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Stability constants for the formation of lead chloride complexes as a function of temperature and ionic strength

Yanxin Luo and Frank J. Millero*

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

Abstract

The stability constants for the formation of lead (Pb^{2+}) with chloride

have been determined using a spectrophotometric method in NaClO_4 solutions as a function of ionic strength (0–6 m) and temperature (15–45 °C). The results have been fitted to the equations:

$$\begin{aligned} \log \beta_1^* &= \log \beta_1 + 0.21I - 8.61I^{0.5} / (1 + 1.2I^{0.5}) + 1927.40 [I^{0.5} / (1 + 1.2I^{0.5})] / T \\ \log \beta_2^* &= \log \beta_2 + 0.32I - 4.67I^{0.5} (1 + 1.2I^{0.5}) + 594.54 [I^{0.5} / (1 + 1.2I^{0.5})] / T \\ \log \beta_3^* &= \log \beta_3 + 0.40I - 2.68I^{0.5} (1 + 1.2I^{0.5}) - 43.98 [I^{0.5} / (1 + 1.2I^{0.5})] / T \end{aligned}$$

with standard errors of 0.05, 0.04 and 0.06, respectively. The thermodynamic values of $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$ at 25.0 °C and the enthalpies of formation of PbCl^+ , PbCl_2^0 and PbCl_3^- are in good agreement with literature values. We have combined our results with the earlier work of Seward (1984) to yield thermodynamic constants that are valid from 15 to 300 °C:

$$\begin{aligned} \log \beta_1 &= 44.82 + 0.031T - 21.21 \log T \\ \log \beta_2 &= 61.42 + 0.046T - 29.51 \log T \\ \log \beta_3 &= 107.97 + 0.071T - 51.46 \log T \end{aligned}$$

with standard errors of 0.05, 0.08 and 0.10, respectively.

1. Introduction

As a major toxic trace metal in natural waters, lead (Pb^{2+}) has been widely studied to obtain a better understanding of its behavior and effect on the environment. Knowledge of its chemical speciation, which is mainly controlled by the complexation with organic and inorganic ligands, is essential. The speciation can be modeled by using ionic interaction models that require reliable stability constants as a function of temperature and ionic strength.

* Corresponding author. Fax: +1 305 361 4144. fmillero@rsmas.miami.edu (F.J. Millero)..

The formation of complexes of lead with various inorganic ligands (X) can be expressed as

Studies have shown that lead is strongly complexed by Cl^{-} and CO_3^{2-} in natural waters (Turner et al., 1981). Because of the lack of reliable stability constants which are necessary to describe the complexation, the speciation between Cl^{-} and CO_3^{2-} is uncertain (Byrne et al., 1988). Studies of lead (II) chloride complexes have been made using potentiometric (Prasad and Prasad, 1980), solubility (Haight and Peterson, 1965; Rafal'skiy and Masalovich, 1981) and spectrophotometric (Tsai and Cooney, 1976; Byrne et al., 1981; Byrne, 1981; Byrne and Kester, 1981; Byrne and Young, 1982; Millero and Byrne, 1984; Byrne and Miller, 1984; Seward, 1984) methods. These results are summarized by Sillén and Martell (1964, 1971), Smith and Martell (1982, 1989) and Högfeldt (1982). Other recent studies include those of Macías-Zamora and Jones (1996) (ASV) and Ntale et al. (2004) (voltammetry). Although many studies have been made on the stability constants of lead chloride complexes, these results show considerable disagreement of the limited studies made as a function of ionic strength and temperature (Figs. 1 and 2). The effect of ionic strength and temperature on the stability constants of metals with inorganic ligands has not been well established (Millero, 2001). The study by Seward (1984) determined thermodynamic constants over a wide range of temperature (25–300 °C), but did not examine the effect of ionic strength on the constants.

In this paper, we have used the methods developed by Byrne et al. (1981) to examine the effect of ionic strength (0–6 m) and temperature (15–45 °C) on the Pb(II)–Cl system. The measurements were made at low $Pb(II)_T$ concentrations to minimize the possible problems associated with precipitation and the formation of polynuclear species (Perera et al., 2001). By combining our measurements with the work of Seward (1984), we have determined temperature coefficients and Pitzer parameters that can be used to calculate activity coefficients and stability constants for the formation of lead chloride complexes up to 300 °C and ionic strength from 0 to 6 m.

