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The activity coefficients of Fe(III) hydroxide complexes in NaCl and $NaClO_4$ solutions

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Abstract

The osmotic coefficients of $FeCl_3$ at 25 °C from 0.15 to 1.7 m [Rumyantsev et al., *Z. Phys. Chem.*, **218**, 1089–1127, 2004] have been used to determine the Pitzer parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) for $FeCl_3$. Since the differences in the Pitzer coefficients of rare earths in NaCl and $NaClO_4$ are small, the values of $Fe(ClO_4)_3$ have been estimated using the differences between $La(ClO_4)_3$ and $LaCl_3$. The Pitzer coefficients for $FeCl_3$ combined with enthalpy and heat capacity data for the rare earths can be used to estimate the activity coefficients of Fe^{3+} in NaCl over a wide range of temperatures (0 to 50 °C) and ionic strength (0 to 6 m).

The activity coefficients of Fe^{3+} in NaCl and $NaClO_4$ solutions have been used to determine the activity coefficients of $Fe(OH)^{2+}$ in these solutions from the measured first hydrolysis constants of Fe^{3+} [Byrne et al., *Mar. Chem.*, **97**, 34–48, 2005]. The activity coefficients of $Fe(OH)_2{}^{+}$, $Fe(OH)_3$ and $Fe(OH)_4{}^{-}$ from 0 to 50 °C have also been determined from the solubility measurements of Fe(III) in NaCl solutions [Liu and Millero, *Geochim. Cosmochim Acta*, **63**, 3487–3497, 1999]. These activity coefficients have been fitted to the Pitzer equations. These results can be used to estimate the speciation of Fe(III) with OH^- in natural waters with high concentrations of NaCl from 0 to 50 °C.

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1. INTRODUCTION

Until recently the osmotic properties of Fe(III) in aqueous solutions were not readily available. This makes it difficult to model the behavior of Fe(III) in natural waters. In early attempts to model the activity coefficients of Fe^{3+} in natural waters, the values were estimated from trivalent ions, Ga^{3+} (Zhu et al., 1992) or the rare earths (Millero et al., 1995). Recently, Rumyantsev et al. (2004) have determined the osmotic coefficients of $FeCl_3$ as a function of concentration at 25 °C. In this paper, we have fitted these osmotic coefficients to the Pitzer equation (1991) and determined the Pitzer coefficients $\beta^{(0)}_{FeCl_3}$, $\beta^{(1)}_{FeCl_3}$ and $C^{\phi}_{FeCl_3}$. We have estimated the Pitzer coefficients for $Fe(ClO_4)_3$ using the differences in the activity coefficients (Millero, 1992) of $LaCl_3$ and $La(ClO_4)_3$. The effect of temperature on the Pitzer parameters has been estimated using enthalpy (Pitzer et al., 1978) and heat capacity data (Criss and Millero, 1996, 1999). This provides equations that can be used to estimate the activity coefficients of $FeCl_3$ and $Fe(ClO_4)_3$ from 0 to 50 °C and 0 to 6 m ionic strength.

The activity coefficients of Fe^{3+} in NaCl solutions have been used to determine the activity coefficients of $FeOH^{2+}$, $Fe(OH)_2{}^{+}$ $Fe(OH)_3$ and $Fe(OH)_4{}^{-}$ from measurements of the hydrolysis constants determined from potentiometric (Byrne et al., 2000, 2005) and solubility measurements of Fe(III) (Liu and Millero, 1999; Byrne et al., 2000). These results can be used to model the hydrolysis of Fe(III) in brines with high concentrations of NaCl from 0 to 50 °C.

1.1. Osmotic and activity coefficients for $FeCl_3$

The osmotic coefficients (ϕ) of $FeCl_3$ solutions have been tabulated by Rumyantsev et al. (2004) and are given

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in Table 1. These osmotic coefficients of $FeCl_3$ at 25 °C have been fitted to the Pitzer equation (1991)

$$\phi_{\mathrm{FeCl_3}} - 1 = -|Z_{\mathrm{Fe}}Z_{\mathrm{Cl}}|0.391I^{0.5}/(1+1.2I^{0.5}) + [2(\nu_{\mathrm{Fe}}\nu_{\mathrm{Cl}})/\nu]m\,B^{\phi}_{\mathrm{FeCl_3}} + m^2[2(\nu_{\mathrm{Fe}}\nu_{\mathrm{Cl}})^{1.5}/\nu]C^{\phi}_{\mathrm{FeCl_3}} \qquad (1)$$

The value of $\nu = \nu_{\mathrm{Fe}} + \nu_{\mathrm{Cl}}$ is the number of ionic species and Z_{Fe} and Z_{Cl} are the charges on the ions Fe^{3+} and Cl^-. The value of B^{ϕ}_{MX} is given by

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

The Pitzer coefficients for $FeCl_3$, $\beta^{(0)}_{\mathrm{FeCl_3}}$, $\beta^{(1)}_{\mathrm{FeCl_3}}$ and $C^{\phi}_{\mathrm{FeCl_3}}$ were determined using the rearranged Eq. (1)

$$Y = \phi_{\mathrm{MX}} - 1 - \mathrm{D.H.} = 6/4m\ \beta^{(0)}_{\mathrm{MX}} + 6/4m\ \beta^{(1)}_{\mathrm{MX}}\exp(-2I^{0.5}) + m^2(3)^{1.5}(C^{\phi}_{\mathrm{MX}})/2 \qquad (3)$$

$\mathrm{D.H.} = -|Z_{\mathrm{Fe}}Z_{\mathrm{Cl}}|\ 0.391I^{0.5}/(1+1.2I^{0.5})$ is the Debye Hückel contribution. Values of Y as a function of molality are shown in Fig. 1. A nonlinear least squares fit gives $\beta^{(0)}_{\mathrm{FeCl_3}} = 0.5382$, $\beta^{(1)}_{\mathrm{FeCl_3}} = 9.4684$, and $C^{\phi}{}_{\mathrm{FeCl_3}} = -0.0604$ ($\sigma = 0.008$ in $\phi_{\mathrm{FeCl_3}}$). Rumyantsev et al. (2004) fitted the osmotic coefficients of $FeCl_3$ using the extra term $\beta^{(2)}_{\mathrm{FeCl_3}}$ $\exp(-12\ I^{0.5})$ added to Eq. (2). We found that the addition of this term did not improve the fit and was not necessary.

Table 1
The osmotic coefficients of $FeCl_3$ solutions calculated from the isopiestic concentrations of NaCl at 25 °C (Rumyantsev et al., 2004)

$FeCl_3$ (m)	$FeCl_3$ (Φ)
0.1566	0.8137
0.2213	0.7962
0.3373	0.8047[a]
0.3559	0.8147
0.4316	0.8545
0.4954	0.8578
0.5114	0.8547
0.5214	0.8623
0.5341	0.8726
0.5692	0.8704
0.5767	0.8837[a]
0.6194	0.8890
0.7417	0.9164
0.7541	0.9172
0.7769	0.9354
0.8785	0.9514
0.8958	0.9555
1.0017	1.0018
1.0094	0.9833
1.0115	0.9851
1.1328	1.0199
1.2049	1.0351[a]
1.2627	1.0701
1.3504	1.0756
1.3792	1.1014
1.4572	1.1158
1.5500	1.1331
1.6110	1.1576
1.6760	1.1616
1.7168	1.1767
1.7509	1.1816
1.7591	1.1866

[a] Points not used in the final fit.

