Icarus 250 (2015) 64–75

Contents lists available at ScienceDirect

Icarus

journal homepage: www.elsevier.com/locate/icarus

Titan's liquids: Exotic behavior and its implications on global fluid circulation

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ARTICLE INFO

Article history:
Received 31 July 2014
Revised 20 November 2014
Accepted 24 November 2014
Available online 4 December 2014

Keyword:
Titan, atmosphere
Hydrology
Surface

ABSTRACT

Based on a validated model for cryogenic chemical systems, referred to as CRYOCHEM ("Cryogenic Chemistry Model"), surface liquids on Titan are shown to exhibit exotic behavior of density increase with temperature but decrease with pressure, unless the temperature falls below 89.8 K. It is also the case for the atmospheric liquid condensates below an altitude where the liquid density is minimum. The exotic behavior is of compositional origin, which does not have an analog in the atmosphere and liquid water on Earth. As the latitudinal and seasonal variations of surface temperature are known, it is possible to map out the global liquid and vapor density variations as well as the equilibrium phase compositions, which will be useful as inputs for atmospheric general circulation models (GCMs) and investigations of Titan's methane-equivalent of Earth's hydrological cycle, local subsurface alkanology (equivalent to hydrology on Earth), lake convection, and clastic and chemical sedimentation in the lakes. Further, the density variations can be used to derive a general idea about global fluid circulation in the upper crust based on averaged conditions on Titan. The surface liquid should tend to flow toward the hottest spot on Titan and a return flow occurs beneath the surface, thus providing analogies with thermohaline circulation in Earth's oceans. The vapor phase, on the other hand, has ordinary properties that make the global atmospheric circulation similar to the Hadley cell on Earth, but Titan's cycle reaches the polar regions. The calculated compositions of surface liquids are more methane-rich than other models indicated, thus qualitatively in the right direction to satisfy polar-lake compositions deduced from loss tangents. However, quantitatively there remains a need to find yet more accurate liquid compositions and an optimum equilibrium within constraints of the atmospheric measurements.

1. Introduction

Titan's atmosphere consists of mostly nitrogen, a few percent of methane, and trace amount of hydrocarbons, nitriles, and other gases (Strobel et al., 2009). The Descent Imager/Spectral Radiometer (DISR) aboard the *Huygens* descent probe showed that Titan's atmosphere was moist. An obscuring haze existed above 75 km. Gradual partial clearing occurred in the lower stratosphere to ~40 km (near the tropopause), with thin haze extending to the surface, including a stratiform haze deck at 21–22 km (Tomasko et al., 2005). Above 40 km the methane mole fraction remained ~0.0148, and downward it increased to ~0.0565 near 6 km (Niemann et al., 2010), then remained nearly constant until touchdown. After the landed probe warmed the surface, methane and traces of ethane and other gases effused from wet soil (Niemann et al., 2005), possibly wet from a recent rainfall.

Lacking seasonally-resolved in-situ measurements across Titan, thermodynamic models are the best way to represent Titan's chemical systems. Constraints come from the single *Huygens* probe descent and the *Cassini* CIRS remote sensing thermal measurements (Cottini et al., 2012). General circulation models (GCMs) of Titan unfortunately still do not include the moist effects of multicomponent liquid solutions that may have important influences on Titan's atmospheric circulation (Friedson et al., 2009) and surface

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http://dx.doi.org/10.1016/j.icarus.2014.11.029
0019-1035/

geology (Tomasko et al., 2005; Perron et al., 2006). To include the effects of multicomponent mixtures, a thermodynamic equation of state (EOS) is needed to calculate the distribution of surface liquid, chemical partitioning among phases, the formation and distribution of condensate clouds, and the phase densities. Therefore, the EOS should be thermodynamically self-consistent so that it can represent experimental data from the literature and reliably predict information that is experimentally unavailable. We have applied such an EOS in our model for cryogenic chemical systems, now referred to as CRYOCHEM, to describe Titan's lower atmosphere with its condensates as well as the surface liquids. CRYOCHEM is a thermodynamic model intended to describe chemical systems at cryogenic conditions relevant to planetary science. Its prototype has been validated to work for vapor (gas), liquid, and solid phases (Tan et al., 2013a, 2013b).

Validation for CRYOCHEM also includes a computation of the vertical profile of the methane mixing ratio (Tan et al., 2013a), which matches the *Huygens* probe data (Niemann et al., 2010). The match also confirms the validity of the assumption of phase equilibrium applied in CRYOCHEM, even though disequilibrating events may have just happened before the landing. In other words, it implies that the time needed for Titan's chemical systems to reach the equilibrium was relatively short. The probe data were obtained during descent on a slightly misty day, and a transition from liquid to solid haze may have taken place near 21 km altitude, correlating with the thin stratiform observed at that level. Although the atmosphere then lacked dense convective clouds, other observations show that Titan's troposphere sometimes develops convectively active, dense clouds near the poles and occasionally in the tropics (Schaller et al., 2009). Dendritic valley networks near the landing site imply erosive surface flows of precipitation runoff (Tomasko et al., 2005; Perron et al., 2006), thus indicating periods of intense rainfall. Evidence of surface wetting (Niemann et al., 2005) and inundations from a low-latitude storm was obtained by *Cassini* imaging (Turtle et al., 2011).

