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# Thermochemistry of Hydrotalcite-like Phases Intercalated with $CO_3^{2-}$, $NO_3^-$, $Cl^-$, $I^-$, and $ReO_4^-$

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The enthalpies of formation of hydrotalcite-like phases containing Mg and Al and intercalated with $NO_3^-$, $Cl^-$, $I^-$, $ReO_4^-$, or $CO_3^{2-}$ were determined using high-temperature oxide melt and room-temperature acid solution calorimetry. The relative stability of phases bearing the various anions was gauged by comparing the enthalpy of formation from the single-cation components ($\Delta_f H^{scc}$). Trends relating $\Delta_f H^{scc}$ to the nature of intercalating anions (halides, $NO_3^-$, and $CO_3^{2-}$) show small stabilization from the mechanical mixtures of single-cation components. The aim of this study was to relate the enthalpy of formation to the nature of interlayer bonding in hydrotalcite-like compounds (HTLCs) bearing various anions, to uncover trends in the relative aqueous solubilities of these phases. The entropy of formation of these compounds was estimated using an approximation based on third-law entropy measurements for the compound $Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}\cdot 0.39H_2O$ which were performed in a previous study. This approximation for the third-law entropy was combined with the enthalpy data from our calorimetric measurements performed in this work in order to calculate the standard-state free energy of formation for the HTLCs. The solubility products for the compounds investigated in this study were calculated from these free energies of formation and were used in geochemical calculations. The results of these calculations support our previous hypothesis that carbonate-intercalated HTLCs are less soluble than phases bearing other anions such as nitrates and halides. We suspect that the solubilities of HTLCs bearing anions other than carbonate may correspond to the solubilities of single-cation phases bearing the same anions.

## Introduction

Hydrotalcite-like compounds (HTLCs) are a class of layered compounds that are receiving attention both as technical materials and as geologically significant phases that influence the cycling of aqueous species in the environment. HTLCs possess a general stoichiometry: $M(II)_{1-x}M(III)_x(OH)_2[A^{n-}]_{x/n}\cdot mH_2O$ where "$x$" represents the mole fraction (based on 1 mol of cations) in the brucite layer, "$A^{n-}$" is the intercalating anion, and "$m$" represents the water content. These materials contain a variety of cations including Mg(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Al(III), Fe(III), and Cr(III) as well as interlayer anions such as $Cl^-$, $CO_3^{2-}$, $NO_3^-$, and $SO_4^{2-}$.

Interest in HTLCs has grown due their use as catalysts, catalyst precursors, and specialty chemicals.[1] Hydrotalcites are also interesting because of their role in controlling the mobility of aqueous metals in the environment.[2−9] HTLCs bearing a variety of anions can be found as significant mineral phases in soils.[3,4,10,11] Green rusts are an example of such phases. HTLCs are layered materials with loosely bound anions, and one particular application for these materials is as anion exchangers.

Even though numerous applications have been developed for HTLCs, and a great deal of research has centered upon their effects on total dissolved concentrations of transition metals in the environments, little work has been done to study their energetics. Standard-state thermodynamic data are essential for development of novel chemical processes and new materials, as well as for more accurate calculations in environmental chemistry.

In our previous work,[12] we proposed that the intercalating anion has a significant effect on the thermodynamic stability

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and therefore the aqueous solubility of hydrotalcite-like compounds. Our calculations comparing the solubility of $NO_3^-$ intercalated phases and $CO_3^{2-}$ predicted that carbonates would be significantly less soluble and that even small amounts of carbonate could change the solubility of a nitrate phase by several orders of magnitude. Efforts have been attempted to determine the aqueous stability of hydrotalcites intercalated with various anions by considering factors such as shape, size, and charge on the strength of the bonding of the anion within the interlayer.[13,14] For example, although $SO_4^{2-}$ and $CO_3^{2-}$ have the same charge, $SO_4^{2-}$ intercalated phases have the ability to retain more interlayer water.[1] It is suspected that the interlayer bonds in the sulfate-bearing HTLCs might be weaker than the interlayer bonds of the carbonate phases. Similar to more simple binary phases, nitrate-bearing HTLCs may be more soluble than their carbonate-bearing counterparts. Such assertions are based on observations during synthesis and characterization, which are based largely on kinetics. None have been examined from a thermodynamic standpoint.

