Aquat Geochem (2007) 13:339–355
DOI 10.1007/s10498-007-9023-y

ORIGINAL PAPER

# Use of Pitzer Equations to Examine the Formation of Mercury(II) Hydroxide and Chloride Complexes in NaClO$_4$ Media

**Melchor González-Dávila · J. Magdalena Santana-Casiano · Frank J. Millero**

Received: 11 September 2007 / Accepted: 22 October 2007 / Published online: 16 November 2007

**Abstract** The thermodynamic stability constants for the hydrolysis and formation of mercury ($Hg^{2+}$) chloride complexes

$$\mathrm{Hg}^{2+} + n\mathrm{H_2O} = \mathrm{Hg(OH)}_n^{(2-n)+} + n\mathrm{H}^+ \qquad \beta_n$$

$$\mathrm{Hg}^{2+} + n\mathrm{Cl}^- = \mathrm{HgCl}_n^{(2-n)+} \qquad \beta_i$$

have been used to calculate the activity coefficients for $\mathrm{Hg(OH)}_n^{(2-n)+}$ and $\mathrm{HgCl}_n^{(2-n)+}$ complexes using the Pitzer specific interaction model. These values have been used to determine the Pitzer parameters for the hydroxide and chloro complexes ($\beta_{\mathrm{ML}}^{(0)}$, $\beta_{\mathrm{ML}}^{(1)}$ and $C_{\mathrm{ML}}$). The values of $\lambda_{ij}$ and $\zeta_{ijk}$ have been determined for the neutral complexes ($\mathrm{Hg(OH)_2}$ and $\mathrm{HgCl_2}$). The resultant parameters yield calculated values for the measured values of log $\beta^*$ to ±0.01 from $I = 0.1$ to 3 m at 25°C. Since the activity coefficients of $\mathrm{Hg(OH)}_n^{(2-n)+}$ and $\mathrm{HgCl}_n^{(2-n)+}$ are in reasonable agreement with the values for Pb(II), we have estimated the effect of temperature on the chloride constants for Hg(II) from 0 to 300°C and $I = 0$–6 m using the Pitzer parameters for $\mathrm{PbCl}_n^{(2-n)+}$ complexes. The resulting parameters can be used to examine the speciation of Hg(II) with $Cl^-$ in natural waters over a wide range of conditions.

**Keywords** Mercury(II) hydroxide · Chloride complexes · NaClO$_4$ · Speciation · Activity coefficients · Pitzer equations

---

M. González-Dávila · J. M. Santana-Casiano · F. J. Millero (✉)
Rosenstiel School of Marine and Atmospheric Science, Marine and Atmospheric Chemistry,
University of Miami, 4600 Rickenbacker Causeway, Miami, FL 33149, USA
e-mail: fmillero@rsmas.miami.edu

M. González-Dávila · J. M. Santana-Casiano
Department of Chemistry, University of Las Palmas Gran Canaria,
35017 Las Palmas Gran Canaria, Spain

M. González-Dávila
e-mail: mgonzalez@dqui.ulpgc.es

## 1 Introduction

Hg is found typically in three chemical forms in the marine environment: elemental Hg ($Hg^0$), in a variety of inorganic and organic complexes of the divalent ionic Hg (Hg(II)), and methylated forms that include both monomethylmercury (MMHg) and dimethylmercury (DMHg). The di-ion $Hg_2^{2+}$, composed of two singly charged ions, is present in most aqueous solutions in ultra trace levels. All of these species are linked in most natural waters. The biogeochemistry, speciation, distribution, behaviour, and fate of mercury in the ocean have recently been presented by Fitzgerald et al. (2007). The inorganic speciation of Hg(II) in natural waters is dominated by chloride (Powell et al. 2005). The hydrolysis reaction of Hg(II) is observed at pH over 1 and must be considered in all equilibrium studies of $Hg^{2+}$-ligand systems (Lamborg et al. 2003; Powell et al. 2005). In oxic seawater and estuarine waters, a series of chloride and hydroxide complexes exist at neutral pH, in the absence of organic complexing agents. In oxic rivers and lakes with low concentrations of chloride, organic complexes are dominant (Benoit et al. 1999; Lamborg et al. 2003; Fitzgerald et al. 2007). Since the methylation processes are not very fast, appreciable amounts of inorganic Hg(II) can be present. Knowledge of its speciation is, therefore, crucial to understand its biological activity and chemical–physical behaviour in natural waters (Von Burg and Greenwood 1991). The inorganic speciation can play an important part in the toxicity and exposure of mercury to living organisms, and influences the transport and control of mercury emissions to the atmosphere (Fitzgerald et al. 2007). The inorganic speciation of Hg can only be modelled by using reliable stability constants and activity coefficients as a function of ionic strength. Recently, Powell et al. (2005) provided a critical evaluation of the equilibrium constants for the complex formation reactions between aqueous Hg(II) and the inorganic ligands $Cl^-$ and $OH^-$ using data from the IUPAC Stability Constants database, *SC-Database*, at 25°C and perchlorate media. These hydrolysis equilibria are given by the general equation

$$Hg^{2+} + nH_2O = Hg(OH)_n^{(2-n)+} + nH^+ \tag{1}$$

where the values of $\beta_i$ are given by

$$\beta^* i = [Hg(OH)_n^{(2-n)+}][H^+]^n/[Hg^{2+}] \tag{2}$$

The chloro complexes equilibria in $NaClO_4$ media are given by the general equation

$$Hg^{2+} + nCl^- = HgCl_n^{(2-n)+} \tag{3}$$

where the values of $\beta_i$ are given by

$$\beta^* i = [HgCl_n^{(2-n)+}]/[Hg^{2+}][Cl^-]^n \tag{4}$$

The recommended values of log $\beta^*$ for chemical speciation modelling of $Hg^{2+}$ and $OH^-$ and $Cl^-$ ligands are presented in Tables 1 and 2. Powell et al. (2005) have extrapolated the measured stability constants to an ionic strength of $I = 0$ mol kg$^{-1}$ using the Specific Interaction model (Grenthe et al. 1997). In this paper, we have examined the effect of ionic strength on these constants using the Pitzer model (1991). The activity coefficients for the formation of mercury chloride and hydroxide complexes have been determined at ionic strength from 0 to 3.5 m $NaClO_4$ media at 25°C. These values have been used to determine Pitzer interaction parameters ($\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$ and $C_{MX}$) for $Hg(OH)_n^{(2-n)+}$ and $HgCl_n^{(2-n)+}$ complexes (where $\beta_{MX}^{(0)}$ and $\beta_{MX}^{(1)}$ account for cation

**Table 1** Equilibrium constants for the hydrolysis of $Hg^{2+}$ in $NaClO_4$ media at 25°C (Powell et al. 2005)

| Reaction | *I* (molality) | Log $\beta_i$ |
|---|---|---|
| $Hg^{2+} + H_2O = HgOH^+ + H^+$ | 0.102[a] | −3.60[a] |
| | 0.513 | −3.69 |
| | 0.513 | −3.67 |
| | 1.052 | −3.82 |
| | 1.052 | −3.63 |
| | 3.419 | −3.43 |
| | 3.503 | −3.3 |
| | 3.503 | −3.48 |
| | 3.503 | −3.51 |
| | 3.503 | −3.41 |
| $Hg^{2+} + 2H_2O = Hg(OH)_2 + 2H^+$ | 0.102[a] | −6.12[a] |
| | 0.513 | −6.28 |
| | 0.513 | −6.23 |
| | 1.052 | −6.34 |
| | 1.052 | −6.25 |
| | 3.419 | −5.85 |
| | 3.503 | −6.31 |
| | 3.503 | −6.08 |
| | 3.503 | −6.09 |
| | 3.503 | −6.05 |
| $Hg^{2+} + 3H_2O = Hg(OH)_3^- + 3H^+$ | 0 | −21.11 |
| $2Hg^{2+} + H_2O = Hg_2OH^{3+} + H^+$ | 0.102[a] | −3.08[a] |
| | 1.052[a] | −2.82[a] |
| | 3.419 | −2.67 |
| | 3.503[a] | −2.66[a] |
| | 3.503 | −2.67 |

[a] Baes and Mesmer (1976)

(M)–anion (X) interactions and $C_{MX}$ for triplet interactions, M–X–M and X–M–X). These results can be used to model the inorganic behaviour of Hg(II) in natural waters.

