EPSC Abstracts
Vol. 10, EPSC2015-201, 2015
European Planetary Science Congress 2015

About the vertical gradient of composition in Titan's lakes

D. Cordier[1], J. Roussel[2] and P. Rannou[3]
[1]Institut UTINAM, CNRS/INSU, UMR 6213, 25030 Besançon Cedex, France
(daniel.cordier@obs-besancon.fr), [2]Ecole nationale supérieure de Chimie de Rennes - 11, allée de Beaulieu - CS50837 - 35708 Rennes cedex 7, France. [3] GSMA, Universite de Reims Champagne-Ardenne, Reims, France.

Abstract

The hydrocarbons seas of Titan, discovered by Cassini/Huygens mission are among the most interesting features of this object. However, their chemical composition remains not well known. Due to the presence of the methane in the atmosphere, only a few indications favoring the existence of some amount of ethane in Ontario Lacus have been brought by observations reported in [2, 10]. Several numerical models have been proposed: Dubouloz *et al*. (1989), Cordier *et al*. (2009,2013) based on the Regular Solution Theory, Glein *et al*. (2013) [4] and Tan *et al*. (2013) [13] respectively based on a RST family model and on the advanced equation of state PC-SAFT[1] [5, 13, 10, 3].
The atmosphere of Titan is dominated by nitrogen and contains a few percents of methane. The latter, photolyzed by solar radiations in the stratosphere, gives rise to a complex organic chemistry yielding to the production of a plethora of compounds [7]. According to numerical models, the most abundant species, produced by photochemistry, should be ethane. Then, the bulk composition of Titan's lakes can reasonably regarded as a mixture of methane and ethane, with some amount of dissolved N_2. This latter has a melting temperature (63.3 K) much below than that for methane (around 91 K) and ethane (101 K determined by Streng, 1971; 89.2 K measured by Timmermans, 1935); as the ground temperature of Titan in the range $90-95$ K, the nitrogen may play a role of an antifreezing solute.
In this work, we investigate the possibility of a vertical chemical composition gradient produced by the joint effects of the pressure and temperature gradients. For that purpose, we built an original model based on the hydrostatic equilibrium

$$\frac{\partial P}{\partial z} = -\rho g \quad (1)$$

where P is the pressure, ρ the density and g the gravity. A thermodynamic equilibrium is hypothesized through the liquid

$$\frac{\partial \Phi_i x_i}{\partial z} = 0 \quad (2)$$

where Φ_i is the activity coefficient of the species i and x_i is its model fraction at the depth z. The coefficient Φ_i and the density ρ are computed in the frame of PC-SAFT.

Beside this, the vertical energy transport is assumed to be governed by the equation (3), adapted from [14, 15] who used the formalism originally introduced in [1]

$$\frac{\partial}{\partial z}\left((\lambda_{\mathrm{L,mix}} + \lambda_e)\frac{\partial T}{\partial z}\right) + \frac{\partial Q}{\partial z} = 0 \quad (3)$$

$\lambda_{\mathrm{L,mix}}$ is the molecular thermal conductivity of the liquid mixture (W.m^{-1}.K^{-1}) and λ_{e} represents the contribution to heat transport by the eddy diffusion, which coefficient κ_{e} scales with the wind speed over the lake and is given by

$$\kappa_{\mathrm{e}} = \frac{0.0325\, exp(-0.01278 z)\, u_r/10}{1+\beta\frac{\partial\rho}{\partial z}} \quad (4)$$

u_r is the wind speed, λ_{e}, and κ_{e} are simply linked by $\lambda_{\mathrm{e}} = \rho C_{\mathrm{P}} \kappa_{\mathrm{e}}$. The Eq. (4) is also used by [15] who adapted it from [16] and [8]. The former determined the value of β and obtained 5×10^5 m^4.kg^{-1}. In Eq. (3), the source term $\partial Q/\partial z$ is due to the absorption of sunlight governed by

$$Q(z) = (1-\alpha)\, S_g\, \exp(-\eta(h-z)) \quad (5)$$

in which S_g is the light initial flux, η is the absorption coefficient and h stands for the liquid height. For individual compounds, several empirical estimation technics are available. We choose the method developped by Latini and his co-workers, published in a series of papers and summarized in [12] (see p. 10.44). In that approah, the thermal conductivity $\lambda_{L,i}$ (W.m^{-1}.K^{-1}) of a compound i is given by

