

DEPENDENCE OF SOLUBILITY OF FINE PARTICLES ON SURFACE CHARGE

Sergey Pivovarov

Institute of Experimental Mineralogy RAS
142432 Chernogolovka, Moscow district, Russia
E-mail: serg@iem.ac.ru

Published on-line 15.06.2015¹

ABSTRACT

Solubility product of hydrous ferric oxide decreases with modulus of surface charge in accordance with empirical correlation: $\log(a_{\text{Fe}}/a_{\text{H}}^3) = 3.4 - 13[\sigma, \text{eq/mol Fe}]^2$, where a_{Fe} and a_{H} are activities of Fe^{3+} and H^+ ions, and $[\sigma, \text{eq/mol Fe}]$ is surface charge in equivalents per mole of Fe in precipitate. Causes of such behavior are considered.

INTRODUCTION

As found by Biedermann and Chou (1966), solubility of hydrous ferric oxide in acidic field is consistent with concentration ratio $[\text{Fe}^{3+}]/[\text{H}^+]^{2.7} = 10^{3.04}$ (25°C, I = 0.5 M NaCl, pH ~ 1.8-3; aged for 3 weeks). Here and so on, symbol of species in square brackets denotes concentration, whereas symbol $[\text{Fe}^{3+}]$, in reality, is $[\text{Fe}^{3+} + \text{FeCl}^{2+} + \text{FeCl}_2^+ \dots]$. It should be noted that the chloride complexation with ferric ion is well known fact (see Byrne et al., 2005 and references herein). However, it is convenient to consider the chloride complexation as medium effect.

Similar “nonintegral slopes”, $d\log[\text{Fe}^{3+}]/d\log[\text{H}^+] < 3$, were obtained by others (Fox, 1988; Byrne and Lyo, 2000; Byrne et al, 2005). The nature of this phenomenon is not known. And this is a problem.

Fig. 1 shows solubility of hydrous ferric oxide, data Liu and Millero (1999). The solid curve was calculated in accordance with solubility product $[\text{Fe}^{3+}]/[\text{H}^+]^3 = 4.2$ and hydrolysis constants given in **Tab. 1**. Dashed curve was calculated in accordance with apparent solubility product $[\text{Fe}^{3+}]/[\text{H}^+]^{2.7} = 10^{3.5}$. Note that the hydrolytic species FeOH^{2+} and $\text{Fe}(\text{OH})_2^+$ give major contribution to solubility in $p[\text{H}^+]$ range ~ 3.2 – 6.3.

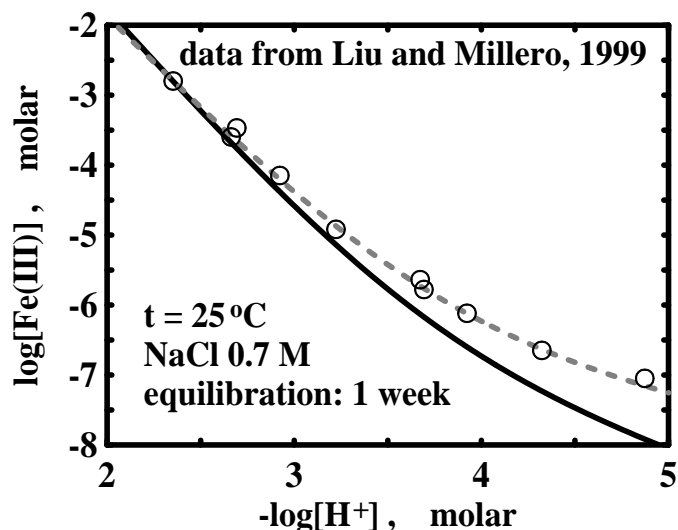
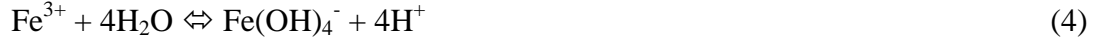


Fig. 1 Solubility of hydrous ferric oxide in acidic field (data from Liu and Millero, 1999). Dashed gray curve: calculated with apparent solubility product $\log[\text{Fe}^{3+}] - 2.7\log[\text{H}^+] = 3.5$ and hydrolysis constants from Tab. 1. Solid curve: $\log[\text{Fe}^{3+}] - 3\log[\text{H}^+] = 4.2$ and the same set of hydrolysis constants. $[\text{Fe}(\text{III})]$ is total concentration of trivalent iron in solution.

¹ With significant correction from 14.09.2015

MONONUCLEAR HYDROLYSIS OF FERRIC ION

To simulate solubility of hydrous ferric oxide, it is necessary to know hydrolysis constants of ferric ion. Reactions of mononuclear hydrolysis of Fe^{3+} are:



As a common rule, activity of water is omitted in reaction quotients for convenience, and results of measurements are reported as:

$$\beta_1 = [\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}] \quad (5)$$

$$\beta_2 = [\text{Fe}(\text{OH})_2^+][\text{H}^+]^2/[\text{Fe}^{3+}] \quad (6)$$

$$\beta_3 = [\text{Fe}(\text{OH})_3^0][\text{H}^+]^3/[\text{Fe}^{3+}] \quad (7)$$

$$\beta_4 = [\text{Fe}(\text{OH})_4^-][\text{H}^+]^4/[\text{Fe}^{3+}] \quad (8)$$

Note that $[\text{Fe}^{3+}]$ in NaCl solutions is, in reality, $[\text{Fe}^{3+} + \text{FeCl}^{2+} + \text{FeCl}_2^+]$.

