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

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Why Study High Pressure Phases of 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.

Although the effects of pressure on pure ice and pure methanol have been extensively studied, the behavior of water-methanol mixtures has not been studied as extensively. In a series of experiments, we plan to explore how various points on the methanol-water phase diagram vary under pressure. For the preliminary investigations reported here, we considered solutions with 40% methanol by weight, inspired by rheological studies on a similar mixture.[2]

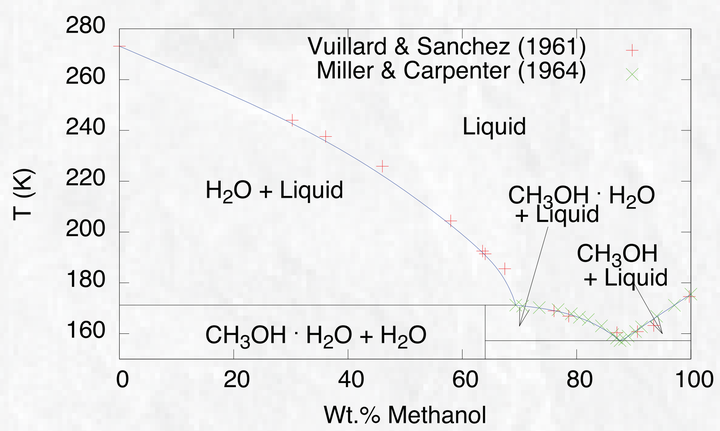

Figure 1: Phase diagram for methanol (CH_3OH) in H_2O at atmospheric pressure, adapted from Kargel [3], and based on data from Vuillard and Sanchez [4] and Miller and Carpenter [5]. The experiments presented here were performed at a concentration of 40 wt.%.

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, similar to that used in previous studies of aqueous salt solutions.[6]

About one mL of sample is contained in the pressure cell, made from a standard high-pressure fitting called a cross, shown in Fig. 2. This stainless steel block has four ports. Two opposing ports contain replaceable plugs that have sapphire windows sealed with epoxy. The third port contains a plug in which a silicon diode thermometer is installed, and the fourth port connects the cell to the pressure system.

Collimated light enters the pressure cell through an optical fiber on the left. The image of the sample is then relayed through a microscope objective into a CCD camera. The bottom port of the cross is connected to a pipe filled with mercury that connects to the pressure system.

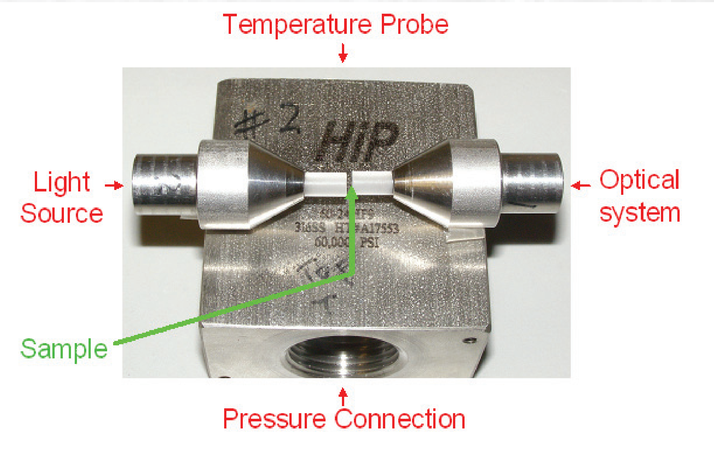

Figure 2: Exploded view of the pressure cell. Sapphire windows in steel plugs are mounted inside a steel cross. The image shows the relative positions of the plugs with windows and the plug containing the thermometer. The visible part of the sample is held in the 1 mm gap between the windows.

As the sample expands or contracts, the vertical height of a magnet floating on top of the mercury is monitored with a transducer. Changes in transducer voltage are approximately proportional to changes in sample volume.

The system is placed in a copper can in a temperature-controlled ethanol-water bath, and the entire apparatus is kept in a heavily-insulated cooler. A chiller is used to control temperatures down to 200 K; below that, cooling is done with liquid nitrogen.

Ice-Ih Regime: Determining the Liquidus Temperature

The results for a run with a 40-wt.% methanol/water solution at a nominal pressure of 50 MPa are shown in Fig. 3.

