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Interaction of Iron(III) with 2-Hydroxybenzohydroxamic Acid in Aqueous Solutions

M. Iuliano* and G. De Tommaso

Dipartimento di Chimica, Università di Napoli “Federico II”, via Cinthia 45 - 80126 Napoli, Italy

The complex formation between the Fe^{3+} ion and 2-hydroxybenzohydroxamic acid (salicylhydroxamic acid, H_2L) has been studied at 25 °C in 1.0 $mol \cdot dm^{-3}$ $(Na)ClO_4$ medium by potentiometric titrations with redox Fe^{3+}/Fe^{2+} and/or glass electrodes. On account of precipitation of Fe(II)−salicylhydroxamates, the redox half-cell was employed only in measuremenrts at $[H^+] > 3 \cdot 10^{-3}$ $mol \cdot dm^{-3}$. The redox and glass electrode data, collected in the concentration ranges ($mol \cdot dm^{-3}$) $1 \cdot 10^{-3} \leq [Fe(III)] \leq 5 \cdot 10^{-3}$, $0 < [H_2L]_{tot} \leq 0.015$, and $0.1 \geq [H^+] \geq 10^{-2}$, are consistent with the presence of the species $FeHL^{2+}$ and $Fe(HL)_2^{+}$. Glass electrode measurements, in solutions where $(10^{-1.5} \geq [H^+] \geq 10^{-4})$ $mol \cdot dm^{-3}$, $(3 \cdot 10^{-4} \leq [Fe(III)] \leq 7 \cdot 10^{-3})$ $mol \cdot dm^{-3}$, and $(1 \leq [H_2L]_{tot}/[Fe(III)] \leq 3)$ $mol \cdot dm^{-3}$, are explained by assuming in addition to $FeHL^{2+}$ and $Fe(HL)_2^{+}$ the complexes FeL_2^{-} and $Fe_5(HL)_5(OH)_8^{2+}$. The pentamer is probably a derivative of the hypothetical hydrolytic complex, $Fe_5(OH)_8^{7+}$. Stability constants for their formation in 1 M $NaClO_4$ as well as in dilute solution are reported.

1. Introduction

In 1987, Springer et al.[1] in a spectrophotometric investigation at 20 °C in 1.0 $mol \cdot dm^{-3}$ $NaClO_4$ found evidence for the formation of the complex $FeHL^{2+}$ (H_2L stands for salicylhydroxamic acid) with a value of the constant $K(Fe^{3+}, HL^-) = 10^{9.09}$.

In 1989, Das et al.[2] studied the complexation equilibrium $Fe^{3+} + H_2L \rightleftarrows FeHL^{2+} + H^+$ in 1.0 $mol \cdot dm^{-3}$ $NaClO_4$ in the range (20 to 50) °C by spectrophotometric (visible) and by kinetic methods. These authors propose at 25 °C the equilibrium constant $K(Fe^{3+}, H_2L, -H^+) = 10^{2.33}$.

In the same year, Shuaib et al.[3] investigated the system at 25 °C in chloride media of ionic strength 0.15 $mol \cdot dm^{-3}$, for $[H^+] < 10^{-1}$ $mol \cdot dm^{-3}$, and 1 $mol \cdot dm^{-3}$ in the H^+ concentration range (0.01 to 1.0) $mol \cdot dm^{-3}$. The model proposed includes an array of ten complexes. FeL^+ with $K(Fe^{3+}, L^{2-}) = 10^{17.22}$; $FeHL^{2+}$ with $K(Fe^{3+}, H^+, L^{2-}) = 10^{19.36}$; FeH_2L^{3+} with $K(Fe^{3+}, 2H^+, L^{2-}) = 10^{19.23}$; FeL_2^- with $K(Fe^{3+}, 2\,L^{2-}) = 10^{29.55}$; FeL_3^{3-} with $K(Fe^{3+}, 3\,L^{2-}) = 10^{38.80}$; $FeLH_{-1}$ with $K(Fe^{3+}, -H^+, L^{2-}) = 10^{8.97}$ spectr., $= 10^{10.39}$ pot.; $FeHL_2$ with $K(Fe^{3+}, H^+, 2\,L^{2-}) = 10^{29.17}$ spectr., $= 10^{31.09}$ pot.; $FeL_2(OH)_2^{3-}$ with $K(Fe^{3+}, -2H^+, 2\,L^{2-}) = 10^{8.49}$ spectr., $= 10^{7.41}$ pot.; $Fe_2LH_{-2}^{2+}$ with $K(2Fe^{3+}, -2H^+, L^{2-}) = 10^{11.40}$; and $Fe_2L_2H_{-3}^{-}$ with $K(2Fe^{3+}, -3H^+, 2\,L^{2-}) = 10^{15.89}$.