In this study we examined the effect of the intercalating anion on the thermodynamic properties of hydrotalcite-like compounds using calorimetric measurements of HTLCs containing Mg and Al in varying ratios and intercalated with $NO_3^-$, $Cl^-$, $I^-$, $ReO_4^-$, and $CO_3^{2-}$. Acid solution calorimetry data were combined with high-temperature oxide melt solution calorimetry to measure the standard enthalpy of formation of several samples of hydrotalcites bearing these anions. The solubility products for a few of these phases were then calculated, on the basis of our calorimetric data and an approximation for the entropy of formation. Using these values we performed geochemical calculations to predict the impact of HTLCs on the speciation of aqueous species in natural waters. This study, unlike our previous work,[12,15−17] focused on investigating the thermodynamics of HTLCs bearing anions other than carbonate. The calorimetric data for these phases are compared to those determined for carbonate-bearing HTLCs.

## Experimental Procedures

**Synthesis and Characterization.** Sources of the hydrotalcites and the reference materials used in this study are described in Table 1. Non-carbonate intercalated HTLCs can be prepared by methods including direct co-precipitation under controlled atmospheres and anion exchange.[1,13,18,19] Samples prepared for this study were synthesized using a "memory-effect"-based synthesis route. Hydrotalcite-like compounds were first synthesized and then calcined at 823 K for 2 h. The calined solid was resuspended in a solution bearing the desired intercalating anion. The exact details of the method are explained elsewhere.[13]

**Table 1. Sample Source and History**

| sample | source/history |
|---|---|
| $Na_2CO_3$ | Alfa |
| $NaCl$ | Alfa |
| $NaNO_3$ | Alfa |
| $NaI$ | Alfa |
| $NaReO_4$ | Alfa |
| $Mg_{0.74}Al_{0.26}(CO_3)_{0.13}(OH)_2{\cdot}0.39H_2O$ | ref 15 |
| $Mg_{0.74}Al_{0.26}[(NO_3)_{0.2}(OH)_{0.06}](OH)_2{\cdot}0.39H_2O$ | synthesized in this study |
| $Mg_{0.74}Al_{0.26}[I_{0.23}(OH)_{0.03}](OH)_2{\cdot}0.39H_2O$ | synthesized in this study |
| $Mg_{0.74}Al_{0.26}[(ReO_4)_{0.17}(OH)_{0.09}](OH)_2{\cdot}0.0.39H_2O$ | synthesized in this study |
| $Mg_{0.73}Al_{0.27}(CO_3)_{0.16}(OH)_{1.95}{\cdot}0.83H_2O$ | synthesized in this study |
| $Mg_{0.73}Al_{0.27}[Cl_{0.22}(OH)_{0.05}](OH)_2{\cdot}0.83H_2O$ | synthesized in this study |

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature on a Siemens Kristalloflex D 500 diffractometer using Cu Kα radiation (Cu Kα radiation, 40 kV, 30 mA; $2\theta = 10-60°$, 0.05° step size, and 1 s count time) and used for crystalline-phase identification. The phases were identified by comparison with the data reported in the JCPDS (Joint Committee of Powder Diffraction Standards) database.

