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Key Points:

- Benzene and ethane readily form a co-crystal under Titan-like conditions
- These co-crystals are likely the dominant form of benzene in Titan evaporites
- Organic co-crystals may be a new class of materials applicable to Titan

Supporting Information:

- Readme
- Data Set S1

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Experimental determination of the kinetics of formation of the benzene-ethane co-crystal and implications for Titan

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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 conditions. Here we investigate the kinetics of formation of this new structure as a function of temperature. We show that the formation process would reach completion under Titan surface conditions in ~18 h and that benzene precipitates from liquid ethane as the co-crystal. This suggests that benzene-rich evaporite basins around ethane/methane lakes and seas may not contain pure crystalline benzene, but instead benzene-ethane co-crystals. 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 new structure may also influence evaporite characteristics such as particle size, dissolution rate, and infrared spectral properties.

1. Introduction

Titan is the only body in the Solar System aside from Earth that has standing liquid on its surface. Due to the low surface temperatures (90–95 K), this liquid phase is comprised of hydrocarbons, primarily methane, and ethane [Brown *et al.*, 2008; Stofan *et al.*, 2007]. These hydrocarbons are involved in processes analogous to the hydrological cycle on Earth—they form clouds in the atmosphere, rain onto the surface, and pool in lakes mostly in the polar regions [Ádámkóvics *et al.*, 2007; Hayes *et al.*, 2008; Tokano *et al.*, 2006]. This occurs in concert with photochemistry in the atmosphere, where solar radiation and energy from Saturn's magnetosphere activate CH₄ and N₂, generating a plethora of organic molecules that range in size from simple molecules like HCN to compounds larger than 10,000 Da [Coates *et al.*, 2007, 2009; Cray *et al.*, 2009; Waite *et al.*, 2007]. These species form multiple haze layers and continue to combine and react as they descend to the surface, where they can fall into the hydrocarbon lakes directly or be moved there via fluvial and/or Aeolian processes [Black *et al.*, 2012; Langhans *et al.*, 2012; Perron *et al.*, 2006].

Modeling of lake composition suggests that some dissolved organics may be present at or near saturation [Cordier *et al.*, 2009]. Evaporation or other processes that reduce lake levels could potentially induce precipitation, forming evaporite deposits around the lakes. This might explain the deposits seen by the Cassini Visual and Infrared Mapping Spectrometer (VIMS) [Barnes *et al.*, 2011, 2013] and Synthetic Aperture Radar (SAR) [Hayes *et al.*, 2008] around some of the northern lakes. Such evaporites would play an important role in the surface chemistry of Titan.

We focus on benzene, a relatively simple organic molecule that has been detected by Cassini in the Titan atmosphere [Clark *et al.*, 2010; Coustenis *et al.*, 2003, 2007; Vinatier *et al.*, 2007; Waite *et al.*, 2007, 2005] and was tentatively identified on the surface by the Huygens probe [Niemann *et al.*, 2005]. Theoretical calculations and laboratory experiments suggest that the solubility of benzene in liquid ethane is low (<20 mg/L) [Raulin, 1987]. Therefore, benzene is a likely constituent of possible Titan lake evaporites, in particular at the edges of deposits where evaporation occurs, as the least-soluble species like benzene should precipitate first. This is supported by Clark *et al.* [2010], who identified benzene in high-resolution (2 km/pixel) VIMS maps of the Titan surface (the 5.05 μm band is unique to benzene) within a feature that appears to be a lake or basin. We recently investigated co-deposition of benzene with methane and ethane under dynamic vacuum (10⁻¹⁰ torr) at 12 K, followed by warming to Titan surface temperature (95 K). Benzene ice maintained approximately 4% trapped methane or ethane for significant amounts of time, leading us to explore the interactions between benzene deposits and liquid ethane in conditions representative of the Titan surface.

