

Short Communications

The Protolytic Properties of Iron(III)-EDTA Complexes in Weakly Alkaline Solution and the Solubility Product of Iron(III) Hydroxide

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As part of an investigation of the feasibility of performing selective extraction of amorphous iron(III) hydroxide mixed with crystalline iron(III) compounds by means of EDTA solutions (EDTA, ethylenediamine-*N,N,N',N'*-tetraacetic acid H_4Y), it was found necessary to reinvestigate the protolytic properties of iron(III)-EDTA in the pH range 6–11 and the solubility product of iron(III) hydroxide. This note presents the acid dissociation constants K_1 ($HY^{3-} \rightleftharpoons H^+ + Y^{4-}$) and K_2 ($H_2Y^{2-} \rightleftharpoons HY^{2-} + H^+$), the constants of the iron(III)-EDTA-hydroxo complexes, and the solubility product of iron(III) hydroxide aged one day determined at ionic strength 1.0 (KNO_3) and 25 °C.

All chemicals were *pro analysis* or of similar purity, and the water was deionized. The pH-meter used was calibrated by means of standard buffer solutions. All the constants given in this paper are mixed constants (*i.e.* molar concentrations except H^+ and OH^- which are activities).

The acid dissociation constants of EDTA. Different solutions of EDTA (Titriplex II, Merck dissolved in KOH solutions) with the ionic strength adjusted to 1.0 (KNO_3) were titrated with 1.000 M KOH solution at 25.0 °C. The constants calculated from these experiments were: $pK_1 = 9.98 \pm 0.02$ and $pK_2 = 6.298 \pm 0.005$ at 25 °C and ionic strength 1.0 in good agreement with the figures of Anderegge¹ ($pK_1 = 9.95$ and $pK_2 = 6.26$ at 20 °C and ionic strength 1.0 (KCl)).

Iron(III)-EDTA-hydroxo complexes. According to Schwarzenbach and Heller² iron(III)-EDTA forms a monohydroxo complex ($pK_{FeY}^H = 7.49$: $FeY^- + H_2O \rightleftharpoons FeYOH^{2-} + H^+$) and a dihydroxo complex ($pK_{FeYO}^H = 9.41$: $FeYOH^{2-} + H_2O \rightleftharpoons FeY(OH)_2^{3-} + H^+$). The existence of the monohydroxo complex has been

confirmed by others^{3,4} together with the occurrence of its dimer. The existence of the dihydroxo complex has, however, to the best of our knowledge not been confirmed. In order to calculate the solubility product of iron(III) hydroxide from dissolution experiments with EDTA⁵ or to calculate the total iron(III) concentration in an EDTA solution in contact with iron(III) hydroxide,⁶ it is important to know whether the dihydroxo complex exists or not in weakly alkaline solution. In an attempt to solve this problem solutions containing iron(III) nitrate and EDTA and adjusted to ionic strength 1.0 (KNO_3) were titrated with 1.000 M KOH at 25.0 °C. An excess of EDTA was added to some solutions to increase the pH range before precipitation of iron(III) hydroxide. The iron(III)/EDTA ratios ranged from 1.0 to 0.125.

Fig. 1 shows the titration curves for a solution (a) containing iron(III) plus an excess

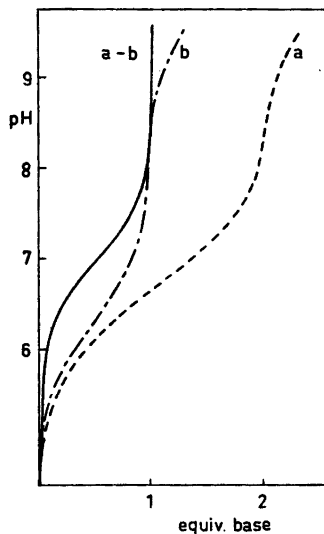


Fig. 1. Titration curves for solutions containing: (a) 2×10^{-2} M iron(III) and 4×10^{-2} M EDTA; (b) 2×10^{-2} M EDTA. (a–b) is the difference between curve (a) and (b) corresponding to the titration of a 2×10^{-2} M iron(III)-EDTA solution. Temperature 25.0 °C and ionic strength 1.0 (KNO_3).

