



Structure of Titan's evaporites



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ABSTRACT

Numerous geological features that could be evaporitic in origin have been identified on the surface of Titan. Although they seem to be water–ice poor, their main properties – chemical composition, thickness, stratification – are essentially unknown. In this paper, which follows on a previous one focusing on the surface composition (Cordier, D., Barnes, J.W., Ferreira, A.G. [2013b]. *Icarus* 226(2), 1431–1437), we provide some answers to these questions derived from a new model. This model, based on the up-to-date thermodynamic theory known as “PC-SAFT”, has been validated with available laboratory measurements and specifically developed for our purpose. 1-D models confirm the possibility of an acetylene and/or butane enriched central layer of evaporitic deposit. The estimated thickness of this acetylene–butane layer could explain the strong RADAR brightness of the evaporites. The 2-D computations indicate an accumulation of poorly soluble species at the deposit's margin. Among these species, HCN or aerosols similar to tholins could play a dominant role. Our model predicts the existence of chemically trimodal “bathtub rings” which is consistent with what it is observed at the south polar lake Ontario Lacus. This work also provides plausible explanations to the lack of evaporites in the south polar region and to the high radar reflectivity of dry lakebeds.

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1. Introduction

Among many other fascinating features, Titan, the largest satellite of Saturn, hosts lakes and seas (Stofan et al., 2007) likely filled by liquid hydrocarbons containing some amount of dissolved atmospheric nitrogen and various organic compounds (Dubouloz et al., 1989; Cordier et al., 2009, 2013a).

In Cordier et al. (2013b) (hereafter PAP1), the authors only derived a chemical composition for the external surface of Titan's

putative evaporites. Butane and acetylene were found to be the most likely main components of these external layers, but this result has several restrictions, the most obvious being the lack of information concerning the spatial structure of the evaporitic deposits. Indeed, in PAP1, neither vertical stratification nor horizontal variations of composition were considered; consequently the model can be labeled “0-D”. The 1-D or 2-D models of evaporitic deposition are of interest as the subsequent structure is potentially observable at the margins of these geological units. Moreover, a future lander could drill into these layers and perform detailed analysis or a Titan boat could directly measure dissolved solids with a mass spectrometer (Stofan et al., 2011).

In a laboratory study, Malaska et al. (2012) obtained interesting and illustrative result on the evaporitic crystallization process with exotic materials. After full evaporation of their working fluid (heptane at room temperature in replacement of methane and/or ethane in cryogenic conditions), a “playa” composed of the sequence of the four organic compounds initially dissolved in the

Abbreviations: PC-SAFT, Perturbed-Chain Statistical Associating Fluid Theory; VIMS, Visual and Infrared Mapping Spectrometer; RST, Regular Solution Theory; EoS, equation of state; VLE, vapor–liquid equilibrium; SLE, solid–liquid equilibrium; NIST, National Institute of Standards and Technology; DST, density functional theory; GCM, Global Circulation Model.

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liquid was left behind. It should be noticed that some species used as analogs in this experimental approach do not follow the expected behavior based on their respective solubilities. This could be explained by the specific conditions of the laboratory simulation. Already in both VIMS¹ and RADAR data, chemical composition gradients appear to surround lakebeds (Barnes et al., 2009, 2011). Barnes et al. (2009) observed several separate *annuli* following the contour of the partially evaporated lake Ontario Lacus at Titan's south pole. Moriconi et al. (2010) tentatively detected organics and nitriles in a ramp along the shore of the same lake, suggesting that sediments and evaporites could coexist around this object. A model of evaporite layer structure may also shed light on the possible cause of the relatively high RADAR reflectivity observed in dry lakebeds. Indeed, as noticed by Barnes et al. (2011), this high reflectivity remains unexplained and could be caused by volume scattering if the evaporite layer is at least several centimeter thick or contains subsurface horizons (see also Section 3.3).

As a first step in PAP1, the Regular Solution Theory (hereafter RST) was employed to mimic the non-ideal effect in cryogenic solutions. Unfortunately, this approach is clearly limited (Cordier et al., 2012). Thus, the model of dissolution has been substantially improved in this work by the use of the Perturbed-Chain Statistical Associating Fluid Theory (hereafter PC-SAFT) equation of state (Gross and Sadowski, 2001) which is widely employed in the chemical engineering community. The PC-SAFT has been successfully introduced to the study of Titan by Tan et al. (2013, 2015) and Luspai-Kuti et al. (2015). Another improvement on the RST approach from PAP1 is the derivation of molar volumes of the relevant molecular solids from the properties of their crystal structure. The influence of the pressure on these volumes is moreover studied using state of the art quantum chemical calculations. We emphasize that the Modified Van Laar (MLV) model developed by Glein and Shock (2013) belongs to the RST family and relies, as does our model, on parameters regressed on empirical data. For the only solid organic considered by Glein and Shock (2013), i.e. acetylene, we have used the same experimental measurements, namely those published by Neumann and Mann (1969).

