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Experimental determination of acetylene and ethylene solubility in liquid methane and ethane: Implications to Titan's surface

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Abstract

In this study, the solubility of acetylene (or ethyne, C_2H_2) and ethylene (or ethene, C_2H_4) in liquid methane (CH_4) and ethane (C_2H_6) has been experimentally determined at Titan surface temperature (90 K) and pressure (1.5 bars). As predicted by theoretical models, the solubilities of acetylene and ethylene are very large at Titan temperature and these species are most likely to be abundantly present in the lakes and as evaporites on the shores or dry lake beds. Our results indicate the solubility of 4.9×10^{-2} mole fraction for acetylene in methane and 48×10^{-2} mole fraction in ethane; for ethylene, 5.6×10^{-1} mole fraction in methane and 4.8×10^{-1} mole fraction in ethane. Assuming the mole fractions from atmospheric models in the lower stratosphere and equilibrium with the surface, we determined that the lakes on Titan that cover ~400,000 km^2 are not saturated. The liquid lakes on Titan act as an important reservoir for both acetylene and ethylene. Assuming difference of methane and ethane content in the lakes at different latitudes, the difference in solubility in liquid methane and ethane, solutes in lakes may change with the temporal evolution (such as; evaporation and condensation) over seasons and geological time scales.

Keywords: Titan; Solubility; Acetylene; Ethylene; Infrared spectroscopy; Planetary surfaces; Atmosphere

1. INTRODUCTION

Since the arrival of the *Cassini-Huygens* mission in the Saturn system in 2004, strong evidence of the presence of liquid bodies has been found on Titan's surface near the poles (Lopes et al., 2007; Stofan et al., 2007; Hayes et al., 2008). Titan possesses a thick atmosphere mainly composed of 95% nitrogen and <5% methane, and experiences an active methane cycle similar to the water cycle on Earth (Lorenz and Lunine, 1997; Hayes et al., 2008). This cycle allows retaining potential liquid hydrocarbons on Titan's surface (Lorenz et al., 2001; Atreya et al., 2006). Although predicted to exist as large oceans (Lunine et al., 1983; Raulin, 1987), free surface liquids have been discovered and interpreted as lakes and seas of various sizes and shapes (Lopes et al., 2007; Stofan et al., 2007; Hayes et al., 2008; Stephan et al., 2010). The observed lake morphologies in *Cassini*'s data is comparable with some terrestrial landforms encountered in semiarid regions, which suggests that the lakes lie in a depression formed by dissolution of a surface soluble porous layer (Bourgeois et al., 2008; Cornet

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et al., 2015). For example, in the Namibian analog, this layer is constituted of calcretes, a rock that is soluble on geological timescales. Indeed, the data acquired during the landing of *Huygens* probe in January 2005 seems to argue of a porous and damp surface and are therefore consistent with this hypothesis (Zarnecki et al., 2005; Lorenz et al., 2006). Photochemical and thermodynamic models (Dubouloz et al., 1989; Cordier et al., 2009), as well as the potential detection of hydrocarbon compounds on Titan's surface (Clark et al., 2010), brought indication about the potential solutes existing in Titan's lakes and as evaporites on the surface.

1.1. Titan's global settings

Atmosphere: Titan's atmosphere is composed of 95% of nitrogen, methane is the second most abundant component, having mixing ratio of 4.92% at near surface (Niemann et al., 2005) and less than 1% of minor species such as dihydrogen (Owen and Niemann, 2009), carbon monoxide (Dekok et al., 2007) argon (Niemann et al., 2005) and ethane (Cordier et al., 2009). The atmosphere of Titan is photochemically active, producing acetylene, ethylene, propane, and benzene as minor components (Mitri et al., 2007; Lavvas et al., 2008a, 2008b; Coustenis and Hirtzig, 2009) that act as solutes.