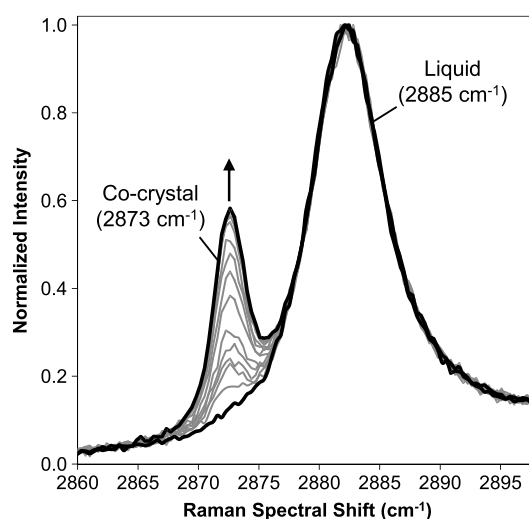


Figure 1. High-resolution Raman spectra of ethane incorporation in solid benzene at 125 K. The feature at 2873 cm^{-1} reaches a maximum value after 14 min, indicating saturation of ethane in the benzene crystal structure. Spectra at $t = 0$ and 14 min are shown in bold; the arrow indicates change in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

Solid benzene forms a co-crystal with ethane at Titan surface temperatures [Vu *et al.*, 2014]. A *co-crystal* is a unique crystalline structure comprised of two or more components in a set stoichiometric ratio, where no formal electronic modifications of the components occur (i.e., no ionic interactions as in typical crystalline salts like NaCl). Instead, co-crystal formation typically involves weaker intermolecular binding forces such as hydrogen bonding, π -stacking, or van der Waals forces. If the lattice completely surrounds or fully encapsulates a guest molecule so that it is trapped in a cage, it is considered a clathrate. Clathrates can therefore be considered a type of co-crystal.

The stability of the benzene-ethane co-crystal is most likely due to van der Waals interactions between the hydrogen atoms of ethane and the π -electron system of benzene, as evidenced by Raman spectral shifts of both ethane and benzene features. A detailed interpretation of the co-crystal Raman spectrum, along with ab

initio calculations supporting the proposed co-crystal structure, is reported elsewhere [Vu *et al.*, 2014]. Here we explore the kinetics of cocrystal formation and the potential implications of benzene-ethane cocrystals as a major component of evaporite basins on Titan.

2. Experimental Methods

2.1. Kinetics Experiments

Ethane (Matheson Tri-Gas, 99.95%) was condensed at Titan surface temperature (90 K) under N_2 atmosphere at ~ 1 bar in a custom-built cryostat. Temperature control to ± 0.1 K was achieved via a temperature controller (Model 321, Lake Shore Cryotronics, Inc.), connected to a PT100 temperature sensor and a wire heater. A $5\text{ }\mu\text{L}$ aliquot of benzene was frozen on a glass substrate in a liquid nitrogen-cooled cryostage (LTS 350, Linkam Scientific Instruments Ltd) maintained at 90 K. A ~ 1 mL aliquot of liquid ethane was then added. The benzene/ethane sample was quickly warmed from 90 K to a specific temperature (110, 115, 120, or 125 K) and monitored by obtaining sequential Raman spectra within the cryostage using a high-resolution confocal dispersive micro-Raman spectrometer (Horiba Jobin Yvon LabRam HR) equipped with a Nd:YAG laser (frequency-doubled 532 nm, 50 mW) as the excitation source. All spectra were obtained using a 1800 grooves/mm grating, providing a resolution of 0.4 cm^{-1} . The sharp 520.7 cm^{-1} band of a silicon chip was used for frequency calibration.