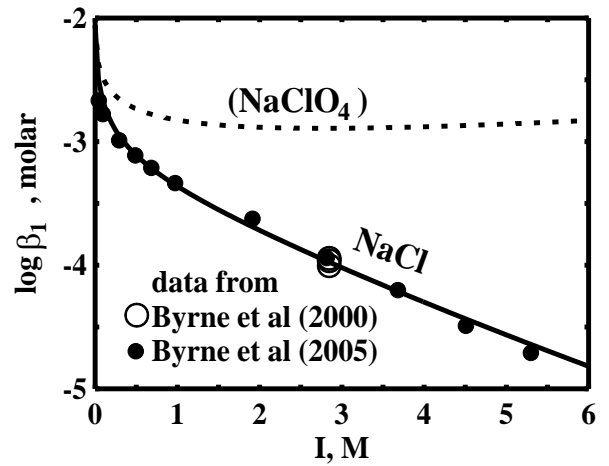
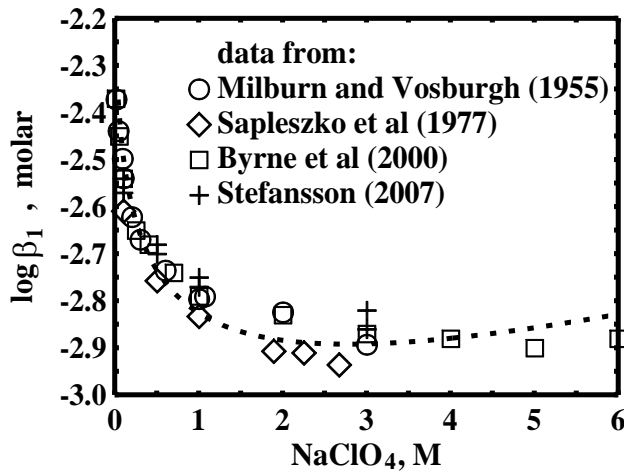


Fig. 2 First hydrolysis constant of ferric ion at $t = 25^\circ\text{C}$ in NaClO_4 solutions. Data from Milburn and Vosburgh (1955), Sapieszko et al (1977), Byrne et al (2000), Stefansson (2007). Dashed curve: Eq (9).

Fig. 3 First hydrolysis constant of ferric ion at $t = 25^\circ\text{C}$ in NaCl solutions. Data from Byrne et al (2000, 2005). Solid curve: Eqs. (11, 12, 9). Dashed curve: Eq. (9).

Fig. 2 shows the values of β_1 in NaClO_4 solutions as measured by Byrne et al (2000), Stefansson (2007), Sapieszko et al (1977), Milburn and Vosburgh (1955). The data were approximated using the SIT approach (see Grenthe et al. 1997):

$$\log\beta_1(\text{NaClO}_4, \text{M}) = -2.06 - 4 \times 0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) + 0.05 \times I \quad (9)$$

Here I is ionic strength (M, moles per dm^3), -2.06 is $\log\beta_1$ at zero ionic strength, factor $-4 = \sum z_{\text{res}}^2 - \sum z_{\text{ini}}^2$, where z_{ini} and z_{res} are charges of initial and resulting compounds of reaction (Eq. 1), 0.51 Debye-Hückel constant, factor 1.5 is fixed model parameter of SIT approach, and 0.05 is adjustable parameter.

In **Fig. 3**, the values of β_1 in NaCl solution are shown (data from Byrne et al 2000, 2005). The values of β_1 in Byrne et al (2005) were measured on molal scale (m, moles per kg H₂O). These data in **Fig. 3** (solid circles) were converted to molar scale in accordance with (fit to conversion factors given by Baes and Mesmer, 1976):

$$[\text{NaCl}, M] = [\text{NaCl}, m] / \{1 + 0.022 \times [\text{NaCl}, m]\} \quad (10)$$

The solid curve in **Fig. 3** (for NaCl solutions):

$$\log \beta_n(\text{NaCl}, M) = \log \beta_n(\text{NaClO}_4, M) - \Delta \log \beta \quad (11)$$

$$\Delta \log \beta = \log(1 + [\text{Cl}^-, M] \times 10^{\{1.37 - 6 \times 0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) + 0.24 \times I\}}) \quad (12)$$

Here (Eq. 11) subscript “n” is 1 for β_1 , 2 for β_2 , etc. As may be seen, depression in activity of Fe³⁺ ion in NaCl as compared with NaClO₄ solution may be successfully approximated by formation of ionic pair FeCl²⁺. Note, however, that Eq. (12) is approximation of all effects (both chloride complexation and medium effects).