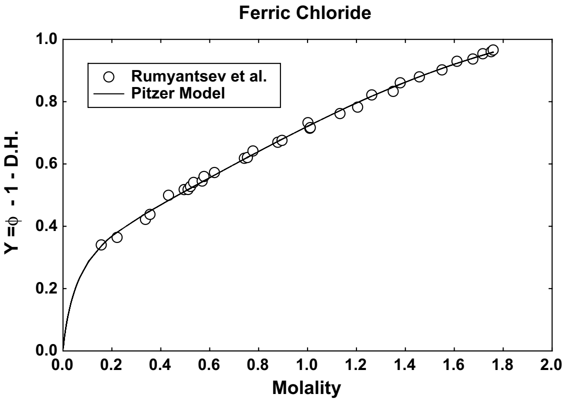

Fig. 1. The fit of $Y = \phi_{\mathrm{MX}} - 1 - \mathrm{D.H.}$ for $FeCl_3$ as a function of the molality (Rumyantsev et al., 2004).

Recently Christov (2004) has estimated the Pitzer coefficients for $FeCl_3$ from the osmotic coefficients tabulated by Mikulin (1968). As discussed by Christov (2004), the earlier results of Kim and Frederick (1988) had large errors and included data of supersaturated solutions (Kangro and Groeneveld, 1962). A comparison of the osmotic coefficients for $FeCl_3$ of Christov (2004), the work of Rumyantsev et al. (2004) and the calculated values for $LaCl_3$ and $AlCl_3$ (Pitzer, 1991) are shown in Fig. 2. The results from Rumyantsev et al. (2004) are in good agreement with the results of Christov (2004) at high concentrations, but differ at low molalities. Since the Rumyantsev et al. (2004) results agree at low molalities with $LaCl_3$ and $AlCl_3$, they appear to be more reliable than the tabulated values of Mikulin (1968).

The Pitzer coefficients for $FeCl_3$ are compared to the values for $LaCl_3$ and $AlCl_3$ in Table 2 (Pitzer, 1991; Chris-

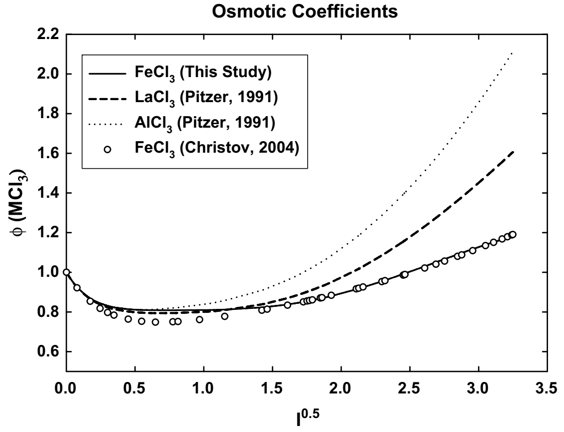

Fig. 2. Comparisons of our values of the osmotic coefficients of $FeCl_3$ with the values of $LaCl_3$ and $AlCl_3$ (Pitzer, 1991) and $FeCl_3$ from Christov (2004) as a function of the square root of the ionic strength.

Table 2
Pitzer parameters for a number of electrolytes at 25 °C used and determined in this study

Electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	σ	Max. Range (m)
HCl[a]	0.1775	0.2945	0.00080	0.0008	6.0
HClO$_4$[a]	0.1747	0.2931	0.00819	0.0082	5.5
NaCl[a]	0.0765	0.2664	0.00127	0.00127	6.0
NaClO$_4$[a]	0.0554	0.2755	−0.00118	0.0004	6.0
FeCl$_3$[b]	0.5382	6.3122	−0.0604	0.008	1.6
	0.34082[c]	1.6285[c]	−0.014[c]	0.00218	6.07
Fe(ClO$_4$)$_3$[b]	0.7213	7.2456	−0.0360		1.6
AlCl$_3$[a]	0.6993	5.845	0.0027	0.002	1.6
LaCl$_3$[a]	0.5889	5.600	−0.0238	0.006	3.9
La(ClO$_4$)$_3$[a]	0.7720	6.5333	0.00062	0.009	2.0

The standard errors are for fits of the osmotic coefficients (ϕ).

[a] Pitzer (1991).

[b] This study.

[c] Christov (2004), a value of $\beta^{(2)} = 1.7199$ was also derived by this worker.

tov, 2004). The activity coefficients of FeCl$_3$ and LaCl$_3$ can be calculated from

$$\ln \gamma_{\mathrm{MX}} = (|Z_{\mathrm{M}}Z_{\mathrm{X}}|/2)f^{\gamma}m\ (2\nu_{\mathrm{M}}\nu_{\mathrm{X}})/\nu B^{\gamma} + m^2\{2(\nu_{\mathrm{M}}\nu_{\mathrm{X}})^{1.5}/\nu\}C^{\gamma} \quad (4)$$

$$f^{\gamma} = -0.391\{I^{0.5}/(1+1.2I^{0.5}) + (2/1.2)\ln(1+1.2I^{0.5})\} \quad (5)$$

$$B^{\gamma}_{\mathrm{MX}} = \beta^{(0)}_{\mathrm{MX}} + \beta^{(1)}_{\mathrm{MX}}[1-(1+I^{0.5})\exp(-2I^{0.5})] \quad (6)$$

$$C^{\gamma}_{\mathrm{MX}} = C^{\phi}{}_{\mathrm{MX}}/(2|Z_{\mathrm{M}}Z_{\mathrm{X}}|^{0.5}) \quad (7)$$

A comparison of the 25 °C activity coefficients of FeCl$_3$, LaCl$_3$, and AlCl$_3$ are shown in Fig. 3. The activity coefficients of FeCl$_3$ are similar to LaCl$_3$ and AlCl$_3$ in dilute solutions. The values for FeCl$_3$ are similar to LaCl$_3$ and other rare earths to $I = 3$ m. The lower values for FeCl$_3$ than LaCl$_3$ at high concentrations can be attributed to stronger interactions between Fe^{3+} and Cl$^-$. Since the differences between the activity coefficients of trivalent ions with Cl$^-$ and ClO$_4^-$ are similar for most rare earth elements (Millero, 1992), one can make an estimate of the Pitzer 25 °C values of Fe(ClO$_4$)$_3$ from the differences between LaCl$_3$ and LaClO$_4$ (Millero, 1992) using

$$\beta^{(0)}_{\mathrm{Fe(ClO_4)_3}} = \beta^{(0)}_{\mathrm{FeCl_3}} + \beta^{(0)}_{\mathrm{La(ClO_4)_3}} - \beta^{(0)}_{\mathrm{LaCl_3}} \quad (8)$$

$$\beta^{(1)}_{\mathrm{Fe(ClO_4)_3}} = \beta^{(1)}_{\mathrm{FeCl_3}} + \beta^{(1)}_{\mathrm{La(ClO_4)_3}} - \beta^{(1)}_{\mathrm{LaCl_3}} \quad (9)$$

$$C^{\phi}_{\mathrm{Fe(ClO_4)_3}} = C^{\phi}_{\mathrm{FeCl_3}} + C^{\phi}_{\mathrm{La(ClO_4)_3}} - C^{\phi}_{\mathrm{LaCl_3}} \quad (10)$$