O’Brien et al.[4] from potentiometric titrations with a glass electrode in 0.2 $mol \cdot dm^{-3}$ KCl at 25 °C found evidence for the formation of $FeHL^{2+}$ and $Fe(HL)_2^{+}$ with equilibrium constants, respectively, $K(Fe^{3+}, L^{2-}, H^+) = 10^{11.92}$ and $K(Fe^{3+}, 2\,L^{2-}, 2H^+) = 10^{22.66}$.

It seems evident, from the analysis of previous work, that the system is complicated and far from conclusive evidence on the composition of the reaction products. In consideration of the fact that hydroxamic acids have numerous biological and medical applications as siderophores, a reinvestigation of the system was thought important. Since the first complexation step leading to the formation of $FeHL^{2+}$ occurs already at $[H^+] > 10^{-2}$ $mol \cdot dm^{-3}$, no reliable information on this equilibrium can be extracted from measurements of only $[H^+]$. We have resorted then to the redox Fe^{3+}/Fe^{2+} couple. This could be used in the acidity range $(0.1 \geq [H^+] \geq 0.003)$ $mol \cdot dm^{-3}$. In less acidic media, the formation of insoluble Fe(II) hydroxamates precludes its proper use. On the other hand, glass electrode data become informative at $[H^+] < 0.01$ $mol \cdot dm^{-3}$. The reaction was, therefore, investigated with a glass electrode up to $[H^+] = 10^{-4}$ $mol \cdot dm^{-3}$ when iron(III) hydroxides start to precipitate.

The potentiometric measurements were carried out at 25.00 °C in 1.0 $mol \cdot dm^{-3}$ $(Na)ClO_4$ ionic medium.[5]

2. Method

The potentiometric titrations were planned to measure in the equilibrium solutions the concentration of the Fe^{3+} ion as well as of H^+ with, respectively, redox Fe^{3+}/Fe^{2+} and glass electrodes. It resulted however that the use of the redox electrode was precluded at $[H^+] < 10^{-2.5}$ $mol \cdot dm^{-3}$ when Fe(II)−hydroxamates of low solubility start to precipitate. Consequently, the measurements were divided according to the acidity range involved in: (a) titrations at pH < 2 with cells I and II; (b) titrations at pH > 1.5 with cell III. Cells I, II, and III had the general composition

$$\text{RE/TS1/Pt} \tag{I}$$

$$\text{RE/TS1/glass electrode} \tag{II}$$

$$\text{RE/TS2/glass electrode} \tag{III}$$

where

$$\text{RE} = \text{Ag,AgCl/0.01 mol} \cdot \text{dm}^{-3}\ \text{AgClO}_4\text{, 0.99 mol} \cdot \text{dm}^{-3}\ \text{NaClO}_4\text{/1.00 mol} \cdot \text{dm}^{-3}\ \text{NaClO}_4$$

$$\text{TS1} = C_3\ \text{mol} \cdot \text{dm}^{-3}\ \text{Fe(ClO}_4)_3,\ C_2\ \text{mol} \cdot \text{dm}^{-3}\ \text{Fe(ClO}_4)_2,\ C_L\ \text{mol} \cdot \text{dm}^{-3}\ \text{H}_2\text{L},\ C_A\ \text{mol} \cdot \text{dm}^{-3}\ \text{HClO}_4,\ (1\text{-}3C_3\text{-}2C_2\text{-}C_A)\ \text{mol} \cdot \text{dm}^{-3}\ \text{NaClO}_4$$

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* Corresponding author. E-mail: miuliano@unina.it.

