

The Stability of Iron(III) Complexes Formed Below pH = 3 with Glycinate, Iminodiacetate, β -Hydroxyethyliminodiacetate, *N,N*-Di-(hydroxyethyl)-glycinate, Nitrilotriacetate and Triethanolamine

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Abstract

The formation of iron(III) complexes with six monoaminopolycarboxylate and monoaminopolyalcohol ligands has been investigated by redox and pH measurements in acidic solutions at $I=1$ (NaClO_4) and 25 °C. The stability of the complexes increases with the number of carboxylate groups and a further enhancement is observed when alcoholic groups are present.

Introduction

The title ligands contain a nitrogen atom, as well as one or more oxygen atoms in suitable positions to form five-membered chelate rings, the oxygen atoms being either an alcoholic or a carboxylate group. Their complexing properties with iron(III) were investigated using potentiometric (pH and redox) measurements by neutralizing solutions containing equimolar amounts of iron(III) and iron(II), and large excesses of perchloric acid and of ligand with sodium bicarbonate. As these ligands form generally weak complexes hydrolysis of iron(III) also occurs. Thus this last process was also investigated separately. The values of the equilibrium constants refer to the metastable hydrolytic equilibria of iron(III), which are normally reached in 5 to 15 min after each addition of base at 25 °C and at the ionic strength 1 using NaClO_4 as inert salt.

Experimental

The ligands H_μL (Fluka, p.a.) were checked by titration with strong base and found pure, within the error of the measurements (0.5%). $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck) was dissolved in perchloric acid and used for the preparation of a 0.1 M iron(III) perchlorate solution as described by Ciavatta *et al.* [1]. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Merck) dissolved in diluted HClO_4 was mixed with an equimolar amount of a $\text{Ba}(\text{ClO}_4)_2$ solution (from BaCO_3 and HClO_4), to give, after the separa-

tion of BaSO_4 , an acidic 0.1 M iron(II) perchlorate solution. Both metal solutions were checked by titration with EDTA as well as photometrically as the trisphenanthroline iron(II) complex. The above solutions as well as those of 2 M HClO_4 , $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ and the ligands were used to obtain the samples to be titrated. The large excess of strong acid, $[\text{H}^+] = 0.04$ M, was used to ensure a low initial degree of complex formation. A stream of N_2 was bubbled through the solutions which were titrated with 1 M NaHCO_3 solutions. Constant potential values were reached within 2 to 5 min using either the glass or the Pt electrode. Ten different solutions ($[\text{Fe}^{3+}]_t = [\text{Fe}^{2+}]_t = 2.5 \times 10^{-4} - 4 \times 10^{-3}$ M; $[\text{L}]_t = 1 - 4 \times 10^{-2}$ M) were investigated giving for each system 200–250 experimental points.

The calculations of the constants were carried out using a program (KVAPO), in which the quantity minimized is the difference between the measured and the calculated values of $\text{pFe} = -\log[\text{Fe}^{3+}]$. The calculated concentration of Fe^{3+} is obtained with a set of values for the corresponding constants by use of the stoichiometric relations, for known concentrations of the components and the measured pH of the solution. The values of the constants were varied in order to obtain the minimum for the sum of the square of the difference minimized over all experimental points.

Results and Discussion

The results obtained by titrating solutions containing the same quantity of iron(III) ($[\text{Fe}^{3+}]_t = 2 \times 10^{-3}$ M) and the same quantity of each ligand ($[\text{L}]_t = 1 \times 10^{-2}$ M) with 1 M NaHCO_3 are shown in Fig. 1. There, the potential of the platinum electrode E_{Pt} is plotted versus the pH value ($\text{pH} = -\log[\text{H}^+]$) of the solutions.

$$E_{\text{Pt}} = E_{\text{Pt}}^{\circ} + 0.05916 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$= E_{\text{Pt}}^{\circ'} + 0.05916 \log [\text{Fe}^{3+}]$$

TABLE I. The Logarithms of the Overall Constants $\beta_{q,p,n} = [\text{Fe}_q\text{H}_p\text{L}_n]/([\text{Fe}]^q[\text{H}]^p[\text{L}]^n)$ at 25 °C and $I = 1$ (NaClO_4). Negative values of p correspond to hydroxo species $\text{Fe}_q(\text{OH})_{-p}\text{L}_n$. The charges of the species have been omitted. For the hydrolysis of iron(III), the following values have been found: $\log \beta_{1,-1,0} = -3.5 \pm 0.5$; $\log \beta_{1,-2,0} = -5.945 \pm 0.3$ and $\log \beta_{2,-2,0} = -3.025 \pm 0.2$