The values of $\beta^{(0)}_{\mathrm{Fe(ClO_4)_3}}$, $\beta^{(1)}{}_{\mathrm{Fe(ClO_4)_3}}$, and $C^{\phi}_{\mathrm{Fe(ClO_4)_3}}$ calculated from these equations are given in Table 2. A comparison of the activity coefficients of FeCl$_3$ and Fe(ClO$_4$)$_3$ determined from these coefficients are shown in Fig. 4. The differences are large, but similar to the differences for the rare earths (Pitzer et al., 1978; Millero, 1992).

Since reliable enthalpies (Pitzer et al., 1978) and heat capacity (Criss and Millero, 1999) are available for trivalent ions, one can make reasonable estimates for the activity coefficients for FeCl$_3$ and Fe(ClO$_4$)$_3$ from 0 to 50 °C from estimates of the effect of temperature on the Pitzer coefficients (Criss and Millero, 1996). The Pitzer parameters for FeCl$_3$ and Fe(ClO$_4$)$_3$ as a function of temperature (T/K) can be determined from relative apparent molal heat capacity (ϕ_{J}) and enthalpy (ϕ_{L}) measurements (Criss and Millero, 1999) at a reference temperature ($T_{\mathrm{R}} = 298.15$) from

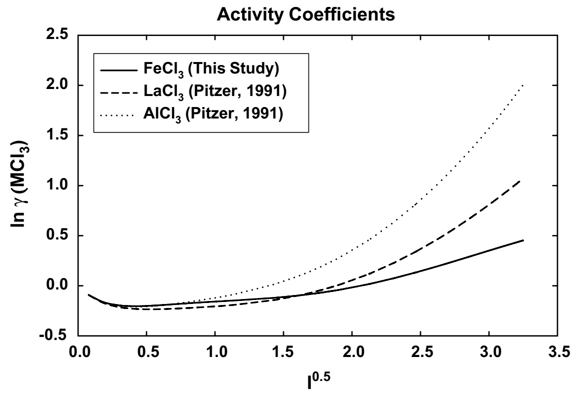

Fig. 3. A comparison of our values for the activity coefficients of FeCl$_3$ with LaCl$_3$ and AlCl$_3$ (Pitzer, 1991) as a function of the square root of the ionic strength.

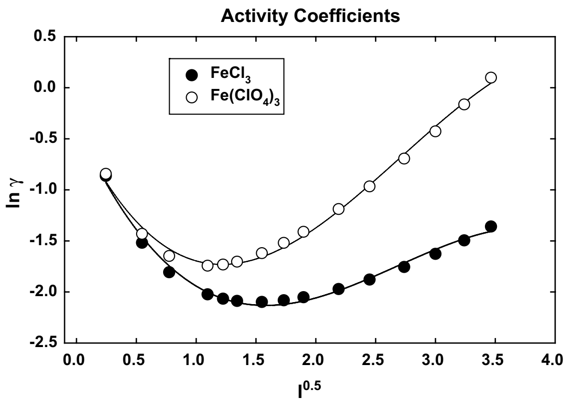

Fig. 4. A comparison of the activity coefficients of FeCl$_3$ and Fe(ClO$_4$)$_3$ solutions at 25 °C as a function of the square root of ionic strength.

Table 3
Values of the $\beta^{(0)\mathrm{L}}$, $\beta^{(1)\mathrm{L}}$, $C^{\phi\,L}$, and $\beta^{(0)J}$, $\beta^{(1)J}$ and $C^{\phi J}$ for some rare earths at 25 °C (Pitzer et al., 1978; Criss and Millero, 1999)

	$10^4\,\beta^{(0)L}$	$10^2\,\beta^{(1)L}$	$10^3\ C^{\phi\,L}$
$LaCl_3$	2.527	0.798	−3.714
$La(ClO_4)_3$	1.519	1.503	−0.672
	$10^5\,\beta^{(0)J}$	$10^5\,\beta^{(1)J}$	$10^7\,\mathrm{C}^{\phi J}$
$LaCl_3$	−1.7647	22.4376	3.5996
$La(ClO_4)_3$	−0.84758	19.3765	2.5315

(a) $\beta^{(0)\,L} = \partial\beta^{(0)}/\partial T$, $\beta^{(1)\,L} = \partial\beta^{(1)}/\partial T$ and $C^{\phi\,L} = \partial C^{\phi}\ /\partial T$.
(b) $\beta^{(0)J} = \partial^2\beta^{(0)}/\partial T^2 + (2/T)\beta^{(0)\,L}$, $\beta^{(1)\,J} = \partial^2\beta^{(1)}/\partial T^2 + (2/T)\beta^{(1)\,L}$ and $C^{\phi\,J} = \partial^2 C^{\phi}\ /\partial T^2 + (2/T)C^{\phi\,L}$.

$$\beta_T^{(0)} = \beta_\mathrm{R}^{(0)} + \mathrm{a}\ (1/T - 1/T_\mathrm{R}) + \mathrm{b}\ (T^2 - T_\mathrm{R}^2) \tag{11}$$

$$\mathrm{a} = (\beta^{(0)\mathrm{J}}/3)\ T_\mathrm{R}^3 - T^2{}_\mathrm{R}\beta^{(0)\mathrm{L}} \tag{12}$$

$$\mathrm{b} = \beta^{(0)\mathrm{J}}/6 \tag{13}$$

The values of $\beta^{(0)\mathrm{L}}$ and $\beta^{(0)\mathrm{J}}$ are given by

$$\beta^{(0)\mathrm{L}} = \partial\beta^{(0)}/\partial T \tag{14}$$

$$\beta^{(0)\mathrm{J}} = \partial^2\beta^{(0)}/\partial T^2 + (2/T)\beta^{(0)\mathrm{L}} \tag{15}$$

Similar equations can be written for $\beta_T^{(1)}$, $\beta^{(1)\,L}$, $\beta^{(1)\,J}$, $C^{\phi}{}_T$, $C^{\phi\,L}$, and $\mathrm{C}^{\phi\,J}$. These quantities for $FeCl_3$ and $Fe(ClO_4)_3$ can be estimated from the known values of $\beta^{(0)\,L}$ and $\beta^{(0)\,J}$ for $LaCl_3$ and $La(ClO_4)_3$ (Pitzer et al., 1978; Criss and Millero, 1999) given in Table 3. Since the activity coefficients of $FeCl_3$ and $LaCl_3$ (Fig. 3) have similar properties in dilute solutions, we feel that their enthalpies and heat capacities should also be similar. The effect of temperature (T/K) on the Pitzer parameters has been fitted to equations of the form

$$P_T = P_{298.15} + A\ (T - 298.15) + B(T - 298.15)^2 \tag{16}$$

The parameter P represents $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} at a temperature T or 298.15/K. The coefficients for Eq. (16) are given in Table 4 for $FeCl_3$ and $Fe(ClO_4)_3$. These equations should yield reasonable estimates for the Pitzer parameters for these systems from 0 to 50 °C that can be used to determine the activity coefficients of Fe^{3+} in NaCl or $Na(ClO_4)_3$ solutions.