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$$\mathrm{TS2} = C_3\ \mathrm{mol \cdot dm^{-3}\ Fe(ClO_4)_3},\ C_L\ \mathrm{mol \cdot dm^{-3}\ H_2L},\ C_A\ \mathrm{mol \cdot dm^{-3}\ HClO_4},\ C_B\ \mathrm{mol \cdot dm^{-3}\ NaHCO_3},\ (1\text{-}3C_3\text{-}C_A)\ \mathrm{mol \cdot dm^{-3}\ NaClO_4}$$

Generally $C_3 = C_2$.

At 25 °C, the EMF of cell I can be written as eq 1

$$E_{\mathrm{red}} = E_{0\mathrm{red}} + 59.16 \log([\mathrm{Fe}^{3+}]/[\mathrm{Fe}^{2+}]) + E_j([\mathrm{H}^+]) \tag{1}$$

whereas that of cells II and III can be written as eq 2

$$E_{\mathrm{glass}} = E_{0\mathrm{glass}} + 59.16 \log[\mathrm{H}^+] + E_j([\mathrm{H}^+]) \tag{2}$$

$E_{0\mathrm{red}}$ and $E_{0\mathrm{glass}}$ are constant in each titration. E_j is the liquid junction potential at the boundary test solution/salt bridge and has been found to be a function of $[\mathrm{H}^+]$ only, i.e., $E_j = -(64 \pm 3)[\mathrm{H}^+]$ in 1.00 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{NaClO_4}$ medium. In the calculation of $[\mathrm{Fe}^{3+}]$ from 1, we set $[\mathrm{Fe}^{2+}] = [\mathrm{Fe(II)}]$. This seems correct since titrations with a glass electrode in solutions of Fe(II)−H_2L, Fe(III) being absent, have excluded the formation of appreciable amounts of Fe(II)−salicylohydroxamate complexes at pH < 2.

Each run consisted of two parts. In the first, measurements, carried out in the absence of H_2L at $C_A \geq 0.01\ \mathrm{mol \cdot dm^{-3}}$, served for the determination of $E_{0\mathrm{glass}}$ and $E_{0\mathrm{red}}$ after a small correction for the hydrolysis of the Fe^{3+} ion. For this purpose, the equilibria 3 and 4 with constants, taken from the paper by Salvatore and Vasca,[6] were assumed

$$\mathrm{Fe}^{3+} + \mathrm{H_2O} \rightleftarrows \mathrm{FeOH}^{2+} + \mathrm{H}^+,\ \log \beta_{1,-1,0} = -2.82 \tag{3}$$

$$2\mathrm{Fe}^{3+} + 2\mathrm{H_2O} \rightleftarrows \mathrm{Fe_2(OH)_2^{4+}} + 2\mathrm{H}^+,\ \log \beta_{1,-1,0} = -2.85 \tag{4}$$

E_0 values constant to within ± 0.1 mV were calculated. In the second part, the ligand was added according to different procedures. In titrations with cells I and II, the ligand was added stepwise while the concentrations of $\mathrm{HClO_4}$ and of Fe(III) were kept essentially constant. In titrations with cell III, the ratio C_3/C_L was kept constant while the acidity was gradually decreased. In Table 1 are summarized the conditions of the various titrations.

Table 1. Survey of Measurements

titrations with cells I and II

C_3 / $10^3\ \mathrm{mol \cdot dm^{-3}}$	C_A / $\mathrm{mol \cdot dm^{-3}}$	C_L / $10^3\ \mathrm{mol \cdot dm^{-3}}$
1.0	0.01	≤ 0.01
2.0	0.01	≤ 0.01
5.0	0.01	≤ 0.015
1.5	0.03	≤ 0.01
2.0	0.10	≤ 0.01

titrations with cell III

C_3 / $10^3\ \mathrm{mol \cdot dm^{-3}}$	C_L / $10^3\ \mathrm{mol \cdot dm^{-3}}$	pH range
0.30	0.30	2.2 to 3.9
0.70	0.70	2.5 to 3.5
1.10	1.10	2.3 to 3.4
2.50	2.50	2.2 to 3.4
7.00	7.00	1.9 to 2.6
0.30	0.50	2.8 to 3.8
0.50	1.00	2.6 to 3.2
0.30	0.60	2.7 to 3.8
0.30	0.90	2.7 to 3.7
1.00	3.00	2.7 to 3.7

