Volumetric and Optical Studies of High Pressure Phases of $Na_2SO_4 \cdot nH_2O$

A. J. Dougherty[1] , J.A. Avidon[1], D. L. Hogenboom[1], and J. S. Kargel[2],
[1]Dept. of Physics, Lafayette College, Easton, PA 18042, e-mail: doughera@lafayette.edu, avidonj@lafayette.edu, hogenbod@lafayette.edu,
[2]Department of Hydrology and Water Resources, The University of Arizona, Harshbarger Building, PO Box 210011, Tucson, AZ 85721-0011, e-mail: kargel@hwr.arizona.edu

Why Study High Pressure Phases of Sodium Sulfate?

Sodium sulfate, along with other hydrated salts such as magnesium sulfate, which we studied previously [1,2], is a likely constituent of Europa's ocean and icy shell [3,4], based on chondrite-evolution models and evidence of excellent matches to NIMS spectra of the non-ice regions of Europa's surface. These salts could depress melting points, alter buoyancy relations of key phases, form thick layers of bedded seafloor sediments, and allow explosive aqueous eruptions. It is therefore useful to know their high pressure and low temperature phase behavior. In addition, sodium sulfate minerals are common terrestrial evaporite phases, and are probably abundant on Mars [5-7].

Background

The three main solid phases of Na_2SO_4 are the anhydrous thenardite, the heptahydrate ($Na_2SO_4 \cdot 7H_2O$), and mirabilite ($Na_2SO_4 \cdot 10H_2O$) [8-12]. For the concentration of 15.5 wt.% used in this experiment, mirabilite is the stable state, though long-lived metastable states of the heptahydrate have been reported[11,12]. Generally, the presence of metastable states and the overall sluggish dynamics of the hydrated salt systems make accurate measurements of the phase boundaries challenging.

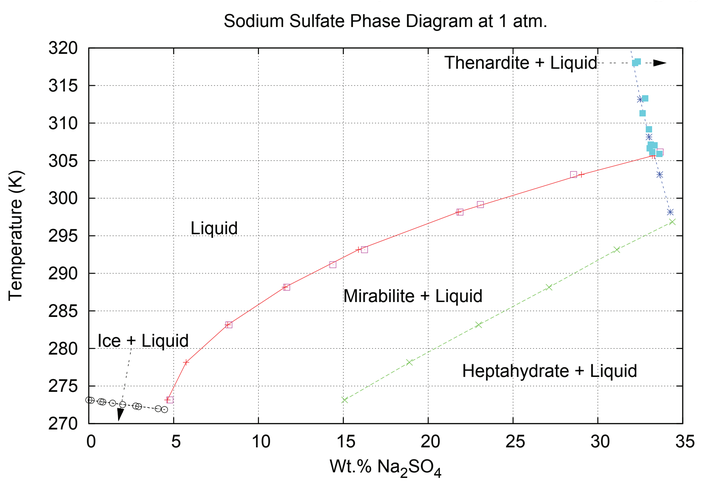

Figure 1: Phase diagram for $Na_2SO_4 \cdot H_2O$ at atmospheric pressure [8-10]. For the concentration of 15.5 wt.% used in this experiment, mirabilite is the expected stable crystal form.

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. About one mL of sample is contained in the pressure cell, made from a standard high-pressure fitting called a cross. 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.

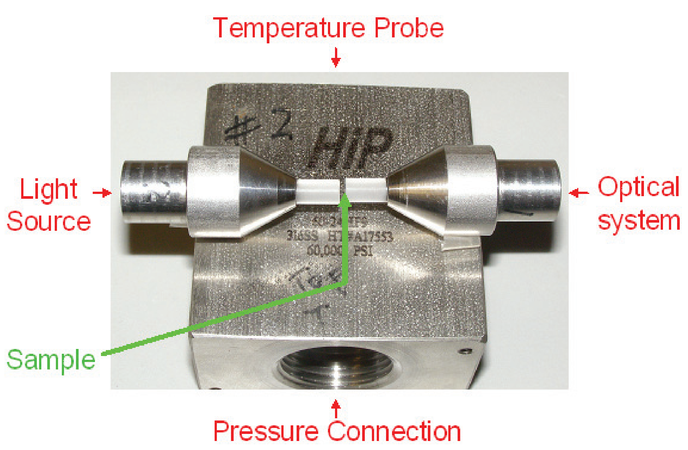

Figure 2: Exploded view of the pressure cell. Sapphire windows in steel plugs are mounted inside a steel cross. The image shows the relative positions of the plugs with windows and the plug containing the thermometer. The window separateion is approximately 1 mm.

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 filled with mercury that connects to the pressure system. 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 vollume.

