Chlorate brines on Mars: Implications for the occurrence of liquid water and deliquescence

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ABSTRACT

Oxychlorine salts (chlorates and perchlorates) are globally important components of surface soils on Mars, and could form liquid water in concentrated salt solutions despite prevailing cold and dry conditions. Although perchlorate salts are well-characterized, basic thermodynamic properties of chlorate solutions, such as water activity (a_w) and even solubility, are poorly known. To address this knowledge-gap, we measured water activities and solubilities in the Na–Ca–Mg–ClO_3 system at 25 °C using the isopiestic method, and fit the data to an aqueous ion-interaction Pitzer model. We find that chlorate solutions have extremely low water activities that could allow liquid water to form on the surface of Mars. Compared to perchlorates, chlorates generally have higher water activities at the same concentration; however, saturated $Mg(ClO_3)_2$ solutions, in particular, are extremely concentrated (7.59 mol kg^{-1}) and have $a_w = 0.2$ at 25 °C, substantially below saturated $Mg(ClO_4)_2$ solutions ($a_w = 0.4$). If $Mg(ClO_3)_2$ salts are present on Mars' surface, then our results suggest a much greater potential for liquid water formation in soils due to freezing point depression or deliquescence than with perchlorates.

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1. Introduction

Oxychlorine salts (e.g., chlorates and perchlorates) have been detected or inferred at several locations on Mars' surface. Perchlorate (ClO_4^-) was first identified on Mars in abundances of 0.4–0.6 wt.% by the Wet Chemistry Laboratory (WCL) experiment on the *Phoenix Lander* (Hecht et al., 2009; Kounaves et al., 2010a; Toner et al., 2014b). Chlorate (ClO_3^-) is also expected on Mars based on its known association with perchlorate. Naturally produced perchlorate and chlorate ions are found in roughly 1:1 ratios in extreme arid regions on Earth (Jackson et al., 2015a; Jackson et al., 2010; Kounaves et al., 2010b; Rao et al., 2010), and in lunar rocks and chondrites (Jackson et al., 2015b). Chlorate has also been found in relatively high abundance in a Mars meteorite ($ClO_3^-/ClO_4^- = 1.95$) (Kounaves et al., 2014a). Associations between chlorate and perchlorate are likely due to similar formation pathways via atmospheric (Catling et al., 2010; Smith et al., 2014) or near-surface photochemical oxidation reactions (Carrier and Kounaves, 2015; Schuttlefield et al., 2011). The presence of oxychlorine salts on Mars is supported by pyrolysis experiments on the *Phoenix Lander* (Cannon et al., 2012; Hecht et al., 2009), the Mars Science Laboratory (Glavin et al., 2013; Leshin et al., 2013; Ming et al., 2013), and the Viking Landers (Navarro-González et al., 2010), suggesting that oxychlorine salts are globally distributed in surface soils (Sutter et al., 2017).

Chlorates and perchlorates have generated interest because their salts substantially lower the freezing point of water, and deliquesce (i.e. absorb water vapor to form brine) at low relative humidity. These properties suggest the potential for liquid water on Mars despite prevailing cold and dry conditions (Gough et al., 2011; Marion et al., 2010; Nuding et al., 2013; Toner and Catling, 2016; Toner et al., 2014a, 2014b, 2015a, 2015b). The stability of aqueous solutions against freezing and evaporation is determined by water activity. Water activity is defined as the equilibrium water vapor fugacity over a salt solution (f) relative to the fugacity of pure saturated water vapor (f^0). At low pressures, fugacity is well approximated by partial vapor pressures, so that $a_w = f/f^0 \approx p/p^0$. If water activity is known as a function of concentration, then activity coefficients of dissolved salts may also be calculated (Lewis et al., 1961); hence, water activities are a fundamental component of chemical models, which can be used to predict salt crystallization sequences from freezing and/or evaporating brines (Marion et al., 2010; Toner et al., 2015a, 2015b).

Although water activities in perchlorate salts have been investigated extensively (Pestova et al., 2005; Robinson et al., 1953; Toner and Catling, 2016), little work has been done on chlorates.

Water activities have been measured in $NaClO_3$ solutions to near saturation (Hanley et al., 2012; Jones, 1947), but the data show significant scatter at higher concentrations. Hanley et al. (2012) present water activities in $Mg(ClO_3)_2$ solutions based on evaporation rates, but the error in the water activity measurement is so large (± 0.1 a_w) that the data cannot be used for developing geochemical models. To our knowledge, water activities in $Ca(ClO_3)_2$ solutions have not been determined, and ternary mixtures in the Na–Ca–Mg–ClO_3 system (e.g., ternary Na–Mg–ClO_3 mixtures) have never been investigated for any thermodynamics properties.

To address the lack of data on chlorate solutions, we have measured water activities to a high level of accuracy in $NaClO_3$, $Ca(ClO_3)_2$, and $Mg(ClO_3)_2$ solutions at 25 °C, as well as ternary Na–Mg–Ca–ClO_3 mixtures. We then use measured water activities to construct a Pitzer model, and explore the solubility of salts in mixtures and the potential for liquid water formation in chlorate brines on Mars.

2. Methods

2.1. Materials

All pure and mixed chlorate salt solutions were prepared by either diluting or mixing $NaClO_3$, $Ca(ClO_3)_2$, and $Mg(ClO_3)_2$ stock solutions. For isopiestic reference solutions we used NaCl, $CaCl_2$, and H_2SO_4. To prepare the NaCl, $CaCl_2$, and $NaClO_3$ stock solutions, we purified the salt by (1) making a saturated salt solution, (2) filtering at 0.45 μm to remove insoluble material, and (3) recrystallizing the solution and discarding the supernatant. We then prepared near-saturated stock solutions from the residual crystals.