3. Experimental Section

3.1. Reagents and Analysis. Salicylhydroxamic acid, Aldrich of pure grade quality, was crystallized and analyzed as described in a previous work.[7] Only freshly prepared solutions were used.

Iron(III) perchlorate stock solutions were obtained from $\mathrm{Fe(ClO_4)_3 \cdot}x\mathrm{H_2O}$ (Aldrich) which was purified by crystallization from 1:1 $\mathrm{HClO_4}$. In the violet crystals, no Cl^- ion and heavy metals could be detected. In the stock solutions, ≈ 0.6 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{Fe(ClO_4)_3}$ and ≈ 0.2 $\mathrm{mol \cdot dm^{-3}}$ $\mathrm{HClO_4}$, the iron(III) concentration was determined gravimetrically as oxinate[8] as well as iodometrically, i.e., by amperometric titration with standard $\mathrm{Na_2S_2O_3}$ of the iodine formed on reducing Fe(III) with NaI in excess. The results agreed to within 0.1 %.

The hydrogen ion excess in the stock solution, $= [\mathrm{ClO_4^-}] - 3[\mathrm{Fe(III)}]$, was determined as follows. Hydrogen gas was bubbled in the presence of platinum black until all the Fe(III) was transformed into Fe(II). The excess acid, now equal to $[\mathrm{ClO_4^-}] - 2[\mathrm{Fe(II)}]$, was titrated potentiometrically (glass electrode) with NaOH and the end-point established by Grans' method.[9] Since the Fe^{2+} ion does not hydrolyze at $[\mathrm{H}^+] > 10^{-5}$ $\mathrm{mol \cdot dm^{-3}}$, linear Grans' plots resulted, from which the hydrogen ion excess in the original stock solution could be evaluated. The analyses agreed within 0.1 %.

The perchlorate ion concentration in the stock $\mathrm{Fe(ClO_4)_3}$ solution was determined gravimetrically as $\mathrm{KClO_4}$. An exactly known excess of $\mathrm{KHCO_3}$ was added dropwise. The precipitated iron(III) hydroxide was removed by filtration, and the excess $\mathrm{KHCO_3}$ in the clear solution was transformed to $\mathrm{KClO_4}$ by adding standard $\mathrm{HClO_4}$ to $[\mathrm{H}^+] = 10^{-5.2}\ \mathrm{mol \cdot dm^{-3}}$, as indicated by methyl red. The solution was finally evaporated, and the $\mathrm{KClO_4}$ crystals dried at 130 °C. The perchlorate concentration in the original sample was calculated by subtracting from the weighed total $\mathrm{KClO_4}$ the equivalents of $\mathrm{HClO_4}$ used to destroy the $\mathrm{KHCO_3}$ excess. The results of a series of three determinations were concordant within 0.2 %. The gravimetric result agreed to within 0.4 % with the sum $3[\mathrm{Fe(III)}] + [\mathrm{H}^+]$, a difference consistent with the various sources of error.

Iron(II) perchlorate solutions were prepared as mentioned above by reduction of $\mathrm{Fe(ClO_4)_3}$ with hydrogen gas in the presence of finely divided platinum.

The sodium hydrogen carbonate solutions were made from $\mathrm{NaHCO_3}$, Merck p.a. quality. The sodium hydroxide solutions were obtained by diluting a 50 % solution, prepared from NaOH Aldrich p.a. pellets, under an inert nitrogen atmosphere. Solutions of bases were standardized with a precision of 0.1 % against $\mathrm{HClO_4}$.

