FREEZING OF METHANOL-WATER MIXTURES AT HIGH PRESSURE WITH APPLICATIONS TO TITAN.

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Introduction: We report measurements of the freezing points for a 40 wt.% methanol-water solution at pressures ranging from 50 to 400 MPa, using simultaneous measurements of pressure, volume, and temperature, coupled with optical images of the sample. The eutectic point for the methanol-water solution appears to increase with pressure, similar to the behavior of the freezing point of pure methanol. Conversely, the liquidus point appears to decrease with pressure in the Ice-Ih regime, consistent with the behavior of pure water. We also find that the Ice-Ih phase is present at somewhat higher pressures than one would expect based on the pure water phase diagram.

Background: The presence of a subsurface ocean on Titan has long been suspected[1], and is consistent with electric field measurements from the *Huygens* probe[2]. The ocean likely contains impurities, such as ammonia and methanol, that act as powerful antifreeze compounds. Sandwiched between an outer Ice-Ih shell and an inner high-pressure ice shell, these compounds could significantly affect both the thickness of the outer shell and the depth of the ocean[3].

The phase diagram for methanol-water solutions at atmospheric pressure is shown in Fig. 1. 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 150 K, the the system solidifies completely. The eutectic concentration is approximately 88 wt%. At higher pressures, the behavior of the peritectic and eutectic temperatures is not known.

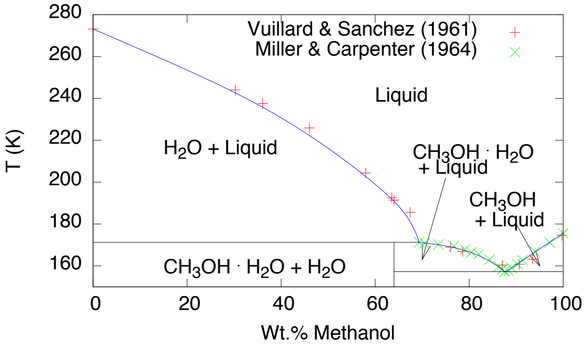

Figure 1: Atmospheric pressure phase diagram for methanol-water solutions, adapted from Kargel[4]. Data are from Vuillard & Sanchez[5] and Miller & Carpenter[6].

Experiment: Approximately 1 mL of sample was loaded into a pressure cell. This cell is made from a 316 stainless steel block with four ports. Two opposing ports contain plugs that have sapphire windows for the imaging system, sealed with epoxy. The third port contains a plug with a silicon diode thermometer, and the fourth connects the cell to the pressure system. A fiber optic light is used to illuminate the sample, and an inverted periscope is used to obtain images. The pressure system includes a transducer that responds approximately linearly to changes in volume of the sample. The pressure cell is insulated, and temperature can be controlled between 200 and 300 K. Cooling below 200 K is done with liquid nitrogen. We generally use very slow cooling and warming so that equilibrium can be closely approximated.

For these preliminary investigations, we chose to study an intermediate concentration of 40 wt.% methanol in water, similar to that used by Zhong *et al.*[7] Although the eutectic concentration is 88 wt.%, the relevant concentrations for planetary applications are likely much lower. Deschamps *et al.* estimate[3] that Titan's primordial ocean might have contained $\sim$ 4wt.% of methanol relative to water.

Sample Run: A sample data run is shown in Fig. 2 for a nominal pressure of 315 MPa.

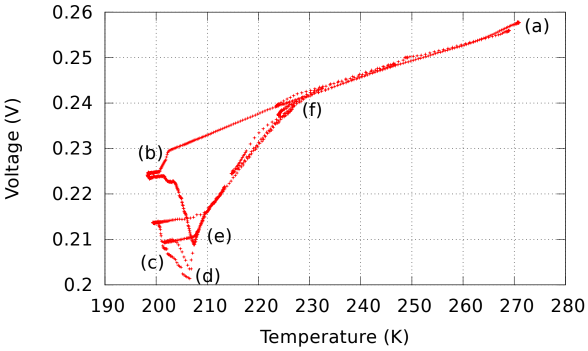

Figure 2: Transducer Voltage (approximately linearly related to volume) *vs.* Temperature for a run at a nominal pressure of 315 MPa.

The system started at point (a) as a homogeneous fluid 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. 3. Based on the atmospheric pressure phase diagram (Fig. 1), it seems likely this solidifying phase was $CH_3OH \cdot H_2O$.