Table 4
Coefficients for Eq. (16) for $FeCl_3$, $Fe(ClO_4)_3$, $Fe(OH)Cl_2$, $Fe(OH)_2Cl$, $Fe(OH)_3$, and $NaFe(OH)_4$

Electrolyte	Parameter	$P_{298.15}$	A	B
$FeCl_3$	$\beta_T^{(0)}$	0.5382	2.6E-04	−1.0E-05
	$\beta_T^{(1)}$	6.3122	0.00802	−2.6E-05
	C_T^{ϕ}	−0.0604	−0.00373	1.3E-05
$Fe(ClO_4)_3$	$\beta_T^{(0)}$	0.7213	0.001531	−9.40E-06
	$\beta_T^{(1)}$	7.2456	0.01501	4.660E-05
	C_T^{ϕ}	−0.0360	−6.76E-04	2.40E-06
$Fe(OH)Cl_2$	$\beta_T^{(0)}$	0.19	0.00160	
	$\beta_T^{(1)}$	5.61	−0.0040	−1.0E-04
	C_T^{ϕ}	0.0087	−0.0033	8.50E-06
$Fe(OH)_2Cl$	$\beta_T^{(0)}$	0.96	0.00260	9.0E-06
	$\beta_T^{(1)}$	−4.1	−0.010	−3.20E-04
	$\beta_T^{(2)}$	−219.8		
	C_T^{ϕ}	−0.39	−0.00250	
$NaFe(OH)_4$	$\beta_T^{(0)}$	0.88	0.00360	
	$\beta_T^{(1)}$	0.16	−0.0060	
	C_T^{ϕ}	−0.25	−0.00220	
$Fe(OH)_3$	λ	3.96		
	ζ	−4.27		

1.2. Hydrolysis constants for Fe(III) in NaCl and $NaClO_4$ solutions

A number of recent measurements (Baes and Mesmer, 1976; Byrne and Kester, 1976a,b, 1978, 1981; Daniele et al., 1994; Liu and Millero, 1999, 2002; Byrne and Luo, 2000; Byrne et al., 2000, 2005, to name a few) have been made on the stability constants for the hydrolysis of Fe^{3+} represented by the equilibria:

$$Fe^{3+} + H_2O \leftrightarrow Fe(OH)^{2+} + H^+ \qquad \beta_1^* \tag{17}$$

$$Fe^{3+} + 2H_2O \leftrightarrow Fe(OH)_2{}^+ + 2H^+ \qquad \beta_2^* \tag{18}$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3{}^0 + 3H^+ \qquad \beta_3^* \tag{19}$$

$$Fe^{3+} + 4H_2O \leftrightarrow Fe(OH)_4{}^- + 4H^+ \qquad \beta_4^* \tag{20}$$

The recent measurements of (Byrne et al., 2000, 2005) for $\log\beta_1^*$ in NaCl and $NaClO_4$ solutions are in good agreement with the literature data they summarized. This work provides the most reliable values of β_1^* in these media and are shown as a function of the ionic strength in Fig. 5. The results of $\log\beta_1^*$ in NaCl and $NaClO_4$ as a function of the molal ionic strength and temperature (T/K), respectively, are given by (Byrne et al., 2000, 2005). We have adjusted these equations assuming that the effect of temperature on the constants are independent of ionic strength. Byrne et al. (2000, 2005) only determined the effect of temperature on the constants at $I = 0.7$ m. The values in NaCl are given by

$$\log\beta_1^* = 2.24 - 1366/T - 2.044I^{0.5}/(1 + 1.7I^{0.5}) - 0.228I \quad (\sigma = 0.02) \tag{21}$$

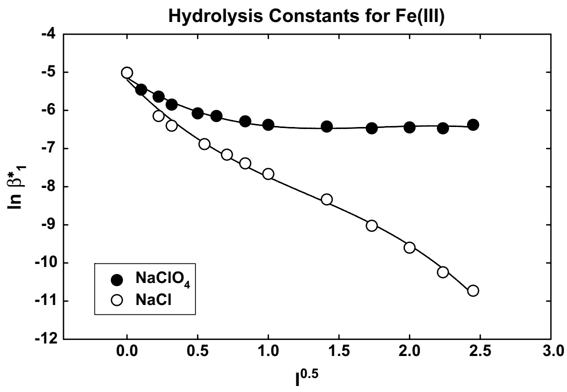

Fig. 5. The values of $\ln\beta_1^*$ for the stepwise hydrolysis constant for the formation of $Fe(OH)^{2+}$ in NaCl and $NaClO_4$ as a function of the square root of ionic strength (Byrne et al., 2000, 2005).

and in $NaClO_4$ by

$$\log \beta_1^* = 5.269 - 2221/T - 2.044\ I^{0.5}/(1 + 2.388\ I^{0.5}) + 0.020\ I \quad (\sigma = 0.01) \tag{22}$$

It should be pointed out that the values of $\log \beta_1$ in pure water at 25 °C extrapolated in the two media differ (−2.18 in $NaClO_4$ and −2.34 in NaCl). Since the extrapolations in NaCl are affected by a larger interaction between Na^+ and Cl^-, measured values have been refit. The equation that extrapolates the results in NaCl to the same value in $NaClO_4$ is given by

$$\log \beta_1^* = 2.40 - 1366/T - 3.450\ I^{0.5}/(1 + 2.8\ I^{0.5}) - 0.237\ I \quad (\sigma = 0.012) \tag{23}$$

