



Magnesium bicarbonate and carbonate interactions in aqueous solutions: An infrared spectroscopic and quantum chemical study

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Abstract

The interaction of magnesium with bicarbonate and carbonate ions in aqueous solutions was studied using infrared spectroscopy and quantum chemical calculations. Using the infrared vibrational bands for HCO_3^- and CO_3^{2-} at 1200–1450 cm^{-1} ($\delta\text{C-OH}$, ν_{S} and ν_3) together with their molar absorptivity (ϵ), the concentrations of the HCO_3^- and CO_3^{2-} ions and the corresponding Mg ion pairs have been determined. In the absence of Mg^{2+} , measured spectra were accurately reproduced assuming that only HCO_3^- and CO_3^{2-} were present in solution. Upon addition of Mg^{2+} at fixed pH, infrared spectra were observed to shift indicating presence of the MgHCO_3^+ and $\text{MgCO}_3(\text{aq})$ ion pairs. From measurements, the second ionization constant of carbonic acid and the MgHCO_3^+ and $\text{MgCO}_3(\text{aq})$ ion pair formation constants have been obtained, these being $\log K_2 = -10.34 \pm 0.04$, $\log K_{\text{MgHCO}_3^+} = 1.12 \pm 0.11$ and $\log K_{\text{MgCO}_3} = 2.98 \pm 0.06$, respectively. To support our experimental infrared measurements and to gain further insight into the molecular nature of the ion pair formation, density functional theory (DFT) calculations with VPT2 anharmonic correction were conducted. The most stable geometries predicted for the MgHCO_3^+ and $\text{MgCO}_3(\text{aq})$ ion pairs were a bi-dentate $[\text{MgHCO}_3]^+(\text{H}_2\text{O})_n$ and a monodentate $[\text{MgHCO}_3]^+(\text{OH})(\text{H}_2\text{O})_n$ complexes, respectively. The predicted frequencies for HCO_3^- , CO_3^{2-} and MgHCO_3^+ were found to shift toward those experimentally measured with an increasing H_2O solvation number where possible band shifts were predicted for $\text{MgCO}_3(\text{aq})$ relative to CO_3^{2-} , this being dependent on the exact structure and hydration of the bulk $\text{MgCO}_3(\text{aq})$ ion pair. Experimentally, the ion pair formations were found to have insignificant effects on the $\delta\text{C-OH}$, ν_{S} and ν_3 vibrational frequencies. The speciation of dissolved inorganic carbon may be significantly influenced by ion pair formation, particularly in alkaline solutions where they may be the predominant species.

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1. INTRODUCTION

Carbon dioxide capture and storage into geological formations is among the more feasible options for permanent CO_2 sequestration. Mineral–fluid interaction involves

release into solution of divalent cations commonly from silicates and formation of stable carbonate minerals like calcite, dolomite, magnesite and siderite. Ultramafic and mafic rocks are particularly favorable and reactive for carbonate mineral formation because of their high magnesium content relative to many other rock types (Seifritz, 1990; Oelkers et al., 2008; Gysi and Stefánsson, 2011).

Magnesite is the most stable magnesium carbonate at all temperatures and CO_2 pressures. Despite its

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thermodynamic stability, precipitation from solution is almost impossible at low temperatures (e.g. Christ and Hostetler, 1970). Instead, hydrated forms of Mg-carbonates like nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) and hydromagnesite ($(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) are formed (Fernandez et al., 2000; Zhang et al., 2006; Hänchen et al., 2008). The difficulty in forming magnesite at low temperatures has been attributed to the structure and energetic properties of the hydrated Mg^{2+} ion (Deelman, 2001). Consequently, the hydration environment around the Mg^{2+} ion is of central importance in evaluating early stage processes of magnesium carbonate formation in solution. The aquated Mg^{2+} ion maintains a hexa-coordinated first solvation shell (Lightstone et al., 2001; Ikeda et al., 2007; Di Tommaso and de Leeuw, 2010). However, according to recent Carr-Parrinello molecular dynamics (CPMD) simulations, the coordination number of Mg^{2+} is reduced, upon substitution of HCO_3^- and CO_3^{2-} , from six to five. In addition, HCO_3^- and CO_3^{2-} ligands may be in direct contact with the ion with mono- or bidentate structures, or alternatively, may be solvent, separated into the second solvation shell (Di Tommaso and de Leeuw, 2010). These changes may have important effects on further reactions of $[\text{MgCO}_3(\text{H}_2\text{O})_n]$ and $[\text{MgHCO}_3]^+(\text{H}_2\text{O})_n$ to form Mg-carbonate and bicarbonate clusters and eventually minerals.

