each time  $t$ . According to equilibrium models (see for instance Cordier *et al.* 2009) the abundance of nitrogen is supposed to be of the order of a percent and its evaporation rate is scaled to the ethane one.

Table 1: Solids assumed to be dissolved in the lakes and their properties.

Species	Precipitation rate $\text{molecules}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$	Melting temperature (K)	Enthalpy of melting ( $\text{kJ}\cdot\text{mol}^{-1}$ )
HCN	$1.3 \times 10^8$ (a)	260.0	8.406
$\text{C}_4\text{H}_{10}$	$5.4 \times 10^7$ (a)	136.0	4.661
$\text{C}_2\text{H}_2$	$5.1 \times 10^7$ (a)	192.4	4.105
$\text{CH}_3\text{CN}$	$4.4 \times 10^6$ (a)	229.3	6.887
$\text{CO}_2$	$1.3 \times 10^6$ (a)	216.6	9.020
$\text{C}_6\text{H}_6$	$1.0 \times 10^6$ (b)	279.1	9.300

(a) Lavvas *et al.* (2008a, 2008b); (b) Vuitton *et al.* (2008).

The quantities of  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  that evaporates during the time interval between  $t$  and  $t + \Delta t$  are computed and new mole fractions  $X_i^{\text{(new)}}$  of solutes are derived. These updated values are compared to the mole fractions at saturation ( $X_i^{\text{sat}}$ ) which are provided by the equation (1)

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

If  $X_i^{\text{(new)}} > X_i^{\text{sat}}$ , then we fix  $X_i^{\text{(new)}} = X_i^{\text{sat}}$ , the exceeding material is assumed to become solid instantaneously at the lake bed, the other mole fractions are adjusted to insure  $\sum X_i = 1$ . Taking into consideration the matter precipitating, the composition of the evaporitic layer ( $X_i^{\text{evap}}$ ) at time  $t + \Delta t$  can be easily calculated. The procedure is repeated until all the initial quantity of solvent is gone. For the sake of simplicity, we first consider here an ideal solution, i.e. a solution for which the activity coefficients  $\Gamma_i$  equal the unity for all species. The calculation is conducted over the evaporation time-scale  $\tau_{\text{CH}_4+\text{C}_2\text{H}_6}$  that way a precise knowledge of evaporation rate  $F_{\text{CH}_4}$  and  $F_{\text{C}_2\text{H}_6}$  is not required. This is a very helpful assumption as these rates depend on numerous and unknown parameters: temperature difference between lake and atmosphere, actual atmospheric mole fraction of methane and ethane, the speed of wind, etc (Mitri *et al.* 2007, Tokano 2009).

**III- The Results** We have considered two kinds of initial liquid mixtures. On one hand (**type 1 mixture**), we chose a mixture with dissolved solids mole fractions scaled to precipitation rates; forcing HCN, the most abundant species in atmospheric precipitations having its mole fraction set to its value at saturation (ideal case). On the other hand (**type 2 mixture**), we took a mixture in which all the species had the same abundance, fixed to the smallest mole fraction at saturation (i.e. that relative to  $\text{C}_6\text{H}_6$ , see Tab. 1). All computations were performed at temperature  $T = 90 \text{ K}$ , typical of the lakes regions.