Unfortunately, at the present time only limited literature data (Byrne and Kester, 1976a,b, 1978; Liu and Millero, 1999; Byrne et al., 2005) are available for the hydrolysis constants β_2^*, β_3^*, and β_4^* for the formation of $Fe(OH)_2^+$, $Fe(OH)_3^0$ and $Fe(OH)_4^-$ in NaCl or other media (see Table 5). Most of the estimates of β_2^*, β_3^*, and β_4^* were determined from solubility measurements. The values of β_2^* and β_3^* in NaCl and seawater from solubility data (Liu and Millero, 1999; Byrne et al., 2000) have been estimated from equations of the form

$$\log[\mathrm{Fe(III)}] = \log K_{so}^* + m \log[\mathrm{H}^+] + \log(1 + \Sigma\beta_j^*/[\mathrm{H}^+]^{-j}) \tag{24}$$

where [Fe(III)] is the total concentration of iron and $K_{so}^* = [\mathrm{Fe}^{3+}][\mathrm{H}^+]^{-m}$ and $[\mathrm{Fe}^{3+}]$ is the free concentration of iron. The Liu and Millero (1999) solubility measurements made in NaCl used a value of $m = 3.0$. Byrne and Luo (2000) have shown that $m = 2.86$ based on their solubility measurements in 0.7 m $NaClO_4$. We have reanalyzed the solubility measurements of Liu and Millero (1999) over a pH range from 2.3 to 7.0 using

$$\log[\mathrm{Fe(III)}] = \log K_{so}^* + m\ \log[\mathrm{H}^+] + \log(1 + \beta_1^*/[\mathrm{H}^+] + \beta_2^*/[\mathrm{H}^+]^2) \tag{25}$$

where K_{so}^*, m and β_2^* were varied and the value of β_1^* was taken from the work of Byrne et al. (2005). The lowest standard deviations between the measured and calculated solubilities at 0.7 m were found when $\log\ \beta_2^* = -6.0 \pm 0.1$ and $\log K_{so}^* = 4.0 \pm 0.2$ and $m = 3.05 \pm 0.03$. The value of K_{so}^* and m is in good agreement with the values found by Liu and Millero (1999), but differ from the values of Byrne and Luo (2000) ($\log\ K_{so}^* = 4.28 \pm 0.05$ and $m = 2.86 \pm 0.009$) in 0.7 m $NaClO_4$. The differences in the values of K_{so}^* are mainly due to the differences in the activity of H_2O, $Fe(OH)_3(s)$ and activity coefficients of Fe^{3+} and H^+ in the two media

$$K_{so} = K_{so}^* \gamma(\mathrm{Fe}^{3+}) a(\mathrm{H_2O})^3/[a(\mathrm{Fe(OH)_3(s)})\gamma^3(\mathrm{H}^+)] \tag{26}$$

The differences in m may be related to differences in the solid phases formed in the two media. The Liu and Millero (1999) solubility measurements were made after equilibrating the samples for at least 7 days. Similar calculations were made at other concentrations of NaCl and the $\log \beta_2^*$ results

Table 5
Hydrolysis constants for the formation of $Fe(OH)_2{}^+$, $Fe(OH)_3$, and $Fe(OH)_4{}^-$ in various media at 25 °C

Media	Molality	Log K^*	$-\log \beta_2^*$	$-\log \beta_3^*$	$-\log \beta_4^*$
NaCl	0.01	4.06[b]	6.5[a], 6.2[b]	13.15[a], 14[b]	21.6[a], 22.4[b]
	0.1	3.6[a], 4.20[b]	6.0[a], 6.5[b]	14.19[a], 15[b]	21.8[a], 22.8[b]
	0.7	4.1[a], 4.16[b]	5.9[a], 6.5[b]	14.94[a], 15[b]	22.7[a], 22.8[b]
	5.0	5.3[a], 5.26[b]	6.4[a], 7.0[b]	15.92[a], 16[b]	24.3[a], 24.3[b]
KNO_3	0.1		5.9[c]		
	0.5		6.0[c]		
	0.7		6.0[c]		
	1.0		5.9[c]		
	3.0		6.3[c]		
SW	0.7		6.8[d]		
			6.0[e]	12.5[e]	21.8[e]
			6.4[f]	13.3[f]	−22.7[f]
		4.13[g]	6.5[g]	13.6[g]	
$NaClO_4$	0.7		7.3[h]		
			7.0[i]		
	1		5.9[i]	>12.54[j]	
	3		6.3[i]		

[a] This study.
[b] Liu and Millero (1999).
[c] Daniele et al. (1994).
[d] Byrne and Kester (1976a,b).
[e] Millero et al. (1995).
[f] Kuma et al. (1996).
[g] Liu and Millero (2002).
[h] Byrne and Kester (1978).
[i] Baes and Mesmer (1976).
[j] Byrne et al. (2000).

are compared to other workers in Table 5 and a few are shown as a function of the $I^{0.5}$ in Fig. 6. The $\log \beta_2^*$ results (−6.0) in 0.7 m NaCl obtained using the Byrne et al. (2005) values for $\log \beta_1^*$ are larger than the value (−6.5) obtained by Liu and Millero (1999), but in reasonable agreement with the values in KNO_3 (Daniele et al., 1994) and $NaClO_4$ (Baes and Mesmer, 1976). The seawater results (Liu and Millero, 2002) are lower than the values determined in NaCl, KNO_3, and $NaClO_4$. This may be related to interactions of $Fe(OH)^{2+}$ with F^- and SO_4^{2-} in seawater (Millero et al., 1995). The resulting values of $\log \beta_2^*$ and K_{so}^* have been fitted to the equation using the temperature data of Liu and Millero (1999).

$$\log \beta_2^* = -0.18 - 1996.5/T + 1.45\ I^{0.5} - 0.56\ I \qquad (\sigma = 0.2) \qquad (27)$$

$$\log K_{so}^* = -14.30 + 5251.6/T + 0.87\ I^{0.5} \qquad (\sigma = 0.06) \qquad (28)$$

As is obvious from the results shown in Fig. 6, more solubility measurements are needed especially at high ionic strengths to determine more reliable values of β_2^*.

Estimates of the values of $\log \beta_3^*$ and $\log \beta_4^*$ from solubility measurements (Byrne and Kester, 1976b; Millero et al., 1995; Kuma et al., 1996; Liu and Millero, 1999; Liu et al., 2000; Byrne et al., 2000) are quite sparse (see Table 5). The measurements of the solubility in seawater are not reliable due to the effect of natural organic ligands on the solubility (Kuma et al., 1996, 1992, 1998a,b; Millero, 1998). The values of $\log \beta_3^*$ and $\log \beta_4^*$ can be calculated from the measured solubility of iron, [Fe(III)], and the value of K_{so}^* determined at low pH from

$$\log \beta_3^* = \log[\mathrm{Fe(III)}] - \log K^*\mathrm{so}\ (\mathrm{pH\ near\ 8}) \qquad (29)$$

$$\log \beta_4^* = \log[\mathrm{Fe(III)}] - \log[\mathrm{H}^+] - \log K_{so}^*\ (\mathrm{pH\ above\ 9}) \qquad (30)$$

