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The Examination of the Activity Coefficients of Cu(II) Complexes with OH^- and Cl^- in $NaClO_4$ Using Pitzer Equations: Application to Other Divalent Cations

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Abstract The stability constants for the hydrolysis of Cu(II) and formation of chloride complexes in $NaClO_4$ solution, at 25 °C, have been examined using the Pitzer equations. The calculated activity coefficients of $CuOH^+$, $Cu(OH)_2$, $Cu_2(OH)^{3+}$, $Cu_2(OH)_2^{2+}$, $CuCl^+$ and $CuCl_2$ have been used to determine the Pitzer parameter ($\beta_i^{(0)}$, $\beta_i^{(1)}$, and C_i) for these complexes. These parameters yield values for the hydrolysis constants ($\log_{10}\beta_1^*$, $\log_{10}\beta_2^*$, $\log_{10}\beta_{2,1}^*$ and $\log_{10}\beta_{2,2}^*$) and the formation of the chloride complexes ($\log_{10}\beta_{\mathrm{CuCl}}^*$ and $\log_{10}\beta_{\mathrm{CuCl_2}}^*$) that agree with the experimental measurements, respectively to ±0.01, ±0.02, ±0.03, ±0.06, ±0.03 and ±0.07.

The stability constants for the hydrolysis and chloride complexes of Cu(II) were found to be related to those of other divalent metals over a wide range of ionic strength. This has allowed us to use the calculated Pitzer parameters for copper complexes to model the stability constants and activity coefficients of hydroxide and chloride complexes of other divalent metals. The applicability of the Pitzer Cu(II) model to the ionic strength dependence of hydrolysis of zinc and cadmium is presented. The resulting thermodynamic hydroxide and chloride constants for zinc are $\log_{10}\beta_{\mathrm{ZnOH^+}} = -9.04 \pm 0.04$ and $\log_{10}\beta_{\mathrm{Zn(OH)_2}} = -16.90 \pm 0.02$. For cadmium the thermodynamic hydrolysis constants are $\log_{10}\beta_{\mathrm{CdOH^+}} = -10.24 \pm 0.05$ and $\log_{10}\beta_{\mathrm{Cd(OH)_2}} = -20.42 \pm 0.07$. The Cu(II) model allows one to determine the stability of other divalent metal complexes over a wide range of concentration when little experimental data are available. More reliable stepwise stability constants for divalent metals are needed to test the linearity found for the chloro complexes.

Keywords Copper complexes · Chloride complexes · Cu(II) hydrolysis · Stability complexes

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1 Introduction

In the aquatic environment, copper is principally present as Cu(II) and is complexed with inorganic and organic ligands. The bioavailability and potential toxicity of copper is directly related to its physico-chemical speciation [1]. Although copper is an essential biological trace metal in natural waters [2–6], free copper is toxic to many organisms at high concentrations [1] whereas the complexed copper is nontoxic. Algae in the marine environment can excrete dissolved organic substances which complex Cu^{2+} and decrease the free concentration of Cu^{2+} [3, 7–11].

In surface waters, the formation of Cu(I) can occur due to the production of H_2O_2 that reduces Cu(II) [12, 13]. The production of H_2O_2 occurs due to the photochemical reaction of organic matter [14, 15]. The Cu(I) is stabilized in seawater due to the formation of Cu^+ chloro complexes that have slower oxidation rates with O_2 and H_2O_2 than free Cu^+ [16, 17].

Knowledge of chemical speciation of copper, which is mainly controlled by the complexation with organic and inorganic ligands, is essential to understand its behavior in natural waters. Speciation models require a reliable set of stability constants to describe the copper equilibria in solutions with low and moderate ionic strength where the ionic interactions are very important. To understand the complexation of Cu^{2+} with organic and inorganic ligands in natural waters, one needs reliable stability constants. In this paper, we use the Pitzer equations [18] to examine the activity coefficients of copper(II) complexes with hydroxide and chloride ions. Pitzer parameters for the Cu(II) complexes and thermodynamic complexation constants (β_i) have been determined.

The aim of this work is to provide divalent metal Pitzer parameters that can be used to estimate the activity coefficients of these complexes and other divalent metals. As shown in Figs. 1a and 1b, the thermodynamic stability constants for the formation of OH^- and Cl^- complexes of divalent metals are related to one another. If this relationship holds at higher ionic strengths, one would expect the activity coefficients for all divalent metal complexes to be similar. In the following sections, we will examine the literature data that describes the formation OH^- and Cl^- complexes with Cu^{2+}.

2 The Cu^{2+}–OH^- System

The hydrolysis equilibria for Cu^{2+} are given by the general equation

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

where the step-wise stability constants at a given ionic strength, β_i^*, are given by

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

The hydrolysis equilibria for Cu^{2+} are given by

$$Cu^{2+} + H_2O \rightleftarrows CuOH^+ + H^+, \quad \beta_1^* = [CuOH^+][H^+]/[Cu^{2+}], \tag{3}$$

$$Cu^{2+} + 2H_2O \rightleftarrows Cu(OH)_2 + 2H^+, \quad \beta_2^* = [Cu(OH)_2][H^+]^2/[Cu^{2+}], \tag{4}$$

$$Cu^{2+} + 3H_2O \rightleftarrows Cu(OH)_3^- + 3H^+, \quad \beta_3^* = [Cu(OH)_3^-][H^+]^3/[Cu^{2+}], \tag{5}$$

$$Cu^{2+} + 4H_2O \rightleftarrows Cu(OH)_4^{2-} + 4H^+, \quad \beta_4^* = [Cu(OH)_4^{2-}][H^+]^4/[Cu^{2+}], \tag{6}$$

$$2Cu^{2+} + H_2O \rightleftarrows Cu_2OH^{3+} + H^+, \quad \beta_{2,1}^* = [Cu_2OH^{3+}][H^+]/[Cu^{2+}]^2, \tag{7}$$