Chemical analysis of the $CO_3^{2-}$ and $ReO_4^-$ HTLC samples were performed by Galbraith Laboratories Inc., Knoxville, TN. The compositions of the remaining samples were analyzed using a Perkin-Elmer SCIEX inductively coupled plasma−mass spectrometer (ICP/MS) for the Mg and Al content, and the anion content was determined using a Dionex ion chromatograph (IC). The $NO_3^-$ HTLC was dissolved in 12.1 N HCl, and the remaining samples were dissolved in 15.8 N $HNO_3$. Commercially available standards (Fischer Scientific) were used for the calibration curves for Mg, Al, Cl, I, and $NO_3$. Four experimental points within the ranges of 0.5 and 2 ppm and 0.1 and 0.75 ppm were obtained for Mg and Al, respectively. Five experimental points within the range of 5 and 80 ppm were obtained for $Cl^-$, $I^-$, and $NO_3^-$. In all cases a linear dependence of the integrated intensity as a function of the elemental concentration was acquired with correlation coefficients $R_i = 0.997$ or better. The water content of these samples was determined by thermogravimetric analysis using a Netzsch 449C STA system. The compositions that were calculated from these analyses are listed in Table 1.

**High-Temperature Oxide Melt Solution Calorimetry.** Enthalpy of drop solution ($\Delta H_{dsol}$) in lead borate ($2PbO{\cdot}B_2O_3$) at 973 K was measured in a twin Tian-Calvet type solution calorimeter.[20] This measurement indicates the heat effect associated with dropping the sample from room temperature into solvent in the high-temperature calorimeter. It includes contributions from the dissolution of the sample in the solvent at calorimeter temperature (with the evolution of $CO_2$ and $H_2O$) and effects due to heat pickup and any phase transitions on heating the sample to calorimeter temperature. Samples in the form of 5 or 15 mg pellets were dropped from room temperature into a platinum crucible containing $2PbO{\cdot}B_2O_3$ at 973 K. A flowing argon atmosphere (60−90 mL/min) was maintained within the calorimeter to drive off $CO_2$ and $H_2O$ that evolved during dissolution of water- and carbonate-bearing phases.[21] The calorimeter was calibrated by measuring the heat content of 5 and 15 mg pellets of corundum. The high-temperature oxide melt calorimetric method has been well-established for the measurement of enthalpies for carbonates.[20,21]

**Acid Solution Calorimetry.** Acid solution calorimetry was used to determine the enthalpies of formation for the phases bearing $NO_3^-$, $Cl^-$, $I^-$, and $ReO_4^-$. The enthalpy of solution ($\Delta H_{sol}$) in 5.0 N HCl (Alfa Aesar, standardized) at 298 K was measured in a

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**Table 2. Heat of Formation Data for End Members and Binary Reference Phases**

| sample | $\Delta H_{sol}$ (kJ/mol) | $\Delta_f H^0$ (kJ/mol) |
|---|---|---|
| $Na_2CO_3$ | −46.81 ± 1.04 (4) | −1129.2 ± 0.3 [24] |
| NaCl | 9.30 ± 0.10 (4) | −411.3 ± 0.10 [24] |
| $NaNO_3$ | 20.77 ± 0.25 (4) | −468.1 ± 0.40 [24] |
| NaI | 18.43 ± 0.40 (4) | −287.9 ± 0.80 [24] |
| $NaReO_4$ | 26.21 ± 3.58 (3) | −1036.00 [25] |
| $MgCO_3$ | | −1111.7 ± 2.55 [15] |
| $Mg(OH)_2$ | | −924.74 ± 2.55 [15] |
| $MgI_2$ | | −376.0 ± 0.60 [24] |
| $MgCl_2{\cdot}6H_2O$ | | −2499.0 [25] |
| $Mg(NO_3)_2$ | | −790.6 ± 1.3 [24] |
| $H_2O$ | 0.40 | 285.83 ± 0.042 [24] |

commercial Hart Scientific IMC-4400 isothermal calorimeter. This measurement indicates the heat effect associated with dropping the sample from room temperature into 5.0 N HCl at 298 K. The enthalpy of acid solution accounts for dissolution of the solid phase, evolution of any gases (in this case $CO_2$), and the enthalpy of dilution (due to dissolution of interlayer water into the acid). Pelletized samples were dissolved in 25 g of acid under vigorous stirring to ensure complete dissolution. The calorimeter was calibrated by dissolving 5 mg pellets of KCl (NIST standard reference material 1655) in 25 g of deionozed water under the same stirring conditions.