In **Fig. 4**, the values of β_2 are shown (data from Hedström, 1953; Byrne et al 2000; Perera and Hefter 2003; Stefánsson 2007). The dashed curve in **Fig. 4** (for NaClO₄ solutions):

$$\log \beta_2(\text{NaClO}_4, M) = -5.8 - 6 \times 0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) + 0.1 \times I \quad (13)$$

The values of β_2 in NaCl solutions (solid curve in **Fig. 4**) were calculated from Eqs. (11, 12, 13).

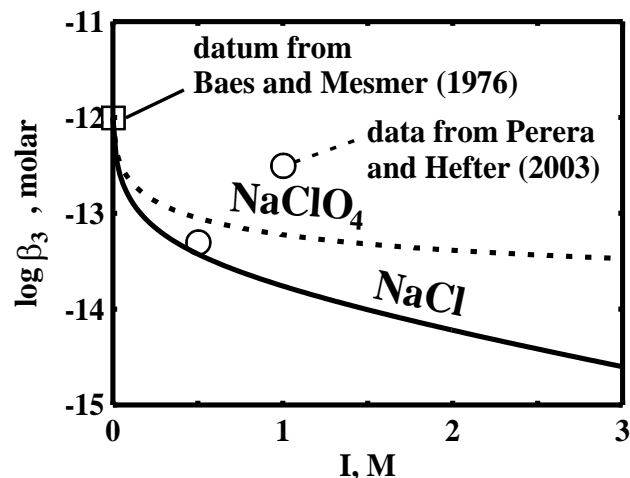
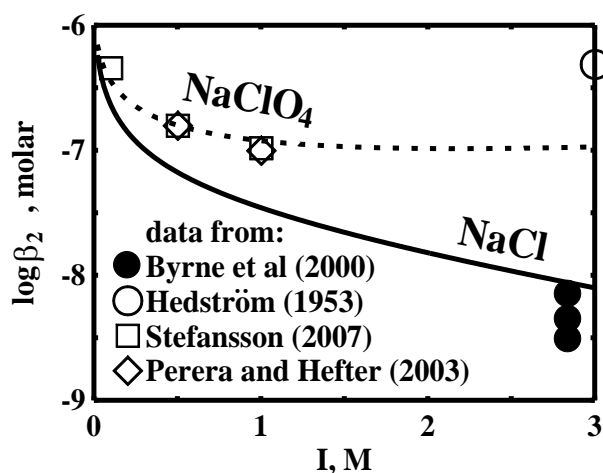


Fig. 4 Second hydrolysis constant of ferric ion at $t = 25^\circ\text{C}$ in NaClO₄ (open symbols) and NaCl solutions (closed symbols). Data from Hedström (1953), Byrne et al (2000), Perera and Hefter (2003), Stefánsson (2007). Solid curve: Eqs (11, 12, 13). Dashed curve: Eq. (13).

Fig. 5 Third hydrolysis constant of ferric ion at $t = 25^\circ\text{C}$. Data from Perera and Hefter (2003), NaClO₄ medium, and zero ionic strength estimate from Baes and Mesmer (1976). Dashed curve: Eq. (14). Solid curve: Eqs. (11, 12, 14).

In **Fig. 5**, some estimates (or, guesses) for β_3 are shown. It should be noted that, due to low solubility of ferric oxides, direct measurements of β_3 are almost impossible. The only spectroscopic measurement (at detection limit) was performed by Perera and Hefter (2003). The value $\beta_3 = 10^{-12}$ at zero ionic strength was estimated by Baes and Mesmer (1976) from solubility data. The dashed curve in **Fig. 5** (for NaClO₄ solutions):

$$\log\beta_3(\text{NaClO}_4, \text{M}) = -12 - 6 \times 0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) \quad (14)$$

Solid curve in **Fig. 5** (for NaCl solutions) was calculated in accordance with Eqs. (11, 12, 14).

In **Fig. 6**, data for β_4 are shown. The value β_4 at zero ionic strength is from Baes and Mesmer (1976). The data from Schindler et al (1963) in NaClO₄ solution, and from Liu and Millero (1999) in NaCl solutions are based on solubility of ferric (hydr)oxides in basic field and solubility products for the same solids. The present model (curves) deviates from these data by ~ 0.6-0.8 log units.

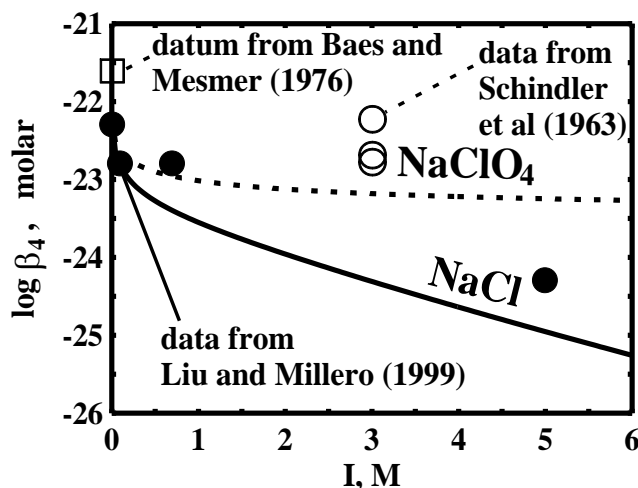


Fig. 6 Fourth hydrolysis constant of ferric ion in NaClO₄ (open circles) and NaCl (closed circles) solutions. Data from Schindler et al (1963), Liu and Millero (1999), and zero ionic strength estimate from Baes and Mesmer (1976). Dashed curve: Eq. (15). Solid curve: Eqs. (11, 12, 15).