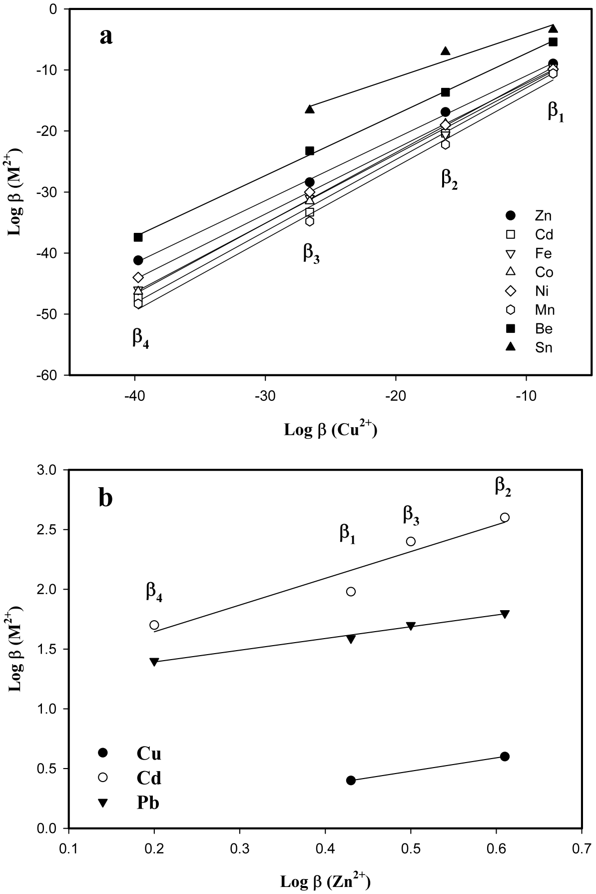


Fig. 1 Standard equilibrium constant relationships for divalent cations for: (**a**) the hydrolysis constants expressed as a function of values for Cu(II), and (**b**) for the formation of chloride complexes with respect to Zn(II). Data for copper hydrolysis constants are taken from [19]. Divalent cations hydrolysis constants are from [23] and chloride complexes values are from [28]

$$2\mathrm{Cu}^{2+} + 2\mathrm{H_2O} \rightleftarrows \mathrm{Cu_2(OH)_2^{2+}} + 2\mathrm{H}^+, \quad \beta^*_{2,2} = [\mathrm{Cu_2(OH)_2^{2+}}][\mathrm{H}^+]^2/[\mathrm{Cu}^{2+}]^2, \tag{8}$$

$$3\mathrm{Cu}^{2+} + 4\mathrm{H_2O} \rightleftarrows \mathrm{Cu_3(OH)_4^{2+}} + 3\mathrm{H}^+, \quad \beta^*_{3,4} = [\mathrm{Cu_3(OH)_4^{2+}}][\mathrm{H}^+]^3/[\mathrm{Cu}^{2+}]^3 \tag{9}$$

Recently Powell et al. [19] have provided the best available hydrolysis constants for Cu^{2+}. Table 1 gives the hydrolysis constants for the formation of copper hydroxide complexes at 25 °C in $\mathrm{NaClO_4}$ solutions at different ionic strengths [19].

3 The Cu^{2+}–Cl^- System

The equilibria for Cu^{2+} and chloride are given by the general equation

$$\mathrm{Cu}^{2+} + n\mathrm{Cl}^- \rightleftarrows \mathrm{CuCl}_n^{(2-n)+} \tag{10}$$

where the values of β^*_i are given by

$$\beta^*_i = [\mathrm{CuCl}_n^{(2-n)+}]/[\mathrm{Cu}^{2+}][\mathrm{Cl}^-]^n \tag{11}$$

Table 1 Stability constants for copper hydroxy complexes at 25 °C in $NaClO_4$ media at different ionic strengths [19]

Reaction	$mol \cdot kg^{-1}$	$\log_{10} \beta^*$
$Cu^{2+} + H_2O \rightleftarrows CuOH^+ + H^+$	0.050	-8.12 ± 0.20
	0.70	-8.09 ± 0.20
	3.503	-7.33 ± 0.20
$Cu^{2+} + 2H_2O \rightleftarrows Cu(OH)_2(aq)$	0.05	-16.40 ± 0.20
	0.70	-16.68 ± 0.20
$2Cu^{2+} + H_2O \rightleftarrows Cu_2OH^{3+} + H^+$	0.101	-6.08 ± 0.30
	0.254	-6.06 ± 0.30
	0.513	-6.07 ± 0.20
	0.779	-6.09 ± 0.20
	1.051	-6.11 ± 0.20
	3.503	-5.75 ± 0.20
	3.503	-6.02 ± 0.10
$2Cu^{2+} + 2H_2O \rightleftarrows Cu_2(OH)_2^{2+} + 2H^+$	0.101	-10.75 ± 0.20
	0.101	-10.72 ± 0.20
	0.254	-10.75 ± 0.20
	0.513	-10.76 ± 0.10
	0.779	-10.75 ± 0.10
	1.051	-10.76 ± 0.10
	3.503	-10.53 ± 0.20
	3.503	-10.86 ± 0.10

The chloride complexation equilibria with Cu^{2+} are given by the equations

$$Cu^{2+} + Cl^- \rightleftarrows CuCl^+, \quad \beta_1^* = [CuCl^+]/[Cu^{2+}][Cl^-] \tag{12}$$

$$Cu^{2+} + 2Cl^- \rightleftarrows Cu(Cl)_2, \quad \beta_2^* = [Cu(Cl)_2]/[Cu^{2+}][Cl^-]^2 \tag{13}$$

Table 2 gives the stability constants for the copper chloride complexes at 25 °C in $NaClO_4$ media at different ionic strengths [19]. Only the mononuclear chloride complexes for copper are considered in this study.