The most compelling evidence for cocrystal formation is a 12 cm^{-1} red shift of the ν_1 stretching vibration of ethane in the Raman spectrum. This shift from 2885 (in liquid ethane) to 2873 cm^{-1} signifies a new molecular environment for ethane: incorporation in the benzene lattice, most likely as a co-crystalline complex [Vu *et al.*, 2014]. The sharpness of this peak (full width at half maximum (FWHM) = 2.5 cm^{-1}) 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). Peak areas were determined using a Gaussian fit with the multipeak fitting tool of Igor Pro (v6.12, Wavemetrics, Inc.). Kinetic curves were normalized to 1 at completion (see Figure 3a) and an exponential of the form $y = y_0 + A \cdot e^{-(x-x_0)/\tau}$ was fitted to the data, following a standard Arrhenius analysis.

Due to the acquisition time of the Raman microscope (≥ 1 min for a set of scans in triplicate with acceptable signal-to-noise) and the size of the liquid nitrogen Dewar used to maintain the temperature of the cryostage, kinetics experiments were limited to the temperature range of 110–125 K.

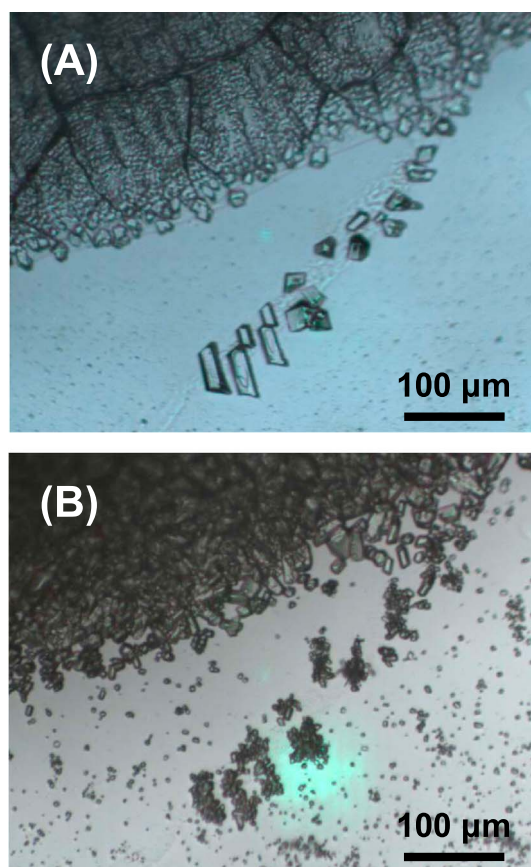


Figure 2. Microscope images (10X) of solid benzene in liquid ethane, (a) before and (b) after co-crystal formation. Evidence of recrystallization, due to incorporation of ethane into the benzene lattice, is easily visible.

strong stacking interaction in solid benzene to accommodate the guest ethane molecules via an attractive van der Waals interaction [Vu *et al.*, 2014]. The 2873 cm^{-1} feature which is 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 (Figure 3a).

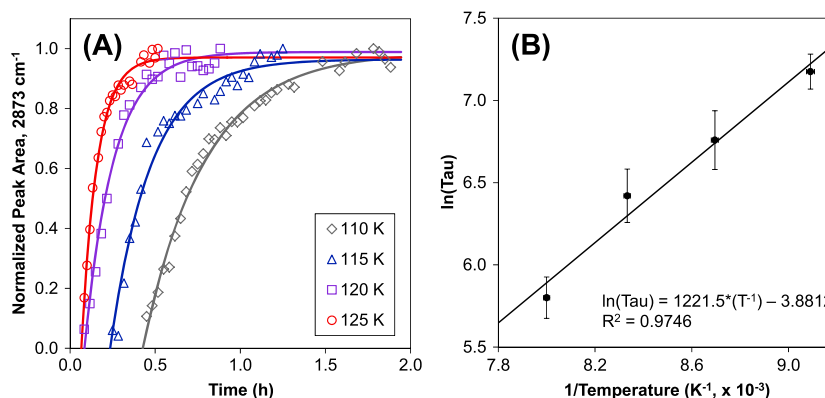


Figure 3. (a) Saturation curves at various temperatures for the 2873 cm^{-1} Raman spectral feature indicative of ethane incorporation in solid benzene. The rate of incorporation increases with temperature. (b) Fit of $\ln(\tau)$ versus $1/T$ for incorporation of ethane in solid benzene. The slope of this fit corresponds to an activation energy of $10.2 \pm 0.2\text{ kJ/mol}$.

