Freezing of Methanol-Water Mixtures at High Pressure with Applications to Titan

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Why Study High Pressure Methanol-Water Mixtures?

Sub-surface oceans have been proposed to exist on many of the large icy moons of the outer solar system. On Titan, any such ocean is likely sandwiched between an outer mostly Ice-Ih shell and an inner high-pressure Ice shell. The thickness of the shell and the depth of the ocean depend on many factors, including the composition and pressure-dependent freezing points of the materials likely to be found in the ocean.

Methanol is a highly-effective anti-freeze compound. Even relatively small amounts can have a significant effect on the freezing temperature. Deschamps, Mousis, Sanchez-Valle and Lunine [1] considered the role of methanol concentrations on the order of a few percent, and found that they could play an important role in the development and maintenance of a sub-surface ocean.

Methanol-Water Phase Diagram

As a methanol-water mixture is cooled, ice crystals precipitate out until the peritectic point is reached, at a temperature of approximately 171 K and a concentration of 69%, at which point $CH_3OH \cdot H_2O$ begins to form. Below the eutectic temperature of 157 K, the system solidifies completely. The eutectic concentration is approximately 88 %. At higher pressures, the behaviors of the peritectic and eutectic temperatures are not known.

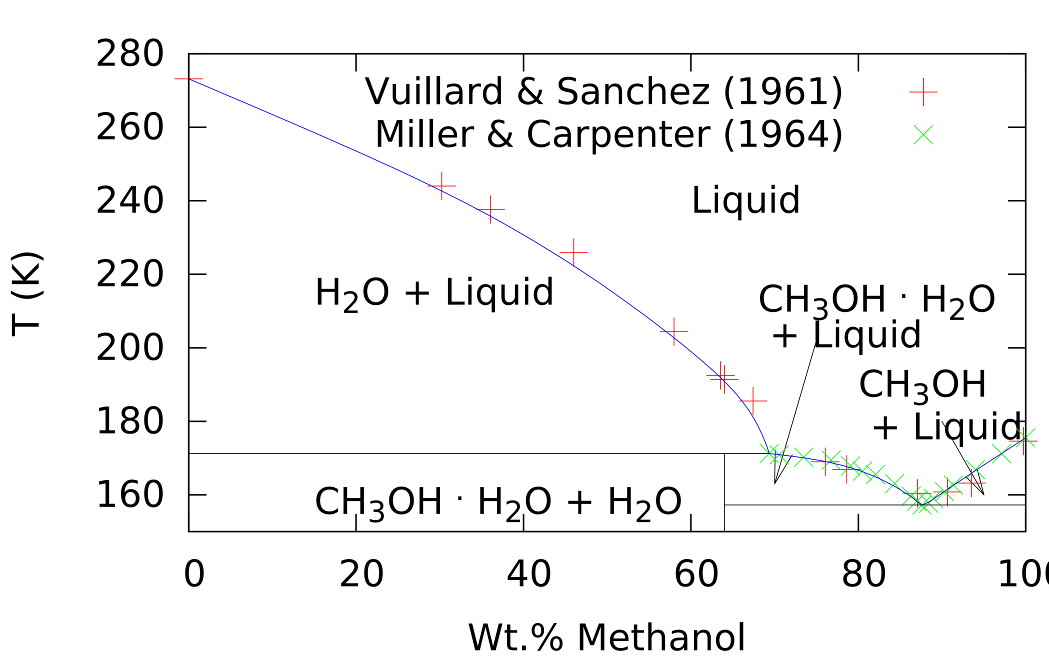

Fig. 1: Atmospheric pressure phase diagram for methanol-water solutions, adapted from Kargel [2]. Data are from Vuillard & Sanchez [3] and Miller & Carpenter [4]. The current experiments have been done at a concentration of 30 wt%.

Experimental Apparatus

The apparatus consists of 3 main parts: a central high-pressure fitting containing the sample fluid, an optical system for imaging the sample, and a pressure system that includes both pressure and volume sensors. Collimated light enters the pressure cell through an optical fiber on the left. The image is then relayed through a microscope objective into a CCD camera. The bottom port of the cross is connected to a pipe that connects to the pressure system, which allows simultaneous measurements of pressure and volume changes.

