

The properties of methane clathrate in the presence of ammonium sulphate solutions with relevance to Titan

Emmal Safi (1), Stephen P. Thompson (3), Aneurin Evans (2), Sarah J. Day (3), Claire A. Murray (3), Annabelle R. Baker (3), Joana M. Oliveira (2), Jacco Th. van Loon (2).

(1) School of Natural and Environmental Sciences, Newcastle University, NE1 7RU, UK (emmal.safi@ncl.ac.uk).

(2) Astrophysics Group, Lennard-Jones Laboratories, Keele University, Keele, Staffordshire, ST5 5BG, UK

(3) Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire, OX11 0DE, UK

Abstract

The source of atmospheric methane on Saturn's satellite Titan is currently unknown. However, one possibility is that it originates from clathrate hydrates formed below the surface. Titan's sub-surface ocean is believed to be composed of saline, rather than pure, water and in situ experimental data on clathrate formation under these conditions are largely absent in literature. Here, synchrotron X-ray powder diffraction (SXRPD) is used to study the properties of methane clathrate hydrates formed in the presence of ammonium sulphate solutions under low temperature conditions with a pressure of 26 bar.

1. Introduction

Apart from Earth, Saturn's largest satellite Titan is the only other body in the Solar System with a dense and predominantly nitrogen atmosphere [4]. The remainder of Titan's atmosphere is composed of CH_4 (1.4%) and H_2 (0.1-0.2%), with trace amounts of C_3H_N , HCN , CO_2 , CO , $(\text{CN})_2$, Ar and He . This makes Titan home to a complex atmospheric chemistry with a surface-atmosphere driven climate [4]. In a current models [1] Titan consists of a rocky core beneath an ice-rich mantle covered by a sub-surface ocean of aqueous $(\text{NH}_4)_2\text{SO}_4$, that sits below a crust composed primarily of methane clathrate and small amounts of ice I, which is a mixture of hexagonal (Ih) and cubic (Ic) ice [5]. An ocean consisting of aqueous $(\text{NH}_4)_2\text{SO}_4$ would have a freezing temperature of approximately 250 K.

In modelling the thermal evolution of such an ocean, [3] it was concluded that the only crystallisation product would be ice. As more ice is formed, the concentration of $(\text{NH}_4)_2\text{SO}_4$ would increase. Therefore, it is possible for a sub-surface ocean of $(\text{NH}_4)_2\text{SO}_4$ to remain liquid up until the present day, and would therefore represent the environment in

which methane clathrate dissociation could occur, contributing a net source of methane to Titan's atmospheric methane.

2. Results

A single-crystal sapphire capillary was filled with the $(\text{NH}_4)_2\text{SO}_4$ solution and sealed into a high pressure gas cell. Cooling was effected using a liquid nitrogen cryostream. Once the solution had frozen at, CH_4 gas was admitted to the cell and gradually increased to 26 bar. A fast position sensitive detector was used to collect the SXRPD data using beamline I11 at the Diamond Light Source. The X-ray wavelength was 0.826220 Å. As the temperature is lowered to 90 K and raised to 270 K, clathrate formation and dissociation are observed. Dissociation temperatures were determined by holding the sample at constant pressure and slowly increasing the temperature in 2 K steps until there were no peaks discernible in the X-ray diffraction pattern.

Comparing the resulting clathrate densities in our temperature range with those of the solutions in which they were formed (1.055 and 1.076 g/cm³ for the 10 wt% and 15 wt% $(\text{NH}_4)_2\text{SO}_4$ solutions respectively) whose concentrations match those of models in current literature [1], we find that the densities of the solutions are higher than the methane clathrate density irrespective of temperature (Fig. 1). This suggests that methane clathrates would always exhibit positive buoyancy and therefore float. In order for a scenario to occur that involved the sinking of the methane clathrates, the density of the ocean (or solution in which they were formed) would need to be ~ 0.91 g cm⁻³ or less.