2. Experimental

2.1. Reagents and materials

All the chemicals used were high-purity reagents (98–99.99%), and the vessels were acid-cleaned before use. Solutions were made using Milli-Q water (18 MΩ cm). All the chemical preparations were made in a class 100 clean laminar flow bench. Stock solutions of 6 M $NaClO_4$ and 4 M $NaCl$ were prepared from $NaClO_4 \cdot H_2O$ (Aldrich, 99.99%) and $NaCl$ (Alfa Aesar, 99.99%, metal basis), respectively, filtered (0.2 μm) and measured gravimetrically (± 0.001 mol/kg). A standard $PbCl_2$ solution (4×10^{-3} M) was prepared from lead (II) chloride (Alfa Aesar, 99.999%, metal basis). The exact concentration was determined by ICP-MS (HP 4500).

2.2. UV–Vis spectrophotometric titration

Absorption spectra of lead (II) chloride complexes were recorded with a spectrophotometer (Hewlett-Packard 8453) at 1 nm intervals from 206 to 300 nm using a 10 cm jacketed quartz

cell. The temperature of the cell was controlled to ± 0.05 °C using a Neslab water bath and was monitored with a calibrated Guildline 9540 Platinum resistance thermometer. The measurements were made in various NaCl–NaClO₄ mixtures as a function of ionic strength (0.01–6 m) and at four different temperatures: 15.1, 25.0, 34.7 and 44.5 °C. Solutions were introduced into the cell using a peristaltic pump (Rainin, Rabbit-Plus) at a speed of 25 rpm and equilibrated for 10 min before measurement, which was sufficient to reach temperature equilibrium.

At different temperatures, molar absorptivities ($\lambda\epsilon_i$) of each lead chloride species were measured in a series of NaCl–NaClO₄ solutions, with Pb(II)_T concentration of 1.476×10^{-5} M and chloride concentrations (HCl + NaCl) from 1.0×10^3 to 1.990 M. The ionic strength was held constant ($I = 2$ M) by varying NaClO₄ from 1.999 to 1.0×10^{-2} M. HCl (*ultratrace*, EMD) was added to maintain constant pH = 3 in all the solutions. The background absorbance of an identical mixture without lead was subtracted from the measured values.

The effect of ionic strength was determined by measuring the absorbance in various NaCl–NaClO₄ solutions, where the ionic strength was varied from 1.0×10^2 to 5 M. The lower ionic strength (0.077–0.325 M) measurements were made in NaCl solutions; while the measurements up to 5 M were made by adding NaClO₄ to a 0.325 M NaCl solution. HCl was added to the NaCl–Na–ClO₄ mixtures to give a pH = 3 in all the solutions.

2.3. Determination of the stability constants

Stability constants for the lead chloride complexes can be expressed as

$$\beta_1^* = [PbCl^+] / [Pb^{2+}] [Cl^-] \quad (2)$$

$$\beta_2^* = [PbCl_2^0] / [Pb^{2+}] [Cl^-]^2 \quad (3)$$

$$\beta_3^* = [PbCl_3^-] / [Pb^{2+}] [Cl^-]^3 \quad (4)$$

The brackets denote the molar concentrations of each species. With each addition of Cl[−], the concentrations of free lead and its various species can be monitored from an ultraviolet spectrophotometer, and thus the cumulative stability constants can be determined.

According to Beer's law, the absorbance of a given lead species is related to its concentration by

$$\lambda A_i = 10 \lambda \epsilon_i [i] \quad (5)$$

where λA_i and $\lambda \epsilon_i$ are the absorbance and molar absorptivity of lead species i at wavelength λ , respectively, and $[i]$ is the molar concentration of each species. The cell path length is 10 cm. The observed absorbance (λA_i) is the sum of the absorbances of free lead ion (Pb²⁺) and its chloride complexes. So Eq. (5) can be written as

$$_{\lambda}A=10_{\lambda}\varepsilon_0 [Pb^{2+}] + 10_{\lambda}\varepsilon_1 [PbCl^+] + 10_{\lambda}\varepsilon_2 [PbCl_2^0] + 10_{\lambda}\varepsilon_3 [PbCl_3^-] \quad (6)$$