## 2 Pitzer Calculations

### 2.1 Formation of Hydroxide Complexes

The hydrolysis equilibria for Hg(II) are given by

$$Hg^{2+} + H_2O = HgOH^+ + H^+ \qquad \beta_1^* = [HgOH^+][H^+]/[Hg^{2+}] \qquad (5)$$

$$Hg^{2+} + 2H_2O = Hg(OH)_2 + 2H^+ \qquad \beta_2^* = [Hg(OH)_2][H^+]^2/[Hg^{2+}] \qquad (6)$$

$$Hg^{2+} + 3H_2O = Hg(OH)_3^- + 3H^+ \qquad \beta_3^* = [Hg(OH)_3^-][H^+]^3/[Hg^{2+}] \qquad (7)$$

$$2Hg^{2+} + H_2O = Hg_2OH^{3+} + H^+ \qquad \beta_{2,1}^* = [Hg_2OH^{3+}][H^+]/[Hg^{2+}]^2 \qquad (8)$$

**Table 2** Equilibrium constants for the formation of chloro complexes of $Hg^{2+}$ in $NaClO_4$ media at 25°C (Powell et al. 2005)

| Reaction | $I$ (molality) | Log $\beta_i$ |
|---|---|---|
| $Hg^{2+} + Cl^- = HgCl^+$ | 0.513 | 6.73 |
| | 0.513 | 6.55 |
| | 0.513 | 6.61 |
| | 1.051 | 6.70 |
| | 3.503 | 7.00 |
| | 3.503 | 7.15 |
| $Hg^{2+} + 2Cl^- = HgCl_2$ | 0.513 | 13.20 |
| | 0.513 | 12.84 |
| | 0.513 | 12.97 |
| | 1.051 | 13.19 |
| | 3.503 | 13.85 |
| | 3.503 | 13.87 |
| $Hg^{2+} + 3Cl^- = HgCl_3^-$ | 0.513 | 13.84 |
| | 0.513 | 13.94 |
| | 0.513 | 13.84 |
| | 0.513 | 14.02 |
| | 0.513 | 13.80 |
| | 1.051 | 14.17 |
| | 1.051 | 14.13 |
| | 2.212 | 14.34 |
| | 3.503 | 14.87 |
| | 3.503 | 14.54 |
| | 3.503 | 14.86 |
| $Hg^{2+} + 4Cl^- = HgCl_4^{2-}$ | 0.513 | 14.88 |
| | 0.513 | 14.93 |
| | 0.513 | 14.88 |
| | 0.513 | 14.83 |
| | 1.051 | 15.10 |
| | 1.051 | 15.16 |
| | 2.212 | 15.33 |
| | 3.503 | 15.78 |
| | 3.503 | 16.07 |
| | 3.503 | 15.76 |
| $Hg^{2+} + HgCl_2(aq) = 2HgCl^+$ | 0.513 | 0.255 |
| | 0.513 | 0.26 |
| | 0.513 | 0.255 |
| | 1.051 | 0.22 |
| | 3.503 | 0.57[a] |
| $Hg^{2+} + Cl^- + H_2O = HgOHCl + H^+$ | 3.503 | 4.12 |
| $HgCl_2 + H_2O = HgOHCl + Cl^- + H^+$ | 1.052 | −9.56 |
| | 3.503 | −9.87 |

[a] This study

The measured values of $\beta_i^*$ are related to the thermodynamic values by

$$\ln \beta_1 = \ln \beta_1^* + \ln \gamma(\mathrm{HgOH}^+) + \ln \gamma(\mathrm{H}^+) - \ln \gamma(\mathrm{Hg}^{2+}) - \ln a_{\mathrm{H_2O}} \tag{9}$$

$$\ln \beta_2 = \ln \beta_2^* + \ln \gamma(\mathrm{Hg(OH)_2}) + 2\ln \gamma(\mathrm{H}^+) - \ln \gamma(\mathrm{Hg}^{2+}) - 2\ln a_{\mathrm{H_2O}} \tag{10}$$

$$\ln \beta_3 = \ln \beta_3^* + \ln \gamma(\mathrm{Hg(OH)_3^-}) + 3\ln \gamma(\mathrm{H}^+) - \ln \gamma(\mathrm{Hg}^{2+}) - 3\ln a_{\mathrm{H_2O}} \tag{11}$$

$$\ln \beta_{2,1} = \ln \beta_{2,1}^* + \ln \gamma(\mathrm{Hg_2OH}^{3+}) + \ln \gamma(\mathrm{H}^+) - 2\ln \gamma(\mathrm{Hg}^{2+}) \ln a_{\mathrm{H_2O}} \tag{12}$$

where $\gamma(i)$ is the activity coefficient of species $i$ and $a_{\mathrm{H_2O}}$ is the activity of water in $NaClO_4$ media which can be estimated from

$$a_{\mathrm{H_2O}} = \exp(-2m\phi/55.51) \tag{13}$$

$m$ is the molality and $\phi$ is the osmotic coefficient of $NaClO_4$ at 25°C. The values of $\phi$ have been calculated from the Pitzer equation (Pitzer 1991)

$$\begin{aligned}\phi_{\mathrm{NaClO_4}} - 1 = &- |Z_{\mathrm{Na}} Z_{\mathrm{ClO_4}}| 0.3915 I^{0.5}/(1 + 1.2I^{0.5}) + [2(v_{\mathrm{Na}}\, v_{\mathrm{ClO_4}})^{1.5}/v)] m B^{\phi}_{\mathrm{NaClO_4}} \\ &+ m^2[2(v_{\mathrm{Na}}\, v_{\mathrm{ClO_4}})^{1.5}/v)] C^{\phi}_{\mathrm{NaClO_4}}\end{aligned} \tag{14}$$

The value of $v = v_{\mathrm{Na}} + v_{\mathrm{ClO_4}} = 2$ is the sum of the ionic species $(v_i)$, $Z_{\mathrm{Na}}$ and $Z_{\cdot\mathrm{ClO_4}}$ are the charges on the ions $Na^+$ and $ClO_4^-$ and $I$ is the ionic strength ($I = m$, mol kg$^{-1}$). The value of $B^{\phi}_{\mathrm{NaClO_4}}$ is given by

$$B^{\phi}_{\mathrm{NaClO_4}} = \beta^{(0)}_{\mathrm{NaClO_4}} + \beta^{(1)}_{\mathrm{NaClO_4}} \exp(-2I^{0.5}) \tag{15}$$

Solving for the unknown activity coefficients gives

$$-\ln \beta_1 + \ln \gamma(\mathrm{HgOH}^+) = -\ln \beta_1^* - \ln \gamma(\mathrm{H}^+) + \ln \gamma(\mathrm{Hg}^{2+}) + \ln a_{\mathrm{H_2O}} \tag{16}$$

$$-\ln \beta_2 + \ln \gamma(\mathrm{Hg(OH)_2}) = -\ln \beta_2^* - 2\ln \gamma(\mathrm{H}^+) + \ln \gamma(\mathrm{Hg}^{2+}) + 2\ln a_{\mathrm{H_2O}} \tag{17}$$

$$-\ln \beta_3 + \ln \gamma(\mathrm{Hg(OH)_3^-}) = -\ln \beta_3^* - 3\ln \gamma(\mathrm{H}^+) + \ln \gamma(\mathrm{Hg}^{2+}) + 3\ln a_{\mathrm{H_2O}} \tag{18}$$

$$-\ln \beta_{2,1} + \ln \gamma(\mathrm{Hg_2OH}^{3+}) = -\ln \beta_{2,1}^* - \ln \gamma(\mathrm{H}^+) + 2\ln \gamma(\mathrm{Hg}^{2+}) + \ln a_{\mathrm{H_2O}} \tag{19}$$