Our paper is organized as follows. In Section 2, we describe our new PC-SAFT based model, and we give details concerning the properties of the different molecular solids involved. We also specify the atmospheric model taken into consideration. Section 3 is devoted to results obtained with our 1-D model: for a given initial state (i.e. depth of liquid, assumed composition of solutes and solvents) a possible vertical structure is proposed. The question of the maximum thickness of evaporite deposited is also addressed. Adopting a plausible topography, in Section 4 we compute what could be the species segregation across a lakebed shore. Finally, we discuss our results and conclude in Sections 5 and 6.

2. The model of solutes properties

Although other possible sources are available in the literature, we have chosen to keep the list of studied solutes from the work of Lavvas et al. (2008a,b). This has the advantage of facilitating the comparisons with previous work (PAP1) and limits the potential sources of uncertainties which are inevitably multiplied by introducing more species. However, in the last section of the paper we will discuss the occurrence and the possible role of the compounds not included in our “standard” mixture. Although theoretical models (Lavvas et al., 2008a,b) argue in favor of their presence, we are aware that acetylene has not yet been firmly detected at the surface (Clark et al., 2010; Moriconi et al., 2010) and that butane has not been observed in the atmosphere.

Beside the solvents, considered as a ternary mixture of N₂, CH₄ and C₂H₆, we therefore consider a set of six species, listed in Table 1, which are assumed to be deposited to the surface of Titan or extracted from the “soil” by cryogenic solvents (after being previously produced in the atmosphere). In photochemical models (Lavvas et al., 2008a,b), they reach their temperature of solidification; therefore it can be hypothesized that they form exotic organic snows. Once they fall to the surface of Titan, these six species (i.e. HCN, C₄H₁₀, C₂H₂, CH₃CN, CO₂, C₆H₆) either remain in the solid state due to local conditions or will be dissolved in cryogenic solvents. Species that have been detected by observations or produced in photochemical models but are never found at temperatures below their freezing point are not considered as potential lake solutes – this is the case for ethylene. The microphysics of the formation of organic snows is ignored, although it could be the subject of interesting research in the future.

In the next section, we describe the adopted solubility theory and the method employed to get reliable molar volumes for organic solids.

2.1. The model of solubility

Similar to what has been done in PAP1, our solubility estimations are made by solving the equation

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

where $X_{i,sat}$ is the mole fraction of the compound i at saturation and Γ_i is the activity coefficient of the considered species. $T_{i,m}$ and $\Delta H_{i,m}$ are melting temperature and enthalpy of melting respectively. The temperature of the system is denoted T , and R is the gas constant. This relation can be found, for instance, in the textbook by Poling et al. (2007). The physical meaning of Eq. (1) is that a thermodynamic equilibrium between the considered precipitated solid i and the liquid solution – Eq. (1) is nothing more than an equality of chemical potential. We emphasize that $X_i < X_{i,sat}$ can easily occur for a stable state, while situations where $X_i > X_{i,sat}$ are metastable. Commonly, metastable states are not sustainable: any perturbation ignites crystallization and the corresponding mole fractions are adjusted such as $X_i = X_{i,sat}$. The overabundance of species i is deposited at the bottom of the system. In PAP1 and in Glein and Shock (2013), the limitation of the validity of Eq. (1) is mentioned, in in depth discussion of that aspect will be put forward in the appendix of this paper. Cordier et al. (2012) have shown the flaws of the RST, as have other authors (Glein and Shock, 2013). At its core, the RST is a generalization of a model established for binary mixtures. The main caveat concerning the RST probably lies in its weak physical foundation. In contrast, the equation of state (EoS) called PC-SAFT² Gross and Sadowski (2001), which belongs to the vast family of the SAFT EoS, is molecular based. Indeed, PC-SAFT is derived, contrary to the RST, from the statistical physics. Each type of molecule is represented by parameters related to its individual microscopic properties. In that sense, PC-SAFT can be considered more profound than theories belonging to the RST family. Furthermore, PC-SAFT has proved to be one of the most powerful types of EoS for the liquid and vapor states. This theory is the subject of numerous works in the field of thermophysics. Here, the activity coefficient Γ_i that appears in Eq. (1) will be computed with the help of PC-SAFT. For this application to solid–liquid equilibrium (SLE), the activity coefficient is written as the ratio $\Gamma_i = \Phi_i^l / \Phi_i^{l0}$, where Φ_i^l is the fugacity coefficient of the species i and Φ_i^{l0} is the fugacity coefficient of the pure subcooled liquid of the same compound. In the frame of PC-SAFT, molecules are considered as “chains” of segments where each molecule is

¹ Visual and Infrared Mapping Spectrometer.

² Perturbed-Chain Statistical Associating Fluid Theory.

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