Eq. (6) provides a way to determine the concentration of each lead species if the molar absorptivities are known. Combining with Eqs. (2)–(4), Eq. (6) can be written in terms of stability constants as well as the free lead concentration:

$$_{\lambda}A=10 [Pb^{2+}] \left(\lambda\varepsilon_0 + \lambda\varepsilon_1\beta_1^* [Cl^-] + \lambda\varepsilon_2\beta_2^* [Cl^-]^2 + \lambda\varepsilon_3\beta_3^* [Cl^-]^3 \right) \quad (7)$$

$$[Pb(II)]_T = [Pb^{2+}] \left(1 + \beta_1^* [Cl^-] + \beta_2^* [Cl^-]^2 + \beta_3^* [Cl^-]^3 \right) \quad (8)$$

Combining Eqs. (7) and (8) on rearranging, we have

$$\frac{A}{10[Pb(II)]_T} = \frac{\lambda\varepsilon_0 + \lambda\varepsilon_1\beta_1^* [Cl^-] + \lambda\varepsilon_2\beta_2^* [Cl^-]^2 + \lambda\varepsilon_3\beta_3^* [Cl^-]^3}{1 + \beta_1^* [Cl^-] + \beta_2^* [Cl^-]^2 + \beta_3^* [Cl^-]^3} \quad (9)$$

From the multi-wavelength analysis, a nonlinear least-squares method (Byrne and Kester, 1978, 1981; Byrne et al., 1981; Matlab 5.3, 1996) was used to determine the molar absorptivities at a given temperature for each lead species using a MatLab program. The molar absorptivities determined from Eq. (9) at a given ionic strength could be used to determine the concentrations for the lead chloride complexes using Eq. (6), and thus the stability constants at a given temperature can be obtained from Eqs. (2)–(4).

3. Results and discussion

A typical spectrum for the lead chloride complexes at 25 °C is shown in Fig. 3. Shorter wavelengths are sensitive to lead speciation changes at low $[Cl^-]$, and longer wavelengths are useful for observing the lead chloride species with high ligand numbers. The multi-wavelength analysis can better define the characteristics of the complexation equilibrium than a single wavelength analysis (Byrne et al., 1981). Molar absorptivity characteristics at 25 °C are shown as an example in Fig. 4. Eq. (9) yields the best fit for the spectrophotometric data. An additional analysis assuming the formation of higher chloride species $PbCl_4^-$ produced a poorer fit than using Eq. (9). The $PbCl_4^-$ complex is a minor species under our experimental conditions. Molar absorptivity data were used to determine lead speciation from $I = 0.1$ – 6 m at 15.1, 25.0, 34.7 and 44.5 °C using the method described above. An example at 25 °C is shown in Fig. 5. The cumulative stability constants for $PbCl^+$, $PbCl_2^0$ and $PbCl_3^-$ as a function of the square root of ionic strength are shown in Fig. 6 and tabulated in Table 1. Our study of the stability constants as a function of temperature and ionic strength were fitted to the empirical equations:

$$\log \beta_1^* = \log \beta_1 + 0.21I - 8.61I^{0.5} / (1 + 1.2I^{0.5}) + 1927.40 [I^{0.5} / (1 + 1.2I^{0.5})] / T \quad (10)$$

$$\log \beta_2^* = \log \beta_2 + 0.32I - 4.67I^{0.5} / (1 + 1.2I^{0.5}) + 594.54 [I^{0.5} / (1 + 1.2I^{0.5})] / T \quad (11)$$

$$\log \beta_3^* = \log \beta_3 + 0.40I - 2.68I^{0.5} / (1 + 1.2I^{0.5}) - 43.98 [I^{0.5} / (1 + 1.2I^{0.5})] / T \quad (12)$$

with standard errors of 0.05, 0.04 and 0.06, respectively. The extrapolated thermodynamic stability constants $\log \beta_n$ ($n = 1, 2, 3$) using the Pitzer equations are described below and the values at different temperatures are given in Table 2. Our β_1 result is in reasonable agreement with literature data (Carmody, 1929; Hannan, 1936; Güntelberg, 1938; Biggs et al., 1955; Fedorov and Shishin, 1976; Yurchenko et al., 1976; Prasad and Prasad, 1980). There are few data available for β_2 and β_3 . A comparison with more recent measurements is given in Table 3. The complex PbCl_2^0 has the highest values indicating it is the dominant species amongst the lead chloride complexes under our experimental conditions.