Determining the Eutectic Temperature

The results for a run at 250 MPa are shown in Fig. 4. The system was initially pressurized to 250 MPa and warmed to point (a) so that the system was a homogeneous liquid. We then supercooled the sample to 271 K (b). The volume decreased due to thermal contraction.

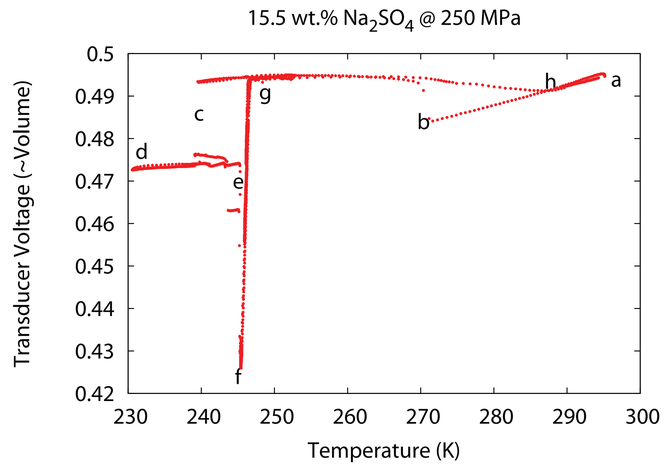

Figure 3: Results for 250 MPa. The eutectic temperature is 246 K.

Rapid crystallization at (b) led to a sharp increase in volume and a small increase in temperature due to the exothermic release of heat of crystallization. Based on the final equilibrium temperature (h), we identified these crystals as mirabilite, similar to that shown in Fig. 4. Although mirabilite is denser than the original solution, the remaining water-rich solution is less dense, leading to a slight overall increase in volume.

Figure 4: Mirabilite crystals at T = 254.9 K, p = 311 MPa.

The mirabilite crystals continued to grow as we cooled to 239.5 K. At point (c), the remaining sample solidified rapidly to an opaque dense mixture. Further cooling to (d) produced no significant changes. Upon warming to (e), incipient melting or softening of the sample allowed pressure equilibrium to be re-established, thus causing a reduction in volume from (e) to (f). Reversibe eutectic melting occured from (f) to (g) near 246 K; the volume increased rapidly, and crystals were seen melting in the window.

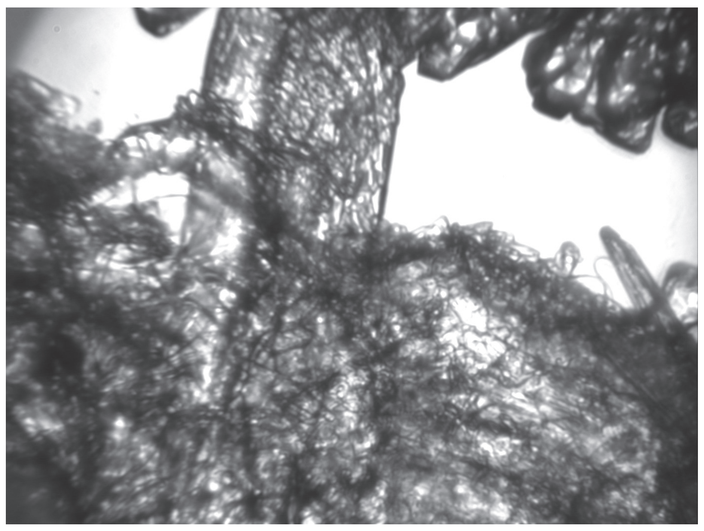

Figure 5: Coexistence of liquid and solid during eutectic melting at T = 249.53 K, p = 295 MPa (on curve Eutectic-IIIb) in Fig. 7.

Finally, the sample was gradualy warmed to point (h), at which point the last mirabilite crystals dissolved.

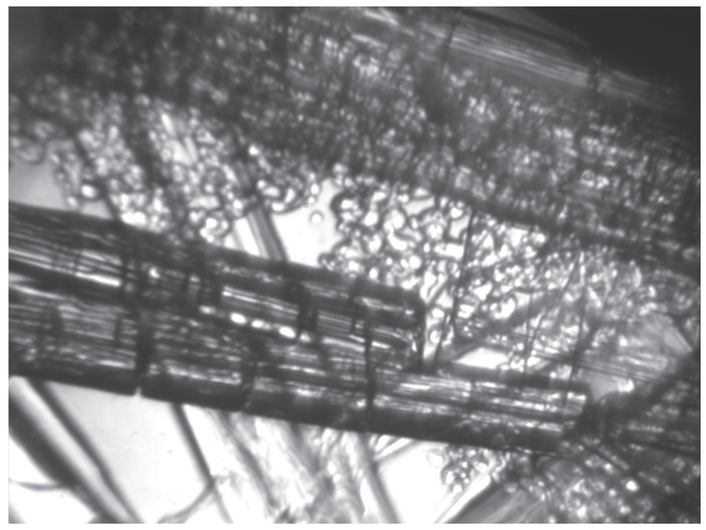

Figure 6: Coexistence of liquid and solid during eutectic melting at T = 253.1 K, p = 314 MPa (on curve Eutectic-IIIa) in Fig. 7.