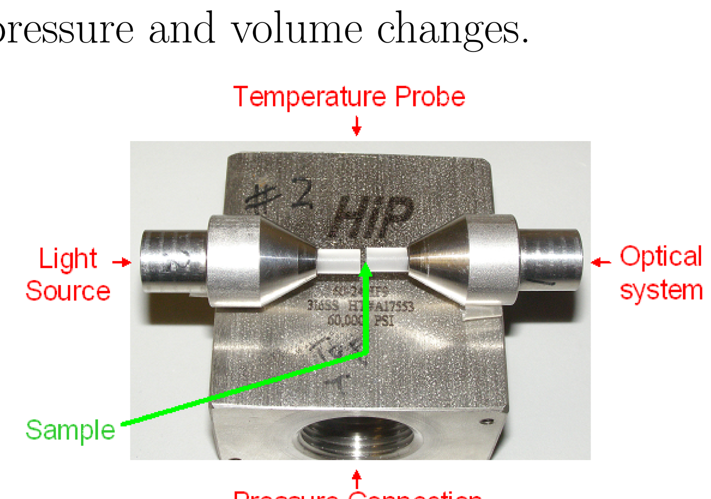

Fig. 2: Exploded view of the pressure cell. Sapphire windows in steel plugs are mounted inside a steel cross. The image shows the relative positions of the plugs.

Determining the Liquidus and Eutectic Temperatures

A sample data run is shown in Fig. 3 for a nominal pressure of 315 MPa.

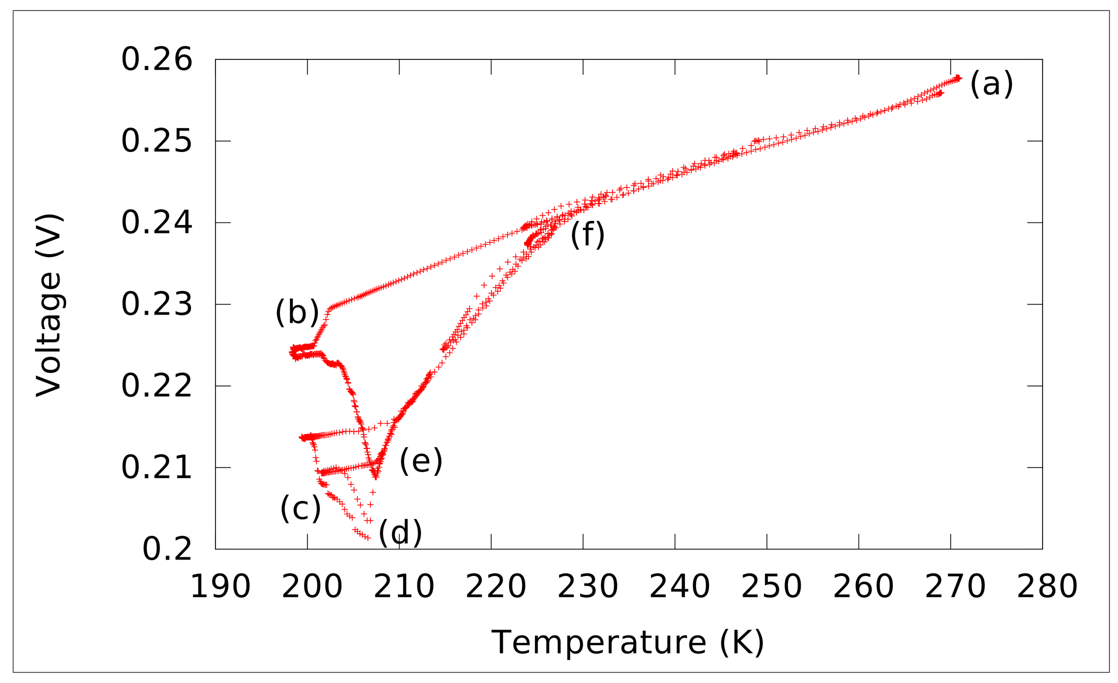

Fig. 3: Transducer voltage (approximately linearly related to volume) *vs.* temperature for a run at a nominal pressure of 315 MPa.

The system started at point (a). As it was cooled, the fluid contracted. After the system became supersaturated, ice crystals precipitated starting at point (b). The volume decreased, indicating that the ice crystals were denser than the surrounding fluid. Upon further cooling, the system froze and became an opaque solid.