3.1. Activity coefficients of lead complexes with Cl^-

The formation of complexes of lead with Cl^- is given by the equation

The thermodynamic equilibrium constant (β_n) for the formation of PbCl_n^{2-n} is given by

$$\beta_1 = \beta_1^* \left\{ \gamma(\text{PbCl}^+) / \gamma(\text{Pb}^{2+}) \gamma(\text{Cl}^-) \right\} \quad (16)$$

$$\beta_2 = \beta_2^* \left\{ \gamma(\text{PbCl}_2^0) / \gamma(\text{Pb}^{2+}) \gamma^2(\text{Cl}^-) \right\} \quad (17)$$

$$\beta_3 = \beta_3^* \left\{ \gamma(\text{PbCl}_3^-) / \gamma(\text{Pb}^{2+}) \gamma^3(\text{Cl}^-) \right\} \quad (18)$$

where $\lambda(i)$ is the activity coefficient of i and β_n^* is the stability constants. From measurements of β_n^* as a function of concentration, it is possible to determine the thermodynamic constants and the activity coefficients of the ion complexes. The values of the activity coefficients for the lead complexes can be formulated by (Millero and Byrne, 1984; Møller, 1988; Pitzer, 1991; Luo and Millero, 2004)

$$\ln \gamma(\text{PbCl}^+) = Z^2 f^\gamma + 2m_{\text{ClO}_4} (B_{\text{PbCl}-\text{ClO}_4} + m_{\text{ClO}_4} C_{\text{PbCl}-\text{ClO}_4}) + 2m_{\text{Cl}} (B_{\text{PbCl}-\text{Cl}} + m_{\text{Cl}} C_{\text{PbCl}-\text{Cl}}) + Z^2 R + ZS \quad (19)$$

$$\begin{aligned}
\ln \gamma \left(\text{PbCl}_2^0 \right) &= 2m_{\text{ClO}_4} \lambda_{\text{PbCl}_2-\text{ClO}_4} \\
&+ 2m_{\text{Na}} \lambda_{\text{PbCl}_2-\text{Na}} \\
&+ 2m_{\text{Cl}} \lambda_{\text{PbCl}_2-\text{Cl}} \\
&+ m_{\text{Na}} m_{\text{ClO}_4} \zeta_{\text{PbCl}_2-\text{ClO}_4-\text{Na}} \\
&+ m_{\text{Na}} m_{\text{Cl}} \zeta_{\text{PbCl}_2-\text{Cl}-\text{Na}}
\end{aligned} \quad (20)$$

$$\ln \gamma \left(\text{PbCl}_3^- \right) = Z^2 f^\gamma + 2m_{\text{ClO}_4} \left(B_{\text{PbCl}-\text{ClO}_4} + m_{\text{ClO}_4} C_{\text{PbCl}-\text{ClO}_4} \right) + 2m_{\text{Na}} \left(B_{\text{PbCl}_3-\text{Na}} + m_{\text{Cl}} C_{\text{PbCl}_3-\text{Na}} \right) + Z^2 R + ZS \quad (21)$$

where f^γ is the Debye–Hückel term. R and S are the media terms given by (Pitzer, 1991)

$$\begin{aligned}
R &= m_{\text{Na}} m_{\text{ClO}_4} B'_{\text{NaClO}_4} + m_{\text{Na}} m_{\text{Cl}} B'_{\text{NaCl}} \\
S &= m_{\text{Na}} m_{\text{ClO}_4} C^\phi_{\text{NaClO}_4} + m_{\text{Na}} m_{\text{Cl}} C^\phi_{\text{NaCl}}
\end{aligned}$$

The rearrangement of Eqs. (19)–(21) gives

$$\begin{aligned}
& - \ln \left\{ \beta_1^* / \gamma \left(\text{Pb}^{2+} \right) \gamma \left(\text{Cl}^- \right) \right\} \\
& - \text{Med} = - \ln \beta_1 + 2m_{\text{ClO}_4} \beta_{\text{PbCl}-\text{ClO}_4}^{(0)} \\
& + 2m_{\text{ClO}_4} \beta_{\text{PbCl}-\text{ClO}_4}^{(1)} \\
& + 2m_{\text{ClO}_4}^2 C_{\text{PbCl}-\text{ClO}_4} \\
& + 2m_{\text{Cl}} \beta_{\text{PbCl}-\text{Cl}}^{(0)} \\
& + 2m_{\text{Cl}} \beta_{\text{PbCl}-\text{Cl}}^{(1)} f^1 \\
& + 2m_{\text{Cl}}^2 C_{\text{PbCl}-\text{Cl}}
\end{aligned} \quad (22)$$

