

EXPERIMENTAL CHARACTERIZATION OF MAGNESIUM CHLORATE PHASE TRANSITIONS: IMPLICATIONS FOR METASTABLE LIQUIDS ON MARS

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Introduction

Pure liquid water is unstable on the Martian surface under the prevailing dry and cold conditions. However, metastable brines may temporarily exist on Mars, for a few percentage of the year for several hours per sol [1]. Oxychlorine brines, particularly perchlorates and chlorates may play a crucial role on modern water cycle of Mars due to their ability to substantially lower the freezing point of water and deliquescence (absorb atmospheric water) [2]. Magnesium chlorate brines have been reported to have a very low eutectic temperature (204 K) [3] and a low deliquescence relative humidity (20.4% RH) [4] and are recognized as an important constituent for the formation of liquid water on Mars if present [5].

The Phoenix lander's WCL detected high levels of (0.4-0.6 wt%) perchlorate [6] but chlorate was not detected. However, the Ion Selective Electrode on the Phoenix was extremely sensitive to perchlorate and any signal from chlorates may have been masked by the perchlorate signal [3]. Perchlorates and chlorates may exist in Gale crater sediments as corroborated by the Sample Analysis at Mars instrument onboard Mars Science Laboratory [7]. In addition, Martian meteorites EETA79001 [8] and Tissint [9] contained a significant amount of chlorates and perchlorates. The co-existence and widespread distribution of these anions across the solar system were further established by the detection of them on Earth, Lunar, and primitive chondrite materials [10].

Although chlorate is a thermodynamically stable oxychlorine species, there's only one study that explored their stability. Hanley *et al.*, 2012 [3] performed evaporation experiments on chlorate salts and calculated the activity of water to construct stability diagrams. Based on this model, magnesium chlorate was predicted to have the lowest eutectic temperature for any brine. However, our literature review suggests that the freezing and melting points of magnesium chlorate brines have not yet been experimentally measured. Here we use Differential Scanning Calorimetry to directly measure the freezing and melting points of pure magnesium chlorate solutions under a range of concentrations to better understand the phase transitions.

Methods

Sample preparation: Magnesium chlorate was synthesized by slowly mixing equimolar amounts of $\text{BaSO}_4 \cdot \text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ under constant stirring, according to the method described by Kossev *et al.*, 2013 [11]. The solution was then filtered under gravity multiple times to remove solid impurities. The initial sample with a concentration of 1 m (16.05 wt%) was freeze dried using a Freeze-Drying Apparatus for ~10 hours to produce a brine solution with a concentration of 3.71 m.

Gravimetry: ~1 mL of Magnesium Chlorate solution was placed in a crucible with a known mass and 12 N HCl was added until the mixture ceased to release gas upon addition. The mixture was then evaporated to dryness on a hotplate and transferred to a muffle furnace at 870 K for 2.5 hours. A second acidification was done using H_2SO_4 , evaporated on a hotplate and dried in the muffle furnace at 870 K overnight. The process converted $\text{Mg}(\text{ClO}_3)_2$ to MgSO_4 .

Measuring freezing and melting points: A dilution series was prepared using the Magnesium chlorate brine and freezing and melting points at different concentrations were measured by a Differential Scanning Calorimeter, Netzsch DSC 200 F3 Maia in sealed crucibles. Two rates of cooling and heating were used (1 K/Min cooling, 5 K/Min heating and 3 K/Min cooling, 3 K/Min heating). The rates were chosen such that liquid nitrogen would not be exhausted during the run while maintaining the temperature profile of 293 K \rightarrow 173 K \rightarrow 293 K. Obtained data is compared with a modeled stability diagram of magnesium chlorate, created by Tu *et al.*, [12]. For this work, we report values for concentrations ranging from 0.48 m to 3.71 m (Fig. 1).

