SOLUBILITIES OF HYDROCARBONS IN THE SEAS OF TITAN AND TESTS FOR EXOTIC LIFE. J.I. Lunine 1, 5, D. Cordier 2, 5, O. Moussis 3 and P. Lavvas 5, 1 Dipartimento di Fisica, Università degli Studi di Roma “Tor Vergata”, Rome, Italy, ilunine@roma2.infn.it, 2 Ecole National Superieure de Chimie de Rennes, Rennes, France, 4 Institut de Physique de Rennes, Rennes, France, 4 Université de Franche-Comté, Institut UTINAM, CNRS/INSU, Besançon, France, 5 Lunar and Planetary Laboratory, The University of Arizona, Tucson AZ USA.

Introduction: Hundreds of km- to hundred-km-sized patches interpreted as lakes, and several areas large enough to be designated seas, have been discovered in the north and south polar regions of Titan [1,2]. We quantified the composition of these lakes and seas by using the equatorial atmospheric abundance measurements taken in 2005 by the Gas Chromatograph Mass Spectrometer (GCMS) aboard the Huygens probe, and recent photochemical models based on the vertical temperature profile derived by the Huygens Atmospheric Structure Instrument (HASI) [3,4]. The calculated composition of lakes is different from what has been expected from earlier models [5] which preceded Cassini-Huygens exploration and used a smaller set of thermodynamic data. Here we explore the astrophysical implications of variations around the calculated lake compositions, and what might be inferred about Titan’s sedimentary and possible biologic history with a chemical analyzer system aboard a lake lander.

Model summary: Our model uses regular solution theory and the assumption of thermodynamic equilibrium between the lake liquid and the atmosphere expressed through the equality of the chemical potentials, using an iterated Newton-Raphson scheme [6]. Data sources have been derived from both the NIST database [7], other published sources [5], and some unpublished data of J. Prausnitz. We calculate both the dissolution of vapor and that of solid particulates in the liquid. Based on laboratory experiments in which thermodynamic consistency was achieved in vapor-liquid equilibrium measurements, the assumption of thermodynamic equilibrium should generally hold for the lakes and seas [8]. However, we cannot rule out the presence of a methane-rich and buoyant layer, deposited through seasonal methane rainstorms and floating transiently atop the main body of liquid [9].

Composition: We found [6] that the main constituents of polar lakes and seas at the Cassini-inferred surface temperature of 90 K [19] are ethane C2H6 (~76%), methane CH4 (10%), propane C3H8 (~7%), and butene C4H8 at 1%. Major aerosol particulates that would be dissolved in the lakes include hydrogen cyanide (HCN) (2%), butane C4H10 and acetylene C2H2, both at about 1%, and benzene C6H6 at 0.02%. Nitrogen dissolved from the atmosphere accounts for less than 0.5% of the polar marine and lacustrine composition. Of the dissolved solids, butane, acetylene and benzene are unsaturated.

Observational implications: The lake/sea composition reported here is lower in methane and nitrogen, and higher in propane, than given in pre-Cassini calculations. The methane abundance remains high enough to give the lakes essentially a black appearance within the methane bands in the near-infrared, making direct detection of liquid methane difficult or impossible, but both ethane and propane should be evident. Ontario Lacus in the southern hemisphere has been observed to be shrinking [10] over the past 4 years of late summer on Titan, and shows evidence for both ethane [11] and propane [12] in spectroscopic data.

Geological implications: The calculated particulate surface liquid composition given here is based on direct precipitation of stratospheric aerosols into the lakes and seas. However, Titan seems to be oblate, with the polar regions at lower elevation than the equator [12]. While it is not known whether this corresponds as well to a polar depression relative to the geoid, it is at least suggestive of the possibility that fluvial flow on a global scale will be toward the poles, and hence some of the aerosol material deposited over large parts of Titan’s surface might be transported into the polar lakes and seas; at least that portion not present in the vast equatorial dune fields. The importance of the poleward transport of photochemically-produced aerosols will depend on the extent of fluvial transport which because of limited Cassini resolution remains poorly-defined [13]. However, aeolian transport may play an important role as well. If the lakes are a repository for significant amounts of solid organics beyond that directly precipitated in the polar regions, species that are not saturated in our model could have higher abundances than we predict, indeed, even be saturated. Differences between our photochemically-generated model abundances for these species, and abundances actually measured aboard a lander in the lakes or seas could allow determination of the extent of such surface and lower-atmosphere transport. Ideally, one would want to measure these abundances both in one of the smaller lakes (which might disappear seasonally or on longer timescales [14]) and a large sea.

Biological implications: Ideas for a very exotic form of life that might exist in hydrocarbon liquids...
have been discussed [15,16], and one should not rule out such a possibility without either direct exploration of the lakes and seas or hard evidence that organic chemistry cannot self-organize toward complex autocatalytic chemical cycles. Chemical evidence for specific metabolic processes in the lakes could come in the form of variations from our model predictions, or from compositions that arguably suggest bulk sedimentary deposition of organics in the lakes. For example, reaction of solid or dissolved-liquid acetylene with atmospheric hydrogen \( \text{C}_2\text{H}_2 + 3\text{H}_2 \rightarrow 2\text{CH}_4 \) generates chemical free energies exceeding what is required on a per mole basis to sustain terrestrial methanogenic or -ganisms [17]. If such a metabolic process were operating in Titan’s lakes and seas, one might expect to find a deficit of acetylene relative to what is predicted in our model, or (if fluvial/aeolian transport to the lakes is efficiently recharging the lakes and seas with solid organics) relative to the abundances of other dissolved particulates that are not energetically favorable reagents for simple metabolic cycles. At the same time, hydrogen immediately above the lake/sea would be depleted, and methane within the liquid and coexisting atmospheric boundary layer enriched. Alternatively, biotic or abiotic processes might consume acetylene to make benzene (also energetically favorable but difficult to reverse); in this case the dissolved benzene-to-acetylene ratio might be larger than expected. This is a useful measurement, as long as both constituents are not saturated. The significantly higher solubilities for the lighter hydrocarbons that we find in our calculations, relative to those reported in experiments done on much heavier plasma-discharge “tholins” [18], makes lake and sea measurements a potentially useful pointer toward nascent or ongoing biological activity.

**Measurements:** Our results suggest that the polar lakes and seas of Titan are an extremely high priority target for future landed missions to Saturn’s largest moon. The solubilities and predicted compositions of major and minor constituents are sufficiently large that standard mass spectrometers flown previously in space are capable of quantifying the compositions of interest. Care would need to be taken to determine whether the layer of liquid being analyzed were representative of the bulk liquid, or a transient layer deposited as a result of meteorological events or seasonal processes. Such a determination might require a relatively long-lived lander (weeks), floating over a significant portion of a lake or sea, and/or sounding measurements that could probe the subsurface properties of the lake or sea.

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**References:**