4 Pitzer Model Calculations for the Cu^{2+}–OH^- System

The Pitzer coefficients for the copper hydrolysis complexes can be determined from the experimentally measured values of β_i^*. These measured values of β_i^* are related to their thermodynamic values β_i by

$$\ln \beta_1 = \ln \beta_1^* + \ln \gamma(CuOH^+) + \ln \gamma(H^+) - \ln \gamma(Cu^{2+}) - \ln a_{H_2O}, \tag{14}$$

$$\ln \beta_2 = \ln \beta_2^* + \ln \gamma(Cu(OH)_2) + 2\ln \gamma(H^+) - \ln \gamma(Cu^{2+}) - 2\ln a_{H_2O}, \tag{15}$$

$$\ln \beta_3 = \ln \beta_3^* + \ln \gamma(Cu(OH)_3^-) + 3\ln \gamma(H^+) - \ln \gamma(Cu^{2+}) - 3\ln a_{H_2O}, \tag{16}$$

$$\ln \beta_4 = \ln \beta_4^* + \ln \gamma(Cu(OH)_4^{2-}) + 4\ln \gamma(H^+) - \ln \gamma(Cu^{2+}) - 4\ln a_{H_2O}, \tag{17}$$

$$\ln \beta_{2,1} = \ln \beta_{2,1}^* + \ln \gamma(Cu_2OH^{3+}) + \ln \gamma(H^+) - 2\ln \gamma(Cu^{2+}) - \ln a_{H_2O}, \tag{18}$$

$$\ln \beta_{2,2} = \ln \beta_{2,2}^* + \ln \gamma(Cu_2(OH)_2^{2+}) + 2\ln \gamma(H^+) - 2\ln \gamma(Cu^{2+}) - 2\ln a_{H_2O}, \tag{19}$$

Table 2 Stability constants for the copper chloride complexes at 25 °C in $NaClO_4$ media at different ionic strengths [19]

Reaction	$mol\cdot kg^{-1}$	$\log_{10}\beta^*$
$Cu^{2+} + Cl^- \rightleftarrows CuCl^+$	1.051	0.05 ± 0.10
	1.051	0.13 ± 0.30
	2.212	0.04 ± 0.10
	3.503	-0.07 ± 0.10
	6.584	0.06 ± 0.20
	6.584	0.04 ± 0.10
	6.584	0.25 ± 0.20
	6.0	0.06 ± 0.20
$Cu^{2+} + 2Cl^- \rightleftarrows CuCl_2(aq)$	1.051	-0.56 ± 0.40
	3.503	-0.54 ± 0.20
	6.584	-0.44 ± 0.30
	6.584	-0.48 ± 0.20
	6.584	-0.07 ± 0.30
	6.0	-0.26 ± 0.30

$$\ln\beta_{3,4} = \ln\beta^*_{3,4} + \ln\gamma(Cu_3(OH)_4^{2+}) + 4\ln\gamma(H^+) - 3\ln\gamma(Cu^{2+}) - 4\ln a_{H_2O} \tag{20}$$

where the activity of water a_{H_2O} in $NaClO_4$ media can be estimated from the osmotic coefficient (ϕ).

$$a_{H_2O} = \exp(-2m\phi/55.51) \tag{21}$$

The osmotic coefficient of $NaClO_4$ at 25 °C has been calculated from the Pitzer equation [18]

$$\begin{aligned}\phi_{NaClO_4} - 1 &= -|z_{Na}z_{ClO_4}|0.3915I^{0.5}/(1+1.2I^{0.5})\\ &\quad + [2(\nu_{Na}\nu_{ClO_4})^{1.5}/\nu)]mB^{\phi}_{NaClO_4} + m^2[2(\nu_{Na}\nu_{ClO_4})^{1.5}/\nu)]C^{\phi}_{NaClO_4}\end{aligned} \tag{22}$$

The value of $\nu = \nu_{Na} + \nu_{ClO_4}$ is the number of ionic species and z_{Na} and z_{ClO_4} are the charges on the ions Na^+ and ClO_4^-. The value of $B^{\phi}_{NaClO_4}$ is given by

$$B^{\phi}_{NaClO_4} = \beta^{(0)}_{NaClO_4} + \beta^{(1)}_{NaClO_4}\exp(-2I^{0.5}) \tag{23}$$

Solving the unknown activity coefficients for the complexes and the thermodynamic constants β for the known constants give the equations

$$-\ln\beta_1 + \ln\gamma(CuOH^+) = -\ln\beta^*_1 - \ln\gamma(H^+) + \ln\gamma(Cu^{2+}) + \ln a_{H_2O}, \tag{24}$$

$$-\ln\beta_2 + \ln\gamma(Cu(OH)_2) = -\ln\beta^*_2 - 2\ln\gamma(H^+) + \ln\gamma(Cu^{2+}) + 2\ln a_{H_2O}, \tag{25}$$

$$-\ln\beta_{2,1} + \ln\gamma(Cu_2OH^{3+}) = -\ln\beta^*_{2,1} - \ln\gamma(H^+) + 2\ln\gamma(Cu^{2+}) + \ln a_{H_2O}, \tag{26}$$

$$-\ln\beta_{2,2} + \ln\gamma(Cu_2(OH)_2^{2+}) = -\ln\beta^*_{2,2} - 2\ln\gamma(H^+) + 2\ln\gamma(Cu^{2+}) + 2\ln a_{H_2O} \tag{27}$$

