

Pitzer model for the speciation of lead chloride and carbonate complexes in natural waters

Ryan J. Woosley, Frank J. Millero *

Rosenstiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA

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ABSTRACT

The speciation of lead in the environment is extremely important in determining its behavior and fate in natural waters. Speciation calculations rely on accurate formation constants, which are often scarce. The constants for Lead Chloride complexes are fairly well known in a wide variety of media, but lead carbonate values are rare and somewhat uncertain. We determined the stoichiometric formation constant (β_{PbCO_3}) of lead carbonate in NaCl solutions from 0.05 to 3.0 m at 25 °C. The thermodynamic formation constant (K_{PbCO_3}) was obtained using a Pitzer model ($\log K_{\text{PbCO}_3} = 6.87 \pm 0.09$). The known thermodynamic and stoichiometric formation constants of PbCl_n^{2-n} in HCl, NaCl, NaClO_4 , MgCl_2 and CaCl_2 , published PbCO_3 values in NaClO_4 , and our new PbCO_3 values in NaCl are fit to a Pitzer model to determine the Pitzer coefficients for PbCl^+ , PbCl_2 , PbCl_3^- , and PbCO_3 . Using this model the speciation of lead can be determined in a wide variety of media relevant to natural waters, including brines and seawater. Calculations of seawater speciation show general agreement with previously published estimates.

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1. Introduction

Lead (Pb^{2+}) has been widely studied in the environment due to its toxicity to organisms (Borgmann et al., 1993; Bryan, 1971; Hannan and Patouillet, 1972) and because of its large anthropogenic input into the environment (Boyle et al., 1994). Since the chemical form, and not the total concentration, is important in determining bioavailability, behavior, and fate of the metal, accurate knowledge of the speciation of Pb^{2+} is essential. Speciation is largely controlled by complexation with organic and inorganic ligands. This complexation is a function of temperature, ionic strength, and type of media; therefore, ionic interaction models require reliable formation constants over a range of temperature, ionic strength, and media. Lead is a somewhat unusual metal because the inorganic speciation is not dominated by one ligand, but by both chloride and carbonate in most natural waters. The formation of lead complexes can be expressed by:



and



Where n is the number of chloride or carbonate ions, and values typically range from 1 to 3 for chloride and 1 for carbonate, although dicarbonato species exist at high pH (Easley and Byrne, 2011). The stoichiometric formation constants (β_i) are then given by:

$$\beta_{\text{PbCl}_n} = [\text{PbCl}_n^{2-n}]/[\text{Pb}^{2+}][\text{Cl}^-]^n \quad (3)$$

$$\beta_{\text{PbCO}_3} = [\text{PbCO}_3]/[\text{Pb}^{2+}][\text{CO}_3^{2-}] \quad (4)$$

where the brackets denote concentration in molality (m). These constants are related to the thermodynamic (pure water) constants (K_i) through the activity coefficients (γ) of the species by:

$$K_{\text{PbCl}_n} = \beta_{\text{PbCl}_n} \{ \gamma(\text{PbCl}_n^{2-n}) / \gamma(\text{Pb}^{2+}) / \gamma^n(\text{Cl}^-) \} \quad (5)$$

$$K_{\text{PbCO}_3} = \beta_{\text{PbCO}_3} \{ \gamma(\text{PbCO}_3) / \gamma(\text{Pb}^{2+}) / \gamma(\text{CO}_3^{2-}) \} \quad (6)$$

Determination of activity coefficients requires reliable formation constants, which are often lacking (Byrne et al., 1988). Powell et al. (2009) critically compiled and reviewed the most reliable constants available for all the lead complexes available in the literature. Byrne et al. (2010) then used these stoichiometric values for chloride to determine the best thermodynamic constants, and fit the stoichiometric constants as a function of ionic strength. As shown by Millero and

* Corresponding author. Tel.: +1 305 421 4707; fax: +1 305 421 4144.
E-mail address: fmillero@rsmas.miami.edu (F.J. Millero).