At low concentrations of $Hg^{2+}$, the trace activity coefficients of $H^+$, $Hg^{2+}$, $HgOH^+$, $Hg(OH)_2$, $Hg(OH)_3^-$ and $Hg_2OH^{3+}$ in a $NaClO_4$ solution can be calculated from the Pitzer equations (Pitzer 1991) as formulated by Millero and Pierrot (2002). We have

$$\begin{aligned}\ln \gamma(\mathrm{H}^+) = &f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{HClO_4}} + EC_{\mathrm{HClO_4}}) + R + S \\ &+ m_{\mathrm{Na}}(2\Theta_{\mathrm{HNa}} + m_{\mathrm{ClO_4}}\Psi_{\mathrm{H-Na-ClO_4}})\end{aligned} \tag{20}$$

$$\ln \gamma(\mathrm{Hg}^{2+}) = 4f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{HgClO_4}} + EC_{\mathrm{HgClO_4}}) + 4R + 2S \tag{21}$$

$$\ln \gamma(\mathrm{HgOH}^+) = f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{HgOH-ClO_4}} + EC_{\mathrm{HgOH-ClO_4}}) + R + S \tag{22}$$

$$\ln \gamma(\mathrm{Hg(OH)_3^-}) = f^{\gamma} + 2m_{\mathrm{Na}}(B_{\mathrm{Hg(OH)_3-Na}} + EC_{\mathrm{Hg(OH)_3-Na}}) + R + S \tag{23}$$

$$\ln \gamma(\mathrm{Hg_2OH}^{3+}) = 9f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{Hg_2OH-ClO_4}} + EC_{\mathrm{Hg_2OH-ClO_4}}) + 9R + 3S \tag{24}$$

$$\ln \gamma(\mathrm{Hg(OH)_2}) = 2m_{\mathrm{Na}}\lambda_{\mathrm{Hg(OH)_2-Na}} + m_{\mathrm{Na}} m_{\mathrm{ClO_4}} \zeta_{\mathrm{Hg(OH)_2-ClO_4-Na}} \tag{25}$$

The value of $\Theta_{HNa}$ is 0.036 (Pitzer 1979) while the $\Psi_{H-Na-ClO_4}$ and $\lambda_{HgOH_2-ClO_4}$ are assumed to be zero (Millero and Pierrot 2002).

The Debye–Hückel term, $f^\gamma$ is given by

$$f^\gamma = -A^\phi[I^{1/2}/(1 + 1.2I^{0.5}) + (2/1.2)\ln(1 + 1.2I^{0.5})] \tag{26}$$

where $A^\phi = 0.3915$ at 25°C is given by Møller (1988) and $I$ is the molal ionic strength. The equivalent molality ($E$) and the ionic strength ($I$) are equal to the molality of the media.

The second ($B_{MX}$) and third ($C_{MX}$) virial coefficients for 1-1, 2-1, 3-1, 4-1 electrolytes MX are given by

$$B_{MX} = \beta^{(0)}_{MX} + (\beta^{(1)}_{MX}/2I)[1 - (1 + 2I^{0.5})\exp(-2I^{0.5})] \tag{27}$$

$$B'_{MX} = (\beta^{(1)}_{MX}/2I^2)[-1 + (1 + 2I^{0.5} + 2I)\exp(-2I^{0.5})] \tag{28}$$

$$C_{MX} = C^\phi_{MX}/(2|Z_M Z_X|^{0.5}) \tag{29}$$

The medium terms $R$ and $S$ in Eqs. 20–24 in $NaClO_4$ are given by (Pitzer 1991)

$$R = m_{Na}m_{ClO_4}B'_{NaClO_4} = m_{Na}m_{ClO_4}(\beta^{(1)}_{NaClO_4}/2I^2)[-1 + (1 + 2I^{0.5} + 2I)\exp(-2I^{0.5})]\} \tag{30}$$

$$S = m_{Na}m_{ClO_4}C_{NaClO_4} = m_{Na}m_{ClO_4}C^\phi_{NaClO_4}/2 \tag{31}$$

The values of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and $C^\phi_{MX}$ for $NaClO_4$, as well as $HClO_4$ are taken from Millero and Pierrot (2002). The values at 25°C are given in Table 3. The rearrangement of equations yields a series of equations that can be used to determined the activity coefficients ($\gamma_i$) of the ions and thermodynamic constants $\beta_i$. In order to solve Eqs. 16–19, one needs to estimate the activity coefficient of $Hg(ClO_4)_2$. Since the coefficients were not available for $Hg(ClO_4)_2$, we have used the values for $Pb(ClO_4)_2$ (Pitzer 1979). In order to justify this selection, the formation constants for mercury and the ionic concentration dependence of lead chloride complexes (Luo and Millero 2007) in $NaClO_4$ media are shown in Fig. 1 as a function of the square root of the ionic strength. The effect of ionic strength between the two metal chloride complexes are in good agreement indicating that ionic interactions of Pb(II) and Hg(II) ions and complexes are similar.

By defining ln $\gamma$ (Ideal) as

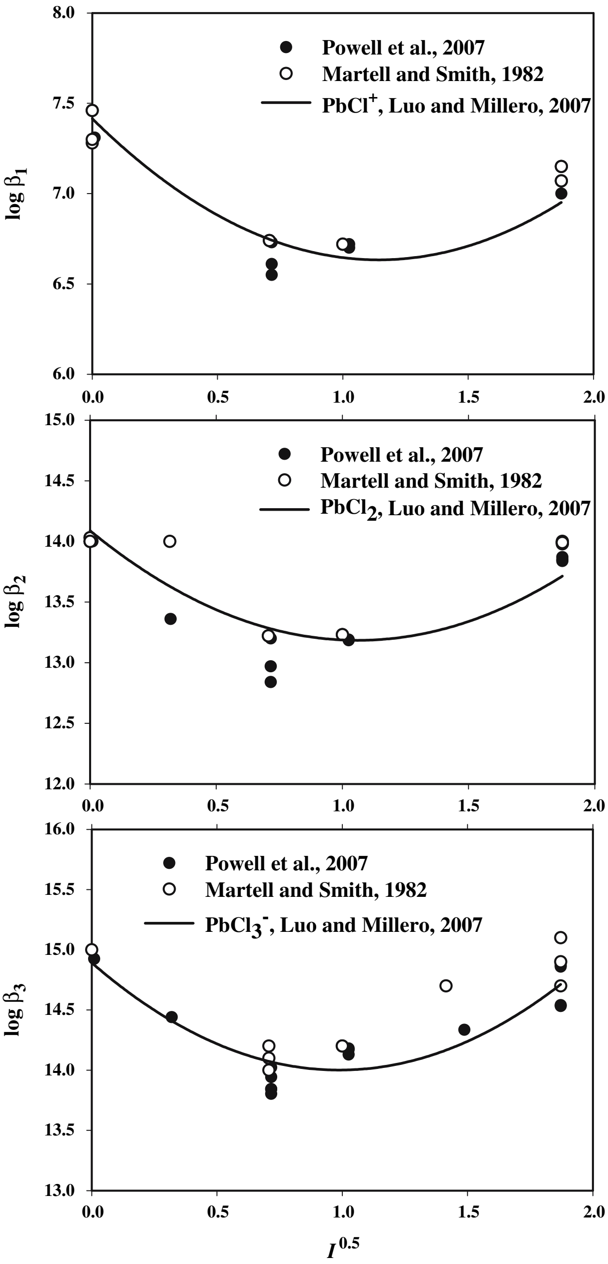
$$\ln\gamma(\text{Ideal}) = Z_i^2 f^\gamma + Z^2 R + |Z|S \tag{32}$$

**Table 3** The Pitzer coefficients for the hydrolysis and chloro complex formations in $NaClO_4$ media at 25°C in Eqs. 20–25 and 62–68

| Electrolyte | $\beta^{(0)}_{MX}$ | $\beta^{(1)}_{MX}$ | $C_{MX}$ |
|---|---|---|---|
| $NaClO_4$ | 0.0554 | 0.2755 | −0.00118 |
| $HClO_4$ | 0.1747 | 0.2931 | 0.00819 |
| NaCl | 0.0765 | 0.2664 | 0.00127 |
| $Hg(ClO_4)_2^a$ | 0.333225 | 1.722 | −0.00884 |

[a] Values for $Pb(ClO_4)_2$ from Pitzer (1979)

**Fig. 1** Values of mercury and lead chloride stability constants as a function of the square root of ionic strength at 25°C (**a**) $HgCl^+$, (**b**) $HgCl_2$, and (**c**) $HgCl_3^-$ species. The solid lines correspond to the results for the concentration effects on the $PbCl_n^{(2-n)+}$ species determined by Luo and Millero (2007)



where $Z$ is the charge and $R$ and $S$ are given by Eqs. 30 and 31, Eqs. 16–19 become

$$\begin{aligned} Y_1 &= -\ln \beta_1^* - \ln \gamma(H^+) + \ln \gamma(Hg^{2+}) + \ln a_{H_2O} - \ln \gamma(\text{Ideal}) \\ &= -\ln \beta_1 + \ln \gamma(HgOH^+) - \ln \gamma(\text{Ideal}) \end{aligned} \quad (33)$$

$$Y_1 = -\ln \beta_1 + 2m_{\mathrm{ClO_4}}\beta_{\mathrm{HgOH-ClO_4}} + 2m_{\mathrm{ClO_4}} f_1 \beta^{(1)}_{\mathrm{HgOH-ClO_4}} + 2m_{\mathrm{Na}} m_{\mathrm{ClO_4}} C_{\mathrm{HgOH-ClO_4}} \tag{34}$$

The value of $f_1$ is given by

$$f_1 = [1 - (1 + 2I^{0.5})\exp(-2I^{0.5})]/(2I)$$

The value of $Y_1$ can be determined from the known quantities $\{\beta_1^*,\ \gamma(\mathrm{H^+}), \gamma(\mathrm{Hg^{2+}}), a_{\mathrm{H_2O}}, \gamma\ (\mathrm{Ideal})$ in $\mathrm{NaClO_4}$ solutions$\}$ and can be used to determine $\beta_1$ and $\gamma(\mathrm{HgOH^+})$.