2.2. Benzene Precipitation Experiment

Approximately 5 mL of ethane was condensed in the custom-built cryostat at 90 K (see section 2.1). Four drops of benzene ($\sim 200\text{ }\mu\text{L}$) were added and allowed to equilibrate with stirring for 1 h. A borosilicate glass microfiber extraction thimble (Whatman® 603G, thickness 1.7 mm, $0.8\text{ }\mu\text{m}$ nominal particle retention) was placed in the ethane/benzene solution with the top of the thimble above the meniscus and allowed to saturate. By pipetting solution from within the thimble, filtered aliquots of the ethane/benzene solution were transferred to the cryostage (approximately 3 mL total over 12 transfers) maintained at 130 K. Nitrogen flow was used to speed evaporation of ethane between transfers. Following evaporation of ethane, a single precipitate crystal was located and analyzed using the Raman microscope.

3. 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. Microscope images (see Figure 2 for a representative example) indicate recrystallization of the sample, which, in association with the changes in Raman signature, strongly suggest the formation of a new crystal structure. This transformation associated with the reaction is most likely due to disruption of the

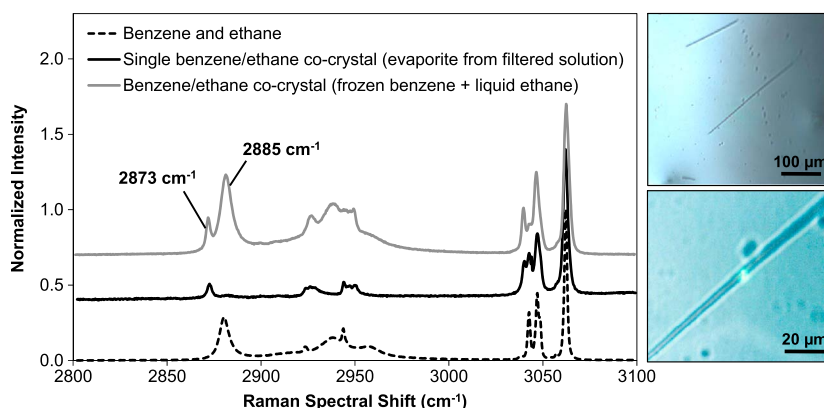


Figure 4. Raman spectrum of benzene evaporite crystal (black) at 130 K compared to a saturated co-crystal (gray) and benzene and ethane prior to co-crystal formation (dashed). All remaining ethane is incorporated within benzene as the co-crystal, as evidenced by the absence of the 2885 cm^{-1} peak and the presence of only the 2873 cm^{-1} peak (black). Images to the right show the unusually long morphology of these evaporite crystals. All spectra are vertically offset for clarity.

A plot of $\ln(\tau)$ versus $1/T$ produced a linear fit, shown in Figure 3b. The slope of this fit, E_a/R , yielded an activation energy (E_a) of $10.2 \pm 0.2\text{ kJ/mol}$. This is comparable to the calculated interaction energy of a stable benzene-ethane heterodimer in the gas phase (9.33 kJ/mol) [Vu *et al.*, 2014] and is very close to the interaction energy of a benzene-acetylene dimer (11.3 kJ/mol) [Boese *et al.*, 2003], which has a similar mode of interaction to that proposed for benzene and ethane.

Extrapolation to 90 K indicates that the incorporation of ethane in benzene ice will reach completion in approximately 18 h 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 (Figure 4), as indicated by the presence of the 2873 cm^{-1} peak. We note that long, thin co-crystalline structures were formed from this experiment that were dissimilar to the small fragments formed during recrystallization (Figure 2b). Regardless of morphology, precipitation of the benzene-ethane co-crystal from a filtered ethane solution suggests that any benzene 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.