Ligand	q,p,n									
		(0, 1, 1)	(0, 2, 1)	(0, 3, 1)	(0, 4, 1)	(1, 0, 1)	(1, 1, 1)	(1, -1, 1)	(2, -2, 1)	(2, -2, 2)
1 TRIET	8.14	—	—	—	—	≤ 7	≤ 9.4	—	—	—
2 GLY	9.65	12.07	—	—	~ 8	11.41 ± 0.07	—	6.80 ± 0.1	—	
3 DHEG	8.34	10.21	—	—	7.35 ± 0.16	9.68 ± 0.1	—	—	12.90 ± 0.16	
4 IDA	9.29	11.87	13.72	—	11.13 ± 0.07	12.02 ± 0.5	8.01 ± 0.16	—	—	
5 HIDA	8.59	10.83	12.29	—	11.60 ± 0.16	13.80 ± 0.1	8.57 ± 0.5	—	—	
6 NTA	8.90	11.10	13.08	14.18	14.78 ± 0.02^a	15.67 ± 0.15	—	—	—	

^a $\log \beta_{1,0,1} = 16.0$, after correction of the Na^+ -complexes.

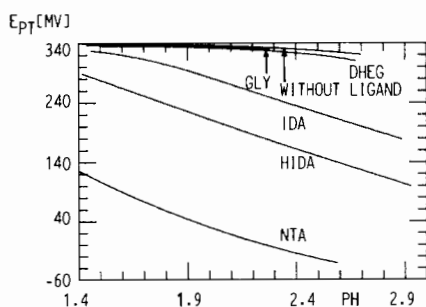


Fig. 1. The potentials of the platinum electrode E_{Pt} vs. pH values, for solutions containing 2×10^{-3} M $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$, 4×10^{-3} M HClO_4 and 1×10^{-2} M ligand, titrated by addition of 1 M NaHCO_3 . Each curve is identified by the abbreviation of the ligand used.

As can be seen from known and estimated stability constants, the concentration of divalent iron is not decreased by complex formation but only as a consequence of dilution. This last effect occurs also for Fe^{3+} , thus the change of E_{Pt} is only due to hydrolysis or complex formation of iron(III). The curve 'without ligand' corresponds to the hydrolysis of iron(III): in the pH range 1.4–2.9 it shows a decrease in E_{Pt} of 20 mV and the concentration of the free iron(III) becomes approximately half of the initial one. Glycinate (GLY) and *N,N*-di-(hydroxyethyl)-glycinate (DHEG) show a further very low decrease of the potential and correspond to the formation of very weak complexes, in addition to the hydrolytic products of iron(III). More remarkable is the potential drop for iminodiacetate (IDA, till 120 mV) and β -hydroxyethyliminodiacetate (HIDA, till 200 mV), which correspond to a decrease of the iron(III) concentration to 1% and 0.1%, respectively, to that observed in the solution without ligand; thus the amount of hydrolytic products is strongly reduced with respect to the solution without ligand. Finally, with nitrilotriacetate (NTA), in the pH range 1.4–2.9, only the complex formation occurs. The curve

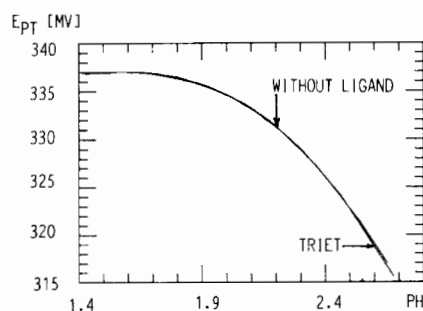


Fig. 2. The potentials of the platinum electrode E_{Pt} vs. pH values, for solutions containing 4×10^{-3} M $\text{Fe}(\text{ClO}_4)_2$ and $\text{Fe}(\text{ClO}_4)_3$, 4×10^{-3} M HClO_4 and 4×10^{-2} M triethanolamine. The E_{Pt} scale has been enlarged by a factor of 15.8 with respect to that of Fig. 1.

with triethanolamine (TRIET) is plotted separately (Fig. 2) because of the slight change of E_{Pt} with respect to that without ligand. This corresponds to the formation of $\sim 4\%$ of complexes whose exact composition cannot be established because of their low concentrations. Only limiting values of their stability constants can be estimated.

