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Solvation of nitrogen compounds in Titan's seas, precipitates, and atmosphere

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ABSTRACT

Saturn's moon Titan, dominated by its low, 90–95 K, surface temperature and methane seas, is shaped by physical and chemical processes unparalleled in any environment on Earth. Titan's upper atmosphere produces a rain of compounds such as acetonitrile, acrylonitrile, and acetylene, more familiar to chemical processing plants than to nature. The interaction of these compounds with Titan's seas is, to a large extent, unknown. As an important first step towards understanding these interactions, we investigate the solvation properties of many of these compounds in methane using multiple theoretical approaches, including cubic equations of state, Statistical Associating Fluid Theory, the Conductor like Screening Model for Real Solvents, and all-atom Molecular Dynamics.

1. Introduction

Saturn's moon, Titan, is the only body other than Earth known to have stable bodies of liquid on its surface. The exact composition of these bodies is not known (Cordier et al., 2009), but the emerging picture based on the high-latitude lakes in the northern hemisphere is that they are substantially methane, with 5–15% dissolved nitrogen, less than 10% ethane, and other organic molecules in lower concentrations (Mastrogiuseppe et al., 2014). The seas interact with Titan's thick nitrogen-based atmosphere to produce a methane cycle, with methane clouds and methane rain. The soluble hydrocarbon surface is eroded by these methane flows, forming meandering channels, valleys, and other features familiar on Earth (Langhans et al., 2012).

In Titan's upper atmosphere, the action of ultraviolet light from the Sun and secondarily energetic particles causes methane and nitrogen to react, producing a range of organic nitrogen-containing compounds, shown in Table 1 (Müller-Wodarg et al., 2014, p. 176). Unlike other compounds observed on Titan, they are strongly polar, allowing them to form structures that could resist dissolving in Titan's nonpolar surface fluids (He and Smith, 2014). The stability and insolubility of these compounds might even cause them to accumulate as grains, pebbles, or more substantial agglomerations in certain areas of Titan, while more soluble hydrocarbons were weathered around them by Titan's surface liquids.

In addition, insolubility in the liquid is the first step toward compartmentalization, the separation of one part of the liquid from another (Strulson et al., 2012; Ferris and Usher, 1983). This is key to the speculations, based on the unusual hydrogen-acetylene consumption of Titan's surface, that Titan might be capable of supporting some form of life (McKay and Smith, 2005; Strobel, 2010; Clark et al., 2010; Niemann et al., 2010).

A fundamental question, then, is the stability of the vapor, liquid and solid phases of nitrogen-rich organic compounds in Titan's surface liquids. Each compound can enter the liquid either by leaving the solid phase or by leaving the atmosphere. Very little is known about the thermodynamic transitions of these molecules at such low temperatures. Data have been gathered using Fourier Transform Infrared Spectroscopy (FTIR) to analyze the composition of cryogenic methane solutions of acetonitrile and acetylene, but no conclusions drawn because of the difficulty of deconvoluting the FTIR spectra (Singh et al., 2014). The solubility of acetylene in methane at saturation has been measured down to 92 K (Neumann and Mann, 1969; Tan et al., 2013). Vapor–liquid equilibria relevant to Titan's chemistry have been studied for the ternary

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Table 1
The most common organic nitrogen species observed spectroscopically in Titan's upper atmosphere. Ranges refer to interpretations of the data via different ion chemistry models (Müller-Wodarg et al., 2014, p. 176).

Name	Formula	Concentration (ppm)
Hydrogen cyanide	HCN	200–240
Cyanoacetylene	HC_3N	0.8–40
Acrylonitrile	C_2H_3CN	0.3–10
Cyanoallene	C_4H_3N	4
Acetonitrile	CH_3CN	1.5–3
2,4-Pentadiynenitrile	HC_5N	1
Propanenitrile	C_2H_5CN	0.15–0.5

system, methane–ethane–nitrogen, down to 95 K (Llave et al., 1987; Trappehl and Knapp, 1987; Gabis, 1991). Depending on the surface ethane fraction, which is unclear on Titan, the fraction of dissolved nitrogen in the liquid at 95 K varies between 3.6% and 14.9% (Gabis, 1991).

This lack of information is understandable: conducting experiments in cryogenic methane is not a simple task. This provides considerable incentive to employ the large toolbox of theoretical approaches that are available to determine the relevant thermodynamic properties. In this vein, predictions of methane–nitrogen vapor–liquid equilibria at ultra-low temperatures have been made using a theoretical approach known as Grand Canonical Monte Carlo (GCMC) simulation. GCMC is a molecular-level simulation in which solute molecules are inserted into the solvent until an equilibrium is reached; here the chemical potential, volume and temperature are kept constant, but the number of particles fluctuates (Firanescu et al., 2011). However, the effectiveness of this method drops off rapidly with increasing solute size, preventing GCMC simulations of other interesting solutes on Titan.