It should be pointed out that these equations assume that the solid state of $Fe(OH)_3(s)$ or K_{so}^* is the same over the entire pH range. As shown elsewhere (Liu et al., 2000) this may not be the case, since the structure of $Fe(OH)_3(s)$ at low pH, pH near 8.0 and at high pH does not appear to be the same. The recalculated values of $\log \beta_3^*$ in NaCl from solubility measurements (Liu and Millero, 1999) as a function of ionic strength and temperature have been fitted to the equation

$$\log \beta_3^* = 0.53 - 4042/T - 3.10\ I^{0.5} + 0.81\ I \quad (\sigma = 0.3) \qquad (31)$$

The recalculated values of $\log \beta_4^*$ in NaCl from solubility measurements (Liu and Millero, 1999) as a function of ionic strength and temperature have been fitted to the equation

$$\log \beta_4^* = 5.26 - 7976/T - 1.28\ I^{0.5} \qquad (\sigma = 0.1) \qquad (32)$$

New solubility measurements in NaCl and $NaClO_4$ solutions as a function of pH and ionic strength are needed to determine more reliable estimates for β_3^* and β_4^*. A summary of the hydrolysis constants for Fe(III) in water is given in

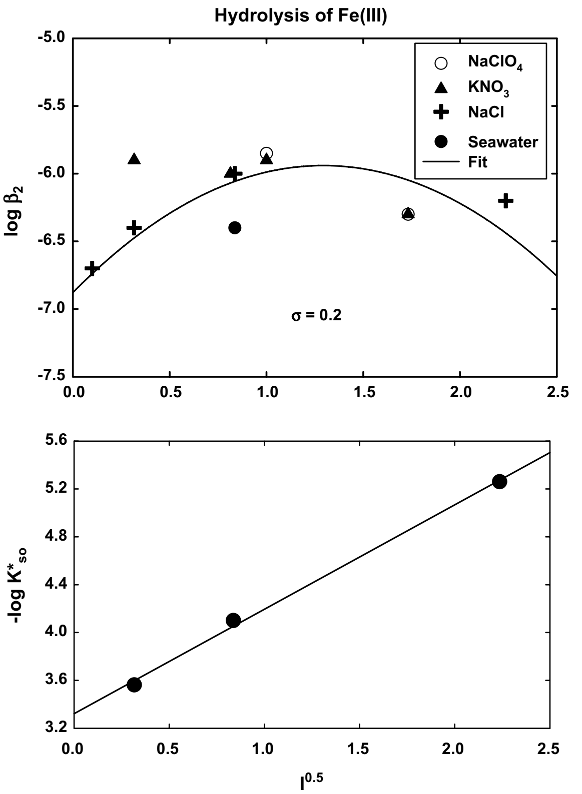

Fig. 6. Values of $\log \beta_2^*$ for the stepwise hydrolysis constant for the formation of $Fe(OH)_2^+$ as a function of the square root of ionic strength in NaCl (Liu and Millero, 1999), $NaClO_4$ (Baes and Mesmer, 1976), KNO_3 (Daniele et al., 1994) and seawater (Liu and Millero, 2002).

Table 6
Thermodynamic hydrolysis constants for the formation of $Fe(OH)^{2+}$, $Fe(OH)_2{}^+$, $Fe(OH)_3{}^0$, and $Fe(OH)_4{}^-$ in water at 25 °C

Constant	Reference
$-\log \beta_1$	
2.18	This study
2.18	Byrne et al. (2000)
2.1	Liu and Millero (1999)
2.20	Millero et al. (1995)
2.19	Baes and Mesmer (1976)
2.17	Kester et al. (1975)
$-\log \beta_2$	
6.9	This study
6.3	Liu and Millero (1999)
5.7	Millero et al. (1995)
5.67	Baes and Mesmer (1976)
7.17	Kester et al. (1975)
$-\log \beta_3^*$	
13.0	This study
14.3	Liu and Millero (1999)
11.8	Millero et al. (1995)
12.9	Byrne and Kester (1976a)
12.0	Baes and Mesmer (1976)
$-\log \beta_4^*$	
22.3	This study
22.3	Liu and Millero (1999)
21.6	Baes and Mesmer (1976)
24.4	Byrne and Kester (1976b)

Table 6 along with some literature results (Kester et al., 1975; Baes and Mesmer, 1976; Byrne and Kester, 1976a,b; Millero et al., 1995; Liu and Millero, 1999; Byrne et al., 2000).

1.3. Pitzer equations for the activity coefficients

The stepwise hydrolysis constants are related to the thermodynamic values (β_j) by

$$\beta_j^* = \beta_j \gamma(\mathrm{Fe}^{3+})\ a(\mathrm{H_2O})^j / \{\gamma(\mathrm{H}^+)^j \gamma(\mathrm{Fe(OH)}_j^{(3-j)})\} \tag{33}$$

This equation demonstrates that the measured values of β_j^* in a given media or two different media are affected by the water activity and activity coefficients of H^+, Fe^{3+} and the ion complexes $(\mathrm{Fe(OH)}_j^{(3-j)+})$. We prefer to attribute the differences of β_j^* in NaCl and $NaClO_4$ media in terms of the activity and activity coefficient rather than the formation of Cl^- complexes (Byrne et al., 2000). As shown by Christov (2004), this can be done when considering the equilibria of Fe^{3+} in various media. The activity of water $a(H_2O)$ and the activity coefficients (γ_i) of the H^+ and Fe^{3+} ions in NaCl and $NaClO_4$ solutions can be estimated from

$$a(\mathrm{H_2O}) = \exp(-2\ m\phi/55.51) \tag{34}$$

and the Pitzer expressions for single ion activity coefficients (Pitzer, 1991)

$$\begin{aligned}\ln\gamma(\mathrm{H}^+) = {} & f^\gamma + 2m_{\ \mathrm{Cl}}\beta^{(0)}_{\mathrm{HCl}} + (\beta^{(1)}_{\mathrm{HCl}})[1-(1+2I^{0.5})\\ & \times \exp(-2I^{0.5})] + 2m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{HCl}}\\ & + m_{\mathrm{Na}}m_{\mathrm{Cl}}(B'_{\ \mathrm{NaCl}} + C_{\mathrm{NaCl}})\\ & + m_{\mathrm{Na}}(2\theta_{\mathrm{Na\text{–}H}} + m_{\mathrm{Cl}}\psi_{\mathrm{HNaCl}})\end{aligned} \tag{35}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe}^{3+}) = {} & 9f^\gamma + 2m_{\mathrm{Na}}\beta^{(0)}_{\mathrm{FeCl_3}} + (\beta^{(1)}_{\mathrm{FeCl_3}})[1-(1+2I^{0.5})\\ & \times \exp(-2I^{0.5})] + 2\ m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{FeCl_3}}\\ & + 9\ m_{\mathrm{Na}}m_{\mathrm{Cl}}B'_{\mathrm{NaCl}} + 3\ m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\end{aligned} \tag{36}$$

(where $B'_{\mathrm{NaCl}} = (\beta^{(1)}_{\mathrm{NaCl}}/2\,I^2)[-1+(1+2\,I^{0.5}+2\,I)\exp(-2\,I^{0.5})$ and $f^\gamma = -A_\phi\ [I^{0.5}/(1+1.2\ I^{0.5}) + (2/1.2)\ \ln\ (1+1.2\ I^{0.5})]$, Millero et al., 1995).

