

SOLUBILITY AND REACTIVITY OF THOLINS IN LIQUID HYDROCARBONS ON TITAN. K.N. Barnett¹, V.F. Chevrier¹. ¹Arkansas Center for Space and Planetary Sciences, University of Arkansas, Fayetteville, AR, USA (knbarnett@uark.edu).

Introduction: Discovery of large, dark features and a vast lake array in the Southern and northern hemispheres of Titan, respectively, in 2005 and 2006 suggested the presence of liquid lakes on Titan's surface [1,2]. Since then, there has been intense scrutiny of these features to determine their chemical composition and physical properties. Despite extensive radar radiometry and VIMS to characterize these Titan features, the chemical composition is still poorly determined, although theoretical thermodynamic models predict the presence of liquid methane and ethane in abundance [3] in addition to organic constituents originating from the Titan's atmosphere. Included in such organic constituents are Titan aerosols or "tholins", resulting from complex chemistry driven by UV in the upper atmosphere. These macromolecular materials have been demonstrated to have a poor solubility in methane [4] and ethane [5], but similar testing in acetonitrile is lacking. Acetonitrile has been determined to be present in Titan's atmosphere in trace amounts [6], and so is thought to exist in Titan lakes and seas as a result of dissolution / precipitation. This abundance of acetonitrile in Titan's lakes and seas is the primary reason for its use as a potential reactant.

This study aims to build upon our previous work showing low solubility in ethane or methane [5], both non-polar molecules (Fig. 1). Acetonitrile being a polar compound, the main objectives of this study are to determine if tholins dissolve in acetonitrile and under what conditions as well as determine if such solubility can be detected by conventional Gas Chromatography / Mass Spectroscopy methods. Here we present desktop experiments examining the possible signature of acetonitrile in contact with laboratory analogs of Titan's aerosols.

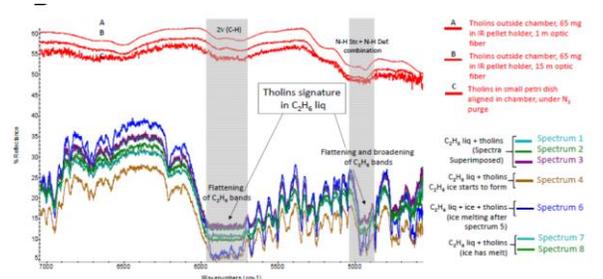


Figure 1: FTIR Spectra of tholins and ethane mixtures at 94 K (liquid C₂H₆) and 87 K (solid C₂H₆). The tholins were synthesized using our own plasma synthesis system, before being transferred into the Titan simulations chamber [5]. Only weak signatures of tholins can be characterized while tholins

appear unchanged before and after the experiment, suggesting low solubility, and thus the need for GC-MS.

Laboratory Investigation: Experiments have been performed in the W.M. Keck laboratory at the University of Arkansas. Titan tholins were first synthesized from July through August of 2015 using the CH₄-N₂ plasma system available in our lab (2014 experiments, Fig. 2).

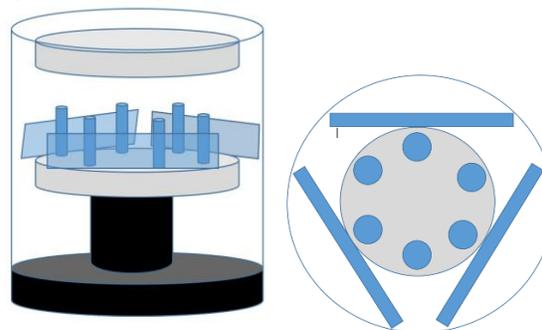


Figure 2: Schematic of CH₄-N₂ plasma system vacuum chamber set up. Blue elements represent small test tubes (circles) and glass slides (rectangles) upon which tholins were allowed to collect. Test tubes were filled with acetonitrile and sealed, glass slides were secured in foil, tholins which had collected on other surfaces were scraped off into larger test tubes. All tholins were labelled according to their collection date and stored in a desiccator which was first vacuumed and then partially filled with argon.

Experiments were performed by subjecting a Titan gas mixture analogue (10% CH₄ in N₂, high purity) to a DC glow discharge (cold plasma) inside a glass vacuum chamber (Technics Hummer II sputtering system, DC current 0-50 mA, DC Voltage 100-3000 V), at a continuous gas flow (flow rate 10-40 sccm) and ambient temperature (293 K). Glassware for tholins collection was prepared so that six small test tubes were arranged on the target stage as per Figure 2; glass slides were set around the perimeter of the target stage to allow direct accumulation for later analysis.

Short term, preliminary experiments were conducted in which a small amount of tholins in increased concentrations were added to Erlenmeyer flasks containing acetonitrile. Temperature was monitored during the addition of the tholins to the acetonitrile with no change noted (average temperature around 20°C). The flasks were covered, sealed, and monitored daily for visible changes. After three days, deionized water was added to the flasks. Environment was ambient temperature, atmosphere, and pressure.