Under gradual warming, this solid phase underwent a repeatable melting transition as the system looped through points (c), (d), and (e). The sample volume changed rapidly, and the crystals could be seen growing or shrinking. Further warming along the from (e) to the liquidus point (f) gradually dissolved the remaining ice crystals.

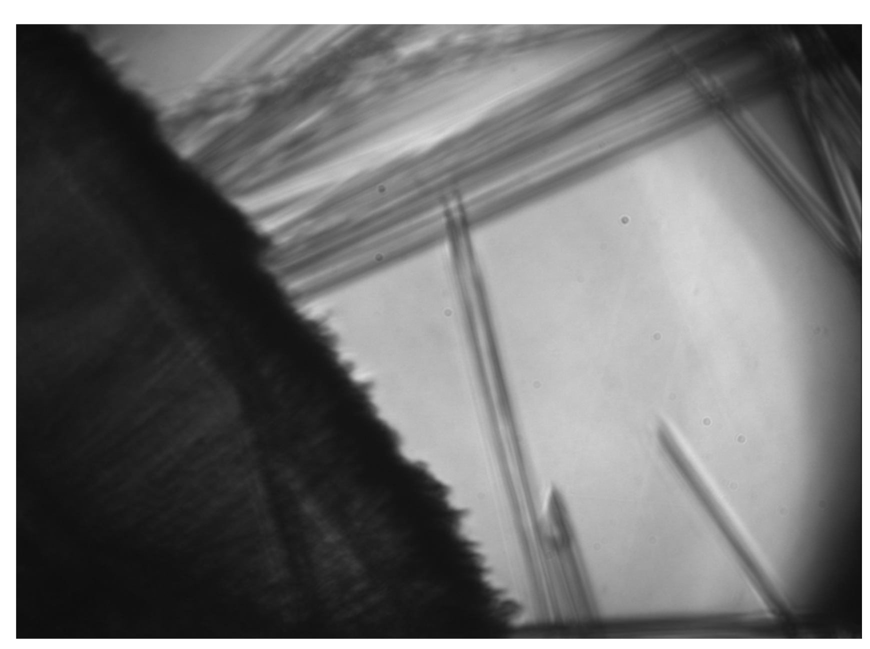

Fig. 4: Image taken during the solidification of a methanol-water solution at a temperature of 201 K and pressure of 314 MPa. The original thin Ice-II crystals are visible against a clear liquid background, with a solidification front approaching from the lower left-hand side of the image. The image is approximately 1 mm across.

Ice-Ih Regime

At lower pressures, typically less than about 200 MPa, the volume increased upon the initial crystallization of Ice-Ih crystals, locking up the volume transducer, and it was not possible to determine the eutectic temperature accurately.

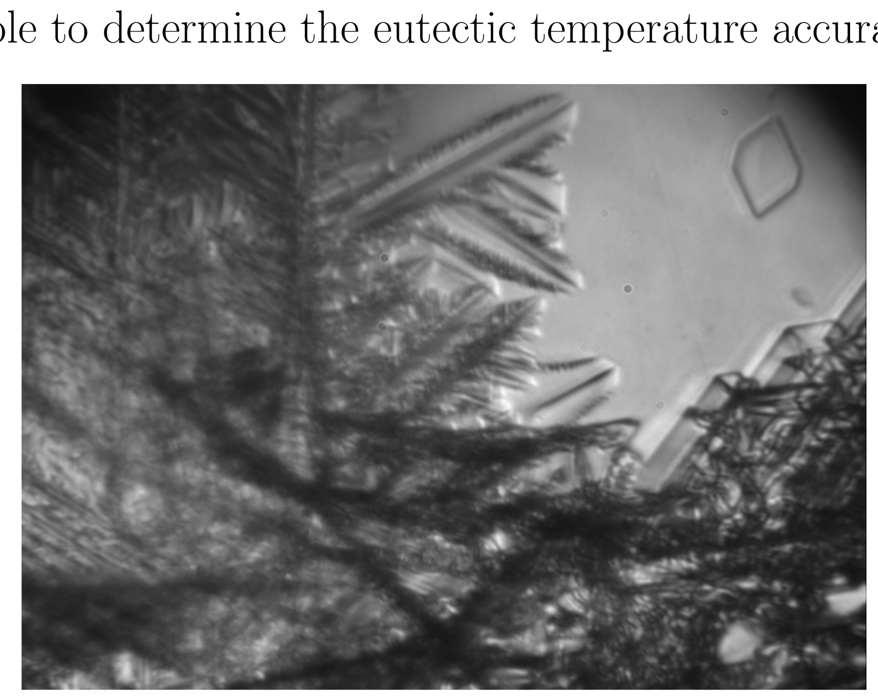

Fig. 5: Ice-Ih crystals growing during the freezing of a methanol-water solution at a temperature of 254 K and pressure of 50 Mpa.