In present study, the values of $\log\beta_4$ were estimated via modeling of the solubility data given by Liu and Millero (1999) with accounting for dependence of solubility on surface charge. The obtained correlation for NaClO₄ solutions (dashed curve in **Fig. 6**):

$$\log\beta_4(\text{NaClO}_4, \text{M}) = -22.2 - 4 \times 0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) \quad (15)$$

The values of β_4 in NaCl solutions (solid curve in Fig. 6) were calculated from Eq. (11, 12, 15). The accepted values of hydrolysis constants of ferric ion in 0.7 M NaCl solutions are given in **Tab. 1**.

Tab. 1 Hydrolysis constants of ferric ion at 25°C, calculated from Eqs. (9, 11, 12, 13, 14, 15) and solubility product of hydrous ferric oxide (corrected on surface charge). Note that $[\text{Fe}^{3+}]$ in NaCl solution is, in reality, $[\text{Fe}^{3+} + \text{FeCl}^{2+} + \text{FeCl}_2^+]$.

Quotient	I → 0	0.7 M NaClO ₄	0.7 M NaCl
$\log\beta_1 = \log\{[\text{FeOH}^{2+}][\text{H}^+]/[\text{Fe}^{3+}]\}$	-2.06	-2.78	-3.22
$\log\beta_2 = \log\{[\text{Fe}(\text{OH})_2^+][\text{H}^+]^2/[\text{Fe}^{3+}]\}$	-5.80	-6.87	-7.31
$\log\beta_3 = \log\{[\text{Fe}(\text{OH})_3^0][\text{H}^+]^3/[\text{Fe}^{3+}]\}$	-12	-13.14	-13.58
$\log\beta_4 = \log\{[\text{Fe}(\text{OH})_4^-][\text{H}^+]^4/[\text{Fe}^{3+}]\}$	-22.2	-22.96	-23.40
$\log\{[\text{Fe}^{3+}]/[\text{H}^+]^3\} - \log\{a_{\text{HFO}}\}$	3.4	4.54	4.98

CORRELATION BETWEEN SOLUBILITY AND SURFACE CHARGE

Fig. 7 shows the surface charge of hydrous ferric oxide, as measured by Pivovarov (2009). For convenience, these data were approximated by empirical equation (curves in Fig. 7):

$$\sigma, \text{ eq/mol Fe} = 0.28/(1 + 10^{(\text{pH} - 5.0 - \log(I))/4}) - 0.28/(1 + 10^{(11.2 - \text{pH} - \log(I))/4}) \quad (16)$$

Here pH is negative logarithm of proton activity in solution.

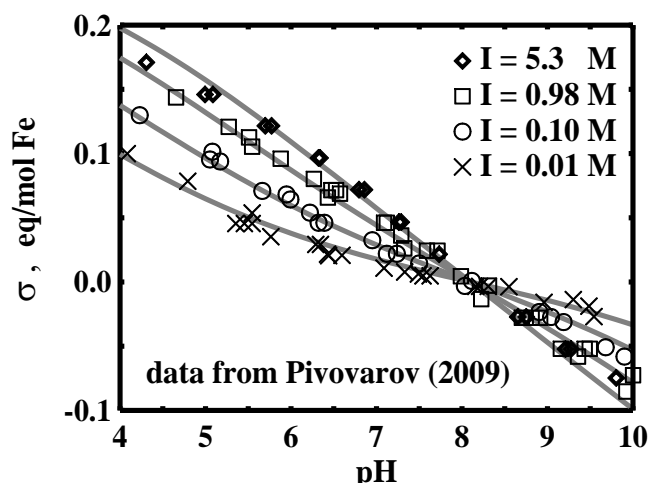


Fig. 7 Surface charge of hydrous ferric oxide (aged for 2 days) in NaCl + 0.01 M NaNO₃ solutions at 25°C. Acid and base titrations. Equilibration: 10-15 min. Data from Pivovarov (2009). Curves: Eq. (16).

For NaCl solutions, conversion of pH to $-\log[H^+]$ (molar scale) may be performed as

$$\text{pH} = -\log[H^+] - \log(\gamma_H) \quad (17)$$

$$\log(\gamma_H), \text{ molar} = -0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) + 0.113 \times I + 0.011 \times I^2 / (1 + 0.077 \times I) \quad (18)$$

Here, as before, I is ionic strength (molar concentration of NaCl). Eq. (18) is fit to mean activity coefficient of HCl from Voznesenskaya (1968), converted to molar scale with use of density data from Zaitcev and Aseev (1988). This approximation is valid up to 7 M HCl. In assumption that the values of activity coefficient of proton in equimolar HCl and NaCl solutions are equal, Eq. (18) gives reasonable estimates for activity coefficient of proton in NaCl solution. At I = 0.7 M, $\text{pH} = -\log[H^+] + 0.105$.

