TITAN IN A FUME HOOD: ROOM-TEMPERATURE SIMULATION OF A TITAN EVAPORITE PLAYA USING A MULTI-COMPONENT MIXTURE OF ORGANIC COMPOUNDS.

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Introduction: Saturn's moon Titan is a world where organic chemistry reigns supreme. The Cassini mission instruments have revealed that the geology appears to be dominated by organic materials [1-3] with erosive processes using hydrocarbon fluids [4, 5]. Previous studies have detailed possible karstic lakes [6], karst-like terrains and poljes [7], evaporite deposits in dry lake beds [8] and evaporite rings around Ontario Lacus [9] that may have resulted from the dissolution, transport, and evaporitic precipitation of Titan surface materials. Figure 1B and 1C show two dry lakes near Ligea Mare that have VIMS-bright signatures in their bottoms that may be evaporite deposits [8].
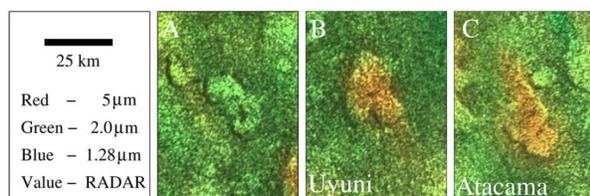

Figure 1. VIMS-RADAR composite from Barnes et al., 2011 [8] showing lakes with and without VIMS-identified evaporite deposits. (A) empty lake with no evaporite deposit. (B) and (C) show two empty lakes with evaporite deposits (orange coloring).

With a frigid surface temperature of 95 K, many of the materials detected on Titan are gases or are reactive at terrestrial temperatures. Previous work has modeled some of Titan's surface processes using a cryogenic chamber to monitor the absorption of methane in water ice [10], the evaporation rate of liquid methane [11], and the precipitation of crystalline materials in Titan lakes [12].

Our approach was to identify organic compounds that can be manipulated at room temperature and serve as a proxy for the materials on Titan that are volatile under terrestrial conditions. This facilitates the development of readily achievable experimental set-ups, as well as provide insights that could bridge experimental results to the actual cryogenic processes.

Recent VIMS work has shown evaporite deposits in several empty lakes [8]. On Earth, the formation of evaporites involves the precipitation of inorganic salts following a known sequence where the least soluble material, typically calcite or dolomite, precipitates first, followed by gypsum, then halite or other chloride ion-containing inorganic salts.

On Titan, evaporation may follow a similar sequence of deposition of organic molecules in reverse order of solubility following evaporation of a hydrocarbon solvent.
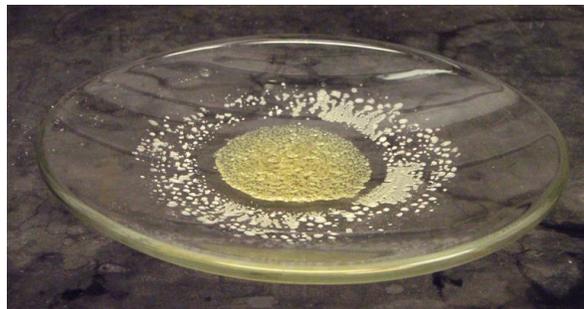

Figure 2. Titan evaporite simultation using a four-component mixture of organic compounds in heptanes on a watch glass

Simulation of the drying of a Titan playa. We simulated the evaporation of the most soluble compounds expected on Titan's surface (Figure 2). As a replacement for liquid methane precipitation and runoff, we used heptanes as the hydrocarbon fluid. We identified easily-obtainable laboratory compounds with solubilities in heptane that would scale to the predicted solubilities of Titan materials in liquid methane [13, 14]. The four compounds chosen for the mixture are shown in Figure 3.
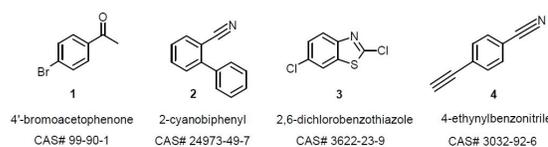
	Experimental solubility in heptane at 298 K (mg/mL)	30x Estimated solubility in 77%CH$_4$ / 23%N$_2$ at 95 K(mg/mL)	Estimated solubility in 77%CH$_4$ / 23%N$_2$ at 95 K(mg/mL)
ethylene (C$_2$H$_4$)		84300	2810
4'-bromoacetophenone [1]	77100		
2-cyanobiphenyl [2]	42200		
acetylene (C$_2$H$_2$)		39000	1300
2,6-dichlorobenzothiazole [3]	37500		
hydrogen cyanide (HCN)		32400	1080
n-butane (C$_4$H$_{10}$)		17400	580
4-ethynylbenzonitrile [4]	2500		
carbon dioxide (CO2)		1320	44

Figure 3. Analog compounds, their experimentally determined solubilities in heptanes, and comparison with estimated solubilites of selected Titan surface materials.

For our initial simulation, we assumed that the heptane fluid was at saturation for each of the four components.