Notwithstanding the dependency on ocean salinity as to whether the clathrates float towards the surface to contribute to the atmospheric methane budget, we also observe that the low temperature phase of ice

and/or the presence of $(\text{NH}_4)_2\text{SO}_4$ precipitate could more readily facilitate the dissociation of clathrates. In the case of ice this is due to the differences in the diffusion pathways provided by Ih and Ic [2]. The low temperature phase provides an easier diffusion pathway because of the presence of grain boundaries and defective zones, hence encouraging clathrate dissociation. Ih however, provides a more challenging route and, because it is the thermodynamically more stable phase, Ih inhibits clathrate dissociation. For Titan this could mean that clathrates dissociate more readily in the ocean and crust, hence never reaching the surface, which would limit the extent to which clathrates may act as a source of the atmospheric methane.

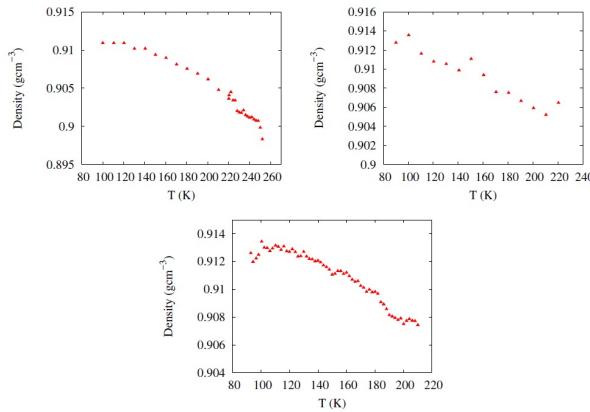


Figure 1. Temperature-dependence of CH_4 clathrate density for 10 wt% $(\text{NH}_4)_2\text{SO}_4$ solution during heating. Top left; cycle 1, top right; cycle 2, and bottom is cycle 3 all at 26 bar. Each panel represents three successive cooling and heating cycles.

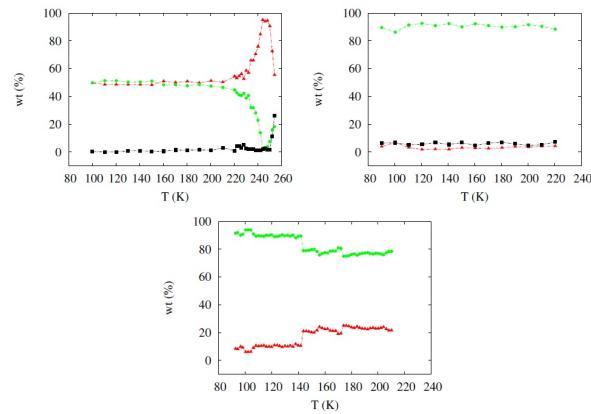


Figure 2: Temperature-dependence of wt% for the 10 wt% solution during heating. Top left; cycle 1, top

right; cycle 2 and bottom; cycle 3 all at 26 bar. Red triangles: clathrates; green circles: Ih ice; black squares: $(\text{NH}_4)_2\text{SO}_4$ precipitate. Each panel represents three successive cooling and heating cycles.

3. Conclusions

By the use of SXRPD we have investigated the formation, dissociation, buoyancy and thermal expansion properties of methane clathrates formed in $(\text{NH}_4)_2\text{SO}_4$ salt solutions. We have found that methane clathrates formed in aqueous solutions of $(\text{NH}_4)_2\text{SO}_4$ should exhibit positive buoyancy due to their lower densities, this is relevant to Saturn's moon Titan, where the ocean salinities are likely such that clathrates could rise to the surface and be a potential source of atmospheric methane.

However, our results also identify a limiting factor in clathrate formation; low-temperature phases of ice. We have shown that, in the presence of a low temperature phase of ice and/or $(\text{NH}_4)_2\text{SO}_4$ precipitate, clathrates seem to dissociate more readily. We conclude that further work on clathrate formation and dissociation in the presence of $(\text{NH}_4)_2\text{SO}_4$ and low-temperature phases of ice is needed to fully quantify the effect of ice and salts on clathrate behavior.

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