## Results and Discussion

**Calorimetry.** The enthalpies of solution for the sodium salt reference phases and single-cation components used in this study are listed in Table 2. The enthalpies of solution for the HTLCs are given in Table 3. For each sample, the reported enthalpy of drop solution or enthalpy of acid solution represents the mean of several measurements with an associated error of 2 standard deviations from the mean. The number of measurements taken per sample is indicated by the number given in parentheses.

**Determination of Heats of Formation.** Although many advances have been made to optimize the calorimetry of carbonates and silicates, high-temperature oxide melt calorimetry techniques have not been optimized for phases containing halides and nitrates. However, acid solution calorimetry is applicable to a number of phases, including those bearing $NO_3^-$, $SO_4^{2-}$, halides, and $CO_3^{2-}$. Therefore we used a combination of acid solution and high-temperature oxide melt calorimetry to determine the enthalpy of formation of the phases in this study. We illustrate the technique by considering the enthalpy determination of a nitrate-bearing HTLC $Mg_{1-x}Al_x(OH)_2(NO_3)_x{\cdot}mH_2O$.

First the enthalpies of acid solution for the carbonate-bearing HTLCs (eq 1) and the non-carbonate-bearing HTLCs (eq 2) were measured separately. Equations 1 and 2 illustrate the dissolution of two idealized (pure anion) phases:

$$\begin{aligned} &M^{II}{}_{1-x}Al_x(OH)_2(CO_3)_{x/2}{\cdot}mH_2O + (2+x)H^+(aq,298K) \rightarrow \\ &\quad (1-x)M^{2+}(aq,298K) + xAl^{3+}(aq,298K) + \\ &\quad \frac{x}{2}CO_2(g,298K) + \left(2 + m + \frac{x}{2}\right)H_2O(l,298K) \end{aligned} \tag{1}$$

$$\begin{aligned} &M^{II}{}_{1-x}Al_x(OH)_2(NO_3)_x{\cdot}mH_2O + 2H^+(aq,298K) \rightarrow \\ &\quad (1-x)M^{2+}(aq,298K) + xAl^{3+}(aq,298K) + \\ &\quad xNO_3^-(aq,298K) + (2+m)H_2O(l,298K) \end{aligned} \tag{2}$$

Sodium salts containing the various anions, in this case $Na_2CO_3$ and $NaNO_3$, were used as the reference phases for the dissolved anion,

$$NaNO_3(s,298K) \rightarrow Na^+(aq,298K) + NO_3^-(aq,298K) \tag{3}$$

$$\begin{aligned} &Na_2CO_3(s,298K) + 2H^+(aq,298K) \rightarrow 2Na^+(aq,298K) + \\ &\quad CO_2(g,298K) + H_2O(l,298K) \end{aligned} \tag{4}$$

The acid solution measurements were combined to calculate an enthalpy of ion exchange:

$$\begin{aligned} &M^{II}{}_{1-x}Al_x(OH)_2(CO_3)_{x/2}{\cdot}mH_2O(s,298K) + \\ &\quad xNaNO_3(s,298K) \rightarrow \\ &M^{II}{}_{1-x}Al_x(OH)_2(NO_3)_x{\cdot}mH_2O(s,298K) + \frac{x}{2}Na_2CO_3(s,298K) \end{aligned} \tag{5}$$

Since the enthalpy is a state function, enthalpies of formation from the elements (standard enthalpies of formation) were used for the known phases and the heat of reaction to calculate the standard enthalpy of formation for any HTLC. Therefore, using the standard enthalpies of formation for the sodium salt reference phases and the standard heat of formation for the carbonate-bearing HTLC, the standard enthalpy of formation for the non-carbonate-bearing phase was calculated. Relatively large errors associated with the enthalpy of formation are due to the propagation of errors[22] associated with the heats of formation of the reference phases used in the calculations.