$$\begin{aligned}
& - \ln \left\{ \beta_2^* / \gamma \left(\text{Pb}^{2+} \right) \gamma^2 \left(\text{Cl}^- \right) \right\} \\
& = - \ln \beta_2 + 2m_{\text{ClO}_4} \lambda_{\text{PbCl}_2-\text{ClO}_4} \\
& + 2m_{\text{Na}} \lambda_{\text{PbCl}_2-\text{Na}} \\
& + 2m_{\text{Cl}} \lambda_{\text{PbCl}_2-\text{Cl}} \\
& + m_{\text{Na}} m_{\text{ClO}_4} \zeta_{\text{PbCl}_2-\text{ClO}_4-\text{Na}} \\
& + m_{\text{Na}} m_{\text{Cl}} \zeta_{\text{PbCl}_2-\text{Cl}-\text{Na}}
\end{aligned} \quad (23)$$

$$\begin{aligned}
& - \ln \left\{ \beta_3^* / \gamma \left(\text{Pb}^{2+} \right) \gamma^3 \left(\text{Cl}^- \right) \right\} \\
& - \text{Med} = - \ln \beta_3 + 2m_{\text{Na}} \beta_{\text{PbCl}_3-\text{Na}}^{(0)} \\
& + 2m_{\text{Na}} \beta_{\text{PbCl}_3-\text{Na}}^{(1)} f^1 \\
& + 2m_{\text{Na}}^2 C_{\text{PbCl}_3-\text{Na}} \\
& + 2m_{\text{Cl}} \theta_{\text{PbCl}_3-\text{Cl}} \\
& + 2m_{\text{ClO}_4} \theta_{\text{PbCl}_3-\text{ClO}_4}
\end{aligned} \quad (24)$$

where $f^1 = [1 - (1 + 2I^{0.5}) \exp(-2I^{0.5})]/2I$. The medium term (Med) is given by

$$\text{Med} = f^\gamma + R + S \quad (25)$$

All terms on the left-hand side of Eqs. (22)–(24) are experimentally known (β_n^*) or can be calculated from Pitzer programs for the ions ($\gamma(\text{Pb}^{2+})$ and $\gamma(\text{Cl}^-)$). The Pitzer coefficients used for the calculation of $\gamma(\text{Pb}^{2+})$ and $\gamma(\text{Cl}^-)$ are tabulated in Table 4. Since the coefficients were not available for PbCl_2 , we have used the values for ZnCl_2 (Millero and Byrne, 1984). A nonlinear least-squares fit of the values of the left side of Eq. (22) as a function of $2m$, $2m f^1$ and m^2 yields the infinite dilution thermodynamic stability constant (β_1) and the Pitzer parameters ($\beta_{\text{PbCl}-\text{ClO}_4}^{(0)}$, $\beta_{\text{PbCl}-\text{ClO}_4}^{(1)}$, $C_{\text{PbCl}-\text{ClO}_4}$, $\beta_{\text{PbCl}-\text{Cl}}^{(0)}$, $\beta_{\text{PbCl}-\text{Cl}}^{(1)}$ and $C_{\text{PbCl}-\text{Cl}}$) for PbCl^+ ion pairs. Similar fits were made for PbCl_2^0 and PbCl_3^- complexes from Eqs. (23) and (24). Since the concentration of Na^+ is independent of Cl^- and ClO_4^- , we have assumed $\lambda_{\text{PbCl}_2-\text{Na}} = 0$ to determine the ionic components of $\lambda_{\text{PbCl}_2-\text{Cl}}$ and $\lambda_{\text{PbCl}_2-\text{ClO}_4}$. The same assumption were made for $\theta_{\text{PbCl}_3-\text{Cl}} = 0$ and $\theta_{\text{PbCl}_3-\text{ClO}_4} = 0$ to derive the Pitzer parameters for the interaction between PbCl_3^- and Na^+ . Plots of the left side values of Eqs. (22)–(24) versus molality for PbCl_n^{2-n} ($n = 1, 2, 3$) complexes in NaClO_4 at 45 °C are shown as an example in Fig. 7. A summary of the Pitzer parameters for lead chloride complexes is given in Table 5. The reliability of these parameters can be demonstrated by comparing the measured and calculated values of β_n^* for the formation of PbCl_n^{2-n} complexes. The differences of $\ln \beta_n^*$ are shown in Fig. 8. The average deviations are ± 0.03 , ± 0.05 and ± 0.07 , respectively.