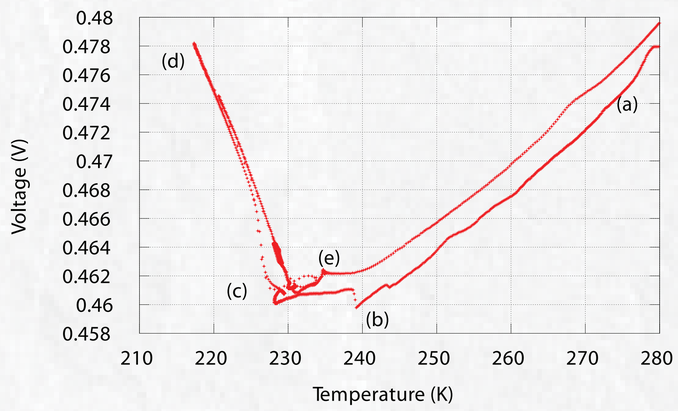

Figure 3: A run at 50 MPa. The vertical axis shows the transducer voltage, which is approximately linearly related to volume, and the horizontal axis shows temperature.

The system started as a warm homogeneous liquid at 280 K (point (a)). As the system cooled to (b), the volume decreased due to thermal contraction. From (c) to (d), rapid crystallization of Ice-Ih was observed, accompanied by significant increases in volume, though the sample remained partially liquid throughout. The crystallization was reversible upon warming, until the last crystals dissolved around point (e), slightly below 235 K. The final approach to equilibrium is quite slow.

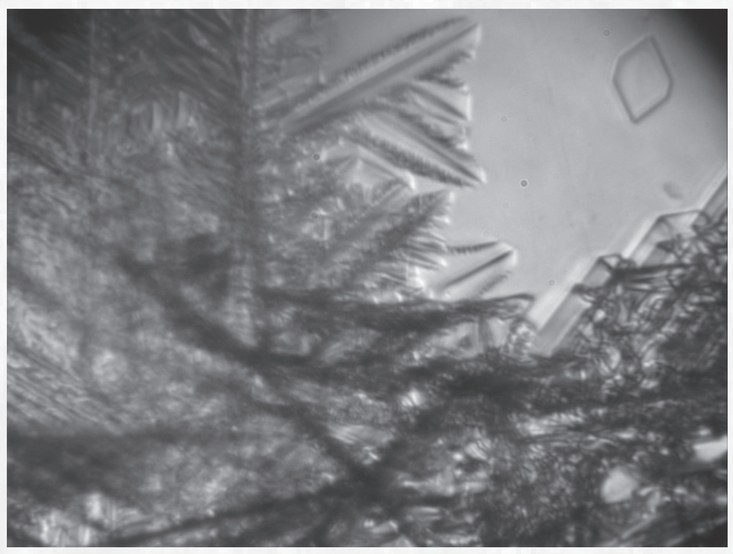

Figure 4: Ice-Ih crystals growing during the initial freezing of a methanol-water solution at a pressure of approximately 49 MPa, and temperature of 225.8 K. The image is approximately 1 mm across.

Ice-II Regime

Results for a run at a nominal pressure of 315 MPa are shown in Fig. 5.

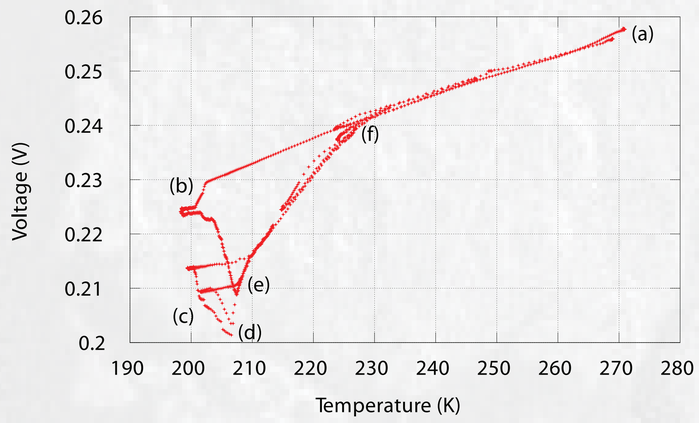

Figure 5: A run at 315 MPa. The vertical axis is approximately linearly related to volume; the horizontal axis shows temperature.

The system started at point (a) as a liquid at about 270 K, and was cooled steadily. As the system 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. Comparison of the temperature to the pure ice phase diagram suggests that the ice phase was Ice-II. Upon further cooling, the system froze and became an opaque solid. An advancing solidification front is shown in Fig. 6. Based on the atmospheric pressure phase diagram (Fig. 1), it seems likely that this solidifying phase was $CH_3OH \cdot H_2O$.