Apparent solubility product for hydrous ferric oxide may be found from solubility data in accordance with (as for hydrolysis constants, activity of water is omitted):

$$\log L = \log\{[Fe^{3+}]/[H^+]^3\} = \log[FeIII] - 3\log[H^+] - \log\{\alpha\} \quad (19)$$

$$\alpha = 1 + \beta_1/[H^+] + \beta_2/[H^+]^2 + \beta_3/[H^+]^3 + \beta_4/[H^+]^4 \quad (20)$$

Correction to zero ionic strength may be estimated from (for NaCl solutions):

$$\log L^0 = \log\{a_{Fe}/a_H^3\} = \log L - 6 \times 0.51 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) - \Delta \log \beta \quad (21)$$

Here a_{Fe} is activity of Fe³⁺ ion and a_H is activity of proton. As before, the value $\Delta \log \beta$ (= 0.44 at I = 0.7 M) is defined by Eq. (12).

Fig. 8 shows the values of $\log L^{\circ}$, calculated from solubility data given by Liu and Millero (1999). It should be noted that in the original study (Liu and Millero, 1999), designation “pH” was used. However, authors write: “electrode was calibrated on free hydrogen scale by titrating a 0.7 M NaCl solution free of CO₂ with strong acid”. Thus, it was assumed that the designation “pH” was used by Liu and Millero (1999) for negative logarithm of molar concentration of free hydrogen ions, $-\log[H^+]$.

So on, the values of $-\log[H^+]$ were first converted to pH (see Eqs. 17, 18), and then, the values of pH were converted into surface charge via Eq. (16). As may be seen in **Fig. 8**, there is distinctive correlation between the solubility product and surface charge. Solid curve in **Fig 8** is:

$$\log L^{\circ} = \log(a_{\text{Fe}}/a_{\text{H}}^3) = 3.4 + \log(a_{\text{HFO}}) \quad (22)$$

$$\log(a_{\text{HFO}}) = -13 \times [\sigma, \text{eq/mol Fe}]^2 \quad (23)$$

Here a_{HFO} is activity of hydrous ferric oxide.

It should be noted, the branch of negative surface charge in **Fig. 8** is artificial, i.e., consistence with Eq. (23) was achieved via adjustment of constant β_4 . Contrarily, selected values of β_1 and β_2 are well supported by experimental data (see Figs 2, 3, 4). Besides, 5 points (last in the right) are not affected by hydrolysis. Thus, correlation, given by Eq. (23) is well grounded, at least, in the field of positive surface charge (i.e. at pH < 8.1).

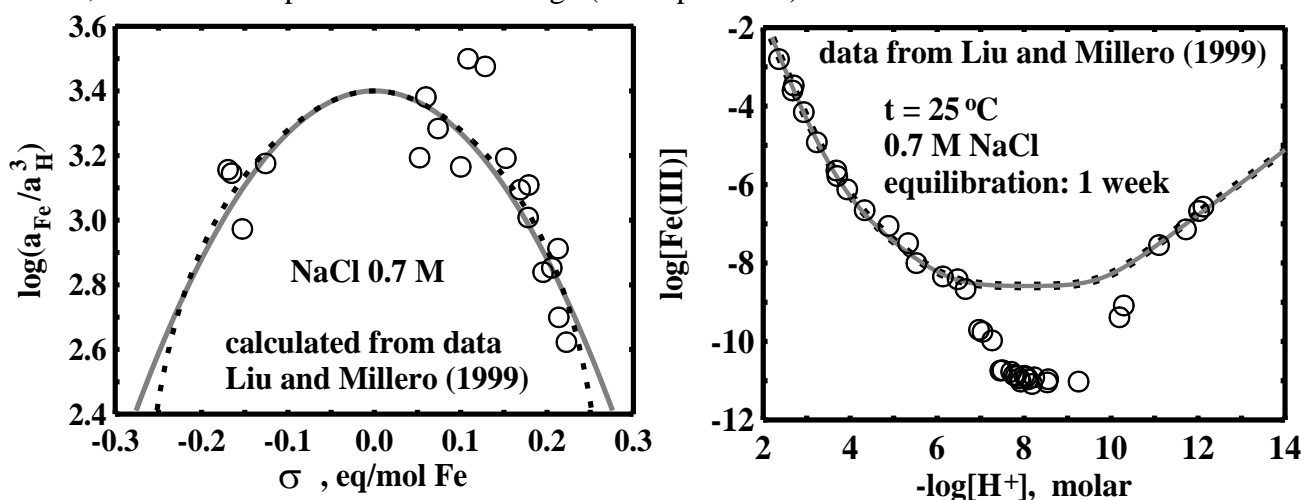


Fig. 8 Correlation between solubility product (corrected to zero ionic strength) and surface charge of hydrous ferric oxide. Calculated from solubility data given by Liu and Millero (1999) and Eqs. (21, 19, 20, 12). Solid gray curve: “hypothesis number one”, Eqs. (22, 23). Dashed curve: “hypothesis number two”, Eqs (22, 33, 16).