**Relative Stability of HTLCs with Anions Other than Carbonate.** The heat of formation from the single-cation components ($\Delta_f H^{scc}$)

$$\begin{aligned} &\left(1 - \frac{3x}{2}\right)M^{II}(OH)_2(s) + \frac{x}{2}M^{II}(A^{n-})_{2/n}(s) + xAl(OH)_3(s) + \\ &\quad mH_2O(l) \rightarrow M^{II}{}_{1-x}Al_x(OH)_2(A^{n-})_{x/n}{\cdot}mH_2O(s) \end{aligned} \tag{6}$$

is presented as a function of the mole fraction of Al(III) in

**Table 3. Heat of Formation Data for HTLCs**

| sample | $\Delta H_{dsol}$ (kJ/mol) | $\Delta H_{sol}$ (kJ/mol) | $\Delta_f H^0$ (kJ/mol) | $\Delta_f H^{scc}$ (kJ/mol) |
|---|---|---|---|---|
| $Mg_{0.74}Al_{0.26}(CO_3)_{0.13}(OH)_2{\cdot}0.39H_2O$ | 197.50 ± 1.18 (5) | −78.67 ± 0.52 (4) | −1165.98 ± 2.06 | −10.49 ± 1.37 |
| $Mg_{0.73}Al_{0.27}(CO_3)_{0.16}(OH)_{1.95}{\cdot}0.83H\ _2O$ | 226.11 ± 1.06 (4) | −91.86 ± 0.49 (4) | −1297.19 ± 1.97 | −7.20 ± 1.27 |
| $Mg_{0.74}Al_{0.26}[(NO_3)_{0.2}(OH)_{0.06}](OH)_2{\cdot}0.39H_2O$ | | −93.72 ± 1.31 (4) | −1119.36 ± 2.50 | −1.58 ± 2.96 |
| $Mg_{0.74}Al_{0.26}[I_{0.23}(OH)_{0.03}](OH)_2{\cdot}0.39H_2O$ | | −90.45 ± 0.89 (4) | −1079.32 ±± 2.32 | −12.26 ± 2.7 |
| $Mg_{0.74}Al_{0.26}[(ReO_4)_{0.17}(OH)_{0.09}](OH)_2{\cdot}0.40H_2O$ | | −135.66 ± 0.44 (4) | −1181.82 ± 2.26 | a |
| $Mg_{0.73}Al_{0.27}[Cl_{0.22}(OH)_{0.05}](OH)_2{\cdot}0.83H_2O$ | | −89.68 ± 0.59 (4) | −1252.34 ± 2.12 | −7.74 ± 2.61 |

[a] Enthalpy data were not available for $MgReO_4$.

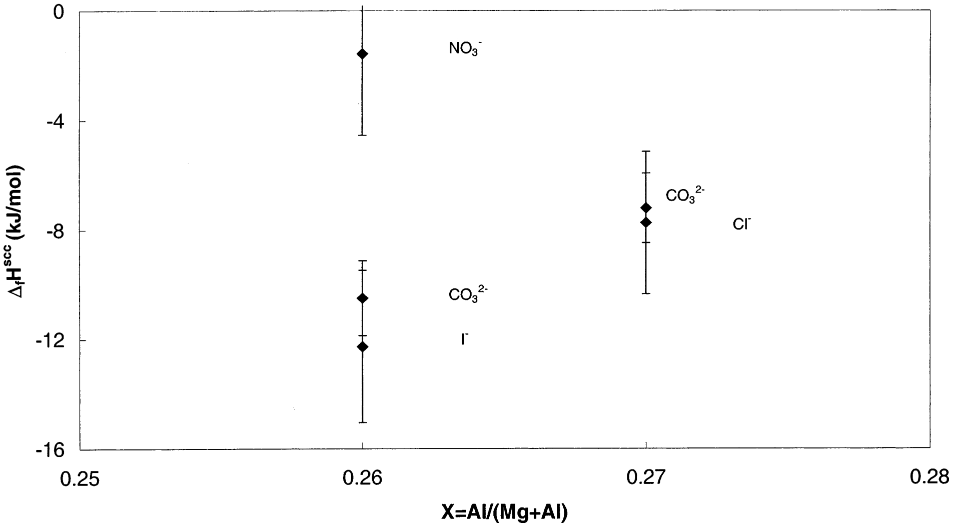

**Figure 1.** Heat of formation from the single-cation components for HTLCs (♦). The counterion is indicated next to the data point. Multiple anions are listed to indicate compositions where data points overlap.