Approaches based on continuum thermodynamics have also been used: The methane–ethane–propane–nitrogen–acetylene system has been studied using the van Laar model, which indicates that solid acetylene will be quite soluble under Titan surface conditions, with erosion similar to that of gypsum in water on Earth (Glein and Shock, 2013; Malaska and Hodyss, 2014). The solubility of solid acetylene in pure liquid methane has been estimated using their pure-substance properties (Preston and Prausnitz, 1970). Similarly, the saturation solubility of HCN and acetylene in liquid ethane have been estimated using the enthalpy of fusion of pure HCN and acetylene (Cordier et al., 2013). The ternary methane–ethane–nitrogen system has been studied very recently using Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) (Luspay-Kuti et al., 2015).

In this paper, we tackle the lack of information on the tendency of nitrogen compounds to dissolve in Titan's cold hydrocarbon seas. We investigate the solvation properties of the most common stable nitrogen compounds observed in Titan's upper atmosphere, and acetylene, using a full complement of techniques from equation of state approaches to all-atom Molecular Dynamics (MD). The equation of state approaches include the Soave–Redlich–Kwong, Peng–Robinson, PC-SAFT, Polar PC-SAFT, and the Conductor-like Screening Model for Real Solvents (COSMO-RS). These methods are described in the next section.

2. Methods

Modeling the thermodynamics of nitrogen-containing systems at Titan is challenging for several reasons. First, nitriles exhibit strong polar interactions which can influence significantly the phase behavior of systems under consideration. Moreover, most equations of state and models do not explicitly take polar interactions into account. Second, the literature lacks any experimental data on the solubility of nitriles in liquid alkanes, neither at Titan conditions, nor at higher temperatures and pressures. As a result, equations of state and models are required to predict the needed solubilities without the use of any fitting parameters.

Knowing how challenging the problem is, we predict the solubility of nitrogen-containing systems in pure liquid methane, methane–nitrogen and methane–ethane–nitrogen mixture using four different thermodynamic models. Peng–Robinson (PR) (Peng and Robinson, 1976) and Soave–Redlich–Kwong (SRK) (Soave, 1972) equations of state have the advantage of being simple correlations of phase behavior that are fitted to reproduce the critical pressure and temperature of components under consideration. However, cubic equations of state do not predict accurate liquid phase densities, and they tend to perform poorly for associating and highly polar compounds.

Another model used here is the conductor-like screening model for realistic solvents (COSMO-RS) (Klamt and Schüürmann, 1993; Klamt and Eckert, 2000; Eckert and Klamt, 2002), as implemented in the ADF molecular modeling suite (Te Velde et al., 2001; Guerra et al., 1998), which uses the COSMO approach developed by Klamt and Schüürmann (1993) to predict activity coefficients through quantum calculations. The advantage of using COSMO-RS is that, without the need to fit parameters, it is as accurate as activity coefficient models fitted to large databases (e.g., UNIFAC). The COSMO approach includes nearest neighbor polar interactions, but it cannot predict compressibility effects.

Finally, we use a molecular equation of state developed by Chapman et al. (1988, 1990) for polar and associating fluids, known as the Statistical Associating Fluid Theory (SAFT). This theory includes association by using a coarse-grained atomic model based on Wertheim's first-order perturbation theory (TPT1) (Wertheim, 1984a,b, 1986a,b, 1987). In reference to Fig. 1, the polar and perturbed chain form of the equation of state (Polar PC-SAFT) (Sauer and Chapman, 2003; Jog and Chapman, 1999; Jog et al., 2001), used here, models molecules as linear chains of polar hard spheres with attached association sites that allow for hydrogen-bonding. We allowed all solutes to be in the solid state and form a solid–liquid equilibrium. More details on the models used in this work can be found in the appendix.

In Fig. 2, we compare the performance of the models versus vapor–liquid equilibria data for components of the Titan atmosphere (and also argon) at cryogenic conditions. In reference to Fig. 2(a) and (b), it can be seen that PC-SAFT was able to predict the most accurate shape of the phase diagram in comparison to the other models. The models performed equally well in predicting the liquid phase of the binary methane–nitrogen system in Fig. 2(c), while PC-SAFT showed superiority in predicting the vapor phase composition. COSMO-RS, as implemented by the ADF molecular modeling suite, does not allow molecular modeling of noble gas-containing systems; hence the model predictions were not included in Fig. 2(d) and (e). Although Fig. 2(b) shows that COSMO-RS failed to predict the methane–propane interaction, this should not be taken as an indictment of its accuracy for more complex systems. Van der Waals interactions are treated within the COSMO approach in an empirical manner. The main advantage behind COSMO-RS relies in its ability to compute short-range interactions through sigma profiles and electron density calculations. As a result, we expect it to perform poorly for systems where dispersion interactions dominate, but perform well for polar systems such as nitriles.

Comparing how the models perform in predicting the solubility of solid hydrocarbons in cryogenic liquids is a necessary step in the validation process. The literature lacks any experimental data on the solubility of nitriles in liquid methane, so, for the sake of comparison, we examined data found on the solubility of non-polar hydrocarbons, CO_2, and H_2S in liquid methane at 110 K. From a