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Formation of aqueous solutions on Mars via deliquescence of chloride–perchlorate binary mixtures

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ABSTRACT

Perchlorate salts, known to exist on Mars, can readily absorb water vapor and deliquesce into aqueous solutions even at low temperatures. The multiple soluble ionic species, such as chloride salts, present in the Martian subsurface may affect this deliquescence. Here we study the deliquescence (solid to aqueous transition) and efflorescence (aqueous to solid transition) of three perchlorate/chloride mixtures: $KClO_4/KCl$ at 253 K, $NaClO_4/NaCl$ at 243 and 253 K, and $Mg(ClO_4)_2/MgCl_2$ at 243 and 253 K. A Raman microscope with an environmental cell was used to monitor the phase transitions of internally mixed ClO_4^-/Cl^- particles as a function of the perchlorate mole fraction. The eutonic relative humidity (where deliquescence begins to occur regardless of ClO_4^- mole fraction), deliquescence relative humidity (DRH, where complete deliquescence occurs), and efflorescence relative humidity (ERH) were measured for several perchlorate mole ratios for each cation system. At the temperatures studied, the eutonic relative humidity was measured to be 28% RH for $Mg(ClO_4)_2/MgCl_2$ mixtures, 38% RH for $NaClO_4/NaCl$ mixtures, and 82% RH for $KClO_4/KCl$ mixtures. The DRH depends on the perchlorate mole ratio, but is below the DRH of the least deliquescent (highest DRH) pure salt. When humidity is lowered around an aqueous salt mixture, we find that efflorescence occurs at an RH below the DRH due to the kinetic inhibition of crystallization. The ERH values of the salt solutions were as low as 5% RH for $Mg(ClO_4)_2/MgCl_2$ mixtures, as low as 13% RH for $NaClO_4/NaCl$ mixtures, and as low as 66% RH for $KClO_4/KCl$ mixtures. The low eutonic RH values for the Na^+ and Mg^{2+} perchlorate/chloride mixtures are important: wherever $Mg(ClO_4)_2$ and $MgCl_2$ or $NaClO_4$ and NaCl coexist at the temperatures studied, mixtures will contain a stable aqueous phase above 28 or 38% RH, respectively, regardless of the perchlorate mole fraction. This liquid water may persist until 5 or 13% RH, respectively.

1. Introduction

1.1. Perchlorate on Mars

Perchlorate (ClO_4^-) salts, recently discovered at the Phoenix landing site (Hecht et al., 2009; Cull et al., 2010), are interesting due to their chemical and physical properties. Like many soluble salts, perchlorates are deliquescent, meaning the crystalline salt can form an aqueous solution by absorption of atmospheric water vapor. It has been suggested that deliquescence of perchlorate was observed by Phoenix (Renno et al., 2009; Smith et al., 2009) and this humidity-induced deliquescence could be an explanation for the formation of brines which may have recently flowed across the Martian surface (McEwen et al., 2011; Chevrier and Rivera-Valentin, 2012).

The deliquescence phase transition occurs when the relative humidity (RH) of the local atmosphere is equal to or greater than the deliquescence relative humidity (DRH) of the salt. Previous laboratory studies by Gough et al. (2011) and Zorzano et al. (2009) have found that the DRH of sodium (Na^+) and magnesium (Mg^{2+}) perchlorate salts can be as low as 38% RH. Although the DRH varies with hydration state, temperature and cation, all Na^+ and Mg^{2+} perchlorates deliquesce at low RH values relative to many salts such as sulfates.

Efflorescence, the recrystallization of salt solution into a crystalline phase, occurs at a lower relative humidity than deliquescence for a given salt at constant temperature. The efflorescence relative humidity (ERH) is lower than the DRH for most inorganic salts (Tang, 1997; Martin, 2000) because the crystallization process is kinetically hindered. Although deliquescence occurs as

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Table 1
DRH and ERH values of the six pure salts used to make the salt mixtures studied here. When known, the hydration state of the salt and the measurement temperature are given for the DRH and ERH values.

Cation	Salt	Solubility at 273 K (mass %)[a]	DRH	ERH
Na^+	$NaClO_4$ (anhydrous)	61.9%	38 (±3)%[b,c]	13 (±2)%[b,c]
	$NaClO_4 \cdot H_2O$		51 (±2)% at 273 K[c] 64 (±4)% at 228 K[c]	13 (±2)%[b,c]
	NaCl (anhydrous)	26.28%	75% at 293 K[d]	44% at 293 K[f]
K^+	$KClO_4$ (anhydrous)	0.70%	92 (±2)% at 253 K[f]	77 (±6)% at 253 K[d]
	KCl (anhydrous)	21.74%	84% at 293 K[d]	59% at 293 K[f]
Mg^{2+}	$Mg(ClO_4)_2 \cdot 6H_2O$	47.8%	42 (±2)% at 273 K[c] 55 (±2)% at 223 K[c]	19 (±3)%[b,c]
	$MgCl_2 \cdot 6H_2O$	33.96%	33.7 (±0.3)% at 273 K[g]	14 (±4)% at 243 K[e]

[a] CRC Handbook, 94th ed.
[b] Independent of temperature between 223 and 273 K.
[c] Gough et al. (2011).
[d] Cohen et al. (1987a).
[e] This work; not previously measured.
[f] Cohen et al. (1987b).
[g] Greenspan (1977).

soon as the free energy of the crystalline and aqueous phases are equal (i.e.: when the transition is thermodynamically favorable), salt crystallization is a phase transition to a more ordered state and requires nucleation. Supersaturated salt solutions are metastable and can exist for significant time periods at RH < DRH. $NaClO_4$ and $Mg(ClO_4)_2$ were found to exhibit this hysteresis; the ERH values of these salts are 13% and 19% RH, respectively (Gough et al., 2011). These low RH values are independent of temperature between 223 and 273 K and suggest that metastable perchlorate solutions may exist on Mars over a large range of RH values. Although DRH values can generally be predicted from thermodynamical calculations, ERH values must be measured by laboratory studies.

