DETECTION AND REACTIVITY OF TITAN THOLINS IN LIQUID HYDROCARBONS CONTAINING POLAR COMPOUNDS. K. Dzurilla[1], D. Nna Mvondo[2,3], D. Mège[4], V.F. Chevrier[1], [1]Arkansas Center for Space and Planetary Science, Fayetteville, AR 72701, [2]Universities Space Research Association, NASA Goddard Space Flight Research Center, [3]University of Maryland, [4]Laboratoire de Planétologie et Géodynamique de Nantes, CNRS France. (kadzuril@uark.edu).

Introduction: Tholins are complex organic materials produced via photolysis of methane and dinitrogen gases in Titan's upper atmosphere. These long-chained hydrocarbons sediment to the Saturnian moon surface and interact with liquid hydrocarbons via methane rain [1-2] and methane-ethane-nitrogen dominated lakes and seas [3-6]. However, preliminary studies have shown that tholins are only weakly soluble in non-polar solvents such as methane and ethane, and soluble in polar solvents [7-11]..

Kawai et al. [12] and He et al. [13] detected amino acids (e.g. glycine, alanine) as products of solubility of tholins dissolved in polar solvents. Studies have found that the solubility of tholins increases as the polarity of the solvent increase [7-10]. Our current study determines the solubility of Titan tholins in solutions of liquid hydrocarbons (hexane) mixed with nitriles, such as acrylonitrile and acetonitrile. These experiments are first steps towards a more comprehensive study of tholins behaviour at the surface of Titan, especially to understand how tholins could contribute to chemical activity within the lakes of Titan.

The objective of this task is double: first, we want to calibrate the future experimental solubilities in liquid methane and ethane. Determining the solubility of tholins at room temperature will quasi-quantitatively inform on the solubilities to expect in the cryogenic solvents (typically if they are in the ppm or percent range). The second objective is to determine the kinetics of the dissolution processes. Then, by determining the kinetics at the three different temperatures, we will be able to extrapolate to the cryogenic conditions in the chamber.

Experimental Methodology: Acetonitrile, hexane, and mixtures of acetonitrile/hexane were used as solvents. While methane and ethane are the abundant liquids on Titan, both are in the gas phase under room temperature and pressure. Therefore, hexane (liquid at ambient conditions) was used as a non-polar alkane solvent instead.

After the addition of tholins to these solvents, the samples were mixed and allowed to react for ~72 hours. A simple vacuum filtration technique was used to separate the liquid sample from the solid residue that remains.

We used a cold plasma discharge (approx. 27mA) simulating charge particle radiation interacting in a 90% nitrogen and 10% methane gas mixture (simulating Titan's atmosphere) to synthesize Titan tholins (as seen in Figure 1). Chamber conditions of 0.5 Torr to 3.00 Torr were maintained at room temperature for 3 days with a continuous flow of the N_2-CH_4 gas mixture.

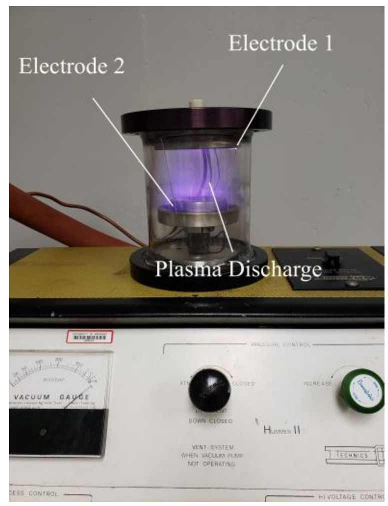

Figure 1: Technics Hummer II sputtering chamber (housed at the Arkansas Center for Space and Planetary Sciences) triggering a DC cold plasma discharge at 30mA that ionizes the Titan-simulated N_2-CH_4 (90%-10%) gas mixture to produce tholins after several days.

Glass slides inside the chamber (Figure 1) collected tholin deposits (Figure 2). Approximately 200 mg of synthesized Titan tholins were produced using this process.