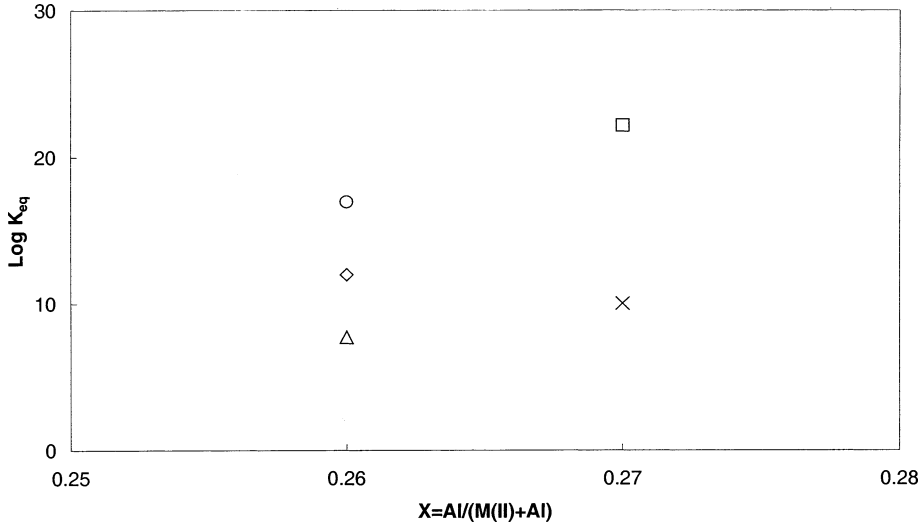

**Figure 2.** Equilibrium constants (eq 7) for the compounds $Mg_{0.74}Al_{0.26}(CO_3)_{0.13}(OH)_2\cdot0.39H_2O$ (△), $Mg_{0.74}Al_{0.26}[(NO_3)_{0.2}(OH)_{0.06}](OH)_2\cdot0.39H_2O$ (◇), $Mg_{0.74}Al_{0.26}[I_{0.23}(OH)_{0.03}](OH)_2\cdot0.39H_2O$ (○), $Mg_{0.73}Al_{0.27}(CO_3)_{0.14}(OH)_2\cdot0.83H_2O$ (×), and $Mg_{0.73}Al_{0.27}[Cl_{0.22}(OH)_{0.05}](OH)_2\cdot0.83H_2O$ (□).

Figure 1. The enthalpy of formation from the single-cation components represents the stabilization of the HTLC from the mechanical mixture and can be used as a measure of the stability gain due the intercalation of various anions. In particular, the enthalpy measurements relate the bonding strength of the interlayer anions to the stability and aqueous solubility of the HTLCs. For example, although $NO_3^-$ possesses the same shape as $CO_3^{2-}$, it is bonded relatively loosely in the interlayer. Hence, one expects that $NO_3^-$ intercalated phases might be more soluble than $CO_3^{2-}$-bearing phases. The relative bonding strengths of the interlayer species was suspected to influence the solubility of HTLCs; i.e., materials that possess stronger interlayer bonds would be less soluble than materials with weaker bonds.

