LABORATORY INFRARED SPECTROSCOPY OF TITAN THOLINS IN LIQUID METHANE AND ETHANE: CAN COMPLEX ORGANICS IN TITAN'S LAKES BE DETECTED?

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Introduction

Since the discover by Cassini ISS and SAR in mid-2005 and mid-2006 of a large dark feature in the Titan south polar region, suggestive of a lake (Ontario lacus) [1] and of a vast array of lake-like features being possibly liquid in the north polar region [2], observation of the Titan's lakes by Radar radiometry and VIMS from the Cassini Orbiter have emerged to characterize the composition and physical properties of the polar lakes. However, currently the chemical composition of these lakes remains poorly determined, due to the presence of strong atmospheric absorptions, mainly CH_4. Theoretical models based on thermodynamic data predict liquid ethane and methane to be abundant in Titan lakes and seas [3] and other organic species from atmospheric precipitation to be additional constitutents such as complex organics including the refractory macromolecular material of Titan's aerosols (Titan tholins). Previous studies have shown that tholins should be poorly soluble in ethane [4] but methane has not been tested, essentially because it is harder to condense and maintain in liquid state for sufficient amounts of time. Moreover, methane and ethane can exhibit very different behaviors with respect to solubility. Indeed, nitrogen is much more soluble in methane than in ethane, while most simple organics exhibit the opposite behavior

The main objectives of this study are to determine if tholins dissolve in liquid hydrocarbons (methane, ethane and their mixtures) and if they can be detected by conventional FTIR spectroscopy methods.. Here we present a Titan's lakes experimental simulation in order to examine the spectroscopic signature of a liquid methane and liquid ethane in contact with laboratory analogs of Titan's aerosols.

Laboratory Simulation of Titan's lakes

Experiments have been performed in the Titan simulation facility of the W.M Keck laboratory at the University of Arkansas [5]. An insulated cylindrical steel cryo-vacuum chamber (internal diameter of 61 cm and height of 208 cm) accommodates out a Titan module that sits inside a main chamber. Titan module contains a temperature control box internally and externally lined with LN2 cooling pipes allowing approaching temperatures relevant to Titan surface (90-94 K). Titan tholins synthesized at NASA Ames Research Center were introduced inside a Petri dish into the sample collection pan sit inside the module. The pressure was maintained at 1.5 bar throughout the experiments to simulate Titan atmospheric pressure at the surface. Once the required temperature and pressure was reached, the sample (methane, ethane) was introduced into the chamber and the module through a condenser using condenser input coils. The behavior of the sample was monitored via FTIR, in the near-infrared from 2.5 to 1.0 µm (4000-10000 cm^{-1}). The mass reading was also monitored.

Results

We have conducted series of several different experiments. Stated with the tholins in liquid methane and then followed by liquid methane and the mixture of liquid ethane/acetoniltrile. Several spectra were acquired during the experiments (Fig.1). The first results show that the tholins infrared signature totally disappears in presence of the solvents and no new absorption bands appear in the spectra. Further IR analysis of the tholins exposed to the solvents neither show modification against the initial tholin optical features. These first results seem to confirm the very low solubility/reactivity or non-solubility of Titan tholins in such solvents as predicted theoretically [4].

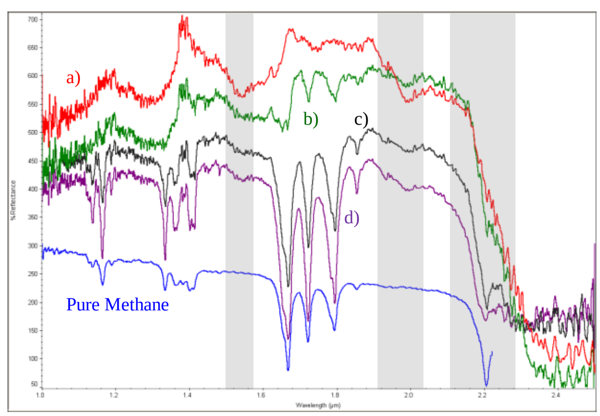

Figure 1: Some of the visible tholins bands are shown in shaded region. a) Tholins spectra at 1.5 bar and at 90K. b)Methane + tholins spectra after evaporating methane @ 138 – 149K. c) Methane + tholins after couple hours into

experiment @ 89K. d) Methane + tholins right after methane pour @ 91 K.

Absorption band of tholins are centered at 1.54, 1.62, 1.74, 1.92, 2.0, and a negative slope at 2.1 µm (Fig. 1). In the mixture of tholins and liquid methane, numerous methane absorbtions band have been detected. Identified methane absorption bands are centered at 1.16, 1.33, 1.41, 1.66, 1.72, 1.79 and 1.85 µm, in agreement with Clark et al. [6]. In the presence of liquid methane the only infrared signature of tholins present are at 1.54, 2.0, and a negative slope at 2.1 µm. In tholins spectra the feature at 1.4 µm is due to water absorption and can not be trusted. Once the methane is evaporated from the mixture all the tholins absorption bands are retrieved and no new feature is noticed resulting in no reactivity/solubility of tholins with liquid methane.

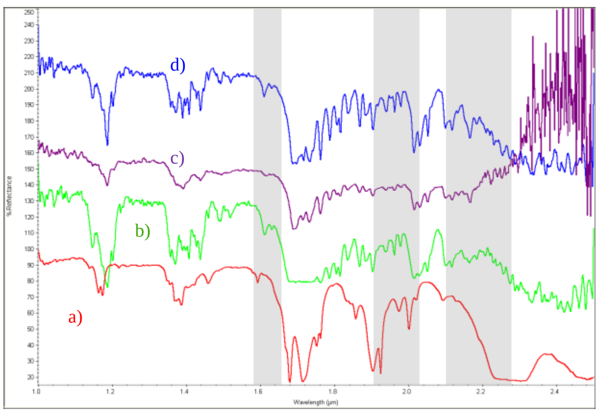

Figure 2: a) Pure acetonitrile @ 89K b) Acetonitrile + ethene + tholins @ 90K c) Pure ethane @ 90K d) Ethane + tholins @ 89K. Some of the visible tholins bands are shown in shaded region.

Fig. 2 shows the pure liquid ethane, acetonitrile, and the mixture of ethane-tholins and ethane-acetoniltrile-tholins spectra. All the tholins absorptions bands are coverd with the liquid ethane features except the negative slope centered at 2.1 µm . In ethane and tholins mixture the negative slope is the only feature tholins. All the other tholins signatures are retrieved once ethane is evaporated resulting in no reactivity. In the mixture of acetonitrile-ethane- tholins same optical behavior of tholins as seen with ethane is observed and thus no reactivity/solubility was noticed.

Conclusions/Future Work

We have observed that tholins when in contact with these solvents are not remaining in suspension. In this case, the refractory material of Titan's aerosols would not be dissolved in the Titan'surface lakes and seas but would rather sinks. However, to confirm these first data, additionnal experiments are needed and are in the prospect of our next work. One of these future experiments is to increase the initial quantity of tholins in contact with the solvents. Our experimental approach and its resulting data can be very relevant in regards to current VIMS observations of Titan's lakes and proposed future missions to Titan like the ESA's Titan Saturn System Mission (TSSM).

Acknowledgements

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