FREEZING OF METHANOL-WATER MIXTURES AT HIGH PRESSURE IN A SUBSURFACE OCEAN

A. Dougherty, R. Chumsky, and D. Morris, Department of Physics, Lafayette College, Easton, PA 18042 USA. doughera@lafayette.edu

Introduction: Enceladus is a surprisingly active world. The observations of water-rich plumes [1, 2, 3, 4, 5] reveal either the presence of a liquid reservoir or highly active melting. The composition of the plumes suggests a liquid reservoir [5, 6], and the measured libration is consistent with a global subsurface ocean, rather than a localized reservoir [7].

Any subsurface ocean would likely contain impurities, such as ammonia[8] and methanol, that act as powerful antifreeze compounds. Small amounts of methanol may have been detected on the surface of Enceladus [9], as well as in the plume [3]. In addition to being a powerful antifreeze, methanol could also play a role in the formation of methane hydrates [10].

Experiment: In this work, we consider the freezing behavior of methanol-water solutions at low temperatures and moderate pressures such as might be encountered in the icy moons of the outer solar system. We report measurements of the liquidus and eutectic points for 30 wt.% and 80 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 phase diagram for methanol-water solutions at atmospheric pressure is shown in Fig. 1.

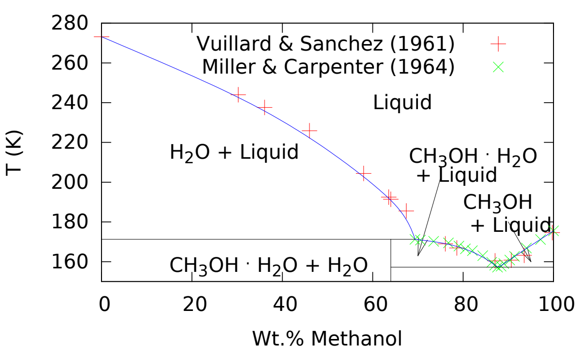

Figure 1: Atmospheric pressure phase diagram for methanol-water solutions, adapted from Kargel [11]. Data are from Vuillard & Sanchez [12] and Miller & Carpenter [13].

Approximately 1 mL of sample was loaded into a pressure cell made from a stainless steel block with four ports. Two opposing ports contain plugs that have sapphire windows for the imaging system. 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 illuminates 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 investigations, we studied two samples, one with a concentration of 30 wt.% methanol in water, and a second with a concentration of 80 wt.%. The higher concentration was chosen to avoid experimental complications due to the expansion of Ice-Ih as it freezes.

Results: The transition temperatures are shown in Fig. 2. The phase boundaries for pure water [14] and methanol [15] are included for comparison. 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.

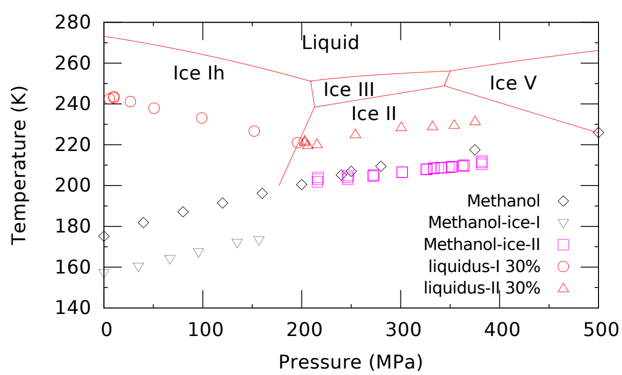

Figure 2: Transition temperatures as a function of pressure for methanol-water mixtures. The freezing temperatures for pure methanol are shown as diamonds. The eutectic temperatures are shown as inverted triangles and boxes in the Ice-Ih and Ice-II regimes, while the liquidus temperatures for 30 wt.% solutions are shown as circles and triangles.

References: [1] M. Dougherty, et al. (2006) *Science* 311 (5766):1406. [2] C. Porco, et al. (2006) *Science* 311 (5766):1393. [3] J. H. Waite, Jr., et al. (2009) *Nature* 460 (7259):1164. [4] C. J. Hansen, et al. (2011) *Geophys Res Lett* 38:L11202. [5] H.-W. Hsu, et al. (2015) *Nature* 519 (7542):207. [6] F. Postberg, et al. (2011) *Nature* 474 (7353):620. [7] P. C. Thomas, et al. (2016) *Icarus* 264:37. [8] D. Hogenboom, et al. (1997) *Icarus* 128 (1):171. [9] R. Hodyss, et al. (2009) *Geophys Res Lett* 36:L17103. [10] G. McLaurin, et al. (2014) *Angewandte Chemie-International Edition* 53 (39):10429. [11] J. S. Kargel (1992) *Icarus* 100:556. [12] G. Vuillard, et al. (1961) *Bull Soc Chim France* 1877–1880. [13] G. A. Miller, et al. (1964) *J Chem & Eng Data* 9 (3):371. [14] W. Wagner, et al. (2011) *J Phys and Chem Ref Data* 40 (4). [15] A. Wurflinger, et al. (1977) *J Phys Chem Solids* 38:811.