Sodium perchlorate, perchloric acid, and silver perchlorate solutions were prepared and analyzed as described elsewhere.[7]

3.2. Apparatus. The potentiometric titrations were carried out with the apparatus described in a previous work in this laboratory.[10] Platinum foils were used as redox electrodes. They were cleaned by boiling in 1:1 $\mathrm{HNO_3}$ and washed with distilled water. The potentials of two or more electrodes immersed in the same solution coincided to within (0.1 to 0.2) mV. Sometimes in highly complexing media the redox electrodes had potentials differing by 0.5 mV or more. These data were disregarded. Glass as well as redox electrodes (10 to 15) min after the addition of reagents acquired potentials that remained constant within 0.1 mV for several hours.

4. Treatment of the Data and Results

The compositions of the reaction products and the corresponding equilibrium constants were evaluated by graphical procedures as well as by the high-speed computer program

Table 2. Values of the Formation Constants of $FeHL^{2+}$ and $Fe(HL)_2^+$

	graphical	SUPERQUAD(3σ)
$\log \beta_{1,-1,1}$	2.40 ± 0.05	2.38 ± 0.01
$\log \beta_{1,-2,2}$	2.9 ± 0.1	2.83 ± 0.05
		$\sigma(E_{red}) = 0.45$ mV

SUPERQUAD.[11] Redox potentials were processed by a special version of SUPERQUAD kindly supplied by Professors Sabatini and Vacca. Data collected in titrations with cells I and II were treated separately from those with cell III.

4.1. Titrations with Redox and Glass Electrodes, Cells I and II. Processing the data by standard graphical methods[12] led to the conclusion that the predominating complexes are $FeHL^{2+}$ and $Fe(HL)_2^+$ with formation constants given in Table 2. In the calculations, the hydrolytic reactions 3 and 4 were accounted for, while the protolysis of H_2L, with acidic constants[7] $pK_{a1} = 7.57$ and $pK_{a2} = 9.67$, could be safely neglected.

The numerical analysis was carried out by minimization of the error square sum $U_{red} = \Sigma(E_{red} - E_{red}^{calc})^2$ where E_{red}^{calc} is a value calculated with a given set of parameters. The constants of hydrolytic reactions 3 and 4 were not allowed to vary. The calculations assuming $FeHL^{2+}$ and $Fe(HL)_2^-$ ended at the constants and agreement factor quoted in Table 2. The agreement between graphical and numerical constants is satisfactory. A standard deviation of 0.45 mV in E_{red} still leaves something to be desired. In the search of a better fit we have tried to add systematically conceivable species, such as $Fe(HL)_3$, $FeL^+ = FeOHHL^+$, and $Fe_2(OH)_2(HL)_2^{2+}$, but the error sum did not decrease significantly. It was therefore concluded that unsuspected analytical errors, medium changes, and inaccurate evaluation of the liquid junction potential, which amounts to several millivolts at the highest acidity studied, contribute to a certain extent to the standard deviation of E_{red}.

4.2. Titrations with Cell III. The particular set of data at $C_3 = C_L$ was first analyzed by graphical procedures before the whole set of measurements was processed by SUPERQUAD. In the graph of Figure 1, Z, the average number of hydrogen ions split off per iron or per ligand, $([H^+] - C_A + C_B)/C_3 = ([H^+] - C_A + C_B)/C_L$, is plotted as a function of log $[H^+]$. Filled symbols represent points of reverse titrations. The coincidence within the limits of estimated accuracy indicates that we are measuring true equilibria. The points $Z(\log [H^+], C_3)$ are seen to fall on different curves which means that polynuclear complexes in Fe and H_2L might prevail.

At increasing acidities, Z tends to unity, and the complex $FeHL^{2+}$ prevails over $Fe(HL)_2^+$, Fe^{3+}, $FeOH^{2+}$, and $Fe_2(OH)_2^{4+}$. As acidity decreases, $FeHL^{2+}$ might hydrolyze to form species such as FeL^+. However, on account of the features of the $Z(\log [H^+])$ function, the reaction products should have a more complicated formula. In an attempt to assign the formula of the main species formed in the pH range 1.5 to 4, we have postulated that the $FeHL^{2+}$ ion undergoes hydrolytic reactions of the type: $m FeHL^{2+} + n H_2O \rightleftarrows (FeHL)_m(OH)_n^{n-m} + nH^+$.