$$\lambda_{L,i} = \frac{A_i(1-T_{r,i})^{0.38}}{T_{r,i}^{1/6}} \quad (6)$$

[1]Perturbed-Chain Statistical Associating Fluid Theory

where

$$A_i = \frac{A^* T_{b,i}^{\alpha}}{M_i^{\beta} T_{c,i}^{\gamma}} \quad (7)$$

the parameters A^*, α, β, and γ, are shown in Table 10-4 of [12]. The current temperature is noted T while $T_{b,i}$ and $T_{c,i}$ are respectively the temperature at the boiling point and the critical temperature. The molecular weight (expressed in g.mol^{-1}) is represented by M_i, the ratio $T_{r,i} = T/T_{c,i}$ is the reduced temperature. Concerning the thermal conductivity $\lambda_{\mathrm{L,mix}}$ of liquid mixture, we adpoted the rule from Vredeveld (1973) [12].
Since $\lambda_{\mathrm{L,mix}}$ depends on the local temperature T, the differential equation (3) is non-linear, then the Crank-Nicholson scheme used by [15] is no longer applicable. Rather, we have employed a finite-differences implicit scheme.

Unfortunately, the methane triple point depression estimation, performed by Mitri *et al*. (2007) [11], relies on a misuse of Landau & Lifshitz (1969) [6]. In addition, this kind of calculation in the context of a triple point, is not relevant for a possible freezing in deep sea liquid, because it assumes the presence of a vapor phase in contact with the liquid.

Alternatively, in order to assess if methane or ethane freezes, we propose a calculation in which we compare the chemical potentials of a species in the liquid phase and in the corresponding solid phase. Then, when the vertical structure is obained by solving the above mentioned equations, we check if the equation

$$\ln \Phi_i \, x_i = -\frac{\Delta H_{i,m}}{R T_{i,m}} \left(\frac{T_{i,m}}{T} - 1 \right) \quad (8)$$

is satisfied at some depth z in the sea. In this equation $\Delta H_{i,m}$ and $T_{i,m}$ denote respectively the melting enthalpy and the temperature of melting of the considered compound (*i.e.* methane or ethane), while Φ_i and x_i are provided by the previously computed vertical structure.

Our study is particularly relevant in the context of the possible furture space missions. Particularly to ones that consists in *in situ* exploration of Titan's lakes (see for instance Lorenz *et al.* (2015) [9]).

References

[1] Bonan, G. B., 1996, Tech. rep.

[2] Brown et al. (2008), *Nature* 454, 607–610.

[3] Cordier et al. (2015), *Icarus*, submitted.

[4] Glein, C. R., Shock, E. L., *Geochim Cosmochim Ac*, 115, 217–240.

[5] Gross, J., Sadowski, G., Jan. 2001. *Ind. Eng. Chem. Res.*, 40, 1244–1260.

[6] Landau, L. D., Lifshitz, E. M., 1969. Statistical Physics – Second Revised and Enlarged Edition (Course pf Theoretical Physics, Vol. 5), 2nd Edition. Pergamon Press.

[7] Lavvas, P. P., Coustenis, A., Vardavas, I. M., *Planet. Space Sci.*, 56, 27–66.

[8] Lawrence, S. P., H. K., Le Core, H., 2002, *Hydrobiologia*, 487, 95-110.

[9] Lorenz, R. D. et al., 2015, *LPI*, 46, 1259.

[10] Luspay-Kuti, Chevrier, Cordier, et al.(2015) *EPSL*, 410C, 75–83.

[11] Mitri, G., Showman, A. P., Lunine, J. I., Lorenz, R. D., 2007, *Icarus*, 186, 385–394.

[12] Poling, B. E., Prausnitz, J. M., O'Connell, J., 2007, 5th Edition. McGraw-Hill Professional, Englewood Cliffs.

[13] Tan, S. P., Kargel, J. S., Marion, G. M., *Icarus*, 222, 53–72.

[14] Tokano, T., 2005, *Advances in Space Research*, 36, 286–294.

[15] Tokano, T., 2009, *Astrobiology*, 9, 147–164.

[16] Witten, A. J., Thomas, J. H., 1976, *Journal of Physical Oceanography*, 6, 85–92.