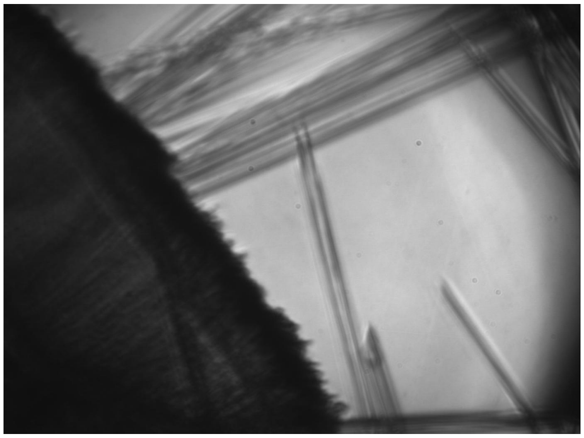

Figure 3: Image taken during the solidification of a methanol-water solution during a run at a nominal pressure of 315 MPa. The original thin ice crystals are visible against a clear liquid background, with a solidification front approaching from the lower left-hand side of the screen. The image is approximately 1 mm across.

Under gradual warming, this solid phase underwent a repeatable melting transition as the system looped through points (c), (d), and (e). 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. The point where the last ice crystals dissolve is the liquidus point. However, the final approach to equilibrium is quite slow, and the apparent value of 230 K in Fig. 2 is likely an overestimate.

At lower pressures, typically less than about 200 MPa, the volume *increased* upon the initial crystallization of ice crystals, consistent with the growth of Ice-Ih. A sample of growing ice crystals at $p = 49\,\mathrm{MPa}$ and $T = 225.8\,\mathrm{K}$ is shown in Fig. 4. Upon warming, the dendrites dissolved and floated upward, again indicating that they were less dense than the surrounding fluid.

At the 40 wt.% concentration used in these experiments, a good deal of ice has to freeze before the eutectic point is reached. In the Ice-Ih regime, that ice takes up a greater volume and tends to both fill up the imaging window and to lock up the volume transducer so that measurements are more difficult to interpret. Future experiments will likely use a higher methanol concentration to avoid this problem.

Results: The resulting transition temperatures are shown in Fig. 5. The phase boundaries for pure water[8] and methanol[9] are included for comparison. The Ice-Ih/Ice-II transition line is taken from Dunaeva *et al.*[10] Only two liquidus points are shown, at 1 and 100 MPa, but the liquidus temperature does appear to decrease slightly with increasing pressure. Generally, the freezing behavior follows that of pure methanol. 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.

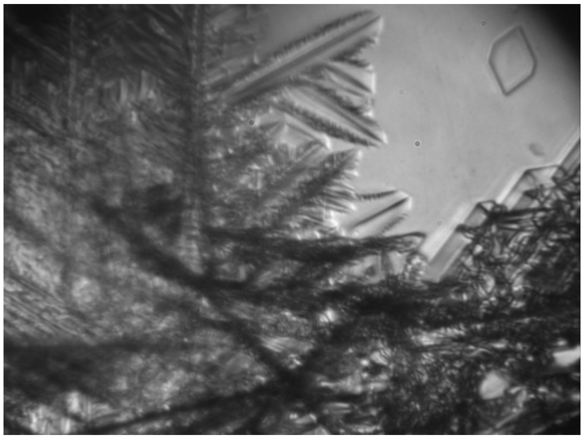

Figure 4: Image of ice crystals growing from a methanol-water solution during a run at a nominal pressure of 50 MPa.

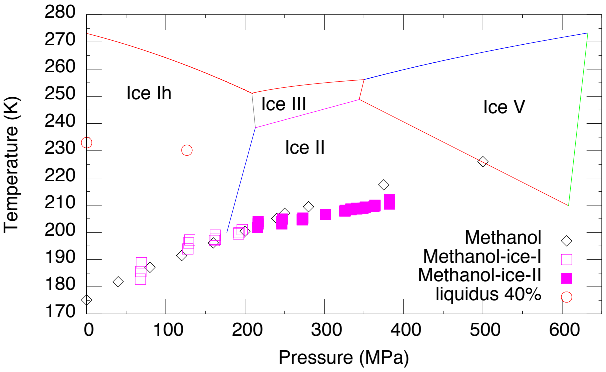

Figure 5: Transition temperatures as a function of pressure for Methanol-Water mixture. Runs where the ice expanded upon freezing are shown as open squares, while runs where the ice contracted upon freezing are shown as solid squares.

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. The results in Fig. 5 indicate that this is a reasonable approximation, at least over the ranges studied to date.

References: [1] J. S. Lewis (1971) *Icarus* 15:174. [2] C. Beghin, et al. (2009) *Planet Space Sci* 57(14–15):1872. [3] F. Deschamps, et al. (2010) *Astrophys Journal* 724:887. [4] J. S. Kargel (1992) *Icarus* 100:556. [5] G. Vuillard, et al. (1961) *Bull Soc Chim France* 1877–1880. [6] G. Miller, et al. (1964) *Journal of Chemical & Engineering Data* 9(3):371. [7] F. Zhong, et al. (2009) *Icarus* 202(2):607. [8] W. Wagner, et al. (2011) *J Phys and Chem Ref Data* 40(4). [9] A. Wurflinger, et al. (1977) *J Phys Chem Solids* 38:811. [10] A. Dunaeva, et al. (2010) *J Solar System Research* 44(3):202.