4. Discussion

Co-crystal formation on Titan would require liquid ethane and benzene to be present together in the same region of Titan's surface. As previously mentioned, benzene has been detected in the Titan atmosphere and tentatively identified on the surface at the Huygens landing site [Niemann *et al.*, 2005]. Modeling of heating data from the Huygens probe indicates that the gas chromatograph mass spectrometer (GCMS) inlet reached an asymptotic value of $145 \pm 2.5\text{ K}$ once it was embedded in the Titan surface [Lorenz *et al.*, 2006a]. A temperature dependence study of liquid ethane and solid benzene in our laboratory is consistent with this value, as liquid ethane begins to evaporate appreciably in simulated Titan surface conditions at 145 K (see supporting information). The Huygens probe data suggest that liquid ethane and benzene coexist on Titan's surface, meaning the conditions are met for benzene-ethane co-crystal formation to occur.

A question that remains is whether co-crystal formation can occur if other species are present. Evaporite composition on Titan should reflect the dominant solid soluble products of the photochemistry, such as acetylene. Recent modeling of Titan evaporite composition suggests that the upper layers of solid precipitates could be rich in butane and acetylene [Cordier *et al.*, 2013]. Solubility experiments conducted in our laboratory indicate that a solution of ethane at 90 K, with benzene and acetylene both at saturation, will generate an evaporite comprised of an acetylene precipitate embedded with hexagonal benzene crystals (see supporting information). This suggests that even in solution with more soluble organics such as acetylene, benzene crystals will still form within mixed organic precipitates as the lake level drops. Co-crystal formation between benzene and ethane should therefore occur even in the presence of other organic precipitates.

Based on the globally averaged surface fluxes of benzene and ethane on Titan, and the assumption that the co-crystal has a 1:1 ratio of benzene to ethane, we estimate that around 0.1% of the total amount of ethane predicted to be on Titan could be sequestered in benzene as a co-crystal (see supporting Information). While not a major ethane sink, this new co-crystal structure may have other properties that could augment our understanding of evaporite surface materials. For example, recrystallization during co-crystal formation appears to break up larger benzene crystals (15–50 μm) into smaller fragments on the order of 1–5 μm (Figure 2), which would alter the light-scattering properties of benzene-rich evaporites and possibly affect their spectroscopic characteristics. These 1–5 μm fragments observed in our experiments are much smaller than the 100–300 μm diameter particles that most likely comprise the dunes [Lorenz *et al.*, 2006b] and could become entrained in the air by quite low winds, leading to aerosolized dust. However, precipitation of dissolved benzene from a filtered ethane solution produced elongated crystals approximately 5 μm in width and up to ~ 250 μm in length (Figure 4). Further work is underway to elucidate the full range of structures possible for a benzene-ethane co-crystal in Titan-like conditions.

We have shown that benzene-ethane co-crystals form rapidly from a mixture of solid benzene and liquid ethane and that these structures form from the evaporation of a saturated solution of benzene in ethane. In fact, co-crystals will likely form anywhere on Titan's surface where significant quantities of liquid ethane and crystalline benzene coexist. Our results imply that the primary form of benzene in Titan's evaporite deposits should be as the co-crystal. The formation of the co-crystal will affect multiple characteristics of the evaporites, such as particle size if formed by interaction of liquid ethane with solid benzene. It is anticipated that the co-crystal will have a dissolution rate and spectral properties distinct from crystalline benzene.

5. 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 whether co-crystal formation can occur in other aromatic-aliphatic systems.

Abbreviations

Da	Daltons
E_a	activation energy
FWHM	full width at half maximum
GCMS	gas chromatograph mass spectrometer
SAR	Synthetic Aperture Radar
VIMS	Visual and Infrared Mapping Spectrometer

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