Similar equations can be written for $NaClO_4$ solutions. The Debye–Hückel limiting law slopes, A_ϕ, at different temperatures are taken from the equation of Møller (1988).

The activity coefficients of the ion pairs $\mathrm{Fe(OH)}^{2+}$, $\mathrm{Fe(OH)_2}^+$, $Fe(OH)_3$, $\mathrm{Fe(OH)_4}^-$ can be determined from the rearrangement of Eq. (33)

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)}^{2+}) = {} & \ln\beta_1 - \ln\beta_1^* + \ln\gamma(\mathrm{Fe}^{3+})\\ & + \ln a(\mathrm{H_2O}) - \ln\gamma(\mathrm{H}^+)\end{aligned} \tag{37}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)_2}^{+}) = {} & \ln\beta_2 - \ln\beta_2^* + \ln\gamma(\mathrm{Fe}^{3+})\\ & + 2\ln a(\mathrm{H_2O}) - 2\ln\gamma(\mathrm{H}^+)\end{aligned} \tag{38}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)_3}) = {} & \ln\beta_3 - \ln\beta_3^* + \ln\gamma(\mathrm{Fe}^{3+})\\ & + 3\ln a(\mathrm{H_2O}) - 3\ln\gamma(\mathrm{H}^+)\end{aligned} \tag{39}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)_4}^{-}) = {} & \ln\beta_4 - \ln\beta_4^* + \ln\gamma(\mathrm{Fe}^{3+})\\ & + 4\ln a(\mathrm{H_2O}) - 4\ln\gamma(\mathrm{H}^+)\end{aligned} \tag{40}$$

A comparison of the activity coefficients of $\mathrm{Fe(OH)}^{2+}$ in NaCl and $NaClO_4$ calculated from Eq. (37) using the direct measurements of Byrne et al. (2000, 2005) is shown in Fig. 7. Below 3 m, the values in NaCl are slightly higher than the values in $NaClO_4$; while above this molality the values in $NaClO_4$ are higher. This is largely related to the differences in the activity coefficients of H^+ and Fe^{3+} in the two media (Fig. 4). The activity coefficients of $\mathrm{Fe(OH)}^{2+}$, $\mathrm{Fe(OH)_2}^+$, $Fe(OH)_3$ and $\mathrm{Fe(OH)_4}^-$ in NaCl determined from Eqs. (37)–(40) using the smoothed hydrolysis constants are shown in Fig. 8. The activity coefficients of $\mathrm{Fe(OH)}^{2+}$, $\mathrm{Fe(\ OH)}_2^+$, $Fe(OH)_3$, and $\mathrm{Fe(OH)_4}^-$ can be fitted to the Pitzer equations in NaCl or $NaClO_4$ which are given by

$$\begin{aligned}\ln\gamma(\mathrm{FeOH}^{2+}) = {} & 4f^\gamma + 2\ m_{\mathrm{Cl}}\beta^{(0)}_{\mathrm{FeOHCl_2}} + (\beta^{(1)}_{\mathrm{FeOHCl_2}})\\ & \times [1-(1+2I^{0.5})\exp(-2I^{0.5})]\\ & + m^2_{\mathrm{Cl}}C^{\phi}{}_{\mathrm{FeOHCl_2}}/|2|^{0.5}\\ & + 4\ m_{\mathrm{Na}}m_{\mathrm{Cl}}B'_{\mathrm{NaCl}} + 2\ m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\end{aligned} \tag{41}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)_2}^{+}) = {} & f^\gamma + 2\ m_{\ \mathrm{Cl}}\beta^{(0)}_{\mathrm{Fe(OH)_2Cl}} + (\beta^{(1)}_{\mathrm{Fe(OH)_2Cl}})\\ & \times [1-(1+2I^{0.5})\exp(-2I^{0.5})]\\ & + (1/36)(\beta^{(2)}_{\mathrm{Fe(OH)_2Cl}})[1-(1+12I^{0.5})\\ & \times \exp(-12I^{0.5})] + m^2_{\mathrm{Cl}}C^{\phi}{}_{\mathrm{Fe(OH)_2Cl}}\\ & + m_{\mathrm{Na}}m_{\mathrm{Cl}}B'_{\ \mathrm{NaCl}} + m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\end{aligned} \tag{42}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)_3}) = {} & 2\ m_{\mathrm{Na}}\lambda_{\ \mathrm{Fe(OH)_3\text{–}Na}} + 2\ m_{\mathrm{Cl}}\lambda_{\mathrm{Fe(OH)_3\text{–}Cl}}\\ & + m_{\mathrm{Na}}m_{\mathrm{Cl}}\zeta_{\mathrm{Fe(OH)_3NaCl}}\end{aligned} \tag{43}$$

$$\begin{aligned}\ln\gamma(\mathrm{Fe(OH)_4}^{-}) = {} & f^\gamma + 2\ m_{\mathrm{Na}}\beta^{(0)}_{\mathrm{NaFe(OH)_4}} + (\beta^{(1)}_{\mathrm{NaFe(OH)_4}})\\ & \times [1-(1+2I^{0.5})\exp(-2I^{0.5})]\\ & + m^2_{\mathrm{Na}}C^{\phi}_{\mathrm{NaFe(OH)_4}} + m_{\mathrm{Na}}m_{\mathrm{Cl}}B'_{\mathrm{NaCl}}\\ & + m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\end{aligned} \tag{44}$$

It has been found necessary to add a $\beta^{(2)}$ term in Eq. (42) in order to fit the data. The values of $\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, and C^ϕ at 25 °C for HCl, NaCl, $NaClO_4$, $FeCl_3$, and $Fe(ClO_4)_3$ used in these calculations are given in Table 2. Upon rearrangement of Eqs. (41)–(44) we have

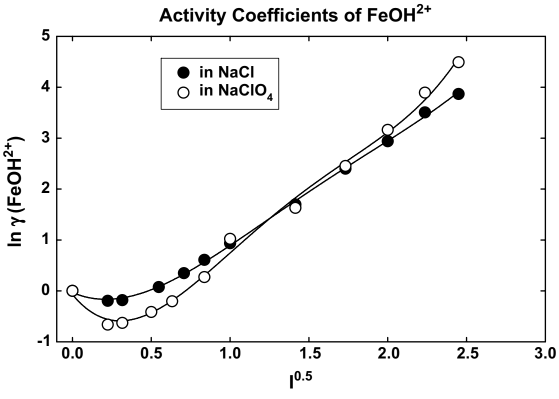

Fig. 7. The activity coefficient of $FeOH^{2+}$ in NaCl and $NaClO_4$ as a function of the square root of ionic strength at 25 °C.

