

FREEZING OF METHANOL-WATER MIXTURES AT HIGH PRESSURE WITH APPLICATIONS TO TITAN. Andrew Dougherty, Ross Chumsky, and Dustin Morris, Department of Physics, Lafayette College, Easton, PA 18042 USA. doughera@lafayette.edu

Introduction: We report measurements of the liquidus and eutectic points for a 30 wt.% methanol-water solution at pressures ranging from 5 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, similar to the behavior of pure water. We also observed Ice-Ih phases 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], and with obliquity measurements[3]. The thickness and rigidity of the outer ice shell would likely have significant influence on surface topography[4]. Any subsurface ocean would likely contain 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 impurities could significantly affect both the thickness of the outer shell and the depth of the ocean[5].

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 $\text{CH}_3\text{OH} \cdot \text{H}_2\text{O}$ begins to form. Below the eutectic temperature of 150 K, the system solidifies completely. The eutectic concentration is approximately 88 wt%. At higher pressures, the behaviors of the peritectic and eutectic temperatures are not known.

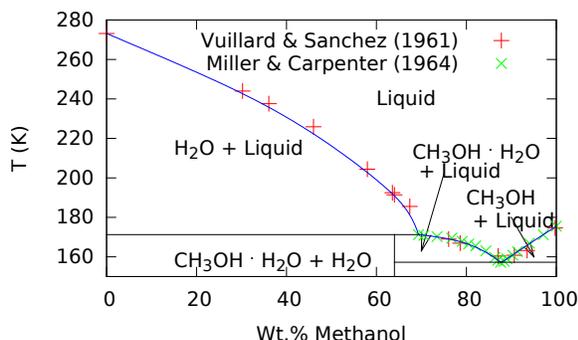


Figure 1: Atmospheric pressure phase diagram for methanol-water solutions, adapted from Kargel[6]. Data are from Vuillard & Sanchez[7] and Miller & Carpenter[8].

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.¹ 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.

For these preliminary investigations, we chose to study an intermediate concentration of 30 wt.% methanol in water, somewhat similar to that used by Zhong *et al.*[9] Although the eutectic concentration is 88 wt.%, the relevant concentrations for planetary applications are likely much lower. Deschamps *et al.* estimate[5] that Titan's primordial ocean might have contained ~ 4 wt.% of methanol relative to water.

Sample Run at Low Pressure: A sample data run is shown in Fig. 2 for a nominal pressure of 10 MPa.

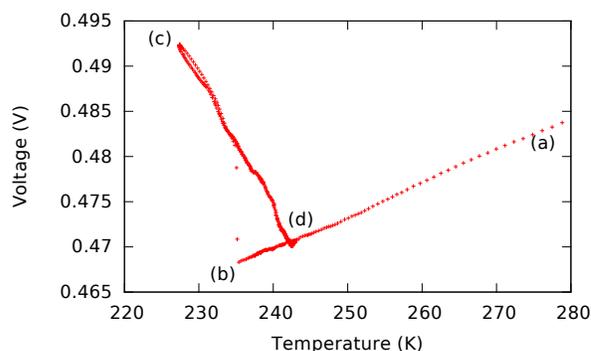


Figure 2: Transducer voltage (approximately linearly related to volume) vs. temperature for a run at a nominal pressure of 10 MPa.

The system started at point (a) as a homogeneous fluid at about 280 K, and was cooled steadily. As the system cooled, the fluid contracted. After the system became supersaturated, dendritic ice crystals precipitated starting at point (b), around 235 K. The volume increased, indicating that the ice crystals were less dense than the surrounding fluid, as would be expected for Ice-Ih. Upon further cooling to point (c), more ice crystals grew, but some liquid remained as well. Under gradual

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warming, the ice crystals slowly melted and floated upward as pieces detached. The last crystals dissolved at the liquidus point (d). In order to ensure thermodynamic equilibrium, the liquidus was approached very slowly, typically over several days at an average rate of less than 0.25°C per hour.

Sample Run at High Pressure: A sample data run is shown in Fig. 3 for a nominal pressure of 315 MPa.

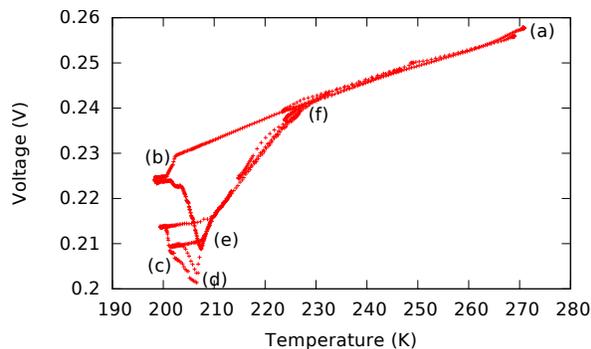


Figure 3: Transducer voltage (approximately linearly related to volume) vs. temperature for a run at a nominal pressure of 315 MPa.

The system started at point (a) as a homogeneous fluid at about 270 K, and was cooled steadily. 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.

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 remaining ice crystals.

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. At the 30 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. Accordingly, we only report eutectic temperatures in the Ice-II regime.

Results: The resulting transition temperatures are shown in Fig. 4. The phase boundaries for pure water[10] and methanol[11] are included for compar-

ison. The Ice-Ih/Ice-II transition line is taken from Dunaeva *et al.*[12] 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.

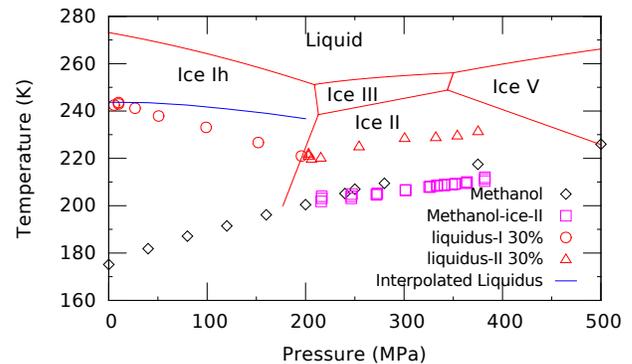


Figure 4: Transition temperatures as a function of pressure for a 30 wt.% methanol-water mixture. The freezing temperatures for pure methanol are shown as diamonds, while the eutectic temperatures are shown as boxes. The liquidus temperatures in the Ice-Ih and Ice-II regimes are shown as circles and triangles respectively. The blue line shows the liquidus estimated by linear interpolation between the ice and methanol curves.

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[5]. The results in Fig. 4 indicate that this is a reasonable approximation, but slightly overestimates the liquidus temperatures at higher pressures.

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: [1] J. S. Lewis (1971) *Icarus* 15:174. [2] C. Beghin, et al. (2009) *Planet Space Sci* 57(14–15):1872. [3] R. M. Baland, et al. (2011) *Astronomy & Astrophysics* 530:A141. [4] D. Hemingway, et al. (2013) *Nature* 500(7464):550. [5] F. Deschamps, et al. (2010) *Astrophys Journal* 724:887. [6] J. S. Kargel (1992) *Icarus* 100:556. [7] G. Vuillard, et al. (1961) *Bull Soc Chim France* 1877–1880. [8] G. A. Miller, et al. (1964) *J Chem & Eng Data* 9(3):371. [9] F. Zhong, et al. (2009) *Icarus* 202(2):607. [10] W. Wagner, et al. (2011) *J Phys and Chem Ref Data* 40(4). [11] A. Wurfinger, et al. (1977) *J Phys Chem Solids* 38:811. [12] A. N. Dunaeva, et al. (2010) *J Solar System Research* 44(3):202.