

DETERMINATION OF THE SOLUBILITIES OF AROMATIC MOLECULES IN CRYOGENIC ETHANE AT 94 K – APPLICATION TO TITAN LAKE FLUIDS. M. Malaska and R. Hodyss, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA. (Michael.J.Malaska@jpl.nasa.gov)

Introduction: One of the major discoveries of the Cassini mission is the existence of large bodies of hydrocarbon lakes in the polar regions of Saturn's moon Titan [1]. This makes Titan and Earth the only worlds in the Solar System with stable liquids on the surface. The complex atmospheric photochemistry on Titan produces a plethora of organic molecules that eventually make their way down to the surface [2, 3]. Evaporite deposits observed in dry lakebeds and also ringing several Titan polar lakes suggest that organic materials are being dissolved, and redeposited as the lake fluids evaporate [4]. However, the exact composition and amounts of the organic materials dissolved in Titan lakes are unknown and will likely require future in situ measurement.

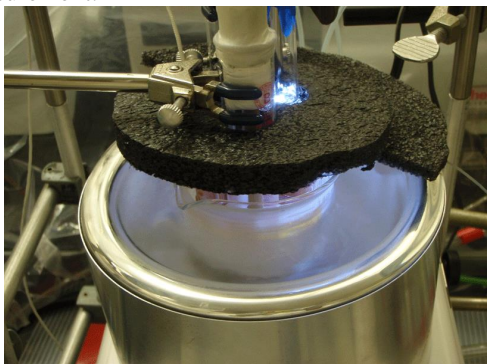
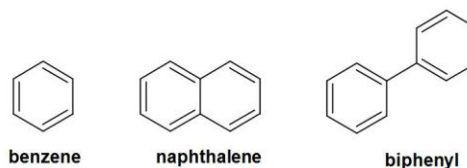


Figure 1. Apparatus for measuring solubilities under Titan conditions. The blue glow is from internal LED illumination.

Our goal was to develop instrumentation and techniques that could quantitatively determine the amounts of organic molecules present in cryogenic hydrocarbons in the laboratory [5]. These measurements will help constrain the values for in situ measurements that could be expected for Titan lake fluids. We examined the solubilities of aromatic molecules benzene, biphenyl, and naphthalene in ethane at 94 K using a UV fiber optic probe and an apparatus capable of maintaining a constant temperature of 94 K (Figure 1) [5].

Among the organic molecules predicted to be on Titan's surface are aromatic molecules such as benzene. Benzene has been detected at high altitudes in Titan's upper atmosphere (another surprising discovery from the Cassini mission) [6] and has been identified on the surface by Cassini's VIMS instrument [7]. Recent laboratory work simulating Titan's atmosphere has shown that the presence of benzene could significantly change the atmospheric production rates and composition of organic aerosols towards more complex aro-

matic molecules [8]. These include molecules such as polyaromatic hydrocarbons (PAHs) or polyphenyls. Naphthalene is the simplest polyaromatic hydrocarbon (PAH) and can be used as an end-member proxy for that entire class of molecules. Naphthalene has been identified in Titan's atmosphere from INMS data [9]. However, that same data was interpreted by Delitsky and McKay to suggest that polyphenyls, which are more likely to form at lower temperatures, were responsible for the ion signals [10]. Polyphenyls are benzene rings linked by a single bond and capable of some (hindered) rotation; the simplest endmember of that series is biphenyl. The detection and relative solubilities of each of these molecules is of interest and may serve to indicate the solubility trend of higher homologues of fused aromatics and linked aromatics.



Experimental: In a typical experiment run, a small amount of solid test sample is placed to an insulated beaker containing 100 mL of liquid ethane held at 94 K. Using differential pressure, some of the solution is pulled past a fritted glass filter into a tube containing a Ocean Optics UV-Vis fiber-optic probe [5]. The absorbance is measured at regular timepoints until equilibrium saturation is reached, and the quantity of material in solution at each time point can be determined by comparison with a calibration. The calibration technique was further validated by adding a known quantity of material to ethane at low temperature and measuring the absorbance. Figure 2 shows the measured spectrum of biphenyl in ethane at 94 K even at sub-milligram per liter concentrations. For comparison, 0.05 mg L^{-1} is the WHO limit for chromium in drinking water.

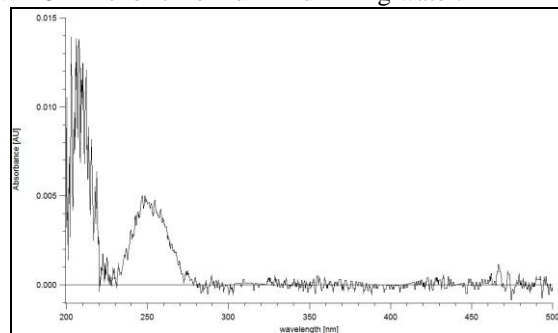


Figure 2. Absorbance spectrum of a saturated (0.039 mg L^{-1}) solution of biphenyl in ethane at 94 K.

Results and Discussion. The equilibrium solubilities of benzene, naphthalene, and biphenyl are listed in Table 1.