Surface: Titan surface temperature is comprised between 93.65 k measured at the *Huygens* landing site (HLS) (Niemann et al., 2005; Tomasko et al., 2008) and 90.5–91.7 K interval inferred from the Composite Infra-Red Spectrometer (CIRS) and the radiometer data at the Titan's poles (Janssen et al., 2009; Jennings et al., 2009; Cottini et al., 2012). The measured surface pressure at the HLS is 1.46 bar (Niemann et al., 2005). The pressure and temperature at the surface lie near the triple point of methane and ethane states (90 K), which suggest both are stable and act as solvents. Titan's surface consists of high-albedo terrains with predominantly high elevation, and low-lying terrains or lower albedo. Exceptions in albedo exist, such as Tui Regio, which is a low-altitude area with high albedo (MacKenzie et al., 2014). Interpretations suggest that the high albedo of the largest highlands region is due to the reflected light of ices (possible solutes) washed down slopes by flash floods instigated by methane/ethane rainfall. Rainfall has been suggested as a cleansing mechanism that might render elevated terrain optically brighter than lowlands (Griffith et al., 1991; Smith et al., 1996). If Titan's bright terrain highlands are made of solid compounds such as acetylene and ethylene, they can easily dissolute in the liquid methane and ethane and transport to the liquid reservoirs at lowlands.

According to photochemical models (Yung and DeMore, 1999; Lavvas et al., 2008a, 2008b), three organic compounds are expected to be in liquid form on Titan's surface: methane, ethane, and to a lesser extent, propane. Several others, such as acetylene and ethylene, are expected to exist in solid phase and are produced abundantly in the atmosphere (Roe et al., 2004). Acetylene and ethylene are the next most abundant hydrocarbons after ethane. Their formation is initiated in the upper atmosphere directly from the products of methane photolysis. In the lower atmosphere, acetylene recycles back to ethylene, hence both acetylene and ethylene are abundant in the atmosphere. The model of Cordier et al. (2009) tends to argue for a lake composition dominated by ethane (more than 70%), propane (7–10%), and methane (5–10%) in which some solid compounds can be dissolved if thermodynamic equilibrium between the lake and the atmosphere is assumed. Tan et al. (2013) and Glein and Shock (2013) present new geochemical models estimating the liquid compositions at the Titan's surface. The equatorial surface liquid is predicted to be dominated by ethane, methane, propane, and nitrogen with mole percent of 53%, 32%, 7%, and 7% respectively (Tan et al., 2013). However, these well-established models tend to argue the need of more information and laboratory experiments to accurately estimate the liquid composition.

Luspay-Kuti et al. (2012, 2015), estimates the lake composition of Ontario Lacus to be ~70–30% of ethane to methane, the major lake in Titan's southern hemisphere. Whereas, northern lakes are thought to be more methane-rich reaching up to 90–10% methane to ethane concentration (Luspay-Kuit et al., 2012, 2015). Depending on the solubility rates of Titan's solids in liquid methane and ethane, we should be able to estimate the amounts of solutes that are present on Titan. A solubility measurement under Titan's conditions in the lab will provide constraints for the atmospheric models and test the limits of these models. In this study, we propose estimations of solubility values of acetylene and ethylene in liquid methane and ethane from experimental measurements under Titan surface conditions.

1.2. Acetylene

Acetylene is known to be one of the end products of methane photolysis in laboratory experiments (Smith and Raulin, 1999; Vuitton et al., 2006; Lavvas et al., 2008a, 2008b). Its photochemistry also plays an important role in the atmosphere of Titan, and is predicted in Titan's lakes as a major component (Cordier et al., 2009, 2013; Glein and Shock, 2013; Tan et al., 2013). Acetylene is the second largest compound after ethane produced in the atmosphere, models predict a net creation of acetylene approximately 125–2000 times greater than other compound produced (Wilson, 2004), and may settle and exist under its solid form at the surface (Cordier et al., 2009, 2013). It has been suggested that over the geological time scale, a solid layer of acetylene a few hundreds of meters thick would have formed on the surface of Titan (Owen and Niemann, 2009). Although, being so abundant in the atmosphere with the stratospheric mixing ratio of a mole fraction of about 3.7×10^{-6} (Coustenis et al., 2010), evidence of acetylene at the surface is still lacking on bright terrains. However, Singh et al. (2016) reports the evidence of acetylene on the low albedo region near equator. Since acetylene is assumed to be abundant on Titan, it is also thought to be highly soluble in Titan liquids (methane and ethane). Several models have previously attempted to determine the solubility of acetylene in methane and ethane (Cordier et al., 2009; Glein and Shock, 2013). Depending on the