EPSC Abstracts
Vol. 6, EPSC-DPS2011-488, 2011
EPSC-DPS Joint Meeting 2011

Cyanide Soap? Dissolved material in Titan's Seas.

R. D. Lorenz(1), J. I. Lunine(2), C. D. Neish (1)
(1) Johns Hopkins University Applied Physics Laboratory, Laurel, MD, USA. (2) Cornell University, Ithaca, NY, USA.
(ralph.lorenz@jhuapl.edu / Fax: +1 443 778 8939)

Abstract

Although it is evident that Titan's lakes and seas are dominated by ethane, methane, nitrogen, and (in some models) propane, there is divergence on the predicted relative abundance of minor constituents such as nitriles and C-4 alkanes. Nitriles such as hydrogen cyanide and acetonitrile, which have a significant dipole moment, may have a disproportionate influence on the dielectric properties of Titan seas and may act to solvate polar molecules such as water ice. The hypothesis is offered that such salvation may act to enhance the otherwise negligible solubility of water ice bedrock in liquid hydrocarbons. Such enhanced solubility may permit solution erosion as a formation mechanism for the widespread pits and apparently karstic lakes on Titan. Prospects for testing this hypothesis in the laboratory, and with measurements on Titan, will be discussed.

1. Introduction

Ever since the serious consideration of hydrocarbon oceans and a hydrological cycle on Titan began in the early 1980s, the question arose of whether water ice – the assumed bulk bedrock on Titan – would appreciably dissolve in the liquid, e.g. [1]. Some early artists impressions of karstic landforms were motivated by laboratory measurements that suggested relatively high solubility of water ice in cryogens—measurements that were subsequently shown to be in error due to misattribution of a CO_2 band in the absorption spectroscopy of the solution (see discussion in [2,3]). Regular solution theory [2] predicts a solubility of water ice in ethane at 92K of the order of 10^{-11} molar.

2. Nitriles as Soaps?

Observations of Titan, especially by the Cassini radar instrument, show many north polar lakes which sit in steep-walled depressions, e.g [4]. One scenario for the formation of these lakes - and similar but apparently dry depressions seen more widely - is that some sort of solution process has etched into the surface as is common in limestone areas on Earth such as Florida or the archetypical karst region in Serbia. However, the weak solubility of ice in Titan liquids challenges this formation mechanism.

There are two solutions (!) to this paradox. One is that the bedrock is not, in fact, water ice but instead a more soluble material. Water ice appears to be rather less commonly exposed than might have been expected, with a robust indication from near-IR spectra and radar dielectric constant data only at Bazaruto Facula (the Sinlap ejecta blanket) [5]. The most likely alternative, acetylene and high-molecular-weight organics, could be more soluble than ice in methane/ethane. Atmospheric photochemistry could perhaps provide enough material over the age of the solar system (although the photochemical budget of solids may be taken up by the volume of material observed in the equatorial sand seas.) Perhaps organic material caused by impact shock-processing of a proto-Titan atmosphere could accumulate in larger quantities than present-day photochemistry, thus forming a ~km-thick veneer of lower-density material above the true ice bedrock, and the solution pits are formed in this material instead.

The other possibility is that Titan fluids are more corrosive/erosive than pure alkanes. An obvious mechanism is the introduction of an intermediate agent that can assist the solvation of a polar molecule like water in a nonpolar solvent, just as surfactants like soaps do with fats in water. Another analogy is the solubility of nonpolar 1-methoxy-4-(1-propenyl) benzene (anethole) in water. This is not itself very soluble, but can be made to dissolve to form a clear solution in water by the introduction of ethanol, as in aniseed beverages such as Pastis in France or Ouzo in Greece. When water is added to these liquors, the ethanol concentration drops and the anethole comes out of solution to form a milky emulsion.

It has already been established, e.g. [6] that tholin material is more soluble in bulk methanol and acetonitrile than in nonpolar solvents like toluene (and indeed, methanol is our preferred cleaning agent for glassware used in tholin experiments). It remains to be explored in laboratory work exactly how minor constituents such as hydrogen cyanide or acetonitrile might act to enhance the solubility of materials, as well as the possible role of carbocations [7]. Such experiments need not be particularly sophisticated, yet could shed important light on the lake formation question, as well as on other intriguing issues such as the capability of such lakes to host chemistry sophisticated enough to be considered an alternative form of life.

3. Composition of the Sea

Ethane, methane and nitrogen have been long expected as the bulk constituents of the seas, and thermodynamic near-equilibrium with the observed atmospheric concentration of 5% methane demands that ethane be the dominant component, and liquid ethane was indeed detected in near-IR spectra of Ontario Lacus.

However, the abundances of minor constituents are impossible to determine remotely from the limited Cassini data (only a few spectral channels in atmospheric windows). Models differ widely in their predictions, since abundances may be limited by modeled photochemical production rates, or by solubility (in most cases, the former is predicted to be the dominant effect). Two post-Cassini models have been published [8,9], and while they both predict ~7% propane liquid, they have very different minor compositions. Cordier [8] suggest high latitude lakes should have 1-2% of butene, butane, acetylene and hydrogen cyanide (such that evaporate solids would be roughly one quarter of each of these), while Raulin [9] instead suggests only a fraction of 1% of butane and isobutane (which would therefore dominate any evaporites), with nitriles present at only tens of ppm levels.

The nitrile abundance in Titan's seas appears to be a major unresolved question. It may be noted that although 1-2% of nitriles will not dramatically affect bulk properties such as density or speed of sound, since nitriles have high dielectric constants (e.g. acetonitrile ~37, hydrogen cyanide ~95) even ~% amounts may measurably affect the permittivity and especially dielectric loss of the liquid.

5. Future Prospects

Conceivably, spectroscopic observations of evaporates around the edges of lakes and seas might at least discriminate between nitrile-rich and hydrocarbon-rich compositions. However, fractional crystallization may mean that the evaporites are not completely representative of the dissolved minor composition. The only way to surely address this question is by analyzing in-situ the composition of a sea. Such a measurement is proposed for the Titan Mare Explorer (TiME) Discovery mission, presently undergoing a Phase A concept study.

Acknowledgements

This work is supported in part by the Cassini RADAR project, managed at the Jet Propulsion Laboratory. The Cassini/Huygens mission is a joint endeavour of NASA, ESA and ASI.

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