For the neutral species, a simpler equation can be used to determine the $\beta_2$ and $\gamma(\mathrm{Hg(OH)_2})$ from

$$Y_2 = -\ln \beta_2^* - 2\ln\gamma(\mathrm{H^+}) + \ln\gamma(\mathrm{Hg^{2+}}) + 2\ln a_{\mathrm{H_2O}} = -\ln\beta_2 + \ln\gamma(\mathrm{Hg(OH)_2}) \tag{35}$$

$$Y_2 = -\ln\beta_2 + 2m_{\mathrm{Na}}\lambda_{\mathrm{HgOH_2-Na}} + 2m_{\mathrm{ClO_4}}\lambda_{\mathrm{HgOH_2-ClO_4}} + m_{\mathrm{Na}} m_{\mathrm{ClO_4}} \zeta_{\mathrm{Hg(OH)_2-ClO_4-Na}} \tag{36}$$

The values of $\lambda_{\mathrm{N-M}}$ and $\lambda_{\mathrm{N-X}}$ account for interactions of the neutral species with cation M and anion X and $\zeta_{\mathrm{N-M-X}}$ with the interactions of N with M and X. The value of $\lambda_{\mathrm{HgOH_2-ClO_4}}$ is assumed to be zero for simplicity.

A nonlinear least-squares fit of the values of the left side of Eq. 36 as a function of $2m$ and $m^2$ yields the infinite dilution thermodynamic hydrolysis constant ($\beta_2$) and the Pitzer parameters $\lambda_{\mathrm{HgOH_2-Na}}$ and $\zeta_{\mathrm{Hg(OH)_2-ClO_4-Na}}$. The results are given in Table 4.

The values of $\gamma(\mathrm{Hg^{2+}})$ can be used to determine $\beta_3$ and ln $\gamma(\mathrm{Hg(OH)_3^-})$ from

$$\begin{aligned} Y_3 &= -\ln\beta_3^* - 3\ln\gamma(\mathrm{H^+}) + \ln\gamma(\mathrm{Hg^{2+}}) + 3\ln a_{\mathrm{H_2O}} - \ln\gamma(\mathrm{Ideal}) \\ &= -\ln\beta_3 + \ln\gamma(\mathrm{Hg(OH)_3^-}) - \ln\gamma(\mathrm{Ideal}) \end{aligned} \tag{37}$$

$$Y_3 = -\ln\beta_3 + 2m_{\mathrm{Na}}\beta^0_{\mathrm{Hg(OH)_3-ClO_4}} + 2m_{\mathrm{Na}} f_1 \beta^1_{\mathrm{Hg(OH)_3-ClO_4}} + 2m_{\mathrm{Na}} m_{\mathrm{ClO_4}} C_{\mathrm{Hg(OH)_3-ClO_4}} \tag{38}$$

Finally, the value of $\beta_{2,1}$ and $\gamma(\mathrm{Hg_2OH^{3+}})$ is determined from

$$\begin{aligned} Y_4 &= -\ln\beta_{2,1}^* - \ln\gamma(\mathrm{H^+}) + 2\ln\gamma(\mathrm{Hg^{2+}}) + \ln a_{\mathrm{H_2O}} - \ln\gamma(\mathrm{Ideal}) \\ &= -\ln\beta_{2,1} + \ln\gamma(\mathrm{Hg_2OH^{3+}}) - \ln\gamma(\mathrm{Ideal}) \end{aligned} \tag{39}$$

$$Y_4 = -\ln\beta_{2,1} + 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\mathrm{Hg_2OH-ClO_4}} + 2m_{\mathrm{ClO_4}} f_1 \beta^{(1)}_{\mathrm{Hg_2OH-ClO_4}} + 2m_{\mathrm{Na}} m_{\mathrm{ClO_4}} C_{\mathrm{Hg_2OH-ClO_4}} \tag{40}$$

The concentration dependency of ln $\beta_i + \ln\gamma(_i)$ are determined from Eqs. 20–25. This results in the values of $\beta_i$ and the Pitzer coefficients $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$ and $C_{\mathrm{MX}}$ for all of the ionic species and $\lambda_{ij}$ and $\zeta_{ijk}$ for the neutral species. These coefficients and log $\beta_i$ are tabulated in Table 4 along with the standard error of the fits in log $\beta_i$. Plots of the $Y_{\mathrm{i}}$ values for Eqs. 33–40 versus molality for $\mathrm{HgOH}_n^{(2-n)+}$ ($n$ = 1, 2, 4) in $\mathrm{NaClO_4}$ at 25°C are shown in Fig. 2. The $\mathrm{Hg(OH)_3^-}$ species was not analyzed due to the scarcity of experimental data for this complex.

**Table 4** Summaries of the hydrolysis constants for $Hg(OH)_n^{(2-n)+} (n = 1, 2)$, stability constants for $HgCl_n^{(2-n)+} (n = 1, 2, 3, 4)$ and for the HgOHCl complex together with Pitzer parameters for mercury hydrolysis and chloride complexes in $NaClO_4$ media at 25°C

| Compound | Log $\beta_i$ | $\beta_{MX}^{(0)}$ | $\beta_{MX}^{(1)}$ | $C_{MX}$ |
|---|---|---|---|---|
| $HgOH^+$ | −3.39 ± 0.08 | $\beta^0_{HgOH-ClO_4} = 0.0888$ | $\beta^1_{HgOH-ClO_4} = 0.3422$ | $C_{HgOH-ClO_4} = -0.0490$ |
| $Hg_2OH^{3+}$ | −3.33 | $\beta^1_{Hg_2OH-ClO_4} = 0.5365$ | $\beta^1_{HgOH-ClO_4} = 3.3639$ | $C_{HgOH-ClO_4} = -0.0190$ |
| $HgCl^+$ | 7.07 ± 0.09 | $\beta^0_{HgCl-ClO_4} = -0.07319$ | | $C_{HgCl-ClO_4} = 0.0277$ |
| $HgCl_2$ | 13.62 ± 0.15 | $\lambda_{HgCl2-Na} = -0.6500$ | $\zeta_{HgCl_2-ClO_4-Na} = 0.2267$ | |
| $HgCl_3^-$ | 14.55 ± 0.13 | $\beta^0_{HgCl3-Na} = -0.3972$ | | $C_{HgCl3\text{-}Na} = 0.0772$ |
| $HgCl_4^{2-}$ | 15.74 ± 0.12 | $\beta^0_{HgCl4-Na} = -0.3489$ | | $C_{HgCl4\text{-}Na} = 0.0576$ |
| | | $\lambda_{HgOHCl-Na}$ | $\zeta_{HgOHCl-ClO_4-Na}$ | |
| $Hg(OH)_2$ | −5.92 ± 0.03 | $\lambda_{Hg(OH)2-Na} = -0.0235$ | $\zeta_{Hg(OH)_2-ClO_4-Na} = -0.1492$ | |
| $HgOHCl^a$ (Eq. 47) | −9.71 ± 0.08 | $\lambda_{HgOHCl-Na} = -0.1957$ | $\zeta_{HgOHCl-ClO_4-Na} = 0$ | |
| $HgOHCl^a$ (Eq. 46) | 4.24 ± 0.11 | $\lambda_{HgOHCl-Na} = -0.1957$ | $\zeta_{HgOHCl-ClO_4-Na} = 0$ | |
| $HgCl^{+b}$ (Eq. 45) | 0.50 ± 0.03 | | | |