In the long term experiments, following each run, the test tubes containing tholins were filled with acetonitrile, sealed, wrapped together in foil, and labeled according to the date of extraction and submersion in acetonitrile. Glass slides with tholins deposits were wrapped in foil; tholins deposited elsewhere within the glass vacuum chamber were scraped into a test tube larger than those used inside the vacuum chamber during synthesis. All were then labelled according to date of extraction and stored within a desiccator. The desiccator was vacuumed and then partially re-inhabited with argon to prevent oxidation of tholins.

Tholins were allowed to dissolve in acetonitrile for three months and then subjected to Gas Chromatography/Mass Spectrometry (GC-MS) for twenty-four minutes.

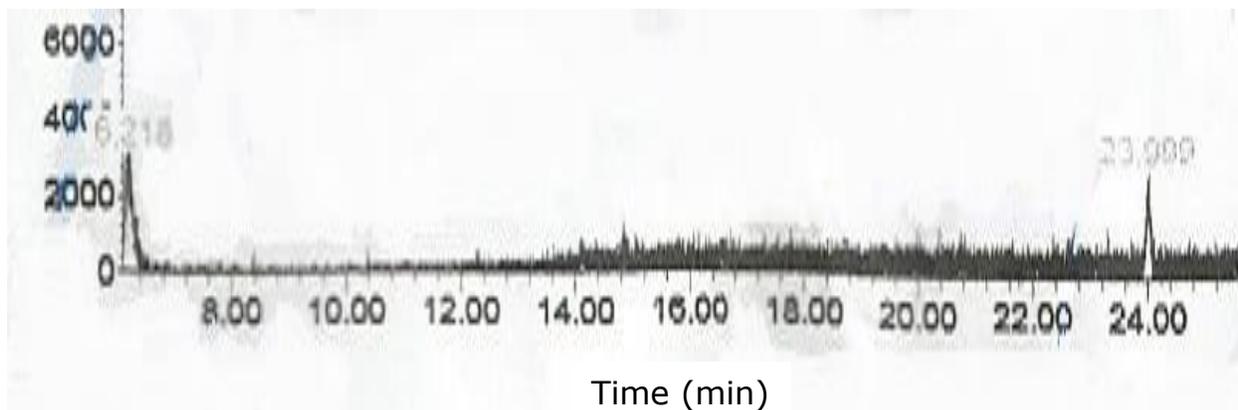


Figure 3: GC-MS results of acetonitrile/tholins mixture. Unanticipated peak at 6.218 minutes indicates presence of carboxylic acid, which has a known aliphatic form) dissolved in the acetonitrile; such aliphatic hydrocarbons are a significant component of Titan tholins [7]. The second peak at 23.999 minutes is indicative of the acetonitrile solvent.

Results: We have conducted a series of several different experiments. We began with preliminary, short term solubility of tholins in acetonitrile with no results; we then added those mixtures to water which elicited an immediate thermal reaction.

After completion of the second set of experiments wherein tholins were allowed to dissolve in acetonitrile over a three-month period, the mixture was analyzed via Gas Chromatography/Mass Spectrometry for twenty-four minutes. Analysis shows a peak at 6.218 minutes and another at 23.999 minutes. The peak at 23.999 minutes is expected and corresponds to the presence of acetonitrile in the mixture. It is the earlier peak which is more interesting; the peak at 6.218 minutes is indicative of the presence of a carboxylic acid.

Carboxylic acid has a known aliphatic form which is significant as aliphatic hydrocarbons are estimated to make-up 29% of Titan tholins [7]. The appearance of this peak in the GC-MS results earlier than that corresponding to the acetonitrile solvent suggests that the carboxylic acid peak is the result of the aliphatic carbons in Titan tholins being liberated from the tholins due to the acetonitrile solvent.

Conclusions/Future Work: We have observed that short-term, ambient conditions are not conducive to solubility of tholins in acetonitrile. However, deionized water added to such mixtures showed a visible and immediate solubility and, additionally, produced a thermal reaction.

We have also observed that tholins placed long term in a pure acetonitrile solvent are reacting; particularly, the aliphatic hydrocarbons appear to be dissolving. Despite these positive findings, there were still visible, undissolved tholins remnants left in the smaller test tubes after GC-MS analysis indicating that a great deal of the refractory material of Titan's aerosols would not be dissolved in Titan's surface lakes and seas, but would rather sink. To confirm these first test data, additional experiments are needed and are in the prospect of our next work.

References:[1] Turtle E. P. et al. (2009) *Geophys. Res. Lett.*, 36(2), L02204. [2] Stofan E. R. et al. (2007) *Nature*, 445, 61–64. [3] Lunine J. I. et al. (1983) *Science*, 222, 1229–1230. [4] Raulin, F. et al. (2012) *Chemical Society Reviews* 41, 5380–5393. [5] Chevrier V.F. et al. (2015) LPSC. [6] Martin A. et al (2002), *IAU 8th Asian-Pacific Regional Meeting*. [7] Derenne S. et al (2012) *Icarus* 221-2, 844-853.