The Surface Energy of "Tholin" and its Implication on Haze-Liquid Interactions on Titan.

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Introduction: Titan's nitrogen-methane atmosphere has enabled rich photochemistry to occur in its upper atmosphere. The photochemistry can create simple hydrocarbons such as ethane, ethylene, acetylene, benzene, and nitrogen-incorporated organics such as hydrogen cyanide, and cyanoacetylene, etc. These simple organics are further processed to form complex organic haze particles that can grow up to ~1 µm before they reach the surface (Tomasko et al., 2005). Methane and many of the photochemically produced simple organics are condensable in certain altitudes of Titan's atmosphere to form clouds. Cassini has observed clouds made of various compositions, including methane, ethane, hydrogen cyanide (HCN), cyanoacetylene (HC_3N), dicyanoacetylene (C_4N_2) (Hörst, 2017). In order to form sufficient observable clouds, heterogenous nucleation is needed for efficient cloud growth. On Earth, water can efficiently nucleate on various species including sea salt, mineral dust, biological debris, anthropogenic aerosols and form clouds. On Titan, the complex organic hazes are proposed to be the main heterogenous cloud condensation nuclei (CCN) for the observed cloud species (e.g., Griffith et al., 2006).

Curtis et al., (2008) studied the adsorption of methane and ethane on the laboratory produced Titan haze analogs, "tholin", and found that tholin can serve as good cloud seeds for methane and ethane clouds on Titan. However, the viability of other kinds of cloud growth on the haze particles has not been studied yet. Laboratory experiments require low temperature nucleation experiments of these hydrocarbon liquids and can be difficult to perform. We approach this question in a different way by first measuring the surface energy ($\boldsymbol{\gamma}_s$) of Titan aerosol analogs "tholin" (Yu et al., 2017; Yu et al., in prep), which can then enable us to theoretically predict the haze-liquid interactions in Titan's atmosphere. By using the surface energy of tholin (γ_s) and surface tensions (γ_l) of various organic species of interest, we can calculate contact angles (θ) between the possible liquid condensates and tholin. This could help us estimate whether haze particles can be good CCN for a certain liquid on Titan. The contact angle study between liquids and haze particles on Titan could also inform us on the interaction of the haze and liquid species in Titan's lake. A recent study suggests the possibility a floating layer of sedimented haze material on Titan's lake surface to damp the surface waves (Cordier & Carrasco, 2019). However, the above scenario requires the lake species (mostly methane, ethane, and nitrogen) to be liquidophobic (θ>90°) to the haze particles. The contact angle study could help assess the viability of a floating film of organics on Titan's lakes and seas.

Methods: We used two different methods, the sessile drop contact angle method and the direct force method to measure the surface energy of the Titan aerosol analogs, "tholin". Tholin samples were produced with two energy sources, cold plasma and UV irradiation, with a cold gas mixture of 5% CH_4/N_2. Both the plasma and UV tholin samples were deposited on acid-washed glass slides for contact angle measurements. The plasma tholin was also deposited on two molecularly smooth mica sheets bonded to cylindrical silica lenses for direct force measurements. Both tholin films are very smooth (RMS roughness < 4 nm) and have sufficient thickness (>100 nm).

Contact angle method: The sessile drop is formed by gently dispensing a set of test liquids through a pipette onto the coated tholin surfaces. The test liquids have a range of surface tensions from 26.5 to 72.8 mN/m, including water, diiodomethane, glycerol, ethylene glycol, dimethyl sulfoxide, formamide, toluene, and tetradecane. An image of each droplet was recorded and measured by using the ImageJ software with the contact angle plugin. We can then use the contact angle data between tholin and various test liquids to estimate the surface energy of tholin. We used four different analytical methods, including the Owens-Wendt-Rabel-Kaelble (OWRK) two-liquids and multi-liquids methods, the harmonic mean method, the van Oss-Chaudhurg-Good (vOCG) method, and the Zisman plot method.