The values of $\gamma(i)$ are the activity coefficients of the i species in the media. At low concentrations of Cu^{2+}, the trace activity coefficients of H^+, Cu^{2+}, $CuOH^+$, $Cu(OH)_2$, Cu_2OH^{3+} and $Cu_2(OH)_2^{2+}$ in a $NaClO_4$ solution can be calculated from the Pitzer equations [18] as formulated by [20]. We have

$$\ln\gamma_H = f^{\gamma} + 2m_{ClO_4}(B_{HClO_4} + \mathrm{E}C_{HClO_4}) + \mathrm{R} + \mathrm{S} + m_{Na}(2\Theta_{HNa} + m_{ClO_4}\Psi_{HNaClO_4}), \tag{28}$$

Table 3 The Pitzer parameters for the hydrolysis and chloro complex formation in $NaClO_4$ media at 25 °C

Solute	$\beta^{(0)}_{MX}$	$\beta^{(1)}_{MX}$	$C^{(0)}_{MX}$
$NaClO_4$	0.0554	0.2755	−0.00118
$HClO_4$	0.1747	0.2931	0.0819
NaCl	0.0765	0.2664	0.00127
$Cu(ClO_4)_2$	0.4897	1.9036	0.00839

$$\ln\gamma(\mathrm{Cu}^{2+}) = 4f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{CuClO_4}} + m_{\mathrm{ClO_4}}C_{\mathrm{CuClO_4}}) + 4\mathrm{R} + 2\mathrm{S}, \tag{29}$$

$$\ln\gamma(\mathrm{CuOH}^{+}) = f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{CuOH\text{-}ClO_4}} + m_{\mathrm{ClO_4}}C_{\mathrm{CuOH\text{-}ClO_4}}) + \mathrm{R} + \mathrm{S}, \tag{30}$$

$$\ln\gamma(\mathrm{Cu_2OH}^{3+}) = 9f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{Cu_2OH\text{-}ClO_4}} + m_{\mathrm{ClO_4}}C_{\mathrm{Cu_2OH\text{-}ClO_4}}) + 9\mathrm{R} + 3\mathrm{S}, \tag{31}$$

$$\ln\gamma(\mathrm{Cu_2(OH)_2^{2+}}) = 4f^{\gamma} + 2m_{\mathrm{ClO_4}}(B_{\mathrm{Cu_2(OH)_2\text{-}ClO_4}} + m_{\mathrm{ClO_4}}C_{\mathrm{Cu_2(OH)_2\text{-}ClO_4}}) + 4\mathrm{R} + 2\mathrm{S}, \tag{32}$$

$$\ln\gamma(\mathrm{Cu(OH)_2}) = 2\lambda_{\mathrm{Cu(OH)_2\text{-}Na}}m_{\mathrm{Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\mathrm{Cu(OH)_2\text{-}Na\text{-}ClO_4}} \tag{33}$$

The Pitzer parameters for $Cu(ClO_4)_2$ in $NaClO_4$ media have been taken from the work of Kim and Frederick [21]. The Debye-Hückel term, f^{γ}, is given by

$$f^{\gamma} = -A^{\phi}[I^{1/2}/(1 + 1.2I^{0.5}) + (2/1.2)\ln(1 + 1.2I^{0.5})] \tag{34}$$

where A^{ϕ} is given by Møller [22] and I is the molal ionic strength. The ionic strength (I) is 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

$$B_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + (\beta^{(1)}_{\mathrm{MX}}/2I)[1 - (1 + 2I^{0.5})\exp(-2I^{0.5})], \tag{35}$$

$$B'_{\mathrm{MX}} = (\beta^{(1)}_{\mathrm{MX}}/2I^{2})[-1 + (1 + 2I^{0.5} + 2I)\exp(-2I^{0.5})], \tag{36}$$

$$C_{\mathrm{MX}} = C^{\phi}_{\mathrm{MX}}/(2|z_{\mathrm{M}}z_{\mathrm{X}}|^{0.5}) \tag{37}$$

The medium terms R and S in Eqs. 28 to 32 in $NaClO_4$ are given by [18]

$$\begin{aligned}\mathrm{R} &= m_{\mathrm{Na}}m_{\mathrm{ClO_4}}B'_{\mathrm{NaClO_4}} = m_{\mathrm{Na}}m_{\mathrm{ClO_4}}(\beta^{(1)}_{\mathrm{NaClO_4}}/2I^{2})\\ &\quad\times[-1 + (1 + 2I^{0.5} + 2I)\exp(-2I^{0.5})]\}, \end{aligned}\tag{38}$$

$$\mathrm{S} = m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{NaClO_4}} = m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C^{\phi}_{\mathrm{NaClO_4}}/2 \tag{39}$$

The 25 °C values of $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and C^{ϕ}_{MX} for $NaClO_4$ as well as Θ_{HNa}(Ψ_{HNaClO_4} is assumed equal zero) are taken from [20] and are tabulated in Table 3.

Rearrangement of Eqs. 29 to 33 yields a series of equations that can be used to determined the activity coefficients (γ_i) of the ions and the thermodynamic constants β_i.

The value of Y_1 can be determined from the known quantities and can be used to determine β_1 and $\gamma(\mathrm{CuOH}^+)$:

$$\begin{aligned}Y_1 &= -\ln\beta_1^{*} - \ln\gamma(\mathrm{H}^+) + \ln\gamma(\mathrm{Cu}^{2+}) - \ln a_{\mathrm{H_2O}} - \ln\gamma(\mathrm{ideal})\\ &= -\ln\beta_1 + \ln\gamma(\mathrm{CuOH}^+) - \ln\gamma(\mathrm{ideal}),\end{aligned} \tag{40}$$

$$Y_1 = -\ln\beta_1 + 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\mathrm{CuOH\text{-}ClO_4}} + 2m_{\mathrm{ClO_4}}f_1\beta^{(1)}_{\mathrm{CuOH\text{-}ClO_4}} + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{CuOH\text{-}ClO_4}} \tag{41}$$

The value of f_1 and $\ln\gamma(\text{ideal})$ are given by

$$f_1 = [1 - (1 + 2I^{0.5})\exp(-2I^{0.5})]/2I, \tag{42}$$

$$\ln\gamma(\text{ideal}) = z_i^2 f^{\gamma} + z^2\mathrm{R} + |z|\mathrm{S} \tag{43}$$

where z is the charge and R and S are given by Eqs. 38 and 39.