The deliquescence and efflorescence behavior of many perchlorates is now well established. However, to better understand the deliquescence and efflorescence of perchlorate salts on Mars, it is important to consider the effect of other species that may be present. In addition to perchlorate, the Wet Chemistry Laboratory (WCL) instrument onboard Phoenix found chloride (Cl^-), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na^+), and potassium (K^+) in the regolith (Hecht et al., 2009). Neither the vertical nor spatial distributions of these ions are known, but all were present in each of the three 1 cm^3 soil samples tested by WCL. It is likely, therefore, that other salts coexist with perchlorate. These additional soluble components of the regolith are present at various concentrations and have different solubilities. Some salts may be more deliquescent than perchlorate, although most are likely to be less. These additional species could affect the deliquescence and efflorescence of perchlorate salts and it is important to understand this effect.

Chloride was found at the Phoenix landing site (Hecht et al., 2009) and chloride deposits are thought to be globally widespread (Osterloo et al., 2010). Quantifying the effect of chloride salts on the deliquescence of perchlorate will help determine the conditions under which water will be absorbed by ClO_4^-/Cl^- mixtures on Mars and may also elucidate the likely behavior of other Mars-relevant salt mixtures. Based on cation measurements performed by WCL, potential Mars-relevant perchlorate salts include $NaClO_4$, $Mg(ClO_4)_2$ and potassium perchlorate ($KClO_4$). Potentially Mars-relevant chloride salts include sodium chloride (NaCl), magnesium chloride ($MgCl_2$) and potassium chloride (KCl). The DRH and ERH values of these six salts, as well as their solubility in water at 273 K, are shown in Table 1. In this paper, we perform laboratory experiments investigating the deliquescence and efflorescence of the following 2-salt mixtures: $KClO_4$/KCl at 253 K, $NaClO_4$/NaCl at 243 and 253 K, and $Mg(ClO_4)_2/MgCl_2$ at 243 and 253 K. We focus particularly on the effect of the perchlorate mole ratio ($m_{ClO_4^-}/(m_{ClO_4^-} + m_{Cl^-})$) on the DRH and ERH of these mixtures, where $m_{ClO_4^-}$ is moles of perchlorate ion and m_{Cl^-} is moles of chloride ion.

1.2. Theory of mixed salt phase transitions

Although the deliquescence and efflorescence of perchlorate-containing mixtures have not been studied, other 2-salt systems have been investigated. The humidity-driven phase transitions of several binary salt mixtures have been studied experimentally (Tang and Munkelwitz, 1993; Tang, 1997; Carroll et al., 2005; Yang et al., 2006) and theoretically (Potukuchi and Wexler, 1995). A schematic of the expected deliquescence behavior of salt mixtures is shown in Fig. 1, plotted as RH (%) vs. mole fraction of salt 1 ($m_{salt\,1}/(m_{salt\,1} + m_{salt\,2})$), where $m_{salt\,1}$ and $m_{salt\,2}$ are the moles of salts 1 and 2 in the mixture, respectively.

When humidity is raised around a 2-salt mixture, the following sequence of events is expected to occur: first, when RH is low (region A), any mixture of salts 1 and 2 consists entirely of a solid phase. When the humidity is raised to the eutonic relative humidity, RH_{eut} (dashed line), an aqueous phase forms. The aqueous salt concentration at RH_{eut} is the eutonic concentration. This initial solution is saturated with both salts 1 and 2 and a solid phase is present in most cases. If the mole ratio of salts in the original mixture is equal to the eutonic concentration, complete deliquescence (full conversion to the aqueous phase) will occur at RH_{eut}. For all other compositions, a solid phase will exist in equilibrium with the aqueous phase when the RH is above RH_{eut} (dashed line) but below the DRH (solid line). The composition of this solid is pure salt 2 if the original mixture was enriched in salt 2 relative to the eutonic concentration (region B) and pure salt 1 if enriched in salt 1 (region C). Continuing to increase the RH around this 2-phase mixture will increase the ratio of aqueous to solid salt. Finally, when the humidity reaches the DRH (solid line), complete deliquescence occurs. Above the DRH (region D) only an aqueous phase is present. At this point, the aqueous phase contains the same mole ratio found in the original solid.

There are two ways that a mixture can boost the formation of an aqueous phase relative to a pure salt. First, RH_{eut} of a 2-salt mixture is always lower than the DRH of either pure component. Therefore, the presence of even small amounts of a more deliquescent salt (salt 1 in Fig. 1) can cause partial dissolution at a RH value far below the DRH of the less deliquescent salt (salt 2). Additionally, the humidity at which a mixture fully deliquesces is