[a] Values of $\lambda_{HgOHCl-Na}$ determined for Eq. 47 were used to compute log $\beta$ for reaction (46)

[b] $\beta^0_{HgCl-ClO_4}$ and $C_{HgCl-ClO_4}$ from Eq. 41 were used to estimate log $\beta$ for reaction (45)

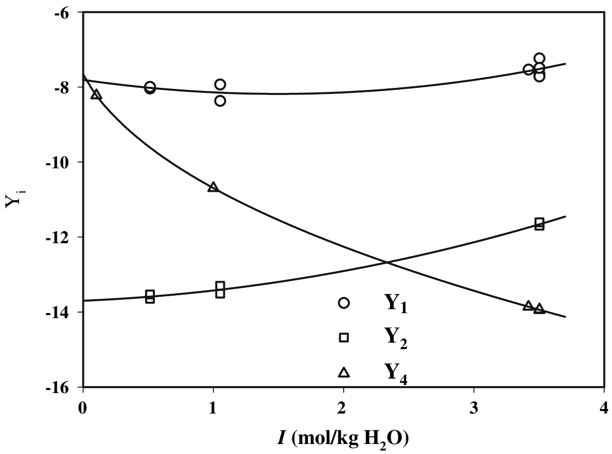


**Fig. 2** Values of $Y_i$ determined from Eqs. 33, 35 and 39 as a function of the ionic strength of $NaClO_4$ at 25°C. ($Y_1$ for $HgOH^+$, $Y_2$ for $Hg(OH)_2$, and $Y_4$ for $Hg_2OH^{3+}$ species). $Y_3$ for $Hg(OH)_3^-$ could not be determined at the present time due to a scarcity of data

### 2.2 Formation of Chloride Complexes

The chloro-complex equilibria for Hg are given by

$$Hg^{2+} + Cl^- = HgCl^+ \qquad \beta_1^* = [HgCl^+]/[Hg^{2+}][Cl^-] \tag{41}$$

$$Hg^{2+} + 2Cl^- = HgCl_2 \qquad \beta_2^* = [HgCl_2]/[Hg^{2+}][Cl^-]^2 \tag{42}$$

$$Hg^{2+} + 3Cl^- = HgCl_3^- \qquad \beta_3^* = [HgCl_3^-]/[Hg^{2+}][Cl^-]^3 \tag{43}$$

$$Hg^{2+} + 4Cl^- = HgCl_4^{2-} \qquad \beta_4^* = [HgCl_4^{2-}]/[H^*][Cl^-]^4 \tag{44}$$

$$Hg^{2+} + HgCl_2 = 2HgCl^+ \qquad \beta_5^* = [HgCl^+]^2/[Hg^{2+}][HgCl_2] \tag{45}$$

$$Hg^{2+} + Cl^- + H_2O = HgOHCl + H^+ \qquad \beta_6^* = [HgOHCl][H^+]/[Hg^{2+}][Cl^-] \tag{46}$$

$$HgCl_2 + H_2O = HgOHCl + Cl^- + H^+ \qquad \beta_7^* = [HgOHCl][Cl^-][H^+]/[HgCl_2] \tag{47}$$

The measured values of $\beta^* i$ are related to the thermodynamic values by

$$\ln\beta_1 = \ln\beta_1^* + \ln\gamma(HgCl^+) - \ln\gamma(Cl^-) - \ln\gamma(Hg^{2+}) \tag{48}$$

$$\ln\beta_2 = \ln\beta_2^* + \ln\gamma(HgCl_2) - 2\ln\gamma(Cl^-) - \ln\gamma(Hg^{2+}) \tag{49}$$

$$\ln\beta_3 = \ln\beta_3^* + \ln\gamma(HgCl_3^-) - 3\ln\gamma(Cl^-) - \ln\gamma(Hg^{2+}) \tag{50}$$

$$\ln\beta_4 = \ln\beta_4^* + \ln\gamma(HgCl_4^{2-}) - 4\ln\gamma(Cl^-) - \ln\gamma(Hg^{2+}) \tag{51}$$

$$\ln\beta_5 = \ln\beta_5^* + 2\ln\gamma(HgCl^+) - \ln\gamma(HgCl_2) - \ln\gamma(Hg^{2+}) \tag{52}$$

$$\ln\beta_6 = \ln\beta_6^* + \ln\gamma(HgOHCl) + \ln\gamma(H^+) - \ln\gamma(Cl^-) - \ln\gamma(Hg^{2+}) - \ln a_{H_2O} \tag{53}$$

$$\ln\beta_7 = \ln\beta_7^* + \ln\gamma(HgOHCl) + \ln\gamma(Cl^-) + \ln\gamma(H^+) - \ln\gamma(HgCl_2) - \ln a_{H_2O} \tag{54}$$

Solving for the unknown activity coefficients give

$$-\ln\beta_1 + \ln\gamma(\mathrm{HgCl}^+) = -\ln\beta_1^* + \ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) \tag{55}$$

$$-\ln\beta_2 + \ln\gamma(\mathrm{HgCl}_2) = -\ln\beta_2^* + 2\ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) \tag{56}$$

$$-\ln\beta_3 + \ln\gamma(\mathrm{HgCl}_3^-) = -\ln\beta_3^* + 3\ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) \tag{57}$$

$$-\ln\beta_4 + \ln\gamma(\mathrm{HgCl}_4^{2-}) = -\ln\beta_4^* + 4\ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) \tag{58}$$

$$-\ln\beta_5 + 2\ln\gamma(\mathrm{HgCl}^+) - \ln\gamma(\mathrm{HgCl}_2) = -\ln\beta_5^* + \ln\gamma(\mathrm{Hg}^{2+}) \tag{59}$$

$$-\ln\beta_6 + \ln\gamma(\mathrm{HgOHCl}) = -\ln\beta_6^* + \ln\gamma(\mathrm{Cl}^-) - \ln\gamma(\mathrm{H}^+) + \ln\gamma(\mathrm{Hg}^{2+}) + \ln a_{\mathrm{H_2O}} \tag{60}$$

$$-\ln\beta_7 + \ln\gamma(\mathrm{HgOHCl}) = -\ln\beta_7^* - \ln\gamma(\mathrm{Cl}^-) - \ln\gamma(\mathrm{H}^+) + \ln\gamma(\mathrm{HgCl}_2) + \ln a_{\mathrm{H_2O}} \tag{61}$$

The trace activity coefficients of $\mathrm{H}^+$ (Eq. 20), $\mathrm{Cl}^-$ and mercury-chloro complexes and activity of water (Eq. 13) in a $\mathrm{NaClO_4}$ solution can be calculated from the Pitzer equations (Pitzer 1991) as formulated by Millero and Pierrot (2002). We have

$$\begin{aligned}\ln\gamma(\mathrm{Cl}^-) = {} & f^\gamma + 2m_{\mathrm{Na}}(B_{\mathrm{NaCl}} + EC_{\mathrm{NaCl}}) + R + S \\ & + m_{\mathrm{ClO_4}}(2\Theta_{\mathrm{Cl-ClO_4}} + m_{\mathrm{Na}}\Psi_{\mathrm{Cl-Na-ClO_4}})\end{aligned} \tag{62}$$

$$\ln\gamma(\mathrm{Hg}^{2+}) = 4f^\gamma + 2m_{\mathrm{ClO_4}}(B_{\mathrm{HgClO_4}} + EC_{\mathrm{HgClO_4}}) + 4R + 2S \tag{63}$$

$$\ln\gamma(\mathrm{HgCl}^+) = f^\gamma + 2m_{\mathrm{ClO_4}}(B_{\mathrm{HgCl-ClO_4}} + EC_{\mathrm{HgCl-ClO_4}}) + R + S \tag{64}$$

$$\ln\gamma(\mathrm{HgCl}_3^-) = f^\gamma + 2m_{\mathrm{Na}}(B_{\mathrm{Na-HgCl_3}} + EC_{\mathrm{Na-HgCl_3}}) + R + S \tag{65}$$

$$\ln\gamma(\mathrm{HgCl}_4^{2-}) = f^\gamma + 2m_{\mathrm{Na}}(B_{\mathrm{Na-HgCl4}} + EC_{\mathrm{Na-HgCl4}}) + 4R + 2S \tag{66}$$

$$\ln\gamma(\mathrm{HgCl}_2) = 2m_{\mathrm{Na}}\lambda_{\mathrm{HgCl_2-Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\mathrm{HgCl_2-ClO_4-Na}} \tag{67}$$

$$\ln\gamma(\mathrm{HgOHCl}) = 2m_{\mathrm{Na}}\lambda_{\mathrm{HgOHCl-Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\mathrm{HgOHCl-ClO_4-Na}} \tag{68}$$

The value of $\lambda_{\mathrm{HgCl_2-ClO_4}}$ and $\lambda_{\mathrm{HgOHCl-ClO_4}}$ are assumed to be zero (Millero and Pierrot 2002).