Fig. 9 Solubility of hydrous ferric oxide in 0.7 M NaCl solution as function of proton concentration. Data from Liu and Millero (1999). Solid gray curve: “hypothesis number one”, Eqs. (24, 20, 23, 16). Dashed curve: “hypothesis number two”, Eqs. (24, 20, 33).

Fig. 9 shows fit to original solubility data from Liu and Millero (1999), solid curve is:

$$\log[\text{FeIII}] = 4.98 - 3\log[H^+] + \log\{\alpha\} + \log\{a_{\text{HFO}}\} \quad (24)$$

Here $4.98 = 3.4 + 3.06 \times I^{0.5} / (1 + 1.5 \times I^{0.5}) + \Delta \log \beta$; $\Delta \log \beta = 0.44$ is that from Eq. 12 (for 0.7 M NaCl); $\log\{\alpha\}$ is that from Eq. (20) and data in Tab. 1; $\log\{a_{\text{HFO}}\}$ is that from Eqs. (23, 16).

It should be noted that the “deep pit” in the pH range ~ 7-11 cannot be simulated via arbitrary adjustment of hydrolysis constants (see Fig. 3 in Liu and Millero, 1999). Presumably,

dissolved iron was lost due to adsorption on filter. Perhaps, $\log[\text{FeIII}] \sim 10^{-9} - 10^{-8}$ in sample is close to adsorption capacity of filter, and higher concentrations of iron are probably not distorted. Apart from this, empirical model gives reasonable agreement with experiment.

HYPOTHESIS NUMBER ONE

The field strength near the charged interface is:

$$E = -\sigma_s/\epsilon_0\epsilon \tag{25}$$

Here E is field strength (V/m), σ_s is surface charge (C/m^2), ϵ_0 is dielectric constant of free space ($= 8.8542 \times 10^{-12} \text{ C} \times \text{V}^{-1} \times \text{m}^{-1}$), and ϵ is relative dielectric constant of medium (78.47 for liquid water at 25°C). Sign minus means that the positive potential decreases with distance from positively charged surface (and otherwise).

The electric force, applied to element $\Delta s = 1$ of charged surface, is electric pressure:

$$P_{el} = f/\Delta s = -\sigma_s \times (E + E_{inn})/2 = -\sigma_s \times (E/2) = \sigma_s^2/2\epsilon_0\epsilon \tag{26} \text{ or}$$

$$P_{el, \text{ bar}} = 7200[\sigma_s, \text{ C}/\text{m}^2]^2 \tag{26a}$$

Here $E_{inn} = 0$ is field strength inside of charged particle, P_{el} is electric pressure at interface ($1 \text{ bar} = 10^5 \text{ Pa}$ or N/m^2). Due to electrostatic repulsion, electric force f (see Eq. 26) is always directed outside from the charged body. This generates expansive stress inside of charged particle, and pressure inside of particle may be negative.

For charged particle in air, “pressure at interface” is simply an atmospheric pressure (see Pivovarov, 2013). In case of charged particle in electrolyte solution, this is not true. “Charged particle in electrolyte solution” is always electrically neutral, because the surface charge is completely compensated by charge of diffuse layer. Consequently, P_{el} (see Eq. 26) is positive pressure in a very fine surface layer, compressed between the diffuse layer and charged surface.

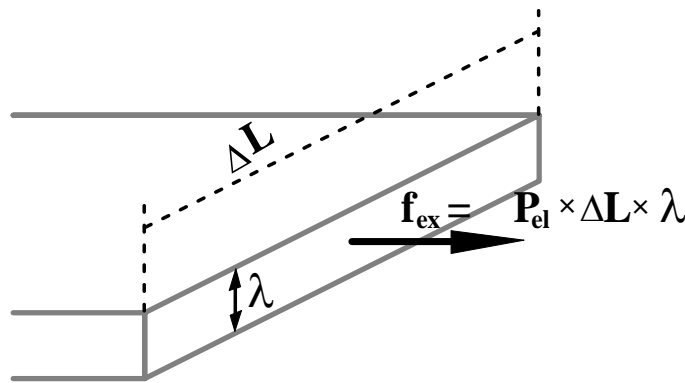


Fig. 10 Expansive force f_{ex} applied to frontier element $\Delta L \times \lambda$ of surface layer.

The expansive force applied to frontier element $\Delta L \times \lambda$ of this “surface layer” (see Fig. 10) is $f_{ex} = P_{el} \times \Delta L \times \lambda$, where λ is thickness of surface layer. Thus, “electric surface tension” may be calculated from:

$$\omega_{el} = -\lambda \times P_{el} = -\lambda \times \sigma_s^2/2\epsilon_0\epsilon \tag{27} \text{ or}$$

$$\omega_{el, \text{ N/m}} = -0.072[\lambda, \text{ \AA}][\sigma_s, \text{ C}/\text{m}^2]^2 \tag{27a}$$

Here $\omega_{el} = -f_{ex}/\Delta L$ is “electric surface tension”, N/m (= J/m²). As common, surface tension is contractive force. However, “electric surface tension”, ω_{el} , is always expansive, and thus, negative.