Experimental: To a 40 mL scintillation vial was added 4'-bromoacetophenone (771 mg), 2-cyano-biphenyl (422 mg), dichlorobenzothiazole (375 mg), and 4-ethynylbenzonitrile (25 mg) in heptanes (10 mL). The mixture was vortexed and passed through a 0.2 micron syringe filter to furnish a clear pale yellow solution which was transferred into a 12.5 cm diameter watch glass. The solution was allowed to evaporate overnight in a variable flow chemical fume hood. After 18 h, the radii of the concentric deposit zones were measured (Figure 4). At the center was a small white globular crystalline deposit immersed in a yellow oil. Further out was a clear zone followed by a feathery crystalline deposit with the main orientation of the crystals radial to the center. Beyond this was a narrow clear zone followed by compact white crystalline globs. Samples were taken at selected locations representative of each region. The samples were weighed, dissolved in CH_3CN, diluted to ca. 0.1-1.0 mg/mL concentration and analyzed by high performance liquid chromatography (HPLC) using UV detection at 254 nm. The molar extinction coefficients and retention times had previously been determined for each component over concentration range from approximately 0.01 mg/mL to 1 mg/mL.
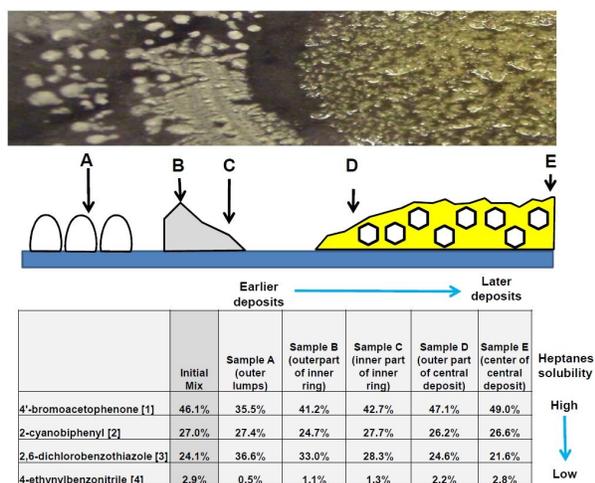

	Initial Mix	Sample A (outer lumps)	Sample B (outer part of inner ring)	Sample C (inner part of inner ring)	Sample D (outer part of central deposit)	Sample E (center of central deposit)	Heptanes solubility
4'-bromoacetophenone [1]	46.1%	35.5%	41.2%	42.7%	47.1%	49.0%	High
2-cyanobiphenyl [2]	27.0%	27.4%	24.7%	27.7%	26.2%	26.6%	
2,6-dichlorobenzothiazole [3]	24.1%	36.6%	33.0%	28.3%	24.6%	21.6%	
4-ethynylbenzonitrile [4]	2.9%	0.5%	1.1%	1.3%	2.2%	2.8%	Low

Figure 4: (upper) Zoom of simulated evaporite seen in Figure 2. (middle) Diagram of zones showing analytical sample points. (lower) Table showing HPLC results expressed as molar ratio (%).

Results and Discussion. The results of the preliminary analysis of the samples are presented in Figure 4. The molar ratio of the most soluble component, 4'-bromo-acetophenone, is depleted at the outer edges and enriched in the center. This is in agreement with halite precipitation in terrestrial playas. In contrast, the next most soluble component, 2-cyanobiphenyl, does not concentrate preferentially. It also has the lowest melting point of all the compounds (35 C) and

may have oiled out from the mixture. It should be noted that the melting point of ethylene (101 K) is only slightly above ambient Titan temperature of 95 K, so under Titan conditions it may also oil out on mixing. The less soluble 2,6-dichlorobenzotriazole shows a decrease in molar ratio as one goes towards the center of the simulated playa. This is also similar to terrestrial playas where the more insoluble components precipitate first. The least soluble material, 4-ethynylbenzonitrile, had a curious behavior - its molar ratio was highest toward the center. This could be explained by the material preferentially mixing in and being partially soluble in phases resulting from the increased concentration of 4-bromoacetophenone. In effect, this would be an extraction of a component material in solution into a solid phase or oil phase deposit.

Conclusions: These initial simulations were designed to scale to the thermodynamic equilibrium solubilities of Titan materials and should mimic the behaviors of saturated solutions. Complex processes, including compounds forming oil phases as well as materials partitioning into oil or solid phases, were observed. From these simulations, we can get a glimpse of the range of possible properties of Titan materials during evaporation. However, kinetic differences between the proxy versus Titan materials at cryogenic temperatures could also affect dissolution and precipitation rates and will need to be considered.

These room temperature simulations provide insight into possible processes occurring on Titan using multi-component organic materials. The information gained can be used to design experiments to examine Titan material behaviors at cryogenic temperatures.

References: [1] Lorenz et al., *GRL* 35 (2008) L02206. [2] Clark et al., *JGR* 115 (2010) E10005. [3] Soderblom et al., *Planetary and Space Sci.* 55 (2007) 2025-2036. [4] Langhans et al., *Planetary and Space Sci.* 2011 in press. [5] Jaumann et al., *Icarus* 197 (2008) 526-538. [6] Mitchell et al., *LPSC* 39 (2008) Abstract 2170. [7] Malaska et al., *LPSC* 41 (2010) Abstract 1544. [8] Barnes et al., *Icarus* 216 (2011) 136-140. [9] Barnes et al., *Icarus* 201 (2009) 217-225. [10] Sotin et al., *LPSC* 40 (2009), Abstract 2088. [11] Luspay-Kuti et al., *LPSC* 42 (2011), Abstract 1736. [12] Hodyss and Choukroun, *EPSC* 6 (2011) EPSC-DPS2011-1026. [13] Raulin, F., *Adv. Space Res.* 7 (1987) 71-81. [14] Cordier et al., *Astrophysical J.* 707 (2009) L128-L131.