**Tab. 2** Notation:  $x.y(-n) = x.y \cdot 10^{-n}$

Species	$X_{\text{sat}}$ (ideal)	Mixture type 1			
		$X_{\text{liq}}^{\text{ini}}$	$X_{\text{sol}}^{\text{ini}}$	$X_{\text{evap}}^{\text{fin}}$	$\Delta$
$\text{CH}_4$	—	10.018%	—	—	—
$\text{C}_2\text{H}_6$	—	88.804%	—	—	—
$\text{N}_2$	—	1.002%	—	—	—
HCN	6.46(-4)	6.46(-4)	3.65(-1)	3.82(-3)	-99 %
$\text{C}_4\text{H}_{10}$	1.22(-1)	5.93(-4)	3.35(-1)	6.48(-1)	+94 %
$\text{C}_2\text{H}_2$	5.40(-2)	3.62(-4)	2.05(-1)	3.20(-1)	+56 %
$\text{CH}_3\text{CN}$	3.73(-3)	5.42(-5)	3.06(-2)	2.21(-2)	-28 %
$\text{CO}_2$	8.72(-4)	3.43(-5)	1.94(-2)	5.16(-3)	-73 %
$\text{C}_6\text{H}_6$	2.20(-4)	8.06(-5)	4.55(-2)	1.31(-3)	-97 %
		Mixture type 2			
Species	$X_{\text{sat}}$ (ideal)	$X_{\text{liq}}^{\text{ini}}$	$X_{\text{sol}}^{\text{ini}}$	$X_{\text{evap}}^{\text{fin}}$	$\Delta$
$\text{CH}_4$	—	10.013%	—	—	—
$\text{C}_2\text{H}_6$	—	88.853%	—	—	—
$\text{N}_2$	—	1.001%	—	—	—
HCN	6.46(-4)	2.20(-4)	1.67(-1)	6.86(-3)	-96 %
$\text{C}_4\text{H}_{10}$	1.22(-1)	2.20(-4)	1.67(-1)	4.71(-1)	+183 %
$\text{C}_2\text{H}_2$	5.40(-2)	2.20(-4)	1.67(-1)	4.71(-1)	+183 %
$\text{CH}_3\text{CN}$	3.73(-3)	2.20(-4)	1.67(-1)	3.96(-2)	-76 %
$\text{CO}_2$	8.72(-4)	2.20(-4)	1.67(-1)	9.26(-3)	-94 %
$\text{C}_6\text{H}_6$	2.20(-4)	2.20(-4)	1.67(-1)	2.34(-3)	-99 %

**Tab. 3** Notation:  $x.y(-n) = x.y \cdot 10^{-n}$

Species	Mixture type 1, methane poor				
	$X_{\text{liq}}^{\text{ini}}$	$X_{\text{sol}}^{\text{ini}}$	$X_{\text{evap}}^{\text{fin}}$	$\Delta$	
$\text{CH}_4$	10.018%	—	—	—	
$\text{C}_2\text{H}_6$	88.804%	—	—	—	
$\text{N}_2$	1.002%	—	—	—	
HCN	6.46(-4)	3.65(-1)	1.52(-4)	-100 %	
$\text{C}_4\text{H}_{10}$	5.93(-4)	3.35(-1)	5.72(-1)	+71 %	
$\text{C}_2\text{H}_2$	3.62(-4)	2.05(-1)	4.20(-1)	+105 %	
$\text{CH}_3\text{CN}$	5.42(-5)	3.06(-2)	7.14(-4)	-98 %	
$\text{CO}_2$	3.43(-5)	1.94(-2)	6.53(-3)	-66 %	
$\text{C}_6\text{H}_6$	8.06(-5)	4.55(-2)	6.82(-4)	-99 %	
		Mixture type 1, methane rich			
Species	$X_{\text{liq}}^{\text{ini}}$	$X_{\text{sol}}^{\text{ini}}$	$X_{\text{evap}}^{\text{fin}}$	$\Delta$	
$\text{CH}_4$	90.160 %	—	—	—	
$\text{C}_2\text{H}_6$	8.662 %	—	—	—	
$\text{N}_2$	1.002 %	—	—	—	
HCN	6.46(-4)	3.65(-1)	6.92(-5)	-100 %	
$\text{C}_4\text{H}_{10}$	5.93(-4)	3.35(-1)	6.69(-1)	+100 %	
$\text{C}_2\text{H}_2$	3.62(-4)	2.05(-1)	3.24(-1)	+58 %	
$\text{CH}_3\text{CN}$	5.42(-5)	3.06(-2)	2.94(-4)	-99 %	
$\text{CO}_2$	3.43(-5)	1.94(-2)	6.03(-3)	-69 %	
$\text{C}_6\text{H}_6$	8.06(-5)	4.55(-2)	3.65(-4)	-99 %	