Byrne (1984) and Byrne and Miller (1984), the stoichiometric constants vary in different media at the same ionic strength, particularly at high ionic strengths.

Very few values for the thermodynamic formation constants of the PbCO_3 complex have been published; many instead rely on correlations with other metals. Thus, Powell et al. (2009) were unable to recommend a reliable thermodynamic value and instead gave an “indicative value” of $\log K = 6.45 \pm 0.72$. Since then Easley and Byrne (2011) have determined the β_{PbCO_3} in NaClO_4 up to 5 m at 25 °C. We have further extended the measured constants by determining the β_{PbCO_3} in NaCl up to 3 m at 25 °C. The constants recommended by Powell et al. (2009) and these recently published stoichiometric and thermodynamic constants are used in the ionic interaction model of Pitzer (1991) to determine a complete set of Pitzer coefficients for PbCl_n^{2-n} in NaCl, NaClO_4 , HCl, HClO_4 , MgCl_2 , and CaCl_2 media at 25 °C and PbCO_3 in NaCl and NaClO_4 . From this model the activity coefficients of the lead-chloro and lead-carbonate complexes can be calculated in a variety of media relevant to natural waters including brines and seawater.

2. Determination of PbCO_3 in NaCl

2.1. Methods

Measurements of PbCO_3 were made using a spectrophotometric technique developed by Byrne and coworkers (Byrne and Yao, 2008; Soli et al., 2008; Easley and Byrne, 2011). All the solutions were made using Milli-Q water. Lead stock solutions (1×10^{-3} m) were made using PbCl_2 (Alfa Aesar, 99.999%, metal basis). A standard solution of 0.2 N NaCO_3 was made from reagent grade NaCO_3 purchased from Sigma Aldrich (St. Louis, MO) and was dried at 110 °C for two hours prior to use. The NaCl solutions were made gravimetrically from reagent grade NaCl purchased from BDH (VWR), exact concentrations were determined by density using an Anton-Par DMA-5000 densitometer and the equations of Lo Surdo et al. (1982). The values of pH of the solutions were monitored by Orion Ross (8101) glass and reference pH electrode and an Orion pH meter (model 720A). The filling solution of the reference electrode was 3 m NaCl. The electrode was calibrated by titration of 0.7 m NaCl with standardized HCl (~ 0.12 mol/L).

Solutions were housed in a thermostated cell containing the electrodes and circulated through a 10 cm quartz microflow cell (Starna Cells, Inc., Asascadero, CA) using a syringe pump (Norgren Kloehn, Inc., Las Vegas, NV). The absorbance was measured at 1 nm intervals between 210 and 350 nm using an HP 8453 spectrophotometer. Experimental solutions with added sodium carbonate (2×10^{-4} to 1×10^{-3} m) were used as a blank for the spectroscopic measurements. Sufficient stock Pb^{2+} solution was then added to give a final concentration of 5 $\mu\text{mol/kg}$ or 10 $\mu\text{mol/kg}$. Concentrations of lead and carbonate were increased at higher ionic strengths to help minimize potential interference of the chloride ion. Measurements were made at 4 different carbonate concentrations for each NaCl solution. The $[\text{CO}_3^{2-}]$ was calculated from the total alkalinity and pH using the dissociation constants of Millero et al. (2007) using the MIAMI model (Millero and Pierrot, 1998). The temperature was held at 25 ± 0.1 °C throughout the experiment using a Neslab RTE7 temperature bath. The solution was constantly stirred using a magnetic stirrer. The pH was kept between 7.85 and 8.5 in order to preclude the formation of $\text{Pb}(\text{CO}_3)_2^{2-}$ at higher pH and minimize PbCl_n^{2-n} formation as much as possible. This narrow pH range limited the number of different carbonate concentrations possible for each NaCl solution.