Following the same assumption for the hydrolysis constants, the activity coefficient for $\mathrm{Hg(ClO_4)_2}$ species was assumed that for $\mathrm{Pb(ClO_4)_2}$ from Pitzer (1979). Eqs. 55–60 become

$$\begin{aligned}Y_1 & = -\ln\beta_1^* + \ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) - \ln\gamma(\mathrm{Ideal}) \\ & = -\ln\beta_1 + \ln\gamma(\mathrm{HgCl}^+) - \ln\gamma(\mathrm{Ideal})\end{aligned} \tag{69}$$

$$Y_1 = -\ln \mathrm{K}_1 + 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\mathrm{HgCl-ClO_4}} + 2m_{\mathrm{ClO_4}}f_1\beta^{(1)}_{\mathrm{HgCl-ClO_4}} + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{HgCl-ClO_4}} \tag{70}$$

The same treatment is applicable for the determination of the formation constants and activity coefficients for the other charged species

$$\begin{aligned}Y_3 & = -\ln\beta_3^* + 3\ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) - \ln\gamma(\mathrm{Ideal}) \\ & = -\ln\beta_3 + \ln\gamma(\mathrm{HgCl}_3^-) - \ln\gamma(\mathrm{Ideal})\end{aligned} \tag{71}$$

$$Y_3 = -\ln\beta_3 + 2m_{\mathrm{Na}}\beta^{(0)}_{\mathrm{HgCl_3-Na}} + 2m_{\mathrm{Na}}f_1\beta^{(1)}_{\mathrm{HgCl_3-Na}} + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{HgCl_3-Na}} \tag{72}$$

$$\begin{aligned} Y_4 &= -\ln\beta_4^* + 4\ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) - \ln\gamma(\mathrm{Ideal}) \\ &= -\ln\beta_4 + \ln\gamma(\mathrm{HgCl}_4^{2-}) - \ln\gamma(\mathrm{Ideal}) \end{aligned} \quad (73)$$

$$Y_4 = -\ln\beta_4 + 2m_{\mathrm{Na}}\beta^{(0)}_{\mathrm{HgCl_4-Na}} + 2m_{\mathrm{Na}}f_1\beta^{(1)}_{\mathrm{HgCl_4-Na}} + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{HgCl_4-Na}} \quad (74)$$

For the neutral species, a simpler equation can be used to determine the $\beta_2$ and $\beta_7$ and $\gamma(\mathrm{HgCl_2})$ and $\gamma(\mathrm{HgOHCl})$ from

$$Y_2 = -\ln\beta_2^* + 2\ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Hg}^{2+}) = -\ln\beta_2 + \ln\gamma(\mathrm{HgCl_2}) \quad (75)$$

$$Y_2 = -\ln\beta_2 + 2m_{\mathrm{Na}}\lambda_{\mathrm{HgCl-Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\mathrm{Na-ClO_4-HgCl_2}} \quad (76)$$

$$\begin{aligned} Y_7 &= -\ln\beta_6^* - \ln\gamma(\mathrm{Cl}^-) - \ln\gamma(\mathrm{H}^+) + \ln\gamma(\mathrm{HgCl_2}) + \ln a_{\mathrm{H_2O}} \\ &= -\ln\beta_7 + \ln\gamma(\mathrm{HgOHCl}) \end{aligned} \quad (77)$$

$$Y_7 = -\ln\beta_7 + 2m_{\mathrm{Na}}\lambda_{\mathrm{HgOHCl-Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\mathrm{HgOHCl-ClO_4-Na}} \quad (78)$$

The values of $\gamma(\mathrm{HgCl_2})$, $\gamma(\mathrm{HgCl}^-)$ and $\gamma$ (HgOHCl) can be used to determine $\beta_5$ and $\beta_6$ for reactions (45) and (46). According to Eq. 51, the values of $\log\beta_5$ for reaction (45) were computed to be 0.50 ± 0.03 (Table 4). In order to be internally consistent, the experimental value of log $\beta^*$ for reaction (45) at $I = 3.503$ is 0.57 ± 0.01 instead of the reported 0.17 ± 0.01 (Powell et al. 2005).

The concentration dependency of $-\ln\beta_i + \ln\gamma(_i)$ is determined from Eqs. 62–68. This results in the values of $\beta_i$ and the Pitzer coefficients $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$ and $C_{\mathrm{MX}}$ for all of the ionic species and $\lambda_{ij}$ and $\zeta_{ijk}$ for the neutral species. The experimental values are well fitted by considering only the $\beta^{(0)}_{\mathrm{MX}}$ and the $C_{\mathrm{MX}}$ terms. These coefficients and ln $\beta_i$ are tabulated in Table 4 along with the standard error of the fits in $\log\beta_i$. Plots of the $Y_i$ values determined for each chloro complex versus molality in $\mathrm{NaClO_4}$ media are shown in Fig. 3. The reliability of these parameters can be demonstrated by comparing the measured and calculated values of $\beta^*$ for the formation of $\mathrm{Hg}_i\mathrm{Cl}_j^{(2-n)+}$ complexes. The differences of log $\beta_n^*$ are shown in Fig. 4. The average deviation for all the seven constants is ±0.01.

The scarcity of data for the reactions (46) and (47) as a function of concentration makes it impossible to compute the value of $\zeta_{\mathrm{HgOHCl-ClO_4-Na}}$, being fitted to the Pitzer coefficient

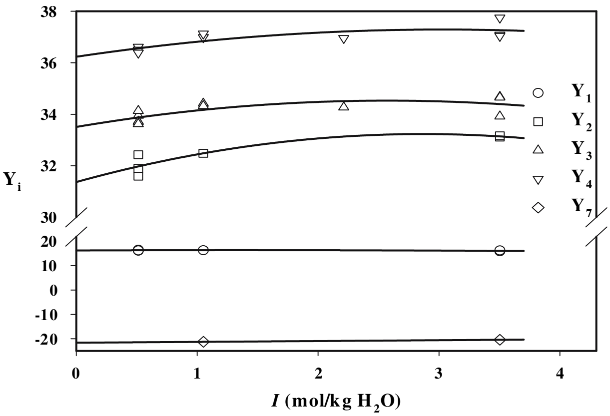


**Fig. 3** Values of $Y_i$ determined following Eqs. 69, 71, 73, 75 and 77 as a function of the ionic strength of $\mathrm{NaClO_4}$ at 25°C. ($Y_1$ for $\mathrm{HgCl}^+$, $Y_2$ for $\mathrm{HgCl_2}$, $Y_3$ for $\mathrm{HgCl_3^-}$ and $Y_7$ for HgOHCl species)

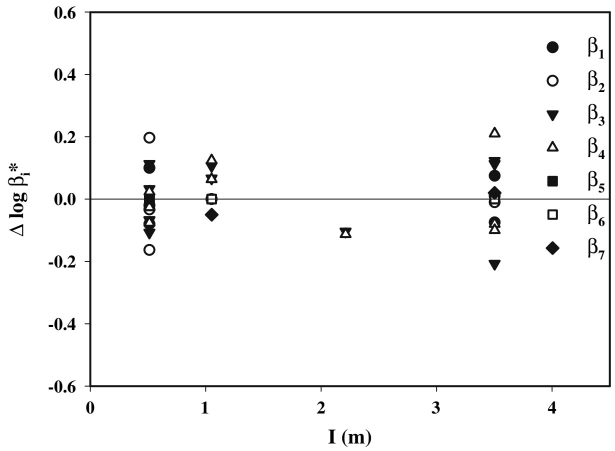


**Fig. 4** The differences between the measured and fitted values of log $\beta_n^*$ for $HgOH_mCl_n^{(2-n-m)+}$ species as a function of ionic strength at 25°C in $NaClO_4$ media

$\lambda_{HgOHCl-Na}$. However, a value of log $\beta^*$ for reaction (46) at 1.052 m $NaClO_4$ of 3.67 was determined by Ciavatta and Grimaldi (1968) and reported by Baes and Mesmer (1976). The inclusion of this value allowed us to compute log $\beta_6$ for reaction (46) of 4.17 and a value of $\lambda_{HgOHCl-Na} = -0.2432$, similar to the values computed from reaction (47) applying Eqs. 77 and 78 (Table 4). With those data, log $\beta_7$ for reaction (47) can be computed from Eq. 61 to be −9.71, similar to the value determined (Table 4) using the data for the formation of HgClOH (Table 2) for reaction (47), confirming the consistency of our calculations.