Results

The eutectic temperature as a function of pressure is shown in Fig. 7. Below 209 MPa, the addition of the salt results in a small depression of the freezing point that ranges from ~0.85 K at low pressure to ~1.5 K near 200 MPa. For all experiments in this pressure range, the crystals observed were consistent with mirabilite.

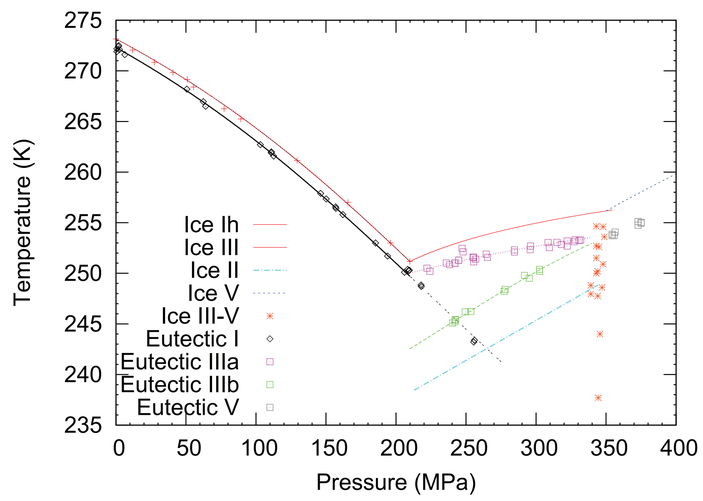

Figure 7: Eutectic temperature as a function of pressure. The melting temperatures for various phases of ice from Ref. [13] are included for comparison.

Above 209 MPa, the results are more complex. In most trials (purple, indicated by 'Eutectic IIIa') the freezing point depression was relatively small, but increased gradually with pressure. The density of the sample increased upon freezing, consistent with an Ice-III eutectic with mirabilite.

In some cases (green, labeled as 'Eutectic IIIb') the eutectic temperature was considerably lower (but well above the Ice II transition). We speculate that this is an Ice-III eutectic with the heptahydrate.

The IIIa and IIIb lines appear to converge near 350 MPa, near the Ice III-V boundary. Above 350 MPa, we only observed one phase. Finally, if we started below 209 MPa with existing Ice Ih crystals and gradually increased the pressure while decreasing the temperature, we obtained the points labeled 'Eutecic I' in Fig. 7. The volume expanded upon freezing, and the eutectic temperatures followed the extrapolation of the low-pressure eutectic line.

Above 209 MPa, both the Eutectic-I and Eutectic-IIIb phases are metastable. By varying the temperature and pressure, the system eventually solidifies as the Eutectic-IIIa phase, presumably mirabilite.

In all cases, the phase changes are accompanied by significant volume changes, and characterzing such changes may help in the development of models of Europa's ocean and icy shell.

References

[1] Dougherty, A.J., Hogenboom, D.L., and Kargel, J.S. (2007) LPS XXXVIII, Abstract #2275. [2] Hogenboom, D.L. et al. (1995) Icarus 115:258-277. [3] McCord, T.B. et al. (1998) Science, 280, 1242. [4] Kargel, J.S. et al. (2000) Icarus 148, 226-265. [5] Squyres, S.W. et al. (2004) Science, 306. [6] Mangold N, Gendrin A, Gondet B, et al. (2008) ICARUS 194, 519-543. [7] Kargel, J.S., Furfaro, R., Prieto-Ballesteros, O., Rodriguez, J.A.P., Montgomery, D.R., Gillespie, A.R., Marion, G.M., Wood, S.E. (2007) Geology, 35,: 975-978. [8] Wuite, J.P. (1913) Z. Physik. Chem. 86, 349-382. [9] Eddy R.D. and Menzies A.W. (1940) J. Phys. Chem, 44, 207-235. [10] Hartley et al. (1908) J. Chem. Soc. Trans. 93:825-833. [11] Hall, C. and Hamilton, A. (2008) Icarus, 198 (1): 277-279. [12] Hamilton, A. (2008) Journal of Physics D-Applied Physics. 41, 212002. [13] Bridgman, P.W. (1911) Proc. Amer. Acad. Arts Sci. 47, 441.