The absorbance of PbCO_3 in NaCl can be described according to the following equation:

$$\lambda A / (l[\text{Pb}]_T) = (\lambda \epsilon_{\text{Pb}} + \lambda \epsilon_{\text{PbCO}_3} \beta'_{\text{PbCO}_3} [\text{CO}_3^{2-}]_T) / (1 + \beta'_{\text{PbCO}_3} [\text{CO}_3^{2-}]_T) \quad (7)$$

where λA is the absorbance at wavelength λ , l is the path length (cm), $[\text{Pb}]_T$ is the total lead concentration, $\lambda \epsilon_i$ is the molal absorptivity of species i at wavelength λ . It is important to note that the β'_{PbCO_3} is slightly different from that defined in Eq. (4). Here β'_{PbCO_3} is defined as:

$$\beta'_{\text{PbCO}_3} = [\text{PbCO}_3] / [\text{Pb}_T^{2+}] [\text{CO}_3^{2-}] \quad (8)$$

where $[\text{Pb}^{2+}_T]$ is the total concentration of lead which is not associated with PbCO_3 , this includes the free lead as well as any lead associated with chloride. These values then must be corrected to the free lead for use in Eq. (4). Derivation of this equation can be found in Byrne (1981) and Soli et al. (2008). A baseline correction was made by subtracting the average of the wavelengths from 305–315 nm from each wavelength and was always less than 0.001. The 4 spectra obtained at each $[\text{Cl}^-]$ were fit to Eq. (7) using nonlinear least squares analysis with the global curve-fitting function in OriginPro 8.6 (OriginLab, Northampton, MA). The model stipulated that molal absorptivity and β'_{PbCO_3} were greater than or equal to 0. The wavelengths used in the analysis were $225 \leq \lambda \leq 250$ nm. There was too much noise in the NaCl media below ~ 215 nm to include the free Pb^{2+} peak as Easley and Byrne (2011) did in perchlorate media.

2.2. PbCO_3 formation results

Typical absorbance spectra at 1.026 m NaCl are shown in Fig. 1. Measurements were made from 0.05 to 3 m NaCl. The formation constant results are given in Table 1. Including all 50 extinction coefficients for each experiment would be excessive and not very useful so only the values at three representative wavelengths are given in Table 2. Interference with chloride ions prevented measurements at higher concentrations and the low solubility of lead prevented measurements at lower concentrations. The results are plotted in Fig. 2 along with the values in NaClO_4 determined by Easley and Byrne (2011). In order to test the reliability of the method two measurements were made in seawater ($S = 35$). The $\log \beta'_{\text{PbCO}_3} = 4.12 \pm 0.01$ was found to be in excellent agreement with the value of Byrne and Yao (2008). The seawater result (corrected to free Pb^{2+}) is also shown in Fig. 2 for comparison. The large difference in formation constants between NaCl and NaClO_4 at high ionic strengths highlights the importance of using constants for the media of interest, not just ionic

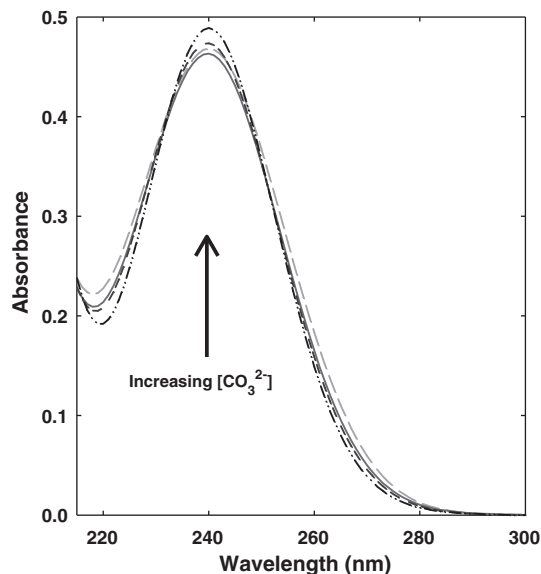


Fig. 1. Absorbance spectra for PbCO_3 at 1.026 m NaCl. The height of the peak increases with increasing carbonate concentration.

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