Table 1. Table of determined equilibrium solubilities (c_{sat}) of aromatic molecules

compound	molecular formula	m.w.	c_{sat} [mg L ⁻¹]	c_{sat} [M]
benzene	C ₆ H ₆	78.11	18.27	2.3×10^{-4}
naphthalene	C ₁₀ H ₈	128.17	0.159	1.2×10^{-6}
biphenyl	C ₁₂ H ₁₀	154.21	0.039	2.5×10^{-7}

Larger aromatic constructs, such as terphenyl or anthracene, would be effectively insoluble, with equilibrium concentrations predicted to fall below 0.001 mg L⁻¹.

Using our technique, we were able to determine the concentration of two components simultaneously. Figure 3 shows the absorbance spectra obtained with a saturated solution of naphthalene (0.16 mg L⁻¹) and added benzene in pentane. From our results, adding benzene (or pentane) did not significantly increase the solubility of naphthalene.

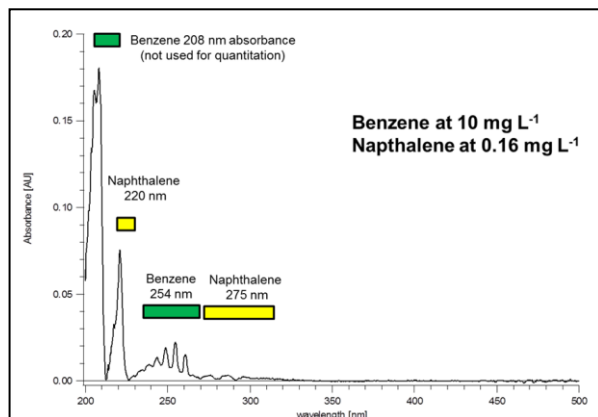
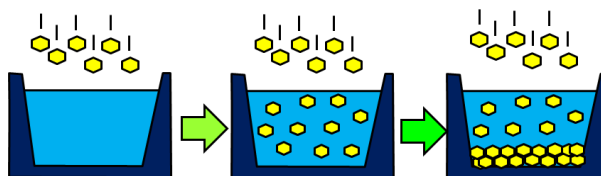


Figure 3. Spectrum of naphthalene at saturation after addition of benzene to bring the solution concentration to 10 mg L⁻¹ benzene in ethane at 94 K.

Implications for Titan lake concentrations and sediments: The time required to achieve saturation from direct atmospheric infall into a Titan lake can be determined from the atmospheric flux rate and equilibrium solubility of the chemical species, and the surface area and volume of a given Titan lake. Until saturation is reached, all the atmospheric materials will dissolve in the lake fluids. After saturation is reached, the excess materials would precipitate out as a sludge on the lake bottom at a rate matching the atmospheric flux. As an example, Ontario Lacus has a surface area of 1.5×10^{10} m². Assuming an average depth of 3 m, this translates to a total lake volume of 4.5×10^{10} m³ ($= 4.5 \times 10^{13}$ L) ethane. Using a benzene flux rate of 1.8 molecules•cm⁻²•s⁻¹ [2], and working through the calcula-

tions, benzene saturation will be reached in 750,000 yr. Assuming a naphthalene and biphenyl flux rate 3 orders of magnitude less than that of benzene, we attain lake saturation of those molecules in 4 Myr. and 800,000 yr. (Biphenyl attains saturation faster due to its lower solubility). These values assume no influx from the drainage area, this only takes into account direct airfall onto the lake surface. Estimates of Titan's surface from the cratering record suggests a young surface less than 1 Gyr. If we assume a constant atmospheric flux rate, we would expect lake saturation to occur on a timescale significantly less than the maximum implied surface age.



Benzene saturation at 18 mg L⁻¹ reached in 0.75 Myr

Figure 4. Graphic showing how airfall from a lake reaches saturation in 750,000 years. Excess is deposited as sediment.

Conclusions: We have successfully measured the equilibrium solubilities of benzene, naphthalene and biphenyl with a fiber optic UV probe at cryogenic temperatures. While benzene is poorly soluble, naphthalene and biphenyl are sparingly soluble and all will attain lake saturation on a geological timescale. It is expected that higher orders of PAHs and polyphenyls will be effectively insoluble in cryogenic hydrocarbons, such as those that exist in Titan's polar lakes.

Acknowledgement: This research was supported by an appointment to the NASA Postdoctoral Program at the Jet Propulsion Laboratory, administered by Oak Ridge Associated Universities through a contract with NASA as well as a grant from the NASA Outer Planets Research (OPR) program. Support from the NASA Astrobiology Institute (Titan) and NASA's Astrobiology Science and Technology Instrument Development (ASTID) program is gratefully acknowledged.

References: [1] Stofan et al., *Science* 445 (2007) 61-64. [2] Krasnopolsky, V.A. (2009) *Icarus* . 201, 226-256. [3] Lavvas et al. (2008) *PSS*, 56, 67-99. [4] Barnes et al., *Icarus* 216 (2011) 136-140 [5] Malaska and Hodyss, (2013) *LPSC 44*, Abstract 2744. [6] Vuitton et al., *JGR* 113 (2008) E05007. [7] Clark et al., *JGR* 115 (2010) E10005. [8] Trainer et al., *The Astrophysical Journal Letters* 766 (2013):L4. [9] Waite et al., *Science* 316 (2007) 870-876. [10] Delitsky and McKay 207 (2010) 477-484.