Table 5 compares the thermodynamic constants determined using the Pitzer equation with those tabulated by Powell et al. (2005). Our results are in reasonable agreement with the extrapolations made by Powell et al. (2005). The Pitzer parameters provided in this study can be used to calculate the hydrolysis and chloride complexes of Hg(II) in $NaClO_4$ media from ionic strengths from 0 to 3.5 m at 25°C.

**Table 5** A comparison of thermodynamic constants (log $\beta_i$) ($I$ = 1, 2, …, $n$) extrapolated using Pitzer equations in this study with data provided in Powell et al. (2005) at 25°C

| | Our study | Powell et al. (2005) |
|---|---|---|
| Log $\beta_{HgOH}$ | −3.39 ± 0.08 | −3.40 ± 0.08 |
| Log $\beta_{Hg(OH)_2}$ | −5.92 ± 0.03 | −5.98 ± 0.06 |
| Log $\beta_{Hg_2(OH)}$ | −3.33 ± 0.03 | −3.33 ± 0.03[a] |
| Log $\beta_{HgCl}$ | 7.07 ± 0.09 | 7.31 ± 0.04 |
| Log $\beta_{HgCl_2}$ | 13.62 ± 0.15 | 14.00 ± 0.09 |
| Log $\beta_{HgCl_3}$ | 14.55 ± 0.13 | 14.92 ± 0.09 |
| Log $\beta_{HgCl_4}$ | 15.74 ± 0.12 | 15.51 ± 0.12 |
| Log $\beta_{HgOHCl}$ | −9.71 ± 0.08 | −9.92 ± 0.02 |
| Log $\beta_{HgOHCl}$ | 4.24 ± 0.11 | 4.27 ± 0.35 |
| Log $\beta_{HgOH}$ | 0.50 ± 0.03 | 0.61 ± 0.12 |

[a] Baes and Mesmer (1976)

## 2.3 Effect of Temperature on the Activity Coefficients and Thermodynamic Constants

Luo and Millero (2007) provided stability constants for the Pb(II)-chloride systems over a wide range of ionic strength (0–6 m) and temperature (15–45°C). Since the equilibrium constants and activity coefficients of $\mathrm{HgCl}_n^{(2-n)+}$ at different ionic strengths are in reasonable agreement with values for Pb(II), we have assumed that the temperature dependence of the Pitzer parameters for lead chloride complexes can be used for the Hg(II) chloride complexes. We realize that this is highly speculative, but feel that is the best that can be done at the present time. New experimental measurements for the effect of temperature on the Hg(II) chloride complexes are needed to provide more reliable estimates. In order to obtain expressions for the effect of temperature on the Pitzer parameter for Pb(II) chloride complexes, we have reanalyzed the published data of Luo and Millero (Table 1, 2007).

**Table 6** Fitting parameters for the $\mathrm{PbCl}_n^{(2-n)+}$stability constants as a function of temperature (Eq. 83) considering data from Luo and Millero (2007) for the 15–45°C range and together with results from Seward (1984) for the range 15–300°C

| Stability constant | $T$ (°C) | $A_i$ | $10^{-3} \cdot B_i$ | $C_i$ | Std. | $A_i$ for $\mathrm{HgCl}_n^{(2-n)+}$ |
|---|---|---|---|---|---|---|
| $\log \beta_1$ | 15–45 | −152.3 | 6.47 | 53.37 | ±0.01 | −146.7 |
| | 15–300 | −104.3 | 4.90 | 36.09 | ±0.07 | −98.7 |
| $\log \beta_2$ | 15–45 | −3.50 | −0.51 | 2.90 | ±0.01 | 8.14 |
| | 15–300 | −160.1 | 7.28 | 55.66 | ±0.13 | −148.5 |
| $\log \beta_3$ | 15–45 | −94.46 | 3.69 | 33.91 | ±0.01 | −81.7 |
| | 15–300 | −183.2 | 8.29 | 63.52 | ±0.32 | −170.4 |

$A_i$ values for $\mathrm{HgCl}_n^{(2-n)+}$ in Eq. 83 is also included

**Table 7** Pitzer parameters for Pb(II) chloride complexes as a function of temperature according to Eq. 84 in the range 15–45°C and corresponding values for Hg(II) chloride complexes

| Complex | Parameters | $A_i$ | $B_i$ | $C$ |
|---|---|---|---|---|
| $\mathrm{PbCl}^+$ | $\beta^{(0)}_{\mathrm{PbCl-ClO_4}}$ | 0.097<br>$-0.109^a$ | 10.93 | |
| | $C_{\mathrm{PbCl\text{-}ClO4}}$ | 0.023<br>$0.055^a$ | −8.10 | |
| | $\beta^{(0)}_{\mathrm{PbCl-Cl}}$ | $-4.93 \cdot 10^3$ | $2.25 \cdot 10^5$ | $1.69 \cdot 10^3$ |
| | $C_{\mathrm{PbCl\text{-}Cl}}$ | $1.26 \cdot 10^4$ | $-5.75 \cdot 10^5$ | $-4.34 \cdot 10^3$ |
| $\mathrm{PbCl_2}$ | $\lambda_{\mathrm{PbCl_2-ClO_4}}$ | −2.58 | 805 | |
| | $\lambda_{\mathrm{PbCl_2-Na}}$ | $-3.55 \cdot 10^3$<br>$-3.55 \cdot 10^{3a}$ | $1.57 \cdot 10^5$ | $1.22 \cdot 10^3$ |
| | $\zeta_{\mathrm{PbCl_2-ClO_4-Na}}$ | 0.015<br>$0.211^a$ | 4.82 | |
| | $\zeta_{\mathrm{PbCl_2-Cl-Na}}$ | $1.09 \cdot 10^4$ | $-4.84 \cdot 10^5$ | $-3.74 \cdot 10^3$ |
| $\mathrm{PbCl_3^-}$ | $\beta^{(0)}_{\mathrm{PbCl_3-Na}}$ | −450.3<br>$-450.1^a$ | $2.02 \cdot 10^4$ | −154.6 |
| | $C_{\mathrm{PbCl_3-Na}}$ | −89.3<br>$-89.2^a$ | $4.00 \cdot 10^3$ | 30.6 |

[a] Value determined for $\mathrm{HgCl}_n^{(2-n)+}$ in Eq. 84

The equations needed to determine the activity coefficient and thermodynamic constants for the Pb(II) complexes in a NaCl–NaClO$_4$ media are given by Luo and Millero (2007).