For neutral species, a simple equation is used to determined β_2 and $\gamma(\mathrm{Cu(OH)_2})$:

$$Y_2 = -\ln\beta_2^* - 2\ln\gamma(\mathrm{H^+}) + \ln\gamma(\mathrm{Cu^{2+}}) + 2\ln a_{\mathrm{H_2O}} = -\ln\beta_2 + \ln\gamma(\mathrm{Cu(OH)_2}), \tag{44}$$

$$Y_2 = -\ln\beta_2 + 2m_{\mathrm{Na}}\lambda_{\mathrm{Cu(OH)_2\text{-}Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\mathrm{Cu(OH)_2\text{-}Na\text{-}ClO_4}} \tag{45}$$

A nonlinear least-squares fit gives values for the interaction parameters $\lambda_{\mathrm{Cu(OH)_2\text{-}Na}}$ and $\zeta_{\mathrm{Cu(OH)_2\text{-}Na\text{-}ClO_4}}$. The values of Y_3 and Y_4 are determined using the same procedure as for in Y_2

$$\begin{aligned} Y_3 &= -\ln\beta_{2,1}^* - \ln\gamma(\mathrm{H^+}) + 2\ln\gamma(\mathrm{Cu^{2+}}) + \ln a_{\mathrm{H_2O}} - \ln\gamma(\text{ideal}) \\ &= -\ln\beta_{2,1} + \ln\gamma(\mathrm{Cu_2OH^{3+}}) - \ln\gamma(\text{ideal}), \end{aligned} \tag{46}$$

$$\begin{aligned} Y_3 &= -\ln\beta_{2,1} + 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\mathrm{Cu_2OH\text{-}ClO_4}} + 2m_{\mathrm{ClO_4}}f_1\beta^{(1)}_{\mathrm{Cu_2OH\text{-}ClO_4}} \\ &\quad + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{Cu_2OH\text{-}ClO_4}}, \end{aligned} \tag{47}$$

$$\begin{aligned} Y_4 &= -\ln\beta_{2,2}^* - 2\ln\gamma(\mathrm{H^+}) + 2\ln\gamma(\mathrm{Cu^{2+}}) + 2\ln a_{\mathrm{H_2O}} - \ln\gamma(\text{ideal}) \\ &= -\ln\beta_{2,2} + \ln\gamma(\mathrm{Cu_2(OH)_2^{2+}}) - \ln\gamma(\text{ideal}), \end{aligned} \tag{48}$$

$$\begin{aligned} Y_4 &= -\ln\beta_{2,2} + 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\mathrm{Cu_2(OH)_2\text{-}ClO_4}} + 2m_{\mathrm{ClO_4}}f_1\beta^{(1)}_{\mathrm{Cu_2(OH)_2\text{-}ClO_4}} \\ &\quad + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\mathrm{Cu_2(OH)_2\text{-}ClO_4}} \end{aligned} \tag{49}$$

The concentration dependency of $-\ln\beta_i + \ln\gamma(i)$ are determined from Eqs. 24 to 27. This results in the values of β_i and the Pitzer coefficients $\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$ and C^{ϕ}_{MX} for all of the ionic species. These coefficients and $\log_{10}\beta_i$ are tabulated in Table 4 along with the standard error of the fits for $\log_{10}\beta_i$. The Y_i values from Eqs. 41, 45, 47 and 49 are plotted in Fig. 2 as a function of ionic strength. Results from Baes and Mesmer [23] for $\mathrm{CuOH^+}$ and $\mathrm{CuCl_2}$ are also shown in Fig. 2.

Table 4 Stability constants and Pitzer parameters for copper hydrolysis and chloride complexes in $\mathrm{NaClO_4}$ media at 25 °C

Species	$\log_{10}\beta_i$	Std. error fit	$\beta_i^{(0)}$	$\beta_i^{(1)}$	C_i
$\mathrm{CuOH^+}$	−7.96	0.02	0.1192		−0.002
$\mathrm{Cu(OH)_2}$	−16.23	0.08		$\lambda = 0.2005$, $\xi = -0.1724$	
$\mathrm{Cu_2OH^{3+}}$	−6.26	0.11	1.1296	4.4234	−0.085
$\mathrm{Cu_2(OH)_2^{2+}}$	−10.58	0.12	0.5954	1.3072	−0.0316
$\mathrm{CuCl^+}$	0.78	0.08	0.5300		−0.0089
$\mathrm{CuCl_2}$	0.41	0.19		$\lambda = 0.268$, $\xi = 0.035$	

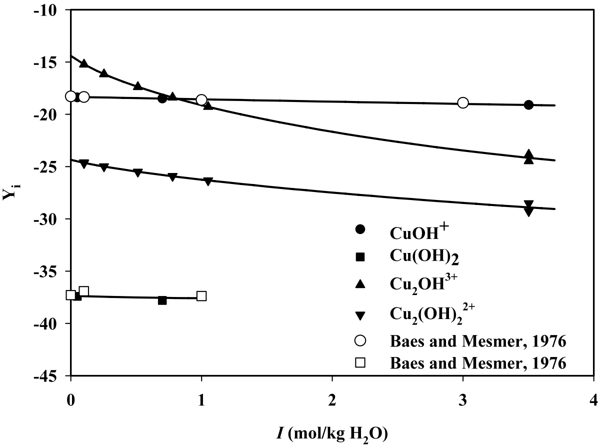


Fig. 2 Y_i values (Eqs. 41, 45, 47 and 49) for copper hydrolysis complexes in $NaClO_4$ as a function of the ionic strength. Data from [22] are also included for $CuOH^+$ and $CuCl_2$