Results

The resulting transition temperatures are shown in Fig. 6. The phase boundaries for pure water [5] and methanol [6] are included for comparison. Generally, the freezing behavior follows that of pure methanol, while the liquidus trend follows that of pure water. We also observe that the Ice-Ih/Ice-II transition appears to occur at higher pressures in this system than has been reported for pure water.

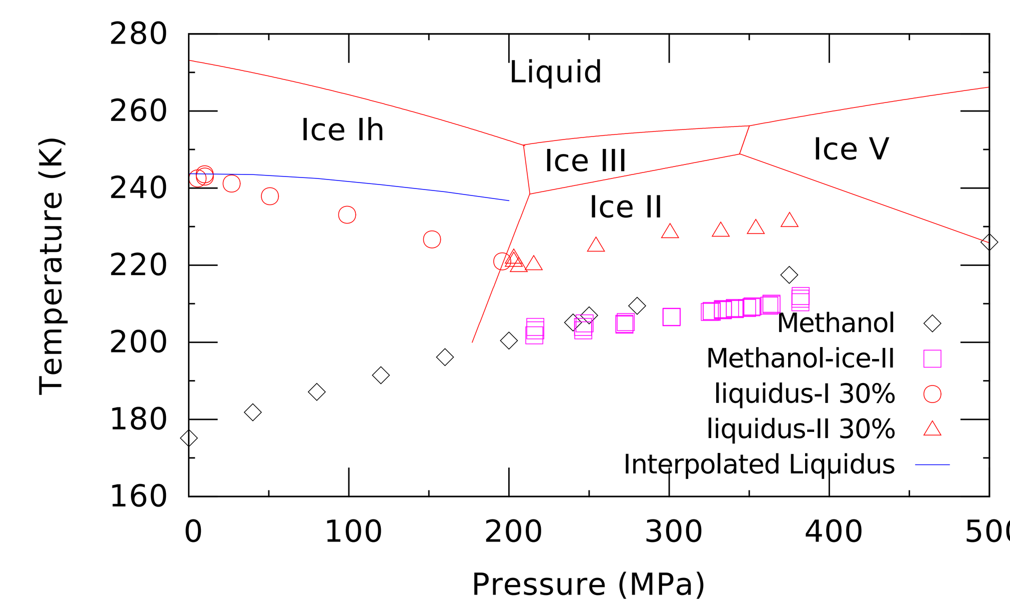

Fig. 6: Transition temperatures for a 30 wt% methanol-water mixture, with pure water and ice values included for comparison. The Ice-Ih/Ice-II transition line is taken from Dunaeva *et al.* [7] The blue line shows the liquidus estimated by linear interpolation between the ice and methanol curves.

Application to Titan

For modeling Titan's ocean, Deschamps *et al.* estimated the crystallization temperature as a function of pressure by interpolating between the pure water and pure methanol values [1]. The results in Fig. 6 indicate that this is a reasonable approximation, but slightly overestimates the liquidus temperatures at higher pressures. For the concentration of 30 wt% studied here, the interpolated estimate is approximately 16 K too high for pressures of 200 MPa.

Future Directions

One set of future experiments will determine the liquidus temperature for the much lower methanol concentrations relevant for Titan. This should allow more accurate modelling of the effects of small concentrations of various impurities in the development of Titan's subsurface ocean.

At atmospheric pressure, there are two separate transitions—one at 171 K, and a eutectic transition at 157 K. In the current experiments at high pressure, there was no clear evidence for the two separate transitions. In the Ice-Ih regime, the expansion of the ice upon freezing prevented any careful monitoring of subsequent freezing of the methanol.

Future experimental work will explore the eutectic temperature in the Ice-Ih regime by using much higher concentrations of methanol. With higher concentrations, we will be able to avoid the complications caused by the large amounts of Ice-Ih in the present system, and anticipate being able to study the freezing transitions in more detail.

References

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