The value of the activity coefficient for the PbCl$^+$ complex in a NaCl–NaClO$_4$ media is given by

$$\begin{aligned}\ln\gamma(\mathrm{PbCl}^+) &= f^\gamma + 2m_{\mathrm{ClO}_4}\left(B_{\mathrm{PbCl-ClO}_4} + m_{\mathrm{ClO}_4}C_{\mathrm{PbCl-ClO}_4}\right)\\ &\quad + 2m_{\mathrm{Cl}}\left(B_{\mathrm{PbCl-Cl}} + m_{\mathrm{Cl}}C_{\mathrm{PbCl-Cl}}\right) + R + S \end{aligned} \tag{79}$$

where $R$ and $S$ are the media terms

$$R = m_{\mathrm{Na}}m_{\mathrm{ClO}_4}B'_{\mathrm{NaClO}_4} + m_{\mathrm{Na}}m_{\mathrm{Cl}}B'_{\mathrm{NaCl}} \tag{80}$$

$$S = m_{\mathrm{Na}}m_{\mathrm{ClO}_4}C_{\mathrm{NaClO}_4} + m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}} \tag{81}$$

The rearrangement of Eq. 79 as shown in Eq. 70 gives

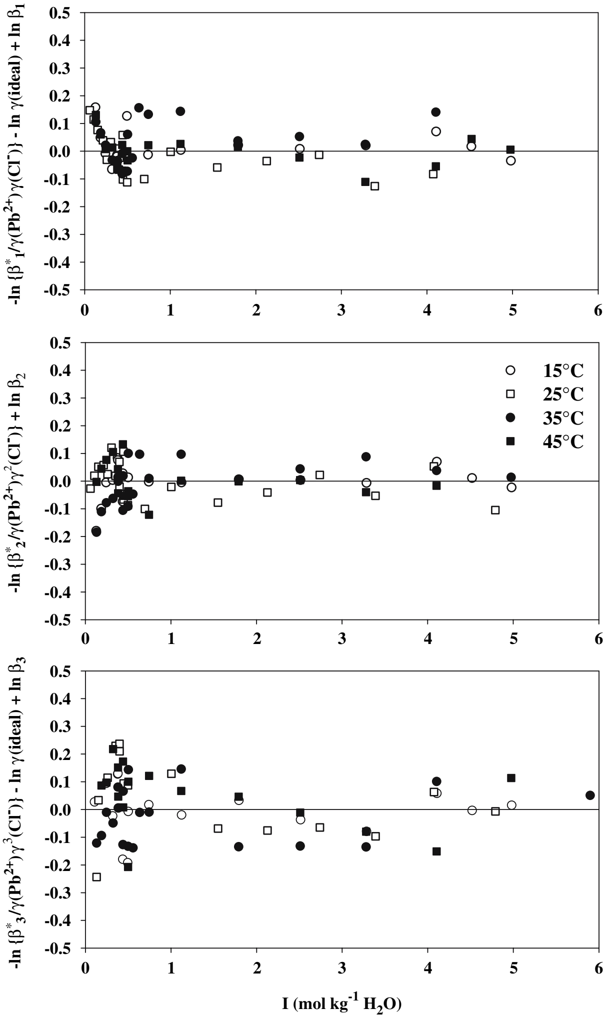


**Fig. 5** The differences between the measured and fitted values of the left side of Eq. 82 for PbCl$^+$ complex and for PbCl$_2$ and PbCl$_3^+$ complexes versus molality in NaClO$_4$–NaCl media at 15, 25, 35 and 45°C

$$\begin{aligned} Y_{\mathrm{PbCl}} - \ln\gamma(\mathrm{Ideal}) + \ln\beta_{\mathrm{PbCl}} &= -\ln\beta_1^* + \ln\gamma(\mathrm{Cl}^-) + \ln\gamma(\mathrm{Pb}^{2+}) - \ln\gamma(\mathrm{Ideal}) + \ln\beta_{\mathrm{PbCl}} \\ &= 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\mathrm{PbCl-ClO_4}} + 2\mathrm{m}_{\mathrm{ClO_4}}\beta^{(1)}_{\mathrm{PbCl-ClO_4}}f_1 + 2m^2_{\mathrm{ClO_4}}C_{\mathrm{PbCl-ClO_4}} \\ &\quad + 2m_{\mathrm{Cl}}\beta^{(0)}_{\mathrm{PbCl-Cl}} + 2m_{\mathrm{Cl}}\beta^{(1)}_{\mathrm{PbCl-Cl}}f_1 + 2m^2_{\mathrm{Cl}}C_{\mathrm{PbCl-Cl}} \end{aligned} \tag{82}$$

We have used these equations to determine the effect of temperature on the thermodynamic constants and Pitzer parameters for all measurements.

Our new extrapolations, for the thermodynamic values derived from Luo and Millero (2007) together with results from Seward (1984) for the range 25–300°C, have been fitted to a general equation

$$\log\beta_i = A_i + B_i/T + C_i\log T \tag{83}$$

The fitting parameters for the $\mathrm{PbCl}_n^{(2-n)+}$ stability constants are shown in Table 6. If we assume that the temperature dependence for Hg-Cl complexes are the same as for Pb(II), values for the $A_i$ term in Eq. 83 for $\mathrm{HgCl}^+$, $\mathrm{HgCl_2}$ and $\mathrm{HgCl}_3^-$ complexes are −146.7, 8.14 and −81.73, respectively, in the temperature range 15–45°C (Table 6).

These equations and parameters in Table 6 fit the thermodynamic constants for mercury complexes with $\mathrm{Cl}^-$ at 25°C and should predict reliable stability constants in the to 300°C range.

The experimental values for the $\mathrm{PbCl}^+$ Pitzer parameters as a function of temperature have been fit to equations of the form

$$\mathrm{Log}\, Y_{\mathrm{MX}} = A + B/T + C\log T \tag{84}$$

The coefficients $A$, $B$ and $C$ for the Pitzer parameters for the various ion pairs are given in Table 7. The coefficients needed to fit the Pitzer parameters were determined using an $F$-test. The reliability of these parameters describing the temperature effects on the Pitzer coefficients for the three Pb(II)-chloride complexes can be demonstrated by comparing the measured and calculated values of the left-hand side of Eq. 82. The differences are shown in Fig. 5. The average deviations are ±0.07, ±0.07 and ±0.11, respectively for the temperature range 15–45°C.

**Acknowledgements** We acknowledge the support of the Oceanographic Section of the National Science Foundation, the National Oceanic and Atmospheric Administration and the Spanish Ministerio de Educacion y Ciencia project CTM2006-09857. MGD wishes to acknowledge the support of the Ministerio de Educacion y Ciencia (PR2007-0163) for his stay in the USA. JMSC acknowledges the support of the Canary Islands Government for her stay in the USA.

## References

Baes CF Jr, Mesmer RE (1976) The hydrolysis of cations. Wiley-Interscience, New-York

Benoit JM, Gilmour CC, Mason RP, Heyes A (1999) Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters. Environ Sci Technol 33:951–957

Ciavatta L, Grimaldi M (1968) The hydrolysis of mercury(II) chloride, $\mathrm{HgCl_2}$. J Inorg Nucl Chem 30:563–581

Fitzgerald WF, Lamborg CH, Hammerschmidt CR (2007) Marine biogeochemical cycling of mercury. Chem Rev 107:641–662

Grenthe I, Plyasunov AV, Spahiu K (1997) Estimations of medium effects on thermodynamic data. In: Grenthe I, Puigdomenech I (eds) Modelling in aqueous chemistry. Organization for Economic Cooperation and Development, Paris, pp 325–426

Lamborg CH, Tseng CM, Fitzgerald WF, Balcom PH, Hammerschmidt CR (2003) Determination of the mercury complexation characteristics of dissolved organic matter in natural waters with "reducible Hg" titrations. Environ Sci Technol 37:3316–3322

Luo Y, Millero FJ (2007) Stability constant for the formation of lead chloride complexes as a function of temperature and ionic strength. Geochim Cosmochim Acta 71:326–334

Millero FJ, Pierrot D (2002) Speciation of metals in natural waters. In: Gianguzza A, Pellizzetti E, Sammartano S (eds) Chemistry of marine water and sediments. Springer-Verlag, Berlin, pp 193–220

Møller N (1988) The prediction of mineral solubilities in natural waters: a chemical equilibrium model for the Na–Ca–Cl–$SO_4$–$H_2O$ system, to high temperature and concentration. Geochim Cosmochim Acta 52:821–837

Pitzer KS (1979) Theory: ion interaction approach. In: Pytkowicz RM (ed) Activity coefficients in electrolyte solutions, vol I. CRC Press, Boca Raton, pp 157–208

Pitzer KS (1991) Ion interaction approach: theory and data correlation. In: Pitzer KS (ed) Activity coefficients in electrolyte solutions, 2nd ed. CRC Press, Boca Raton, pp 75–153

Powell KJ, Brown PL, Byrne RH, Gajda T, Glenn H, Staffan S, Wanner H (2005) Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: the $Hg^{2+}$-$Cl^-$, $OH^-$, $CO_3^{2-}$, $SO_4^{2-}$, and $PO_4^{3-}$ aqueous systems. Pure Appl Chem 77:739–800

Seward TM (1984) The formation of lead (II) chloride complexes to 300°C: a spectrophotometric study. Geochim Cosmochim Acta 48:121–134

Von Burg R, Greenwood MR (1991) Mercury. In: Merian E (ed) Metals and their compounds in the environment: occurrence, analysis, and biological relevance. VCH, Weinheim, pp 1045–1088