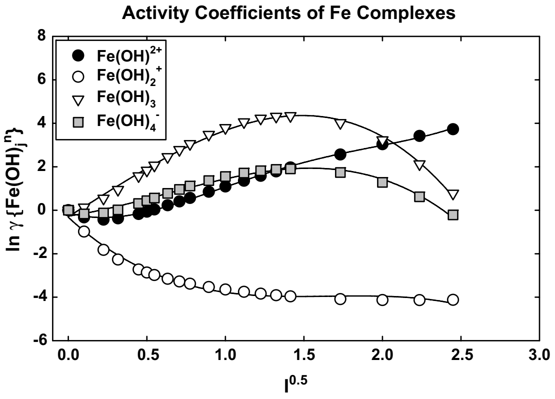

Fig. 8. The activity coefficient of $FeOH^{2+}$, $Fe(OH)_2{}^+$, $Fe(OH)_3$ and $Fe(OH)_4{}^-$ in NaCl solutions as a function of the square root of ionic strength at 25 °C.

$$\begin{aligned}Y_1 &= \ln\gamma(\mathrm{FeOH}^{2+}) - 4f^{\gamma} - 4\ m_{\mathrm{Na}}m_{\mathrm{Cl}}B'_{\mathrm{NaCl}} - 2\ m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\\ &= 2\ m_{\mathrm{Cl}}\beta^{(0)}_{\mathrm{FeOHCl_2}} + (\beta^{(1)}_{\mathrm{FeOHCl_2}})[1-(1+2I^{0.5})\exp(-2I^{0.5})]\\ &\quad + m^2_{\mathrm{Cl}}C^{\phi}_{\mathrm{FeOHCl_2}}/|2|^{0..5} \qquad (45)\end{aligned}$$

$$\begin{aligned}Y_2 &= \ln\gamma(\mathrm{Fe(OH)_2}{}^{+}) - f^{\gamma} - m_{\mathrm{Na}}m_{\mathrm{Cl}}\ B'_{\mathrm{NaCl}} - m\ _{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\\ &= 2\ m_{\mathrm{Cl}}\beta^{(0)}_{\mathrm{Fe(OH)_2Cl}}\\ &\quad + (\beta^{(1)}_{\mathrm{Fe(OH)_2Cl}})[1-(1+2\ I^{0.5})\exp(-2\ I^{0.5})]\\ &\quad + (1/36)(\beta^{(2)}_{\mathrm{Fe(OH)_2Cl}})[1-(1+12I^{0.5})\exp(-12\ I^{0.5})]\\ &\quad + m^2_{\mathrm{Cl}}C^{\phi}{}_{\mathrm{Fe(OH)_2Cl}} \qquad (46)\end{aligned}$$

$$\begin{aligned}Y_3 &= \ln\gamma(\mathrm{Fe(OH)_3}) = 2\ m_{\mathrm{Na}}\lambda_{\mathrm{Fe(OH)_3-Na}}\\ &\quad + 2\ m_{\mathrm{Cl}}\lambda_{\mathrm{Fe(OH)_3-Cl}} + m_{\mathrm{Na}}m_{\mathrm{Cl}}\zeta_{\mathrm{Fe(OH)_3NaCl}} \qquad (47)\end{aligned}$$

$$\begin{aligned}Y_4 &= \ln\gamma(\mathrm{Fe(OH)_4}{}^{-}) - f^{\gamma} - m_{\mathrm{Na}}m_{\mathrm{Cl}}\ B'_{\mathrm{NaCl}} - m_{\mathrm{Na}}m_{\mathrm{Cl}}C_{\mathrm{NaCl}}\\ &= 2\ m_{\mathrm{Na}}\beta^{(0)}_{\mathrm{NaFe(OH)_4}} + (\beta^{(1)}{}_{\mathrm{NaFe(OH)_4}})[1-(1+2I^{0.5})\exp(-2\mathrm{I}^{0.5})]\\ &\quad + m^2_{\mathrm{Na}}C^{\phi}_{\mathrm{NaFe(OH)_4}} \qquad (48)\end{aligned}$$

The values of $\beta^{(0)}_{FeOHCl_2}$, $\beta^{(1)}{}_{FeOHCl_2}$, and $C^{\phi}_{FeOHCl_2}$ in NaCl and $NaClO_4$ at 25 °C are given in Table 4. The standard errors in the fits are 0.034 and 0.035, respectively, for ln β^*_1 in NaCl and $NaClO_4$ solutions. The 25 °C values of $\beta^{(0)}_{MX}$, $\beta^{(1)}{}_{MX}$, $\beta^{(2)}_{MX}$, and C^{ϕ}_{MX} in NaCl for $FeOHCl_2$, $Fe(OH)_2Cl$, and $NaFe(OH)_4$ and $\lambda_{Fe(OH)_3-Na}$ and $\zeta_{Fe(OH)_3NaCl}$ for $Fe(OH)_3$ are given in Table 7. The value of $\lambda_{Fe(OH)_3-Cl}$ is assumed to be zero (Millero, 2000). We were unable to get a reasonable fit for the $Fe(OH)_3$ data past $I = 1$ m. Therefore, the Pitzer parameters for this complex are only valid for ionic strengths below 1 m. Similar calculations have been made as a function of temperature and the resulting Pitzer coefficients have been fitted to Eq. (16). The coefficients for Eq. (16) for $FeOHCl_2$, $Fe(OH)_2Cl$, $Fe(OH)_3$ and $NaFe(OH)_4$ are tabulated in Table 4. No temperature dependence was found for the $Fe(OH)_3$ parameters for ionic strength below 1 m.

The values in NaCl with appropriate estimates of Pitzer parameters for enthalpy and heat capacity can be used to estimate the values of β^*_i in natural waters over a wide range of temperature and ionic strength (Liu and Millero, 1999). Hopefully in the future, new solubility measurements will become available from pH 7 to 12 that can be used to improve the reliability of the values of log β^*_3, and log β^*_4 estimated in this paper.

Table 7
The Pitzer coefficients for $Fe(OH)Cl_2$, $Fe(OH)_2Cl$, $Fe(OH)_3{}^0$, and $NaFe(OH)_4$ in NaCl solutions at 25 °C

Species	Parameter	σ (ln β^*_i)
$Fe(OH)Cl_2$		
$\beta^{(0)}$	0.19 ± 0.01	0.039
$\beta^{(1)}$	5.61 ± 0.05	
C^{ϕ}	0.0087 ± 0.006	
$Fe(OH)_2Cl$		
$\beta^{(0)}$	0.96 ± 06	0.08
$\beta^{(1)}$	−4.1 ± 0.3	
$\beta^{(2)}$	−219.8 ± 5	
C^{ϕ}	−0.39 ± 0.02	
$Fe(OH)_3{}^0$		
λ	3.96 ± 0.1	0.14
ζ	−4.27 ± 0.3	
$NaFe(OH)_4$		
$\beta^{(0)}$	0.88 ± 0.1	0.21
$\beta^{(1)}$	0.16 ± 0.4	
C^{ϕ}	−0.25 ± 0.4	

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