5 Pitzer Calculations for the Cu^{2+}–Cl^- System

The measured values of β_i^* for the copper chloride complexes are related to the thermodynamic values β_i by

$$\ln\beta_1 = \ln\beta_1^* + \ln\gamma(\mathrm{CuCl}^+) - \ln\gamma(\mathrm{Cu}^{2+}) - \ln\gamma(\mathrm{Cl}^-), \tag{50}$$

$$\ln\beta_2 = \ln\beta_2^* + \ln\gamma(\mathrm{CuCl_2}) - \ln\gamma(\mathrm{Cu}^{2+}) - 2\ln\gamma(\mathrm{Cl}^-) \tag{51}$$

Solving for the unknown activity coefficients for β constants gives

$$-\ln\beta_1 + \ln\gamma(\mathrm{CuCl}^+) = -\ln\beta_1^* + \ln\gamma(\mathrm{Cu}^{2+}) + \ln\gamma(\mathrm{Cl}^-), \tag{52}$$

$$-\ln\beta_2 + \ln\gamma(\mathrm{CuCl_2}) = -\ln\beta_2^* + \ln\gamma(\mathrm{Cu}^{2+}) + 2\ln\gamma(\mathrm{Cl}^-) \tag{53}$$

The values of the activity coefficients of species i in the media

$$\ln\gamma(\mathrm{CuCl}^+) = f^\gamma + 2m_{\mathrm{ClO_4}}(B_{\text{CuCl-ClO}_4} + \mathrm{E}C_{\text{CuCl-ClO}_4}) + \mathrm{R} + \mathrm{S}, \tag{54}$$

$$\ln\gamma(\mathrm{CuCl_2}) = 2\lambda_{\text{CuCl}_2\text{-Na}}m_{\mathrm{Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\text{CuCl}_2\text{-Na-ClO}_4} \tag{55}$$

The rearrangement of Eqs. 54 and 55 yields a series of equations that can be used to determined the activity coefficients (γ_i) of the ions and thermodynamic constants β_i.

The value of Y_1 can be determined from the known quantities and can be used to determine β_1 and $\gamma(\mathrm{CuCl}^+)$:

$$\begin{aligned} Y_1 &= -\ln\beta_1^* + \ln\gamma(\mathrm{Cu}^{2+}) + \ln\gamma(\mathrm{Cl}^-) - \ln\gamma(\text{ideal}) \\ &= -\ln\beta_1 + \ln\gamma(\mathrm{CuCl}^+) - \ln\gamma(\text{ideal}), \end{aligned} \tag{56}$$

$$Y_1 = -\ln\beta_1 + 2m_{\mathrm{ClO_4}}\beta^{(0)}_{\text{CuCl-ClO}_4} + 2m_{\mathrm{ClO_4}}f_1\beta^{(1)}_{\text{CuCl-ClO}_4} + 2m_{\mathrm{Na}}m_{\mathrm{ClO_4}}C_{\text{CuCl-ClO}_4}, \tag{57}$$

$$Y_2 = -\ln\beta_2^* + \ln\gamma(\mathrm{Cu}^{2+}) + 2\ln\gamma(\mathrm{Cl}^-) = -\ln\beta_2 + \ln\gamma(\mathrm{CuCl_2}), \tag{58}$$

$$Y_2 = -\ln\beta_2 + 2m_{\mathrm{Na}}\lambda_{\text{Cu(Cl)}_2\text{-Na}} + m_{\mathrm{Na}}m_{\mathrm{ClO_4}}\zeta_{\text{Cu(Cl)}_2\text{-Na-ClO}_4} \tag{59}$$

This results in the values of β_i and the Pitzer coefficients ($\beta^{(0)}_{\mathrm{MX}}$, $\beta^{(1)}_{\mathrm{MX}}$ and C_{MX}) are tabulated in Table 4 for copper chloro complexes along with the standard error of the fits in $\log_{10}\beta_i$. The plots of Y_i for chloride complexes as a function of ionic strength are presented in Fig. 3.

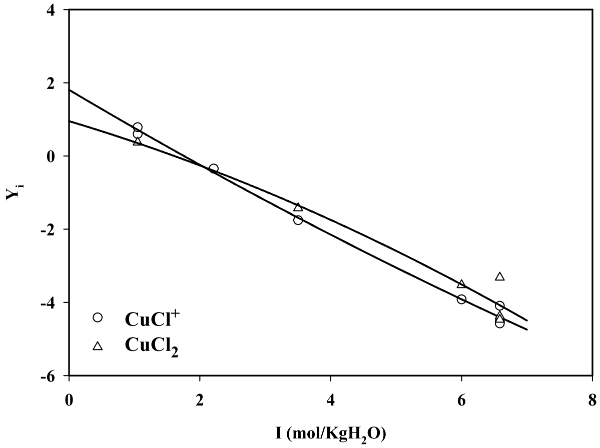


Fig. 3 Y_i values (Eqs. 57 and 59) for copper chloride complexes in NaClO$_4$ as a function of the ionic strength

Table 5 Comparison between the thermodynamic constants extrapolated using Pitzer equations in this study and data provided in [19] at 25 °C