of EDTA and a solution (b) containing only EDTA. The third curve (a-b) in Fig. 1 is the difference between these two curves and corresponds to the titration curve obtained by the titration of an equimolar solution of iron(III) and EDTA. It may be seen that the curve (a-b) has an inflection at $\text{pH} \sim 7$ corresponding to the monohydroxo complex, but up to $\text{pH} \sim 9.5$ no further inflections occur. All the other titration curves showed a similar pattern. This indicates that the $\text{p}K_{\text{FeYOH}^{\text{H}}} = 9.41^2$ for the reaction $\text{FeYOH}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{FeY}(\text{OH})_2^{\text{H}} + \text{H}^+$ is too low and that the dihydroxo complex may be ignored in weakly alkaline solution. $\text{p}K_{\text{FeY}^{\text{H}}}$ and the equilibrium constant for the dimerization of the monohydroxo complex ($K_{\text{d}}: 2\text{FeYOH}^{2-} \rightleftharpoons (\text{FeYOH})_2^{4-}$) were calculated from the titration curves. $\text{p}K_{\text{FeY}^{\text{H}}} = 7.48$ and $\text{p}K_{\text{d}} = -2.6$ at 25°C and ionic strength 1.0 (KNO_3) in good agreement with the literature.^{3,3,4,7} Thus, Schwarzenbach and Heller² found $\text{p}K_{\text{FeY}^{\text{H}}} = 7.49$ at 20°C and ionic strength 0.1 (KCl), Gustavson and Martell³ $\text{p}K_{\text{FeY}^{\text{H}}} = 7.58$ and $\text{p}K_{\text{d}} = -2.8$ at 25°C and ionic strength 1.0 (KCl), Schugar *et al.*⁴ $\text{p}K_{\text{d}} = -2.53$ at 26°C and ionic strength 1.0 (NaClO_4), and McLendon *et al.*⁷ $\text{p}K_{\text{d}} = -2.5$ at 25°C and ionic strength 0.5 (ammonia buffer).

The solubility product of iron(III) hydroxide. The figures given in the literature⁸ for the solubility product of iron(III) hydroxide differ from $10^{-35.5}$ to $10^{-39.4}$. Iron(III) hydroxide is thermodynamically unstable compared with crystalline iron(III) oxide hydroxides and oxides and suspensions of iron(III) hydroxide in water turn into these compounds on ageing.

It was our intention to determine the solubility product of X-ray amorphous iron(III) hydroxide, *i.e.* before crystalline iron(III) compounds were formed. Therefore, different solutions were prepared containing iron(III) and EDTA with pH at the time of preparation in the range 9.5 to 11 and the ionic strength adjusted to 1.0 (KNO_3). All the solutions were supersaturated and iron(III) hydroxide started to settle out immediately. The suspensions were aged at 25.0°C and the pH and the iron(III) concentration in solution were determined from time to time after centrifugation. The iron(III) concentration was determined by atomic absorption spectrophotometry. Some of the precipitates were washed several times with ethanol and acetone and X-rayed (Ni-filtered $\text{CuK}\alpha$). As crystalline iron(III) compounds (goethite and/or hematite) appeared after a few days of ageing, it was decided to use only the measurements from suspensions aged one day. From these measurements combined with the acid dissociation constants of EDTA, and the stability constant for the normal,⁹ the monohydroxo, and the monohydroxo dimer complexes of iron(III)-EDTA, the solubility product may be calculated as $10^{-38.4 \pm 0.2}$ at ionic strength 1.0 (KNO_3) and

25°C . This figure agrees quite well with the more recently published values in the literature.^{5,8} The solubility product of iron(III) hydroxide was also calculated by taking into account the stability constant of the iron(III)-EDTA-dihydroxo² complex besides the above-mentioned constants. These calculations gave figures which decreased as a function of pH supporting further evidence to the statement that the stability constant of the iron(III)-EDTA-dihydroxo complex given by Schwarzenbach and Heller² is incorrect.

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Received July 11, 1977.