Direct force method: We used a surface force apparatus (SFA) for the direct force measurements (e.g., Israelachvili & McGuiggan, 1990). During the SFA measurements, two coated tholin surfaces were brought into contact and then separated, the pull-off forces ($F_{\text{pull-off}}$) at separation can be measured through the deflection of the double-cantilever spring, and the contact radius (R) was continuously monitored by multi-beam optical interference between the silver films coated on the back of the mica sheets. The surface energy of tholin can be approximated by using the Johnson-Kendall-Roberts (JKR) theory: γ_s=$F_{\text{pull-}}$

$_{\mathrm{off}}/3\pi R_{\max}$, where $R_{\max}$ is the maximum contact radius.

Results and Discussion: *Surface energy of tholin.* The surface energy of plasma and UV tholins are calculated with multiple analytical methods and the results are summarized in Table 1. It is interesting that the tholins made with different energy sources have similar overall surface energy and similar partitioning pattern. Both tholins have significant polar components, indicating the abundance of polar structures of the materials. The OWKR two liquids method is the most widely used surface energy derivation methods, and gives similar value as the SFA measurement for plasma tholin. Here we took this value for the following contact angle calculations.

Table 1: Derived surface energy of tholin from different methods, all units in mJ/m^2.

Methods	*Plasma Tholin*		
	γ_s^d	γ_s^p	γ_s^{tot}
OWRK two-liquids	39.6	28.5	68.1
OWRK multi-liquids	26.5	27.7	54.1
Harmonic mean	40.2	31.9	72.1
vOCG method	38.4	12.1	50.5
SFA measurement	n/a	n/a	66
	UV tholin		
OWRK two-liquids	41.1	24.9	66.0
OWRK multi-liquids	27.3	23.9	51.2
Harmonic mean	41.5	29.0	70.5
vOCG method	39.8	2.9	42.7

Contact angle between Titan condensates and tholin. We also calculated the contact angle between possible hydrocarbon liquids on Titan and tholin. So far the calculations include methane and ethane (Table 1). We found that both methane and ethane on Titan would completely wet the tholin surface based on the contact angle calculation. Tholin is hardly soluble in most non-polar hydrocarbon liquids [e.g., He & Smith, 2014], which indicate the Titan haze particles may not be the most ideal cloud condensation nuclei (CCN). But insoluble particles could still serve as CCN if the solid-liquid contact angle is less than 10° [e.g., Mahata & Alofs, 1975], which is the case between tholin and methane and ethane liquids on Titan. Thus, we suggest that Titan haze particles are likely good cloud seeds for methane and ethane clouds, which are frequently observed. The extremely low contact angle between methane and ethane on Titan and tholin also rule out the possibility of a film of organics floating on Titan's lakes as proposed by Cordier and Carrasco (2019), which needs large contact angle ($\theta > 90°$) between the lake species and haze particles.

Table 2: Calculated contact angle between Titan condensates and tholin. Literature contact angle is from Rannou et al., (2019) for tholin produced in another laboratory.

Surface Tension	γ_s^d	γ_s^p	γ_s^{tot}	Θ this work	Θ literature
Methane	16.7	0	16.7	0°	6.3°
Ethane	32.9	0	32.9	0°	15.0°
	0.55	0.05			

Conclusion and future work: To understand various physical processes involving the haze on Titan, we quantified an important physical property of the Titan haze analogs "tholin", the surface energy. The total surface energy of tholin measured by different methods is around 65-70 mN/m.

With the surface energy of tholin, we estimated the contact angle between the main liquid condensates on Titan (methane and ethane) and tholin and found that both methane and ethane would completely wet the tholin surface. This indicates that the Titan haze particles are likely good cloud condensation nuclei for methane and ethane clouds. While when the Titan haze particle sediment down and reach the lakes, they would probably sink into the lakes instead of forming a floating wave-damping layer suggested by Cordier and Carrasco (2019).

For future work, we would like to expand our contact angle calculations to more condensate species on Titan that are hard to measure with laboratory adsorption studies.

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