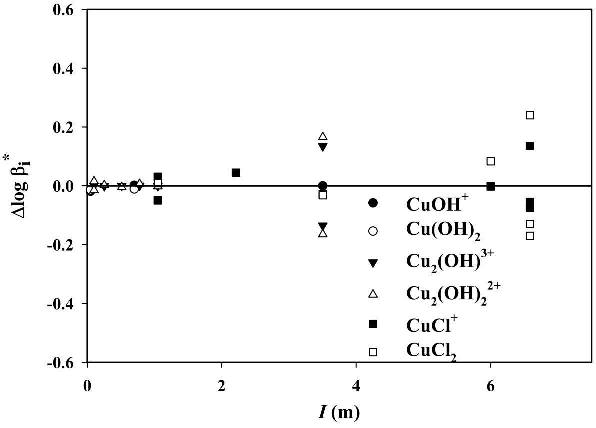
Species	$\log_{10}\beta_i$ this study	$\log_{10}\beta_i$ Powell, 2007
$CuOH^+$	-7.96 ± 0.02	-7.95 ± 0.16
$Cu(OH)_2$	-16.23 ± 0.08	-16.2 ± 0.2
Cu_2OH^{3+}	-6.26 ± 0.11	-6.40 ± 0.12
$Cu_2(OH)_2^{2+}$	-10.58 ± 0.12	-10.43 ± 0.07
$CuCl^+$	0.78 ± 0.08	0.83 ± 0.09
$CuCl_2$	0.41 ± 0.19	0.6 ± 0.3

6 Values of $\log_{10}\beta_i$ and Pitzer Parameters

In the Cu^{2+}–OH^- system, seven species have been identified [19]. The formation of the first monomeric hydrolysis species $CuOH^+$ is described in this study by Eq. 3, and the formation of the second monomeric hydrolysis species $Cu(OH)_2$ by Eq. 4. The species $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$ described by Eqs. 5 and 6 are formed in alkaline solutions at pH higher than 10. The formation of the polynuclear species Cu_2OH^{3+}, $Cu_2(OH)_2^{2+}$ and $Cu_3(OH)_4^{2+}$ are described by Eqs. 7, 8 and 9. In slightly acidic solutions with moderate copper concentrations ($\sim$ mmol·dm^{-3}), $Cu_2(OH)_2^{2+}$ is the predominant species. Cu_2OH^{3+} is formed at high copper concentrations (mol·dm^{-3}) and pH lower than 3.5. The formation of trimeric species is observed at high copper concentrations and pH about 6 [19]. Taking this into consideration, in the natural environment the species more favorable are $CuOH^+$ and $Cu(OH)_2$. Polynuclear species of Cu(II) are only formed at high concentrations of Cu(II). In Table 5, a comparison between the values of $\log_{10}\beta_i$ obtained from the Pitzer equation in this study and the values obtained from [19] are given.

In the Cu^{2+}–Cl^- system four chloride-complexes are identified [19]. The formation of $CuCl^+$ and $CuCl_2(aq)$ formation is described by Eqs. 12 and 13. The $CuCl^+$ and $CuCl_2(aq)$ are weak and $CuCl_3^-$ and $CuCl_4^{2-}$ are extremely weak and only form at very high chloride concentrations. In this case, the species more favorable in natural environments at high ionic strength are $CuCl^+$ and $CuCl_2(aq)$. In Table 5 comparison between the values of $\log_{10}\beta_i$ obtained from the Pitzer equation in this study and the values obtained from [19] for these

Fig. 4 Comparison between measured and calculated values of β_i for different hydrolysis and chloride complexes



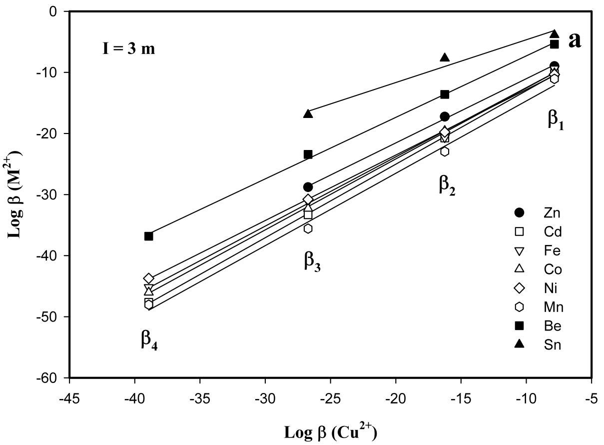


Fig. 5 Equilibrium constant relationships for divalent cations at an ionic strength of 3 mol·kg^{-1} for: (**a**) the hydrolysis expressed as a function of values for Cu(II), and (**b**) for the formation of chloride complexes with respect to Zn(II). Data for copper hydrolysis complexes constants are from [19]. Divalent cation hydrolysis constants are from [23] and data for chloride complexes are from [28]

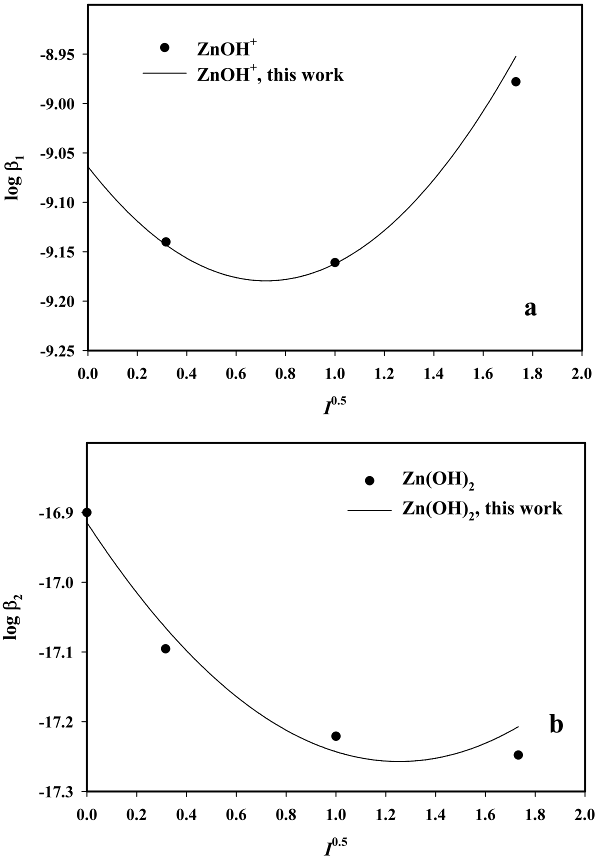


Fig. 6 Zinc hydrolysis constants [23] for: (**a**) ZnOH^+ and (**b**) Zn(OH)_2, together with the theoretical fit considering Pitzer parameters as a function of the ionic strength for the corresponding copper hydrolysis complexes from Table 4

chloride copper complexes are shown. The agreement is quite good and within the experimental error of the two studies.