3.2. Effect of temperature on Pb–Cl complexes

The effect of temperature on the values of $\log \beta_n$ ($n = 1, 2, 3$) can be used to determine the enthalpies for the formation of PbCl_n^{2-n} ($n = 1, 2, 3$) using the van't Hoff equation

$$\log \beta_i = A_i - C_i/T \quad (26)$$

where A_i and C_i are constants and given in Table 6. H_i is related to C_i by

$$\Delta H_i = -R(2.303 - C_i) \quad (27)$$

where R is the gas constant ($8.314 \text{ kJ mol}^{-1} \text{ K}^{-1}$). The values of $\log \beta_n$ ($n = 1, 2, 3$) as a function of $1/T$ (K) are shown in Fig. 9. The resulting enthalpies for lead complexes are summarized and compared with literature data (Seward, 1984; Smith and Martell, 1982, 1989) in Table 7. The available literature data are few and considerably scattered. Seward (1984) fitted the stability constants to a five-parameter function of T (K); hence the

enthalpies are a function of temperature. The values of $\log \beta_n$ ($n = 1, 2, 3$) from his study between 25 and 50 °C were used to estimate enthalpies for a comparison with our results. The enthalpies for the formation of PbCl^+ , PbCl_2^0 and PbCl_3^- from this study are in good agreement with the values of Seward (1984). The values for the formation of PbCl^+ and PbCl_2^0 are also in reasonable agreement with the values from Smith and Martell (1982, 1989), but the enthalpy for PbCl_3^- is much higher than the result of Smith and Martell (1989).

Our results of the thermodynamic stability constants from 15 to 45 °C have been combined with the work of Seward (1984) from 25 to 300 °C and are shown as a function of temperature (°C) in Fig. 10. The data have been fitted to the equations:

$$\log \beta_1 = 44.82 + 0.031T - 21.21 \log T \quad (28)$$

$$\log \beta_2 = 61.42 + 0.046T - 29.51 \log T \quad (29)$$

$$\log \beta_3 = 107.97 + 0.071T - 51.46 \log T \quad (30)$$

which are valid from 15 to 300 °C at $I = 0$ m. The standard errors of the fits are 0.05, 0.08 and 0.10, respectively. These equations should predict reliable stability constants for lead complexes with Cl^- in fresh waters.

Acknowledgments

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Fig. 1.
Literature values of lead chloride stability constants as a function of ionic strength.

Fig. 2.
Literature values of lead chloride stability constants as a function of temperature.

Fig. 3.
A typical spectrum of lead chloride complexes at 25 °C.

Fig. 4.
Molar absorptivity characteristics of lead species at 25 °C.

Fig. 5.

Lead speciation derived from the observed spectrum ($I = 2.740$ m, $[\text{Cl}^-] = 0.350$ m, 25°C) using molar absorptivities. The spectrum can be described by: $\lambda A = 10_{\lambda}\epsilon_0 1.479 \times 10^{-6} + 10_{\lambda}\epsilon_1 3.659 \times 10^{-6} + 10_{\lambda}\epsilon_2 4.291 \times 10^{-6} + 10_{\lambda}\epsilon_3 1.294 \times 10^{-6}$.

Fig. 6.

The stability constants for PbCl_n^{2-n} ($n = 1, 2, 3$) complexes as a function of the square root of ionic strength at different temperatures.

Fig. 7.
The left side of Eqs. (25)–(27) versus molality for PbCl^+ complexes in NaClO_4 at 45 °C.

Fig. 8.
The differences between the measured and fitted values of $\ln \beta_n^*$ as a function of ionic strength at 45 °C.

Fig. 9.

The measured values of $\log \beta_n$ ($n = 1, 2, 3$) as a function of temperature.

Fig. 10. Effect of temperature on the values of $\log \beta_n$ ($n = 1, 2, 3$) from 15 to 300 $^{\circ}\text{C}$. The results from 15 to 45 $^{\circ}\text{C}$ are based on our measurements and the results from 25 to 300 $^{\circ}\text{C}$ are from the work of Seward (1984).