Results and Discussion

Figure 1 shows the results of a representative DSC experiment of a 1 K/Min cooling rate followed by 5 K/Min heating rate for the concentration of 3.6 m. The data clearly show the freezing point upon cooling and two melting signals were noticed in both heating curves of samples with 3.71 m and 3.6 m concentrations. These two melting events correspond to transitions from water ice + solid $\text{Mg}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ to $\text{Mg}(\text{ClO}_3)_2$ liquid + water ice at 223.4 (1) K and the melting of water ice in the $\text{Mg}(\text{ClO}_3)_2$ liquid + water ice mixture at 246.0 (1) K. The observed transitions

and transition temperatures are in good agreement with transitions in the modeled phase diagram for $\text{Mg}(\text{ClO}_3)_2$ by Hanley *et al.* [3].

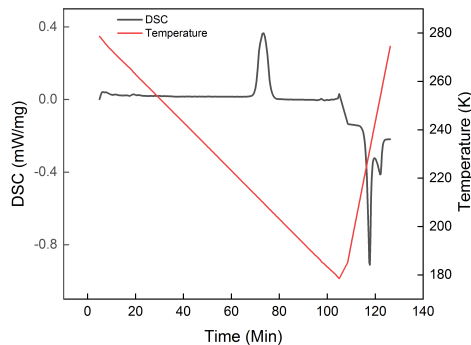


Figure 1: The complete cooling (1 K/Min)/heating curve (5 K/Min) of the sample with 3.6 m. Black solid curve represents the DSC signal and red line shows the temperature profile.

In Figure 2, the phase transition temperatures from all the runs are plotted adjacent to the modeled stability diagram of magnesium chlorate generated by Tu *et al.*, [13]. The preliminary data from our study are in general agreement with the model, however, more data are required to compare and interpret the phase transitions accurately.

Our experimental data show that the freezing and melting temperatures increase with decreasing concentration of $\text{Mg}(\text{ClO}_3)_2$ (Fig. 2) as it is expected based on modeling of the $\text{Mg}(\text{ClO}_3)_2$ phase diagram using newly measured Pitzer parameters [12]. Additionally, in general the experimentally determined freezing points are noticeably lower at fast cooling rates (Fig. 2). This is a result of supercooling effect which depends on several factors such as salt composition, concentration, cooling rate, pressure, and ionic impurities [13]. Faster cooling rates typically yields substantial supercooling due to the limited time for crystallization. The supercooling effect is more pronounced at higher concentrations (Fig 1) and the lowest freezing point was recorded as 191.8(1) K at 3.6 m. This is a significant result as the observed freezing point is about 12 K lower than the freezing point of 204 K at the eutectic based on the phase diagram by Hanley *et al.*, [3]. This might be an indication that the actual eutectic point is at a different concentration than previously suggested by [3]. This also suggests that liquid magnesium chlorate is stable at lower temperatures than previously realized. At all concentrations measured thus far, the observed freezing point temperatures are close to or below the

mean annual temperature on Mars, and vital for metastability of liquids on Mars.

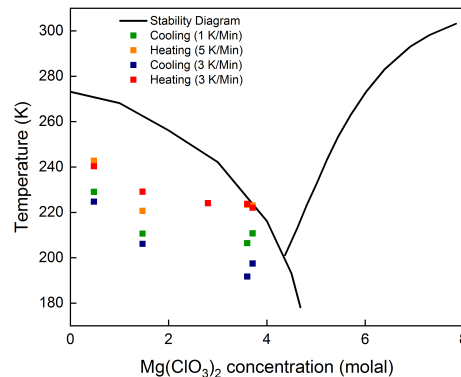


Figure 2: Freezing and melting points of all runs (squares) plotted alongside the modeled phase stability diagram (solid line) by Tu *et al.* [13]

Conclusions and Future Work

Currently, the thermodynamic data for magnesium chlorates are insufficient and the available stability diagram models require experimental validation. Data from our study can be utilized into the models of surface liquescence to investigate the metastability of liquids on Mars. The outcome can be used to interpret the real behavior and phase transitions of magnesium chlorate. Future work includes the acquisition of data covering a wide range of concentrations and integration of soil and salt mixtures.

Acknowledgments

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