

The Stability of the Ferric Complex with EGTA

KNUT HENNING SCHRØDER

Kjemisk Institutt, Norges Lærerhøgskole, Trondheim, Norway

The stability constant of the Fe(III)EGTA complex is determined by means of a spectrophotometric method which eliminates the absorbance of uncomplexed iron in the calculations by means of successive approximations, giving a geometrical series. The constant is found to be $10^{20.5}$. The unexpected hydrolytic properties of the complex compared with those of EDTA are discussed and can seemingly be explained by the difference in coordinating groups in the two molecules.

Ethyleneglycolbis(β -aminoethylether) N,N,N',N'-tetraacetic acid (EGTA) forms stable complexes with many metal ions¹⁻², and like ethylenediaminetetraacetic acid it is found valuable in complexometric titrations. In contrast to EDTA, EGTA forms much less stable complexes with magnesium than with calcium and this is utilized in determinations of the two metals³⁻⁸. Many of the complexes are coloured and this is used in the colourimetric methods of analysis⁹⁻¹³. The behaviour of trivalent iron is quite different in EGTA than in EDTA solutions. With EDTA a homogeneous solution exists to pH about 11, but with EGTA iron hydroxide is precipitated near pH 5. Iron forms weakly coloured complexes with EDTA but with EGTA it produces a much more intense colour. This has made it possible to use EGTA as an analytical reagent for colourimetric determinations of iron¹². The stability constant for trivalent iron with EGTA has not previously been determined; it is established in this investigation in order to discuss the properties of the complex in relation to the hydrolyses to hydroxide.

In the preliminary investigation the compound was studied with polarographic and potentiometric methods, but without satisfactory results. It was necessary to use very acid solutions with pH below 5 to prevent precipitation. In polarography the anodic wave of mercury interfered with the Fe(III)—Fe(II) wave in these acid solutions, and redox potential methods gave too small pH interval for appropriate measurements. However, spectrophotometric determinations were favourable because the complex partially dissociates into free EGTA acid and iron(III) ions in the acid solutions.

REAGENTS AND APPARATUS

Stock solutions of trivalent iron were made by dissolving a known amount of metallic *p.a.* iron in dilute *p.a.* perchloric acid, and were oxidized to the trivalent state by boiling with an excess of the concentrated acid. Stock solutions of EGTA were made by dissolving a known amount of the reagent (Fluka, Switzerland) in standardized KOH (in order to increase the solubility). To keep the ionic strength constant (= 0.1) appropriate amounts of *p.a.* NaClO₄ were added to all solutions.

The Beckman Zeromatic pH-meter and Beckman DU Spectrophotometer with 1.000 cm quartz cells were used for the measurements. Thermostating of the solutions was not possible with the spectrophotometer available, but the temperature was held at 25°C by keeping the solutions in a water bath at 25°C before making recordings.

CALCULATIONS

The stability constant of the ferric complex is given by:

$$K = \frac{[\text{FeX}^-]}{[\text{Fe}^{3+}][\text{X}^{4-}]} \quad \text{X} = \text{EGTA} \quad (\text{I})$$

As the complex dissociates very appreciably in acid solutions, knowledge of of the total acidity and of the total concentrations of ferric iron and EGTA should enable one to evaluate the stability constant. If $K_1 \dots K_4$ denote the ionization constants of EGTA, one can write:

$$K = \frac{[\text{FeX}^-](\text{[H}^+]^4 + K_1[\text{H}^+]^3 + K_1 K_2[\text{H}^+]^2)}{(C_{\text{Fe}^{3+}} - [\text{FeX}^-]) X K_1 K_2 K_3 K_4} \quad (\text{II})$$

Here C represents initial concentrations, $[\]$ is actual concentrations, and X is the actual sum of the concentration of uncombined EGTA in different degrees of protonization. If $[\text{FeX}^-]$ is determined and the only complex formed is FeX^- , then the stability constant K (in a known ionic strength) can be calculated.

In determination of $[\text{FeX}^-]$ the spectrophotometric method was employed. The optical density D , defined by Beer's law, becomes

$$D = l \varepsilon_{\text{Fe}^{3+}}[\text{Fe}^{3+}] + l \varepsilon_{\text{FeX}^-}[\text{FeX}^-] \quad (\text{III})$$

It is assumed that the ferric ion and the complex are the only absorbing species and that the absorption obeys Beer's law. In the equation, l denotes the length of the light path and ε represents the molar extinction coefficients which may be calculated from standard curves. It is seen that, for solutions in which the formation is incomplete, optical density measurements at two wave lengths permit the calculation of all species in the equilibrium expression. In case of the Fe(III)-EGTA complex, however, experimental results show that the ratio of the two molar extinction coefficients is very nearly constant at different appropriate wave lengths. This will cause serious errors in the calculations. However, $\varepsilon_{\text{FeX}^-}$ is much larger than $\varepsilon_{\text{Fe}^{3+}}$ and the following calculations can be performed:

In a first approximation it is assumed that FeX^- is the only absorbing species. The concentration of FeX^- is given by

$$[\text{FeX}^-]_0 = \frac{D}{l \varepsilon_{\text{FeX}^-}} \quad (\text{IVa})$$

This gives the concentration of Fe^{3+}

$$[\text{Fe}^{3+}]_0 = C_{\text{Fe}^{3+}} - \frac{D}{l \epsilon_{\text{FeX}^-}} \tag{IVb}$$

The calculation of $[\text{FeX}^-]$ is repeated, but the contribution to the optical density due to Fe^{3+} is subtracted:

$$[\text{FeX}^-]_1 = \frac{D - k_1}{l \epsilon_{\text{FeX}^-}} \tag{IVc}$$

with

$$k_1 = [\text{Fe}^{3+}]_0 l \epsilon_{\text{Fe}^{3+}} \tag{IVd}$$

A new value of the iron concentration is calculated:

$$[\text{Fe}^{3+}]_1 = C_{\text{Fe}^{3+}} - \frac{D - k_1}{l \epsilon_{\text{FeX}^-}} \tag{IVe}$$

This gives a revised values of the concentration of the complex:

$$[\text{FeX}^-]_2 = \frac{D - k_2}{l \epsilon_{\text{FeX}^-}} \tag{IVf}$$

with

$$k_2 = [\text{Fe}^{3+}]_1 l \epsilon_{\text{Fe}^{3+}} \tag{IVg}$$

With further operations, $k_3, k_4 \dots$ may be computed to give more exact values of the concentrations.

To determine the absorbing corrections (k_i), the following equations are written:

$$k_0 = 0 \tag{Va}$$

$$k_1 = \left(C_{\text{Fe}^{3+}} - \frac{D - k_0}{l \epsilon_{\text{FeX}^-}} \right) l \epsilon_{\text{Fe}^{3+}} \tag{Vb}$$

$$k_2 = \left(C_{\text{Fe}^{3+}} - \frac{D - k_1}{l \epsilon_{\text{FeX}^-}} \right) l \epsilon_{\text{Fe}^{3+}} \tag{Vc}$$

.....

$$k_i = \left(C_{\text{Fe}^{3+}} - \frac{D - k_{i-1}}{l \epsilon_{\text{FeX}^-}} \right) l \epsilon_{\text{Fe}^{3+}} \tag{Vd}$$

.....

The expression of k_i is rearranged:

$$k_i = C_{\text{Fe}^{3+}} l \epsilon_{\text{Fe}^{3+}} - \frac{D \epsilon_{\text{Fe}^{3+}}}{\epsilon_{\text{FeX}^-}} + \frac{\epsilon_{\text{Fe}^{3+}}}{\epsilon_{\text{FeX}^-}} k_{i-1} \tag{VI}$$

or

$$k_i = k_1 + \frac{\epsilon_{\text{Fe}^{3+}}}{\epsilon_{\text{FeX}^-}} k_{i-1} \tag{VIa}$$

This shows that k_i can be calculated by means of a geometrical series which converges towards ($k_\infty = k$):

$$k = \frac{k_1}{1 - \frac{\varepsilon_{\text{Fe}^{3+}}}{\varepsilon_{\text{FeX}^-}}} = \frac{\varepsilon_{\text{Fe}^{3+}} (l \varepsilon_{\text{FeX}^-} C_{\text{Fe}^{3+}} - D)}{\varepsilon_{\text{FeX}^-} - \varepsilon_{\text{Fe}^{3+}}} \quad (\text{VII})$$

(As $\varepsilon_{\text{FeX}^-}$ is much larger than $\varepsilon_{\text{Fe}^{3+}}$, the series converges very rapidly.)

With this value of k , eqn. (II) becomes:

$$K = - \frac{1}{X} \frac{([\text{H}^+]^4 + K_1 [\text{H}^+]^3 + K_1 K_2 [\text{H}^+]^2)}{K_1 K_2 K_3 K_4} \frac{D - C_{\text{Fe}^{3+}} l \varepsilon_{\text{Fe}^{3+}}}{D - C_{\text{Fe}^{3+}} l \varepsilon_{\text{FeX}^-}} \quad (\text{IIX})$$

with

$$X = C_{\text{EGTA}} - \frac{D - C_{\text{Fe}^{3+}} l \varepsilon_{\text{Fe}^{3+}}}{l (\varepsilon_{\text{FeX}^-} - \varepsilon_{\text{Fe}^{3+}})} \quad (\text{IX})$$

EXPERIMENTAL AND RESULTS

It has previously been reported that the Fe—EGTA complex obeys Beer's law in the measured concentration range and wave lengths¹². The results were checked and found to be satisfactory. The composition of the complex is postulated to be FeX^- (where X^{4-} is the tetraacetate ion of EGTA). Job's method of continuous variation with a constant concentration sum of ligand and metal ions, together with the mole ratio method (constant concentration of iron and different quantity of EGTA) showed that the mole ratio is 1:1. This was independent of the wave length chosen, indicating that only one complex is formed. The existence of appreciable amounts of hydrogenated complex seems improbable because no spectral change was observed when pH was changed in the range used in this investigation. The condition for utilizing Job's method and the mole ratio method is to keep the pH constant. This might be done with buffer solutions, but to avoid errors arising from complex formation with the buffer, the pH was carefully adjusted with a few drops of dilute HClO_4 . (This makes no significant change in ionic strength.) The pH-meter was standardized with HClO_4 at known concentrations (10^{-1} and 10^{-2} M); NaClO_4 was added to bring the ionic strength to 0.1.