The results presented in Figure 1 show moderate differences in the stability of HTLCs bearing $NO_3^-$, $Cl^-$, $I^-$, and $CO_3^{2-}$. We could not make this calculation for the $ReO_4^-$ HTLC since there are no data for the compound $MgReO_4$. The data show negligible differences in $\Delta_f H^{scc}$ between samples intercalated with $Cl^-$ or $I^-$ versus the carbonate-bearing analogues, while the equivalent samples intercalated with $NO_3^-$ show significant differences in stabilization from the carbonate-bearing counterparts. The added enthalpic stability of the halides over the carbonates also may be due to a hydration enthalpy contribution. Carbonates do not exhibit large hydration enthalpies[23] such as those shown by sulfates and halides,[24] and thus the stabilization from the single-cation components for carbonates may be less than $\Delta_f H^{scc}$ for the halide-bearing HTLCs.

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Aqueous solubility calculations were used to gauge the effect of $\Delta_f H^{scc}$ on the relative solubilities of HTLCs as a function of their anion content. We considered the equilibrium of HTLC gibbsite ($Al(OH)_3$)

$$M^{II}_{1-x}Al_x(OH)_2(A^{n-})_{x/n}\cdot mH_2O(s) + (2-3x)H^+(aq) \rightarrow (1-x)M^{2+}(aq) + xAl(OH)_3(s) + x/nA^{n-}(aq) + (2+m-3x)H_2O \quad (7)$$

where M(II) = Mg and $A^{n-} = CO_3^{2-}$, $NO_3^-$, $I^-$, and $Cl^-$,

Figure 2 compares the equilibrium constants for the compounds $Mg_{0.74}Al_{0.26}(CO_3)_{0.13}(OH)_2\cdot 0.39H_2O$, $Mg_{0.74}Al_{0.26}[(NO_3)_{0.2}(OH)_{0.06}](OH)_2\cdot 0.39H_2O$, and $Mg_{0.74}Al_{0.26}[I_{0.23}(OH)_{0.03}](OH)_2\cdot 0.39H_2O$, $Mg_{0.73}Al_{0.27}(CO_3)_{0.16}(OH)_{1.95}\cdot 0.83H_2O$ and $Mg_{0.73}Al_{0.27}[Cl_{0.22}(OH)_{0.05}](OH)_2\cdot 0.83H_2O$ based on the above reactions. The free energy of formation of the HTLCs was calculated by combining the heat of formation data with an estimate for the entropy contribution to the free energy ($T\Delta S$ term on the order of − 3.0 kJ/mol), based on entropy measurements of the compound $Mg_{0.74}Al_{0.26}(OH)_2(CO_3)_{0.13}\cdot 0.39H_2O$.[15] The equilibrium constants were then calculated for the hydrotalcites in this study considering the equilibrium specified in eq 7. The exact details of these types of calculations are specified elsewhere.[16,17]

The equilibrium constants predict dramatic decreases in the ability of the nitrate-, chloride-, and iodide-bearing phases to retain metals, in this case Mg, with respect to the carbonate-bearing analogues. The results for the nitrate- and chloride-bearing HTLCs may be considered analogous to the corresponding single-cation phases in that single-cation nitrates and chlorides are highly soluble in aqueous solutions. Our results agree with our previous conjecture that the carbonate-bearing HTLCs will be less soluble than HTLCs bearing other anions.

## Conclusions

In this study the effect of the intercalating anion on the thermodynamic properties of hydrotalcite-like compounds was examined, by considering: $NO_3^-$, $Cl^-$, $I^-$, $ReO_4^-$, and $CO_3^{2-}$. The aim of this study was to relate the enthalpy to the nature of interlayer bonding in HTLCs and to uncover trends in the relative aqueous solubilities of these phases. The results suggest that, in several cases, the difference in $\Delta_f H^{scc}$ between the carbonate, nitrate, and halide phases are small. The calculated aqueous solubilities demonstrate that the carbonate-bearing phases are less soluble than HTLCs bearing nitrates and halides by more than an order of magnitude. The results of these calculations support our previous conjecture that carbonate-intercalated HTLCs are less soluble than phases bearing other anions such as nitrates and halides. The aqueous solubilities of HTLCs bearing anions other than carbonate may be better understood by considering the solubilities of the single-cation analogues.

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