The values obtained are given in the Table I together with the estimated standard deviations and the protonation constants used, which were checked by us. Comparison of the values of $\beta_{1,0,1}$ with literature data (NTA: $\log K_1 = 15.80$ ($I = 0.1$ (KCl), 20 °C [2]); HIDA: $\log K_1 = 11.61$ ($I = 0.1$ (KCl), 20 °C [3]); GLY: $\log K_1 = 10.0$ ($I = 1$ (NaClO_4 [4]), 20 °C)) shows that only in the first two cases the agreement is very good.

The most important factor governing the stability of the iron(III) complexes of the ligands used, appears to be the number of carboxylate groups, which also represents the charge μ of the ligands. The hydroxyl group shows also an enhancing effect, but it is relatively small. Therefore, it is surprising that triethanolamine and *N,N*-di-(hydroxyethyl)-glycine are used to sequester Fe(III). Přibil proposed the use

of triethanolamine [5] as masking agent for iron(III) in compleximetric titrations: when added to an iron(III) solution triethanolamine imparts a light yellow color to the alkaline solutions and allows the determinations of other cations by EDTA. If the iron(III)–triethanolamine solution is left some days under those conditions, one observes a very slow quantitative deposition of $\text{Fe}(\text{OH})_3 \cdot \text{aq}$, showing that the complex formed is not stable. Probably a kinetic effect occurs, for which the complex formed in acidic solution decomposes slowly. Further, it is a known phenomenon that different substances are able to maintain in solution some polynuclear $\text{Fe}(\text{OH})_3$ species. Both effects can play a role in the sequestration of Fe(III) with the latter two ligands.

The stability constants of the protonated complex $[\text{Fe}(\text{HL})]^{(4-\mu)+}$; i.e. $K(\text{M}(\text{HL})) = [\text{MHL}]/([\text{M}][\text{HL}]) = 10^{\beta_{1,1,1}/\beta_{0,1,1}}$ can be obtained using the values of the second and the seventh column of Table I ($10^{1.7}$ (GLY), $10^{1.3}$ (DHEG), $10^{1.3}$ (TRIET), $10^{2.7}$ (IDA), $10^{5.2}$ (HIDA), and 10^5 (NTA)). In $\text{HL}^{(3-\mu)+}$ the proton is bound to N as it is the more basic atom. As the ligands contain carboxylate groups, the values of $K(\text{M}(\text{HL}))$ can be compared with that of acetate. In the case of ligands with one carboxylate group, the values are quite near to that expected for a substituted acetate, taking into consideration the difference in basicity of the carboxylate group ($\text{p}K$ of CH_3COOH : 5.02, $\log K_1(\text{FeL}) = 3.2$, $I = 3$ (NaClO_4) [1]). The values of $K(\text{M}(\text{HL}))$ of the iminodiacetates and of nitrilotriacetate are larger, indicating that their complexes contain chelate structures. By analogy with the case of the protonated EDTA complexes, in these complexes the proton is probably bound to a carboxylate group. Further, in the case of HIDA the alcoholic O atom seems to be coordinated.

In addition to the complexes $[\text{ML}]^{(3-\mu)+}$ and $[\text{MHL}]^{(4-\mu)+}$ hydrolytic products are present. Their composition differs depending on the particular stability of the complexes. Glycine and di-(hydroxyethyl)-glycine form weak complexes in a pH range in which a large concentration of the dimeric cation $\text{Fe}_2(\text{OH})_2^{4+}$ is present, thus giving complexes with that cation. For ligands containing more than one carboxylate group, more stable complexes are found and the hydrolytic species are derived from $[\text{ML}]^{(3-\mu)+}$ by deprotonation of a coordinated water molecule, which in the case of the iminodiacetates have $\text{p}K$ values of *ca.* 3 and in that of NTA of 4 [2].

In conclusion, equilibrium studies in acidic medium between the possible monoamino-polycarboxylate and -polyalcohol ligands and iron(III) show that those with larger charge are preferred.

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