Table 1. Molar extinctions at different wave-lengths; 25°C.

	$\varepsilon_{\text{FeX}^-}$	$\varepsilon_{\text{Fe}^{3+}}$
330 $m\mu$	4680	560
340 $m\mu$	3970	460
350 $m\mu$	3460	360

Table 2. Observed extinctions of solutions at different concentrations and pH; 25°C.

pH	Extinction (<i>D</i>)		
	330 m μ	340 m μ	350 m μ
1.73 ^a	0.155	0.131	0.109
1.87 ^a	0.224	0.194	0.166
1.95 ^a	0.271	0.236	0.200
1.85 ^b	0.470	0.407	0.343
1.87 ^c	0.392	0.340	0.310
1.90 ^d	0.488	0.418	0.357

^a $C_{\text{Fe}^{3+}} = C_{\text{EGTA}} = 7.50 \times 10^{-5}$ M

^b $C_{\text{Fe}^{3+}} = C_{\text{EGTA}} = 1.50 \times 10^{-4}$ M

^c $C_{\text{Fe}^{3+}} = 1.00 \times 10^{-4}$ M, $C_{\text{EGTA}} = 2.00 \times 10^{-4}$ M

^d $C_{\text{Fe}^{3+}} = 2.00 \times 10^{-4}$ M, $C_{\text{EGTA}} = 1.00 \times 10^{-4}$ M

Absorption spectra were recorded of solutions with an excess of EGTA and different amounts of ferric iron at pH 2.58 and 3.00. Plots of the absorbance *vs.* added iron gave equal slopes, so it was assumed that the Fe(III) was all chelated in the form FeX^- at pH = 2.58, and the extinction coefficients were obtained from these measurements. The results are given in Table 1. The extinction of the uncomplexed iron does not strictly follow Beer's law, but as the absorbance is small compared with that of the complex, this will not affect the calculated stability constants. The absorbance of the uncomplexed iron is nearly independent of pH in the measured range.

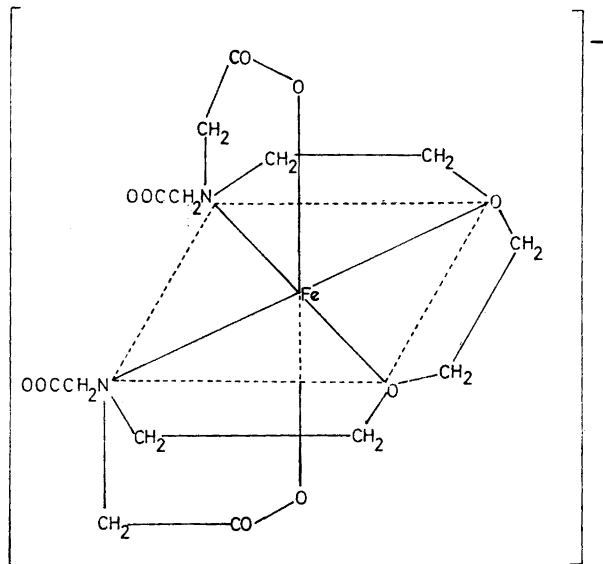
Absorbance of solutions at different pH and concentrations are listed in Table 2.

By use of the reported values of the protolytic constants of EGTA¹⁴: $\text{p}K_1 = 2.0$; $\text{p}K_2 = 2.68$; $\text{p}K_3 = 8.85$; $\text{p}K_4 = 9.43$, the stability constant is calculated to a mean logarithmic value $\log K = 20.49$, with a standard deviation of 0.14.

DISCUSSION

The hydrolytic properties of the FeEGTA^- complex are quite different from those of the related complex with EDTA, and the difference in stability cannot alone be responsible for this fact. The FeEDTA^- complex is converted into $\text{Fe}(\text{OH})\text{EDTA}^{2-}$ and $\text{Fe}(\text{OH})_2\text{EDTA}^{3-}$ with increasing pH and no precipitate is formed¹⁵. It is suggested that one of the carboxylic acid groups bound to the iron is set free by means of hydroxyl ions for each of the OH complexes formed. The precipitation in the Fe(III)-EGTA solutions above pH = 5 might be due to the FeEGTA^- complex not being converted into stable, soluble hydroxyl complexes.

The following structure of FeEGTA^- is proposed:



Only one carboxylic acid group from each nitrogen atom is bound to iron, and the structure is therefore very similar to that of $\text{Fe}(\text{OH})_2\text{EDTA}^{3-}$. When one carboxylic acid group from nitrogen is not engaged in complex bonds, this might increase the strength of the bond from the other group to the central atom. The result will be that $\text{Fe}(\text{OH})\text{EGTA}^{2-}$ is not formed, and precipitation occurs owing to total dissociation and hydrolysis.

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