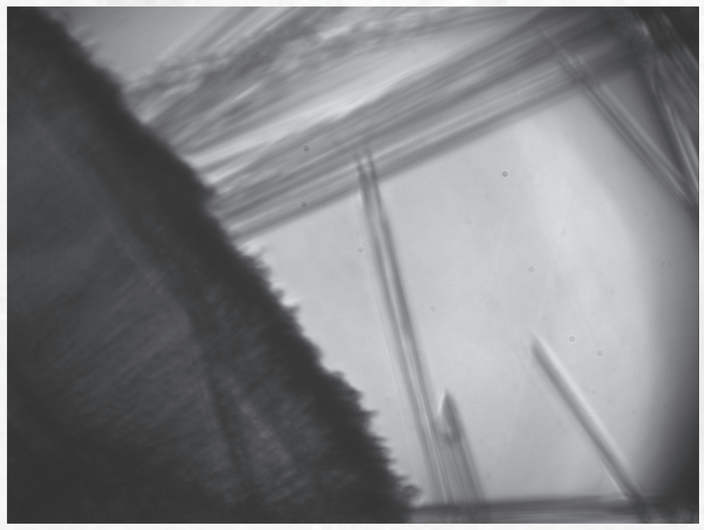

Figure 6: Image taken during the solidification of a methanol-water solution at T = 201 K and p = 314 MPa. The original thin Ice-II crystals are visible against a clear liquid background, with a solidification front approaching from the lower left-hand side of the image. The image is approximately 1 mm across.

Under gradual warming, this solid phase underwent a repeatable melting transition as the system looped through points (c), (d), and (e) in Fig. 5. The sample volume changed rapidly, and the crystals could be seen growing or shrinking in the images. Further warming along the curve from (e) to (f) gradually dissolved the ice crystals.

Results

The observed transition temperatures as a function of pressure are shown in Fig. 7. Overall, the liquidus temperature appears to decrease slowly with pressure, though we only have data at relatively low pressures. Although there are two different transition temperatures for methanol apparent in Fig. 1, we were unable to distinguish two separate transitions in these experiments. The observed freezing temperature appears to follow the trend for pure methanol; the transition from the Ice-Ih phase to the Ice-II phase does not appear to play a significant role. We do observe Ice-Ih at slightly higher pressures than has been reported for pure water ice.[7]

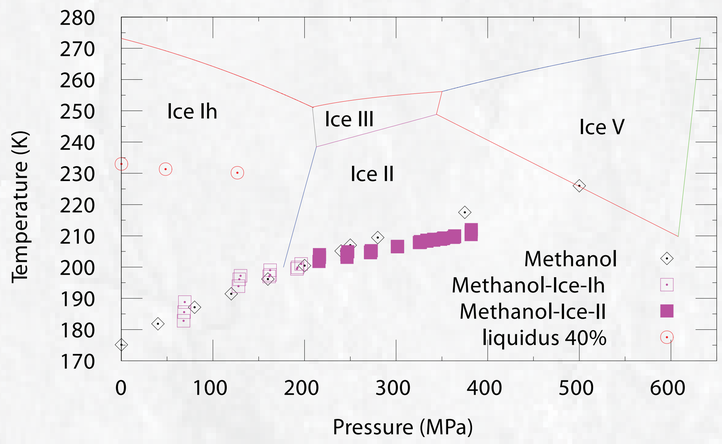

Figure 7: Transition temperatures as a function of pressure for a 40-wt.% methanol-water mixture. Runs where the ice expanded upon freezing are shown as open squares, while runs where the ice contracted upon freezing are shown as solid squares. Values for pure methanol (from Wurflinger et al.[8]) and pure water [7,9] are shown for comparison.

References

[1] Deschamps, F., Mousis, O., Sanchez-Valle, C., and Lunine, J.I., Astrophys. J. 724:887-894, 2010 December 1. [2] Zhong, F., Mitchell, K.L., Hays, C.C., Choukroun, M., Barmatz, M., and Kargel, J.S. Icarus, 202 (2009) 607-619. [3] J. S. Kargel (1992) Icarus 100:556. [4] G. Vuillard, et al. (1961) Bull. Soc. Chim. France 1877-1880. [5] G. Miller, et al. (1964) J. Chem. & Engr. Data 9(3):371. [6] Hogenboom, D.L., Kargel, J.S., Ganasan, J.P., and Lee, L. (1995) Icarus 115, 258-277. [7] The Ice-Ih-II transition is taken from Dunaeva, A. *et al.* (2010) J. Solar System Research 44(3):202. [8] Wurflinger, A. *et al.* (1977) J. Phys. Chem. Solids 38:811.
[9] Wagner, W. *et al.* (2011) J. Phys. and Chem. Ref. Data 40(4).
Background image: Titan Lake Country, NASA/JPL-Caltech/University of Arizona, http://photojournal.jpl.nasa.gov/catalog/PIA16844