Table 1
The stability constants for PbCl_n^{2-n} ($n = 1, 2, 3$) complexes at different temperatures and ionic strengths

I (m)	15.1 °C			25.0 °C			34.7 °C			44.5 °C		
	$\log \beta_1^*$	$\log \beta_2^*$	$\log \beta_3^*$	$\log \beta_1^*$	$\log \beta_2^*$	$\log \beta_3^*$	$\log \beta_1^*$	$\log \beta_2^*$	$\log \beta_3^*$	$\log \beta_1^*$	$\log \beta_2^*$	$\log \beta_3^*$
0.13	0.80	1.30	1.16	0.88	1.31	1.18	1.00	1.45	1.34	1.03	1.43	1.39
0.18	0.73	1.20	1.17	0.83	1.24	1.18	0.94	1.35	1.21	0.99	1.33	1.23
0.24	0.68	1.12	0.96	0.79	1.19	0.99	0.91	1.29	1.12	0.96	1.27	1.18
0.32	0.65	1.09	0.97	0.74	1.12	0.97	0.89	1.24	1.10	0.93	1.22	1.17
0.38	0.63	1.05	0.88	0.75	1.13	0.97	0.84	1.13	1.04	0.98	1.28	1.15
0.44	0.62	1.05	0.89	0.74	1.12	0.98	0.87	1.20	1.05	0.96	1.26	1.14
0.50	0.62	1.04	0.91	0.77	1.16	0.95	0.85	1.17	1.02	0.97	1.29	1.17
0.74	0.60	1.03	0.89	0.70	1.11	0.92	0.78	1.12	0.96	0.93	1.25	1.12
1.12	0.59	1.03	0.93	0.72	1.10	0.95	0.78	1.12	1.00	0.92	1.25	1.11
1.79	0.63	1.11	1.02	0.78	1.22	1.07	0.87	1.26	1.20	0.96	1.34	1.31
2.51	0.70	1.24	1.23	0.83	1.32	1.30	0.92	1.38	1.37	1.04	1.48	1.52
3.28	0.79	1.43	1.48	0.94	1.51	1.54	1.01	1.55	1.61	1.15	1.68	1.77
4.11	0.88	1.61	1.72	0.98	1.65	1.78	1.06	1.68	1.81	1.22	1.84	1.99
4.52	0.97	1.75	1.91	1.10	1.80	1.93	1.18	1.82	2.01	1.22	1.88	2.06
4.98	1.07	1.90	2.10	1.24	1.95	2.16	1.27	2.01	2.20	1.29	2.01	2.23
5.89	1.45	2.39	2.47	1.48	2.41	2.57	1.51	2.45	2.61	1.57	2.51	2.65

Table 2

Values of the thermodynamic constants for PbCl_n^{2-n} ($n = 1, 2, 3$) complexes at different temperatures

	15.1 °C	25.0 °C	34.7 °C	44.5 °C
$\log \beta_1$	1.42 ± 0.02	1.45 ± 0.02	1.52 ± 0.04	1.59 ± 0.02
$\log \beta_2$	1.87 ± 0.06	1.98 ± 0.02	2.06 ± 0.02	2.16 ± 0.02
$\log \beta_3$	1.75 ± 0.06	1.83 ± 0.03	1.90 ± 0.03	2.00 ± 0.05

Table 3

A comparison of thermodynamic constants ($\log \beta_n$) ($n = 1,2,3$) extrapolated using the Pitzer equations in this study with literature data at 25 °C

	Our study	Millero and Byrne (1984)	Seward (1984)
$\log \beta_1$	1.45 ± 0.02	1.48 ± 0.01	1.41 ± 0.05
$\log \beta_2$	1.98 ± 0.02	2.03 ± 0.01	1.97 ± 0.04
$\log \beta_3$	1.83 ± 0.03	1.86 ± 0.02	1.66 ± 0.08

Table 4

Pitzer parameters for chloride and perchloride salts for Eqs. (22)–(24)

