Effects of ammonia on the stability of cyclopentane and tetrahydrofuran clathrate hydrates

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Abstract

The Cassini-Huygens mission led to a better understand of Titan’s atmosphere and surface features. Methane is the second most abundant constituent of its atmosphere (which is made up of 94-98% N₂). However, active photochemistry would make the current methane component disappear in 30-100Myr, which requires replenishment processes from Titan’s interior. In addition, the Huygens probe data provide substantial evidence that ammonia is the primordial source of Titan’s atmospheric N₂. Ammonia is known to suppress the melting point of ices, which have profound implications for Titan’s current internal structure. Given Titan’s near-surface conditions, clathrate hydrates are the stable form of methane and ice together, making them a likely methane reservoir in the subsurface. The effect of ammonia on the stability of clathrates is poorly understood to date. We present a detailed experimental investigation of phase behavior of clathrate hydrates in the ternary H₂O-NH₃-CP (cyclopentane) and H₂O-NH₃-THF (tetrahydrofuran) systems using micro-Raman spectroscopy, differential scanning calorimetry, and X-ray diffraction.

1. Introduction

Clathrate hydrates are crystalline compounds consisting of water molecules forming cages within which gas molecules are trapped. On Earth, these clathrate hydrates naturally form in the permafrost or sediments of the continental margins where conditions of sufficiently low temperature and high pressure are present. Primarily consisting of methane, these natural gas hydrates are considered as a reserve of potential fossil energy [1]. Outside Earth, temperature and pressure conditions on many Solar System bodies suggest that gas hydrates could exist in the Martian permafrost [2,3], on the surface and subsurface of Titan, as well as in icy satellites of the giant planets [4-6]. Cassini-Huygens data suggest that methane and ammonia (before conversion into N₂) originated from Titan’s interior and played a key role in the development and evolution of the atmosphere. Moreover, there is an interest in the role of ammonia on Saturn’s moons Titan and Enceladus as the presence of water, methane and ammonia under temperature and pressure conditions of the surface and the interior make these moons likely to harbor clathrate hydrates. In addition, some methane could be released by substitution process with ethane from the lakes and would therefore participate in the hydrocarbon cycle [7].

However, the paucity of experimental data on the stability of clathrate hydrates in presence of ammonia, and exchanges between methane and ethane, propane, nitrogen (all major constituents of the lakes) severely hinders our ability to incorporate these effects in geophysical models. The goal of this study is to investigate experimentally the stability and composition of clathrates in the presence of ammonia, under thermodynamic conditions relevant to Titan, in order to evaluate the role of ammonia in the stability of clathrates and replenishment of methane to Titan’s atmosphere. We will present these results and the link with geophysical modeling settings which could allow to explain the important amount of methane present in the atmosphere of Saturn’s largest moon.

2. Experimental methods

As a starting point, we investigate clathrate hydrates that can form easily at atmospheric pressure, such as tetrahydrofuran (THF) and cyclopentane (CP). CP and THF are both different, especially in term of water solubility since CP is hydrophobic and THF is fully miscible in water. Raman spectroscopy, X-rays diffraction (XRD) and Differential Scanning Calorimetry (DSC) have been use to identify the structure, the different phases formed and their transitions depending on the temperature (from 90 K...
to 280 K) and the ammonia concentration (from 0 to 26 wt%).

3. Results and Discussion

The effect of NH$_3$ on THF clathrates is found to be almost identical to that of NH$_3$ on water ice, suggesting it is the formation of hydrogen bonds with the H$_2$O skeleton that is responsible for these effects [8, 9]. Figure 1 shows dissociation curves of H$_2$O-NH$_3$, H$_2$O-NH$_3$-CP and H$_2$O-NH$_3$-THF systems. CP clathrate hydrate stability curve seems to be slightly higher than that of THF, but they are very close. XRD and DSC data suggest that, apart from clathrates, several solid phases could be formed depending on the temperature like ammonia hydrates (monohydrate and dihydrate). Moreover, since the THF is hydrophilic, a THF-NH$_3$ rich phase seems to be stable at low temperatures (160-210 K) with a 15 wt% NH$_3$ concentration [8].

![Figure 1: Phase diagram of H$_2$O-NH$_3$, H$_2$O-NH$_3$-CP and H$_2$O-NH$_3$-THF systems depending on ammonia concentration (adapted from [8] and [9]).](image)

4. Concluding Remarks

We showed that the dissociation temperature of THF and CP clathrates, with a similar magnitude to that on water ice. Future investigations will examine the effects under methane pressure, which is a gas with a low solubility in water. It would be then valuable to study the cage occupancy dependence with the NH$_3$ concentration, since methane molecules can occupy the both type of cages in the clathrate structure, to allow a better characterization of the methane reservoir on Titan and its properties (e.g., density).

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References