The reliability of the Pitzer parameters for copper hydrolysis complexes and copper chloride complexes can be demonstrated by comparing the measured and calculated values of β_i^* for the formation of the different complexes. The difference between the measured and calculated values of $\log_{10}\beta_i^*$ are shown in Fig. 4. The average deviations for the hydroxy complexes $\text{Cu}_2\text{OH}^{3+}$ and $\text{Cu}_2(\text{OH})_2^{2+}$ are ±0.03 and ±0.06 and for the chloride complex CuCl^+ and CuCl_2 are ±0.03 and ±0.07, respectively.

7 Copper(II) Pitzer Parameters as a Model for Other Divalent Metals

One of the difficulties of modeling the speciation of metals in natural waters is in determining the activity coefficients of metal complexes [24–27]. Since the stability constants of Cu(II) and other divalent trace metals with hydroxy and chloride are quite similar, one

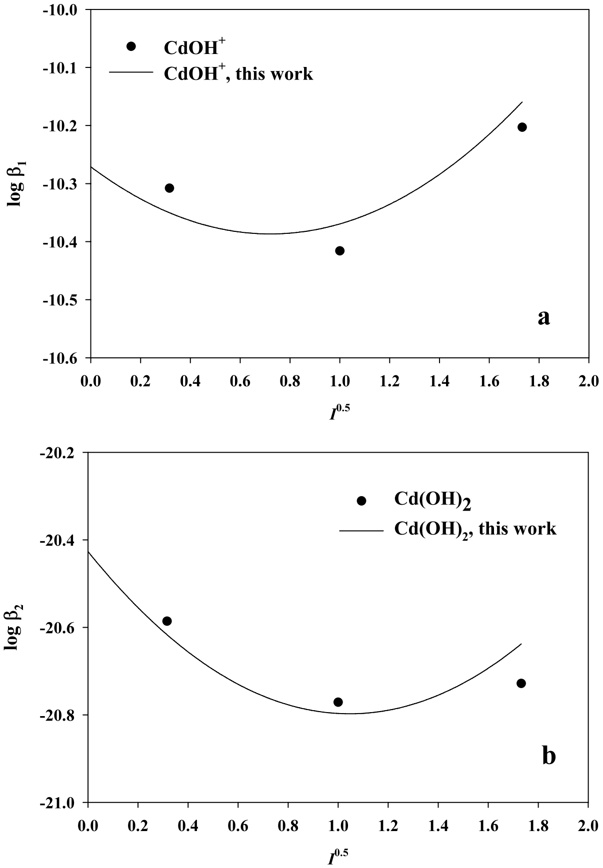


Fig. 7 Cadmium hydrolysis constants [23] for: (**a**) $CdOH^+$ and (**b**) $Cd(OH)_2$, together with the theoretical fit considering Pitzer parameters as a function of the ionic strength for the corresponding copper hydrolysis complexes from Table 4

might expect our results for Cu(II) may be used for other divalent metals. The linear relationships observed for the thermodynamic constants (Fig. 1) holds to 3 mol·kg^{-1}, as shown in Fig. 5a for the hydrolysis constants and in Fig. 5b for the chloride complexes, and support this notion. We applied the Pitzer parameters calculated for hydroxide and chloride complexes of copper to estimate the stability constants of the complexes formed with other divalent cations and their ionic strength dependences. The results for the hydrolysis constants [23] for zinc and cadmium as a function of ionic strength are shown in Figs. 6 and 7 together with the theoretical constants using the Cu(II) Pitzer parameters from Table 4. Standard errors of estimated constants are ±0.05 and ±0.02 for $ZnOH^+$ and $Zn(OH)_2$, respectively. The thermodynamic hydrolysis constants found are $\log_{10}\beta_{ZnOH^+} = -9.04 \pm 0.04$ and $\log_{10}\beta_{Zn(OH)_2} = -16.90 \pm 0.02$, in agreement with the values of -8.96 and -16.9, respectively, estimated by Baes and Mesmer [23]. For cadmium hydrolysis, the standard errors of the estimated constants are ±0.05 and ±0.04 for $CdOH^+$ and $Cd(OH)_2$, respectively, whereas $\log_{10}\beta_{CdOH^+} = -10.24 \pm 0.05$ and $\log_{10}\beta_{Cd(OH)_2} = -20.42 \pm 0.07$, which are similar to the values of -10.08 and -20.35 estimated by Baes and Mesmer [23].

In this study, the equations of Pitzer have been used to calculate the activity coefficients of copper hydroxide and copper chloride complexes in $NaCO_4$ medium. These Pitzer parameters for copper complexes have been shown to serve as a model for other divalent metal cations. Further measurements of the stability constants of copper complexes need to be made at even higher ionic strengths and as a function of temperature. Since it has been shown elsewhere that the Pitzer parameters for ions in NaCl are linearly related to the values in $NaClO_4$ [26, 27], these results should prove useful in determining the speciation of divalent metals in natural waters with high concentrations of NaCl.

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