With known surface tension, activity of hydrous ferric oxide may be calculated from Gibbs equation (see Kaptay, 2011):

$$\ln(a_{\text{HFO}}) = \{\omega_{el} \times S \times M\} / \{RT\} \quad (28)$$

Applying $S = 600 \text{ m}^2/\text{g FeOOH}$ (Dzombak and Morel, 1990), $M = 88.85 \text{ g/mol FeOOH}$, $R = 8.3144 \text{ J} \times \text{mol}^{-1} \times \text{K}^{-1}$, $T = 298.15 \text{ K}$, and Faraday constant 96485 C/eq , one may obtain numerical relation:

$$\log(a_{\text{HFO}}) = -2.20 \times [\lambda, \text{Å}] \times [\sigma_s, \text{eq/mol Fe}]^2 \quad (\text{at } S = 600 \text{ m}^2/\text{g FeOOH}) \quad (29)$$

Thus, as may be found from Eqs. (23, 29), “thickness of surface layer” is $13/2.2 = 5.91 \text{ Å}$, which is close to doubled diameter of water molecule. From volume per molecule in liquid water at 25°C, 30 Å^3 , diameter of water molecule is about of 3.11 Å .

HYPOTHESIS NUMBER TWO

As it was suggested by Biedermann and Chou (1966), true chemical formula for the hydrous ferric oxide is $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$, which was found to be consistent with measured slope, $d\log[\text{Fe}^{3+}]/d\log[\text{H}^+]$. However, this is not true, because Fe:OH ratio in precipitate varies with pH in accordance with:

$$\text{OH:Fe ratio} = 3 - [\sigma, \text{eq/mol Fe}] \quad (30)$$

One may suggest that OH:Fe ratio in precipitate gives true slope $d\log\{a_{\text{Fe}}\}/d\log\{a_{\text{H}}\}$:

$$d\log\{a_{\text{Fe}}\}/d\log\{a_{\text{H}}\} = 3 - [\sigma, \text{eq/mol Fe}] \quad (31)$$

Consequently, differential of activity of hydrous ferric oxide (= $d\log\{a_{\text{Fe}}/a_{\text{H}}^3\}$) may be found from:

$$d\log(a_{\text{HFO}}) = [\sigma, \text{eq/mol Fe}] \times dpH \quad (32)$$

Integration of Eq. (32) with $[\sigma, \text{eq/mol Fe}]$ taken from Eq. (16) gives the following relation:

$$\begin{aligned} \log(a_{\text{HFO}}) = & -0.28 \times 4 \times \log(1 + 10^{\{(\text{pH} - 5.0 - \log(I))/4\}}) \\ & -0.28 \times 4 \times \log(1 + 10^{\{(11.2 - \text{pH} - \log(I))/4\}}) \\ & + 0.28 \times 4 \times 2 \times \log(1 + 10^{\{(3.1 - \log(I))/4\}}) \end{aligned} \quad (33)$$

Dashed curve in **Fig. 8** was calculated with use of Eqs. (22, 33), with conversion of pH to surface charge via Eq. (16). As may be seen in **Fig. 8**, both approaches are very close each other. It is interesting, that the “hypothesis number two” has no adjustment parameters. Nevertheless, it gives excellent fit to experimental data, even better than adjustable “hypothesis number one”. Fit of “hypothesis number two” to original solubility data in **Fig. 9** (dashed curve) is indistinguishable from that of “hypothesis number one” (solid gray curve).

Differentiation of Gibbs equation (Eq. 28) gives the following equality:

$$d\log(a_{\text{HFO}}) = \{SM/RT\ln(10)\}d\omega_{\text{el}} \quad (34)$$

Thus, from Eqs. (32, 34) one may obtain relation:

$$\begin{aligned} d\omega_{\text{el}} &= \{RT\ln(10)/SM\}[\sigma, \text{eq/mol Fe}]dpH = \{RT\ln(10)\}[\Gamma_{\text{H}} - \Gamma_{\text{OH}}, \text{mol/m}^2]dpH = \\ &= - \{RT\ln(10)\}([\Gamma_{\text{H}}, \text{mol/m}^2]d\log\{a_{\text{H}}\} + [\Gamma_{\text{OH}}, \text{mol/m}^2]d\log\{a_{\text{OH}}\}) = \\ &= - ([\Gamma_{\text{H}}, \text{mol/m}^2]dG_{\text{H}} + [\Gamma_{\text{OH}}, \text{mol/m}^2]dG_{\text{OH}}) \end{aligned} \quad (35)$$

Here Γ_{H} is adsorption of proton, Γ_{OH} is adsorption of hydroxide ion ($\Gamma_{\text{H}} - \Gamma_{\text{OH}} = \sigma$); $dG_{\text{H}} = RT \times d\ln\{a_{\text{H}}\}$, and $dG_{\text{OH}} = RT \times d\ln\{a_{\text{OH}}\}$ are differentials of chemical potentials of hydrogen and hydroxide ions. As may be seen, Eq. (35) is Gibbs adsorption equation (Fridrichsberg, 1974). Thus, Eq. (32) is consistent with Gibbs adsorption theory.