To prepare the $Ca(ClO_3)_2$ stock solution, we mixed an excess of gypsum ($CaSO_4 \cdot 2H_2O$) with $Ba(ClO_3)_2 \cdot H_2O$. Similarly, to prepare the $Mg(ClO_3)_2$ stock solution, we mixed stoichiometric quantities of anhydrous $MgSO_4$ and an excess of $BaCO_3$ with $Ba(ClO_3)_2 \cdot H_2O$. The Ba^{2+} precipitates as insoluble $BaSO_4$, leaving behind the soluble chlorate salt. The $BaCO_3$ addition combines with excess $MgSO_4$ to precipitate insoluble $BaSO_4$ and $MgCO_3$ salts. We separated the resulting slurries by centrifuging and then filtering the supernatant at 0.45 μm. Finally, we slowly recrystallized the solutions, discarded the excess supernatant, and prepared stock solutions from the residual crystals.

We measured the concentrations of the NaCl, $CaCl_2$, and $NaClO_3$ stock solutions gravimetrically by dehydration in a vacuum oven overnight at 250 °C and 0.02 mbar. For the H_2SO_4 stock solution, we determined the concentration as ammonium sulfate by neutralizing the acid with ammonia hydroxide and drying the solution on a hotplate overnight at 150 °C.

We attempted to directly measure the $Ca(ClO_3)_2$ and $Mg(ClO_3)_2$ stock solutions gravimetrically, as for $NaClO_3$, but our results were inconsistent and suggested that a fraction of the salt decomposed at high temperatures. Decomposition is likely due to hydrolysis in extremely concentrated Ca^{2+} and Mg^{2+} solutions, leading to acidic conditions that promote the partial decomposition of the chlorate anion. To measure these solutions gravimetrically, we acidified the solutions with concentrated HCl and evaporated the solutions to dryness over a hotplate, and then heated the residue to 600 °C in a muffle furnace. This decomposed the chlorate to chloride. We then acidified the samples a second time with an excess of concentrated H_2SO_4 and evaporated to dryness on a hotplate. We heated the final residue in a muffle furnace to 600 °C overnight, and determined the concentration as anhydrous $MgSO_4$ or $CaSO_4$. The measured stock solution concentrations and the error in triplicate determinations are given in Table 1.

Salt	Source	Initial purity (%)	Stock concentration (mol kg^{-1})
NaCl	Fisher	≥ 99	6.078 ± 0.002
$CaCl_2$	Sigma Aldrich	≥ 99	6.693 ± 0.001
H_2SO_4	Sigma Aldrich	99.999	15.67 ± 0.01
$NaClO_3$	Sigma Aldrich	≥ 99	8.775 ± 0.001
$Ca(ClO_3)_2$	Alfa Aesar	~ 98	9.373 ± 0.004
$Mg(ClO_3)_2$	Alfa Aesar	~ 98	6.656 ± 0.002

2.2. Isopiestic measurements

The isopiestic method measures water activity by equilibrating an unknown solution with a reference solution over the vapor phase. Water vapor will transfer between the two solutions until the water vapor pressures over the reference and unknown solutions are equivalent, i.e. until their water activities are equivalent. Concentrations in the solutions can be accurately determined by gravimetrically measuring the water loss or uptake. Hence, the known water activity of the reference solution gives the water activity of the unknown solution at its measured concentration.

The isopiestic method has several requirements. These are (1) a well-defined reference solution, (2) equivalent temperatures in the reference and unknown solutions, (3) the evacuation of residual air over the solutions, and (4) a stirring mechanism to aid equilibration of the solutions. Salt solutions such as NaCl and H_2SO_4 have been investigated by many authors (Archer, 1992; Clegg and Brimblecombe, 1995), and so are generally used as isopiestic reference standards. Precise thermal equilibrium is needed because the partial vapor pressure of water over solution is strongly dependent on temperature. As a result, a small temperature difference causes significant errors in the water activity measurement. Finally, the headspace over the solutions needs to be evacuated, leaving only water vapor, because residual gases greatly slow the rate of vapor transfer. Platford (1979) provides a detailed review of the isopiestic method.

Isopiestic apparatus have traditionally been built of costly and bulky materials, such as a large copper block to promote thermal equilibrium between solutions and gold-plated dishes to hold the samples; however, relatively recent approaches have developed the use of cost effective and efficient glass isopiestic apparatus (Lin et al., 1996; Ochs et al., 1990; Thiessen and Wilson, 1987). We developed a set of ten glass isopiestic apparatus comprised of two ~10 ml glass flasks, each containing a small magnetic stir-bar (2×7 mm) to agitate the solutions, and connected to a glass manifold via ground-glass joints using hydrocarbon-based grease (Fig. 1). The glass manifold has an outlet controlled by a high-vacuum glass stopcock.

In a typical isopiestic experiment, we first clean grease from the glass vials with a solvent such as toluene, weigh the empty vials to an accuracy of ± 0.01 mg, and then weigh solutions of known concentration into the vials. We then connect the vials to the glass-manifold using a hydrocarbon-based grease. To remove all residual air from the isopiestic apparatus, we first freeze the solutions using dry ice, and then evacuate the apparatus down to 0.02 mbar with a vacuum pump. It is necessary to first freeze the samples prior to applying the vacuum to prevent sample loss due to boiling of the solution.

To equilibrate the evacuated samples, we place the apparatus in a large water bath. For temperature control of the bath, we use a Lakeshore Cryogenic Temperature Controller, which monitors the temperature using a Platinum Resistance Thermometer calibrated to ± 0.01 °C and adjusts the power output to a 25 W cartridge heater using a Proportional-Integral-Derivative control loop. The water bath is stirred using a large magnetic stir bar, which also