Electrolyte	15.1 °C			25.0 °C			34.7 °C			44.5 °C		
	$\beta^{(0)}$	$\beta^{(1)}$	C	$\beta^{(0)}$	$\beta^{(1)}$	C	$\beta^{(0)}$	$\beta^{(1)}$	C	$\beta^{(0)}$	$\beta^{(1)}$	C
HCl	0.1802	0.2911	0.001505	0.1757	0.2978	0.001369	0.1702	0.3092	0.001564	0.1637	0.3250	0.002059
NaCl	0.06707	0.2848	-0.03739	0.07536	0.2952	-0.03884	0.08173	0.3040	-0.04005	0.08683	0.3121	-0.04109
HClO ₄	—	0.2513	2.525E-05	—	0.2755	-1.180E-03	—	0.2964	-2.286E-03	—	0.3150	-3.334E-03
NaClO ₄	—	0.2483	4.907E-04	—	0.2755	-1.180E-03	—	0.2937	-2.697E-03	—	0.3043	-4.119E-03
PbCl ₂	0.2642	1.6078	-0.08839	0.2602	1.6425	-0.08798	0.2558	1.6793	-0.08759	0.2509	1.7192	-0.08720
Pb(ClO ₄) ₂	0.3397	1.6708	-0.004892	0.3332	1.7220	-0.008840	0.3280	1.7707	-0.01246	0.3237	1.8187	-0.01590

Table 5

Summaries of the Pitzer parameters for lead chloride complexes

Complexes	Parameters	15.1 °C	25.0 °C	34.7 °C	44.5 °C
PbCl^+	$\beta^{(0)}(\text{PbCl}-\text{Cl})$	2.52 ± 0.12	-6.64 ± 0.10	-2.33 ± 0.22	-2.26 ± 0.20
	$\beta^{(1)}(\text{PbCl}-\text{Cl})$	7.04 ± 0.04	12.07 ± 0.09	4.72 ± 0.12	4.99 ± 0.09
	$C(\text{PbCl}-\text{Cl})$	0.43 ± 0.22	4.51 ± 0.25	1.41 ± 0.31	0.59 ± 0.42
	$\beta^{(0)}(\text{PbCl}-\text{ClO}_4)$	-0.004 ± 0.28	0.16 ± 0.05	-0.08 ± 0.05	-0.19 ± 0.02
	$\beta^{(1)}(\text{PbCl}-\text{ClO}_4)$	2.67 ± 0.11	3.69 ± 0.20	2.70 ± 0.21	2.76 ± 0.14
	$C(\text{PbCl}-\text{ClO}_4)$	0.017 ± 0.004	-0.016 ± 0.008	0.003 ± 0.005	0.044 ± 0.003
PbCl_2^0	$\lambda(\text{PbCl}_2-\text{ClO}_4)$	0.09 ± 0.01	-0.106 ± 0.006	-0.008 ± 0.005	0.474 ± 0.004
	$\lambda(\text{PbCl}_2-\text{Cl})$	-0.52 ± 0.13	-0.19 ± 0.02	-0.19 ± 0.03	0.055 ± 0.005
	$\xi(\text{PbCl}_2-\text{Na}-\text{ClO}_4)$	-0.11 ± 0.02	0.008 ± 0.007	-0.045 ± 0.004	-3.896 ± 0.072
	$\xi(\text{PbCl}_2-\text{Na}-\text{Cl})$	0.62 ± 0.25	0.21 ± 0.07	0.20 ± 0.06	-1.0 ± 0.1
PbCl_3^-	$\beta^{(0)}(\text{PbCl}_3-\text{Na})$	0.47 ± 0.17	-0.20 ± 0.08	0.18 ± 0.06	-0.27 ± 0.04
	$\beta^{(1)}(\text{PbCl}_3-\text{Na})$	-1.26 ± 0.62	1.11 ± 0.23	-0.28 ± 0.60	0.9 ± 0.1
	$C(\text{PbCl}_3-\text{Na})$	-0.08 ± 0.02	0.02 ± 0.01	0.04 ± 0.01	0.038 ± 0.005

Table 6

Constants for the PbCl_n^{2-n} ($n = 1,2,3$) ion complexes for Eq. (26)

Complexes	A_i	C_i
PbCl^+	3.28 ± 0.25	-539.70 ± 77.08
PbCl_2^0	4.96 ± 0.10	-889.59 ± 31.67
PbCl_3^-	4.40 ± 0.18	-765.85 ± 53.67

Table 7Enthalpies (kJ mol^{-1}) for the PbCl_n^{2-n} ($n = 1,2,3$) ion complexes

Complexes	This study	Smith and Martell (1982)	Smith and Martell (1989)	Seward (1984) (25–50 °C)
PbCl^+	10.3 ± 1.5	18	9	8 ± 4^a
PbCl_2^0	17.0 ± 0.6	—	13^a	18 ± 3^a
PbCl_3^-	14.7 ± 1.0	—	4^a	10 ± 6^a

^aBased on measurements between 25 and 50 °C.