CONCLUDING REMARKS

Solubility of fine particles decreases with modulus of surface charge. ‘‘Hypothesis number two’’ seems to be relevant. This is supported by consistence with experimental data, by absence of adjustable model parameters, and by concordance with Gibbs adsorption theory. However, this does not mean that the ‘‘hypothesis number one’’ is wrong. Interfacial pressure (up to few kbar) is reality.

REFERENCES

- Baes Ch.F.Jr and Mesmer R.E. (1976) The hydrolysis of cations. Wiley: New York, London, Sidney, Toronto.
- Biedermann G., and Chou J.T. (1966) Studies on hydrolysis of metal ions. Part 57. The hydrolysis of the iron(III) ion and the solubility product of $\text{Fe}(\text{OH})_{2.70}\text{Cl}_{0.30}$ in 0.5 M $(\text{Na}^+)\text{Cl}^-$ medium. Acta Chemica Scandinavica 20, 1376-1388.
- Byrne R.H., and Lyo Y.-R. (2000) Direct observations of nonintegral hydrous ferric oxide solubility products: $K_{s0}^* = [\text{Fe}^{3+}][\text{H}^+]^{-2.86}$. Geochim. Cosmochim. Acta 64, 1873-1877.
- Byrne R.H., Lyo Y.-R., and Young R.W. (2000) Iron hydrolysis and solubility revisited: observations and comments on iron hydrolysis characterizations. Marine Chem. 70, 23-35.
- Byrne R.H., Yao W., Lyo Y.-R., and Wang B. (2005) The dependence of Fe^{III} hydrolysis on ionic strength in NaCl solutions. Marine Chem. 97, 34-48.
- Dzombak D.A., and Morel F.M.M. (1990) Surface complexation modeling. Hydrous ferric oxide. Wiley: New York.
- Fox L.E. (1988) The solubility of colloidal ferric hydroxide and its relevance to iron concentrations in river water. Geochim. Cosmochim. Acta 52, 771-777.
- Fridrichsberg D.A. (1974) Kurs kolloidnoy himii. (Course of colloid chemistry. In Russian) ‘‘Himiya’’, Leningrad.
- Grenthe I., Plyasunov A.V., Spahiu K. (1997) Estimations of medium effects on thermodynamic data. In: Grenthe I., Puigdomenech I. (Eds) Modelling in aquatic chemistry. OECD NEA, Paris.
- Hedström B.O.A. (1953) The hydrolysis of metal ions. VII. The hydrolysis of iron(III) ion, Fe^{+++} . Arkiv Kemi. 6, 1-16.

Kaptay G. (2011) The Gibbs equation versus the Kelvin and Gibbs-Thomson equations to describe nucleation and equilibrium of nano-materials. *J. Nanosci. Nanotechnol.* 12, 1-9.

Liu X., and Millero F.J. (1999) The solubility of iron hydroxide in sodium chloride solutions. *Geochim. Cosmochim. Acta.* 63, 3487-3497.

Milburn R.M. and Vosburgh W.C. (1955) A spectrophotometric study of the hydrolysis of iron(III) ion. II. Polynuclear Species. *J. Am. Chem. Soc.* 77, 1352-1355.

Perera W.N., and Hefter G. (2003) Mononuclear cyano- and hydroxo-complexes of iron(III). *Inorg. Chem.* 42, 5917-5923.

Pivovarov S. (2009) Diffuse sorption modeling. *J. Colloid Interface Sci.* 332, 54-59.

Pivovarov S. (2013) Charge and energy of the ball lightning. *Basis* 1, 21-25.

(http://basisj.narod.ru/Basis2013_21-25.pdf)

Sapieszko R.S., Patel R.C., Matijević (1977) Ferric hydrous oxide sols. Thermodynamics of aqueous hydroxo and sulfato ferric complexes. *J. Phys. Chem.* 81, 1061-1068.

Schindler von P., Michaelis W., und Feitknecht W. (1963) 46. Löslichkeitsprodukte von Metalloxiden und -hydroxiden. 8 Mitteilung. Die Löslichkeit gealterter Eisen(III)-hydroxid-Fällungen. (46. Solubility product of metal oxides and hydroxides. 8. Communication. Solubility of aged Iron(III) hydroxide precipitate. In German.) *Helvetica Chim. Acta XLVI*, 444-449.

Stefánsson (2007) Iron(III) hydrolysis and solubility at 25°C. *Environ. Sci. Technol.* 41, 6117-6123.

Voznesenskaya E. (1968) Rasshirennie tablici koefficientov aktivnosti i osmoticheskikh koefficientov vodnih rastvorov 150 elektrolitov pri 25°C. (Extended tables of activity coefficients and osmotic coefficients of aqueous solutions of 150 electrolytes at 25°C. In Russian) In: Mikulin G.I., (Ed.) *Voprosi fizicheskoy himii rastvorov elektrolitov.* (Questions of physical chemistry of electrolyte solutions. In Russian) "Himiya", Leningrad.

Zaitcev I.D., and Aseev G.G. (1988) Fiziko-himicheskie svoystva binarnih i mnogokomponentnih rastvorov neorganicheskikh veschestv. (Physico-chemical properties of binary and multicomponent solutions of inorganic substances. In Russian) "Himiya", Moscow.