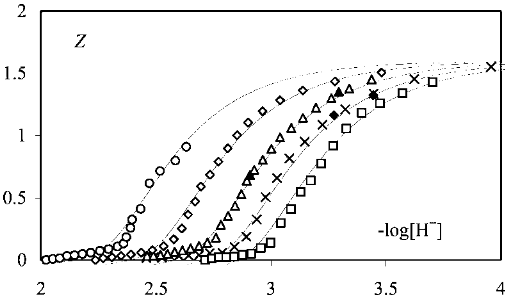

Figure 1. Data at $C_3 = C_L$. Z, average number of hydrogen ions split off per Fe^{3+} ion, as a function of pH. $C_3 \cdot 10^3$ $(mol \cdot dm^{-3})$ = squares, 0.3; crosses, 0.65; triangles, 1.2; diamonds, 2.5; circles, 7.0. Filled symbols refer to reverse titrations. The curves have been calculated by assuming the constants given in eqs 3and 4and Tables 2 and 3.

The Z(pH) curves are of nearly the same shape and of a constant spacing $(\Delta \log C_3/(\Delta \log [H^+])_Z = 2$. Then, all the data may be reduced to a single curve by plotting Z vs $\log(C_3[H^+]^{-2})$, as the graph of Figure 2 shows. This means that according to Sillén[12] the complexes have the general formula $(FeHL)_{n+1}(OH)_2)_n$, where n is an integer and may take a series of values.

The equilibria then can be represented by

$$(n+1)FeHL^{2+} + 2nH_2O \rightleftarrows (FeHL)_{n+1}(OH)_{2n}^{\ 2+} + 2nH^+, K_n \quad (5)$$

To obtain the most important values of n and K_n the graph $Z(\log(C_3[H^+]^{-2}))$ was confronted with model functions representing different hypotheses. The comparison of the experimental graph with curves[13,14] calculated with a single $n = N$ is shown in Figure 2. It is evident that the best fit is produced by the model curve calculated with $N = 4$, i.e., by $(FeHL)_5(OH)_8^{2+}$, while systematic deviations are observed with adjacent N values. The model curve giving the best fit was calculated with $\log K_4 = -10.9 \pm 0.5$. The uncertainty was estimated on the basis of the spread of the points especially in the region of Z from 1 to 1.3. From this K_4 and $\beta_{1,-1,1}$ given in Table 2, the constant $\log \beta_{5,-13,5} = 1.0 \pm 0.6$ was evaluated. We may thus infer that in solutions in which metal and ligand are in equimolecular ratio the pentamer $(FeHL)_5(OH)_8^{2+}$ is the main reaction product in the pH range 2 to 4.

In the analysis of the whole set of data by SUPERQUAD, the constants $\beta_{1,-1,0}$ and $\beta_{2,-2,0}$ in eqs 3 and 4 and $\beta_{1,-1,1}$ and $\beta_{1,-2,2}$ in Table 2 were not allowed to vary. The calculations were founded on the search of the minimum $U_{glass} = \Sigma(E_{glass} - E_{glass}^{calc})$, where E_{glass}^{calc} is a value calculated with a given set of constants. The results are summarized in Table 3.

First, models with two species in addition of $FeHL^{2+}$ and $Fe(HL)_2^+$ were tested. The minimum of U_{glass} was found assuming model 1, i.e., the formation of $Fe_5(OH)_{13}(H_2L)_5^{2+}$ and $Fe(OH)_4(H_2L)_2^-$. Replacing the pentamer with $Fe_6(OH)_{18}(H_2L)_6^{2+}$ yielded the next best fit but with an increase of the minimum by about 50 %. The agreement factor did not improve significantly with three species models. Among the several models tested, we quote model 3 and model 4 which in addition to the pentamer and $Fe(OH)_4(H_2L)_2^-$ comprise, respectively, $Fe(OH)_3$ (H_2L) or $Fe_6(OH)_{18}(H_2L)_6^{2+}$. In our opinion, however, a decrease inferior to 10 % in U_{glass} is not convincing evidence for the formation of either $Fe_6(OH)_{18}(H_2L)_6^{2+}$ or $Fe(OH)_3(H_2L)$. A resolution of the question demands the collection of more accurate experimental data.