The first step in Mg^{2+} and HCO_3^- and CO_3^{2-} interactions in an aqueous solution is associated with ion pair formation. These processes have been experimentally studied using potentiometry and solubility measurements to 150 °C (Greenwald, 1941; Rafflaub, 1960; Garrels et al., 1961; Hostetler, 1963; Nakayama, 1971; Larson et al., 1973; Reardon et al., 1973; Reardon and Langmuir, 1974; Siebert and Hostetler, 1977a, 1977b; Stefánsson et al., 2014). According to these results, interactions between Mg^{2+} and HCO_3^- and particularly CO_3^{2-} to form ion pairs are relatively strong and important in neutral to alkaline Mg-containing carbon dioxide solutions. However, there is no direct experimental verification of the existence of aqueous magnesium carbonate species in CO_2 -rich solutions; instead their stabilities have been calculated from indirect pH and solubility measurements. In addition, the values for the reported ion pair constants at infinity dilution are scattered by 0.5 log units, whereas only limited data are available at higher temperatures.

In this study we report the results of infrared measurements of magnesium solutions containing dissolved bicarbonate and carbonate and the formation of magnesium bicarbonate and carbonate ion pairs. To support our experimental infrared measurements, density functional theory (DFT) calculations have been undertaken to gain insight into the molecular nature of the interactions between Mg^{2+} , HCO_3^- and CO_3^{2-} and solvation with water molecules.

2. METHODS

2.1. Infrared spectroscopy

All solutions were prepared from deionized MilliQ water (<18 mΩ) by weight. The ionic media was NaCl (Sigma

Aldrich, puriss). Stock solutions of 0.1 mol kg⁻¹ HCl were made from 2 M HCl (Fluka) by dilution and standardized against tris-(hydroxomethyl)-aminomethan (Trizma-base, Aldrich) with methyl red indicator. Stock solutions of CO_2 free 0.1 mol kg⁻¹ NaOH solutions were prepared from 50% NaOH solutions (Sigma–Aldrich) by dilution with degassed water. The solution obtained was standardized by acid-base titration using the standardized 0.1 mol kg⁻¹ HCl solution. The source of magnesium was $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (Sigma–Aldrich, ACS reagent) and was either used directly as salt or as a 0.2 mol kg⁻¹ solution. The Mg concentration was determined using ion chromatography within analytical precision based on duplicate analysis at the 95% confidence level of <3%. Carbonate solutions were made from Na_2CO_3 (Sigma–Aldrich, ACS reagent) and NaHCO_3 (Sigma–Aldrich, ACS reagent) that had been dried at 120 °C for >4 h. and at 80 °C for >24 h. prior to use, respectively, and subsequently kept under vacuum. Fresh solutions were prepared for each experimental run from freshly degassed water.

For the infrared spectroscopic measurements, a total of 50 solutions were prepared in the systems $\text{MgCl}_2 + \text{NaHCO}_3 \pm \text{NaOH} \pm \text{HCl}$ and $\text{MgCl}_2 + \text{Na}_2\text{CO}_3 \pm \text{NaOH} \pm \text{HCl}$. The experimental solution composition was 0–0.154 mol kg⁻¹ NaHCO_3 , 0–0.051 mol kg⁻¹ Na_2CO_3 , 0–0.027 mmol kg⁻¹ HCl, 0–0.147 mol kg⁻¹ NaOH, 0–0.161 mol kg⁻¹ MgCl_2 , and the pH was 6.46–12.23 (Table 1).

The experimental solutions were pumped into a flow-through cell with ZnSe windows and path length varying from 25 to 75 μm. The spectra were recorded using a Thermo Scientific Nicolet 5700 spectrometer. Background and sample spectra were obtained from 400 scans with a resolution of 4 cm⁻¹. All experiments were carried out at 25 ± 2 °C. Prior to the infrared measurements, the pH of the solutions was measured using a glass electrode (Mettler Toledo, DG-114-SC) calibrated against standard buffers and ionic strength corrected buffers. The ionic medium used was NaCl. Using this approach, the absolute errors on the pH measurements were estimated to be ±0.05. The results were obtained by comparing the measured pH of several solutions using an electrode calibrated with the above method and using a more rigorous standard addition calibration that involved acid-base titration and determination of standard potential, Nernstian slope and acid and alkaline liquid junction potentials.

The molar concentration of the absorbing species measured by the infrared spectroscopy were quantified using the Beer–Lambert law,

$$A = l \sum_i \varepsilon_i c_i \quad (1)$$

where A is the measured absorbance, l is the path length, ε_i is the molar absorptivity and c_i (or $[i]$) is the molar concentration of the i -th aqueous species, respectively. The vibrational bands observed at 1200–1450 cm⁻¹ (Rudolph et al., 1996) were used for the quantification of HCO_3^- and CO_3^{2-} including $\delta\text{C-OH}$ and ν_{S} for HCO_3^- , and MgHCO_3^+ and ν_3 for $\text{MgCO}_3(\text{aq})$ (Fig. 1). The molal concentrations of the solutions were converted to molar concentration

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