**Tab. 4** Notation:  $x.y(-n) = x.y \cdot 10^{-n}$

Species	Mixture type 2 methane poor				
	$X_{\text{liq}}^{\text{ini}}$	$X_{\text{sol}}^{\text{ini}}$	$X_{\text{evap}}^{\text{fin}}$	$\Delta$	
$\text{CH}_4$	10.013 %	—	—	—	
$\text{C}_2\text{H}_6$	88.853 %	—	—	—	
$\text{N}_2$	1.001 %	—	—	—	
HCN	2.20(-4)	1.67(-1)	2.18(-4)	-100 %	
$\text{C}_4\text{H}_{10}$	2.20(-4)	1.67(-1)	4.95(-1)	197 %	
$\text{C}_2\text{H}_2$	2.20(-4)	1.67(-1)	4.95(-1)	197 %	
$\text{CH}_3\text{CN}$	2.20(-4)	1.67(-1)	1.04(-3)	-99 %	
$\text{CO}_2$	2.20(-4)	1.67(-1)	8.54(-3)	-95 %	
$\text{C}_6\text{H}_6$	2.20(-4)	1.67(-1)	9.55(-4)	-99 %	
		Mixture type 2, methane rich			
Species	$X_{\text{liq}}^{\text{ini}}$	$X_{\text{sol}}^{\text{ini}}$	$X_{\text{evap}}^{\text{fin}}$	$\Delta$	
$\text{CH}_4$	90.119 %	—	—	—	
$\text{C}_2\text{H}_6$	8.747 %	—	—	—	
$\text{N}_2$	1.001 %	—	—	—	
HCN	2.20(-4)	1.67(-1)	6.97(-5)	-100 %	
$\text{C}_4\text{H}_{10}$	2.20(-4)	1.67(-1)	6.68(-1)	301 %	
$\text{C}_2\text{H}_2$	2.20(-4)	1.67(-1)	3.25(-1)	95 %	
$\text{CH}_3\text{CN}$	2.20(-4)	1.67(-1)	2.97(-4)	-100 %	
$\text{CO}_2$	2.20(-4)	1.67(-1)	6.03(-3)	-96 %	
$\text{C}_6\text{H}_6$	2.20(-4)	1.67(-1)	3.67(-4)	-100 %	

**IV- Discussion** We have checked that reasonable variations in the temperature or in the nitrogen abundance do not alter significantly the observed tendency concerning the chemical composition of possible evaporites. However Eq. (1) is an approximation of Eq. (2)

$$\ln \Gamma_i X_{i,\text{sat}} = -\frac{\Delta H_{i,m}}{RT_{i,m}} \left( \frac{T_{i,m}}{T} - 1 \right) - \frac{1}{RT} \int_{T_m}^T \Delta c_p dT + \frac{1}{R} \int_{T_m}^T \frac{\Delta c_p}{T} dT \quad (2)$$

Unfortunately the  $\Delta c_p$ 's are not known for the relevant range of temperature and the regular solution theory (activity coefficients  $\Gamma_i$  calculation) suffers from uncertainties (see Cordier *et al.* 2012), this is why laboratory experiments of dissolution of organic solids in methane/ethane mixtures are required for an improved understanding of the Titan's evaporites formation.

**References** Sagan & Dermott, *Nature*, 300, 731, (1982). Stofan, et al. *Nature*, 445, 61, (2007). Stephan, et al. *GRL*, 37, L07104 (2010). Turtle, et al. *GRL*, L02204 (2009). Barnes, et al. *Icarus*, 216, 136 (2011). Barnes, et al. *Icarus*, 201, 217 (2009). Wall, et al. *GRL*, 37, L05202 (2010). Mitri, et al. *Icarus*, 186, 385 (2007). Tokano, *Astrobiology*, 9, 147 (2009). Brown, et al. *Nature*, 454, 607 (2008). Dubouloz, et al. *Icarus*, 82, 81 (1989). Cordier, et al., *ApJL*, L128 (2009). Cordier, et al., *PSS*, 61, 99 (2012).