In concluding, we assume model 1 as the “best” to describe measurements with cell III.

5. Discussion

The main conclusion of the present investigation is that in solutions of pH < 4, before the onset of precipitation of basic salts, the complexes $FeHL^{2+}$, $Fe(HL)_2^+$, $Fe(OH)_4(H_2L)_2^-$ (equivalent to FeL_2^-), and $Fe_5(OH)_{13}(H_2L)_5^{2+}$ (equivalent to $Fe_5(OH)_8(HL)_5^{2+}$) are formed in appreciable concentration. Distribution curves in different conditions indicate that the $FeHL^{2+}$ species is sufficiently stable to form in appreciable

Table 3. Treatment by SUPERQUAD of Data with Cell III (271 Data Points)

	$\log \beta_{p,q,r} \pm 3\sigma$	$\log \beta_{p,q,r} \pm 3\sigma$	$\log \beta_{p,q,r} \pm 3\sigma$	$\log \beta_{p,q,r} \pm 3\sigma$
species	model 1	model 2	model 3	model 4
$Fe_5(OH)_{13}(H_2L)_5^{2+}$	1.57 ± 0.06		1.53 ± 0.07	1.46 ± 0.09
$Fe(OH)_4(H_2L)_2^-$	−4.48 ± 0.08	−4.52 ± 0.09	−4.52 ± 0.09	−4.49 ± 0.07
$Fe_6(OH)_{18}(H_2L)_6^{2+}$		1.21 ± 0.09		0.54 ± 0.12
$Fe(OH)_3\ (H_2L)$			−5.1 ± 0.3	
σ, mV	0.63	0.76	0.61	0.61
χ^2	15.5	72.5	11.5	13.8
U_{glass}, mV^2	103	150	97.5	96.5

amount even at pH = 1. The polynuclear complex is probably a derivative of hydrolytic complexes of the Fe^{3+} ion. In the absence of complexing agents and before iron hydroxides start to precipitate, the hydrolysis has been described[15] with $FeOH^{2+}$ and $Fe_2(OH)_2^{4+}$ as the main species and with small quantities of $Fe(OH)_2^+$ and $Fe_3(OH)_4^{5+}$, which form near the onset of precipitation. In complexing media, the precipitation of iron(III) hydroxides is shifted to lower acidities and the conditions become favorable for the formation of detectable amounts of soluble hydrolytic species having higher nuclearity. In a previous study[9] on iron(III) acetate complexes, evidence was found for the formation of $Fe_3(OH)_5^{4+}$ favored in the special conditions created by the complexing milieu. We suppose that at the acidities investigated in the present work the free Fe^{3+} concentration is too small to cause the precipitation of the hydroxide but sufficiently large to favor hydrolytic species of nuclearity higher than 3. These are stabilized by completing the coordination of the metal with the hydroxamate group. As an illustrative example, we may quote the UO_2^{2+} ion hydrolysis in the Na_2SO_4 medium. Peterson[16] in a study in $1.5Na_2SO_4$ (and other authors[17−20]) found evidence for the formation of $(UO_2)_5(OH)_8^{2+}$, a species that has never been detected in a noncomplexing medium[21] as $NaClO_4$.

Equilibrium analysis data give no information on the structure of the complexes. Attempts are in course to precipitate basic iron(III) hydroxamates in well-crystallized form to assign the structure of the pentamer.

In a future attack on the system, we intend to extend the investigation at lower acidities on dilute metal solutions, $\leq 2 \cdot 10^{-4}$ mol·dm^{-3}, employing spectrophotometric techniques.