Condensation in Titan's troposphere is more complicated than Earth's because Titan's atmosphere consists of many chemical components that together can undergo phase transitions as it equilibrates with its liquid and/or solid solutions. In contrast, among Earth's major tropospheric gases, only water vapor condenses. CRYOCHEM can calculate the pressure- and temperature-dependent densities and compositions of Titan's condensates, hence their variations with altitude/elevation and latitude. We found that the vertical distribution above the *Huygens* landing site has ethane-dominated liquid on the surface and becomes methane-dominated at altitudes above 1.5 km. Latitude-wise, the liquid composition in the polar regions is dominated by methane while the liquids near the equator are dominated by ethane due to a 3.7 K temperature contrast (Tan et al., 2013a). The liquid compositions in both regions were also modeled by Cordier et al. (2009), but their liquids in polar regions are predicted to be ethane-rich as well. Recent evidence that supports our model comes from the T91 *Cassini* fly-by data acquired across Ligeia Mare (one of the largest polar season Titan), which demonstrated that the sea is extremely transparent at *Cassini* RADAR (microwave) wavelengths. The analysis of bathymetry and radio attenuation (microwaves absorption) imposes a constraint on the loss tangent of the liquids, which carries compositional information (Mastrogiuseppe et al., 2013). The estimated low loss tangent, when combined with the laboratory measurements of the dielectric properties of liquid nitrogen (Smith et al., 1991), liquid alkanes (Mitchell et al., 2014), and the environmental conditions on Titan, essentially indicates that Ligeia Mare's liquid is dominated by methane with a minor quantity of ethane and nitrogen.

Our previous calculations did not account for seasonal and local variations. We now address these matters and consider how temperature- and pressure-driven variations of surface-liquid compositions and densities would drive Titan's liquid circulation. In discussing the implication of our calculation results on the fluid circulation, we will only consider the thermodynamic phase equilibrium conditions, without taking into account the heat transfer, mass transfer, and fluid dynamics, the parameters of which are mostly uncertain. The equilibrium calculations serve as a reasonable approximation or baseline to capture some of the complexity in a qualitative way, from which large local perturbations due to specific local circumstances and short-term variations can be expected in real situations. Furthermore, this work is also important to provide thermodynamic phase-equilibrium data for investigations of global circulation of Titan's atmosphere (Friedson et al., 2009), of Titan's methane-equivalent of Earth's hydrological cycle (Atreya et al., 2006; Mitri et al., 2007; Lunine and Lorenz, 2009; Hayes, 2011; Lorenz, 2014), local subsurface alkanology (equivalent to hydrology on Earth; Vance et al., 2012), lake convection, and clastic and chemical sedimentation in the lakes. For comparison, seawater and atmospheric density differences cause a dynamic global circulation on Earth. The density variations of seawater are due to the temperature and salinity. The thermohaline cycle involves surface and subsurface flows from the more dense to less dense areas and vice versa, with density differences brought about by differential evaporation and sea ice formation, and freshwater influx from rivers, rainfall, and melting glaciers and sea ice. In the atmosphere, the global Hadley circulation involves air rising over the tropical areas and sinking in subtropical areas (Wallace and Hobbs, 2006).

As also previously demonstrated (Tan et al., 2013a), the condensate with ever-changing composition on Titan has an exotic behavior in its density that increases with temperature. Liquids in the polar regions are less dense than those near the equator due to the compositional effects on density exceeding those of thermal expansivity. As shown later, such behavior also occurs with pressure, i.e., the liquid density decreases with pressure, something counter-intuitive for those who are used to working with aqueous systems on Earth or any pure liquid. These exotic behaviors will affect the global circulation of fluids on Titan as discussed in this paper.

2. Data and methods

2.1. Data of Titan's condition

2.1.1. Surface temperature

The global distribution of Titan's surface temperature, which was correlated from the CIRS data between September 2006 and May 2010 (Cottini et al., 2012; Jennings et al., 2011) and between December 2010 and December 2013 as shown in Fig. 1, can be expressed in Kelvin as follows:

$$T = 86.1 + 7.47\cos[0.0106\{L - (5.18Y - 2.98)\}] \quad (1)$$

where L is latitude (in degrees) and Y is the number of years elapsing from the equinox, so that $Y = -4.60$ and 4.32 for January 2005 and December 2013, respectively. These periods have almost symmetrical temperature profiles with respect to the equator as seen in Fig. 1A; it was winter in northern hemisphere in January 2005, and summer almost 9 years later.

The correlation curves in Fig. 1 for four consecutive periods of measurements were calculated using Eq. (1) with the values of Y as follow: −2.100 (June 2007), −0.017 (August 2009), 1.900 (July 2011), and 3.817 (June 2013), respectively. Eq. (1) is likely correct within ±0.3 K for dates even prior to 2006. However, the cosine function only characterizes the recorded data and it remains