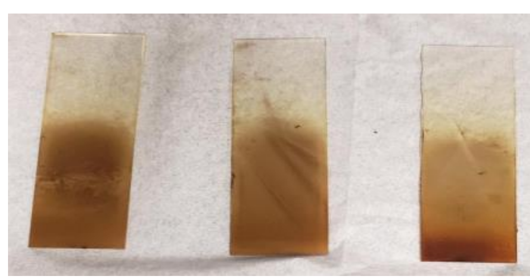

Figure 2: Tholins produced using the noted experimental conditions.

We determined the solubility of tholins at three temperatures close to room temperature (248 K, 273 K, and 298 K).

Matrix Assisted Laser Desorption/Ionization (MALDI) analysis was used to determine structural molecular changes in the solid residue. At different times of the solubility experiment, we sampled a few microliters of the liquid portions of the samples for GC-MS measurements.

Results: From our tholin production, direct desorption from the chamber disk that had tholin residue directly deposited was analysed using MALDI (Figure 3). Additionally, solid tholin residues remaining after solubility studies were analysed with MALDI (Figure 4). This result shows a loss of mass equal to 2 carbon. This makes for an interesting result as we have no previous observations of carbon loss in the molecular structures alone.

A loss of 2 carbon without an associated hydrogen loss provides interesting insight into the molecular formation. These suggest that C to C bonding throughout a fused ring like structures, similar to those seen in Buckminsterfullerene. These structures occurrence on Titan could facilitate more interesting chemical reactions that effect its habitability.

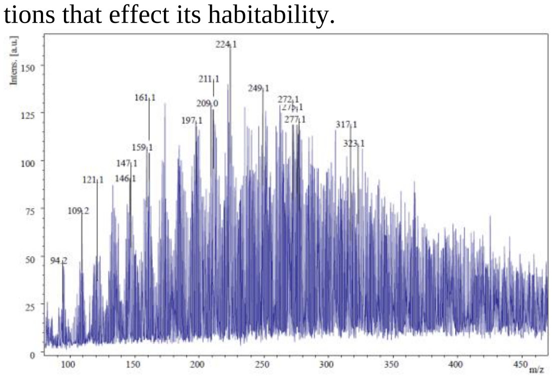

Figure 3: MALDI direct desorption analysis from tholin deposits before dissolution in any solvent.

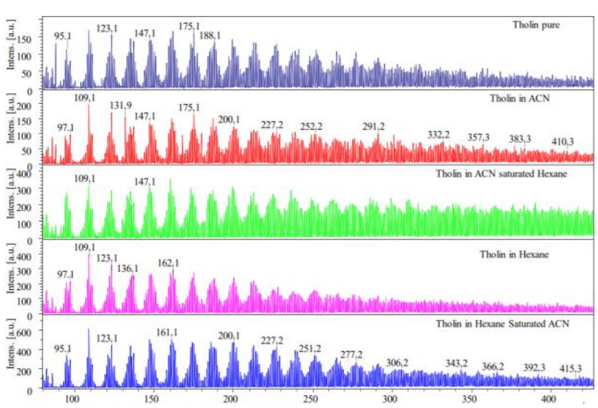

Figure 4: MALDI direct desorption analysis from solid tholin residue remaining from solubility studies of acetonitrile, hexane, acetonitrile saturated hexane, and hexane saturated acetonitrile.

Conclusions: This study aims to investigate the prebiotic chemistry of Titan and the fate of tholins and production of complex organic molecules on the Saturnian moon's surface. As much as there have been extensive experimental work on the formation of tholins in Titan's atmosphere, as well as their potential hydrolysis, there is virtually no extensive study of their further reactivity with liquid hydrocarbons once deposited on the surface. We present preliminary results obtained so far for this solubility study. The first and most straightforward significance of our work provides new solubility data on polar compounds in liquid hydrocarbons. Our second significance is characterizing the potential reactivity of tholins in the presence of liquid non-polar hydrocarbons with dissolved polar species. This could demonstrate the possibility for heterogeneous chemical reactions in exotic liquid solvents. Results of this study at room temperature will be used to constrain our future experiments of the solubility of tholins in liquid methane-ethane mixed with the same polar compounds at Titan's temperature and pressure. This future work will give insights into the habitability of Titan and ultimately provide crucial questions for the future Dragonfly mission.

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