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What is on those Titan Beaches?

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Abstract

Benzene is found on Titan and is a likely constituent of the putative evaporite deposits formed around the hydrocarbon lakes. We have recently demonstrated the formation of a benzene-ethane co-crystal under Titan-like surface condition as a function of temperature. We show that the formation process would reach completion under Titan surface conditions in ~18 hours, and that benzene precipitates from liquid ethane as the co-crystal. This suggests that evaporite basins rich in benzene may not contain just pure crystalline materials, but instead the beaches or basins may be replete with co-crystals of various forms. These new structures may influence evaporite characteristics, such as particle size and infrared spectral properties. This co-crystalline form of benzene with ethane represents a new class of materials for Titan's surface, analogous to hydrated minerals on Earth. This work is being extended to explore the interaction of benzene with methane and propane at Titan temperatures. We are also investigating other molecules such as acetylene and pyridine to determine if co-crystal formation can occur in these systems as well.

1. Introduction

Cassini's investigation of Titan continually surprises us with exciting new results. Lakes were discovered in polar areas [1], and spectral features observed by the Cassini VIMS instrument around some of these lakes have been interpreted as putative evaporitic materials [2]. Although thermodynamic models [3] give some clues on the composition of lakes and potential evaporites, we are sadly lacking in interpreting some of these results because of the dearth of experimental data. This work describes some of our initial thoughts on how to interpret the notion of 'beaches' around the Titan seas. Are these beaches just deposited organics from the atmosphere, materials precipitated out from the ethane/methane lakes or both? Are crystalline or co-crystalline (such as the 1:1 acetylene-benzene co-crystal observed by [4]) complexes formed from the interaction of dissolved materials? Experiments we have initiated begin to shed light on this conundrum. We have slowly evaporated large volumes (10 mL) of saturated solutions of benzene and acetylene in pure ethane and mixtures of ethane/methane and other possible solvents. Macroscopic quantities of crystals have been generated for analysis of morphology and size distribution and the crystals analysed with Raman spectroscopy, infrared spectroscopy and optical microscopy. To maintain the integrity of the sample and determine how these materials mix, the Raman microscopy is performed in a cryo-stage. We will later compare the spectroscopy of some of these simulated 'beaches' with data obtained from VIMS on Cassini.

2. Results

Formation of benzene-ethane co-crystals by interaction of solid benzene with liquid ethane was monitored at four different temperatures: 110, 115, 120 and 125 K. The most compelling evidence for co-crystal formation is a 12 cm^{-1} red shift of a peak in the Raman spectrum characteristic of an ethane stretching vibration. This shift from 2885 to 2873 cm^{-1} signifies a new molecular environment for ethane: incorporation in the benzene lattice, most likely as a co-crystalline complex [5]. The sharpness of this peak is also indicative of a highly specific interaction, as would be expected in a crystalline material. We monitored the area of this 2873 cm^{-1} peak over time to determine the kinetics of ethane incorporation into crystalline benzene (Figure 1) Microscope images indicate recrystallization of the sample, which, in association with the changes in Raman signature, strongly suggest the formation of a new crystal structure. This reorganization associated with the reaction is most likely due to disruption of the strong stacking interaction in solid benzene to accommodate the guest ethane molecules via an attractive van der Waals interaction [5]. The 2873 cm^{-1} feature characteristic of ethane incorporation in the co-crystal emerged and grew over time until saturation was reached for that temperature (Figure 1). As expected, the rate of incorporation increases with temperature. A plot of ln(τ) versus 1/T produced a linear fit, with the slope of this fit, Ea/R, yielded an activation energy (Ea) of 10.2 ± 0.2 kJ/mol. Extrapolation to 90 K indicates that the incorporation of ethane in benzene ice will reach completion in approximately 18 hours at Titan surface temperatures. This implies formation of the benzene-ethane co-crystal will occur readily in Titan ambient conditions. Further, precipitation of benzene out of a filtered ethane solution, followed by evaporation of ethane, yielded the co-crystal. Precipitation of the benzene-ethane co-crystal from a evaporitic deposits on Titan formed by evaporation of an ethane-rich liquid will most likely be in the co-crystal form, as opposed to pure crystalline benzene.

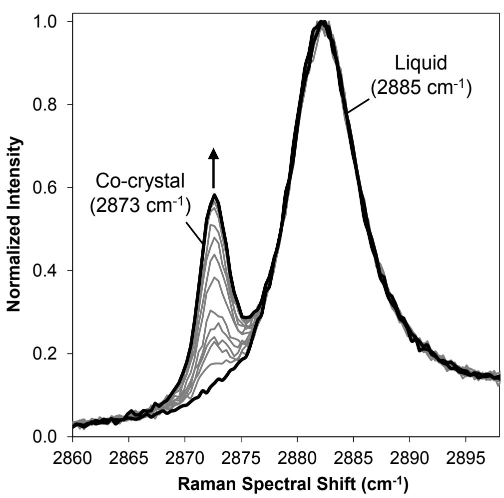

Figure 1: High resolution Raman spectra of ethane incorporation in solid benzene at 125 K. The feature at 2873 cm-1 reaches a maximum value after 14 minutes, indicating saturation of ethane in the benzene crystal structure. Spectra at t = 0 and 14 min are shown in bold; the arrow indicates change in amplitude with time.

3. Summary and Conclusions

We have determined the kinetics of formation of a benzene-ethane co-crystal from solid benzene and liquid ethane, at temperatures ranging from 110 to 125 K. We have used these temperature-dependent data to infer the activation energy associated with the incorporation of ethane into the benzene crystal lattice. We find that this phenomenon could occur readily (within hours) under Titan's surface conditions, and that the benzene/ethane co-crystal is likely the dominant form of benzene on Titan's surface. This form of benzene and ethane represents a new class of materials for Titan's surface, in some ways conceptually analogous to hydrated minerals on Earth. We are currently extending this work to explore the interaction of benzene with methane and propane at Titan temperatures. We are also investigating other molecules such as acetylene and pyridine to determine if co-crystal formation can occur in these systems as well.

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