5.1. Comparison of Results from Previous Work. The constant $\log \beta_{1,-1,1}$ evaluated in this work agrees quite well with 2.33 determined by Das et al.[2] under identical experimental conditions and with the 2.36 recalculated from results at 20 °C in 1 mol·dm^{-3} medium by Springer et al.[1] Also, the $\log \beta_{1,-1,1} = 1.92$ recalculated from data by Shuaib et al.[3] is substantially concordant. The small discrepancy is only apparent and explainable with the complexation of the Fe^{3+} ion with the chloride ion of the medium. On the other hand, the formation constants of $FeHL^{2+}$ and of $Fe(HL)_2^+$ proposed by O'Brien et al.[4] differ by orders of magnitude. From the results reported by these authors, we obtain $\log \beta_{1,-1,1} = -5.28$ and $\log \beta_{1,-2,2} = -11.76$. The incongruity is simply explainable by misprints in the data of Table 1 in ref 4.

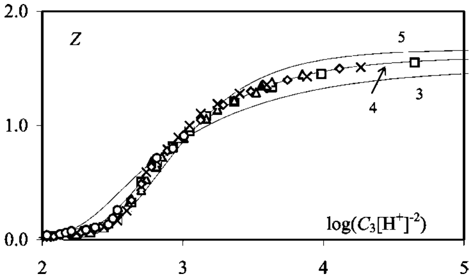

Figure 2. Z as a function of $\log(C_3[H^+]^{-2})$. Symbols as in Figure 1. The curves represent different N values indicated on the graph. The curves were calculated with $\log K_3 = 8.4$, $\log K_4 = 10.9$, and $\log K_5 = 14.0$.

The species $Fe(OH)_4(H_2L)^-$ assumed in our final model has been detected also by Shuaib et al.[3] with a value of $\log \beta_{1,-4,1} = -5.33$. This, in consideration of the different experimental conditions, is in acceptable agreement with our $\beta_{1,-4,1}$.

5.2. Equilibrium Constants at the Infinite Dilution Reference State. The constants $°\beta_{p,q,r}$, valid at zero ionic strength, were obtained by assuming the validity of the specific ion interaction theory.[22,23] The equilibrium constants were converted to the molal scale using densities of $NaClO_4$ solutions compiled by Söhnel and Novotný.[24] The interaction coefficients necessary for the calculations were assumed as follows. $b(Fe^{3+}, ClO_4^-) = 0.56 \pm 0.03$, $b(H^+, ClO_4^-) = 0.14 \pm 0.02$, and $b(Na^+, OH^-) = 0.04 \pm 0.01$ were taken from ref 21 and $b(HL^-, Na^+) = 0.12 \pm 0.01$, $b(L^{2-}, Na^+) = 0.17 \pm 0.02$, and $b(H_2L, NaClO_4) = -0.05_5 \pm 0.01$ from ref 5. The interaction coefficients $b(FeHL^{2+}, NaClO_4) = 0.62 \pm 0.05$, $b(Fe(HL)_2^+, NaClO_4) = 0.27 \pm 0.05$, and $b(FeL_2^-, NaClO_4) = 0.30 \pm 0.05$ were estimated with the empirical rule proposed previously.[23] The water activity in 1.05 mol·kg^{-1} of $NaClO_a$, $a_w = 10^{-0.014}$, was deduced from osmotic coefficients tabulated by Robinson and Stokes.[25]

More crucial is the estimate of the interaction coefficient of the pentamer with medium ions. It has been pointed out[16] that the charge of the ionic species is determinant. Since species with charge 2+ have interaction coefficients ranging from 0.15 to 0.5, a plausible value for the pentamer would be the average 0.3 ± 0.2. In addition, we suggest another rule based on the hypothesis that the complex has a closed structure in which the core "$Fe_5(OH)_8$" is surrounded by chelating groups HL^-. In the complex, metal ions are buried by hydroxide and ligand ions so that they have no chance to interact with short-range forces with medium ions. In other words, short-range ineractions of medium ions are possible only with HL^- groups in $Fe_5(HL)_5(OH)_8^{2+}$. According to the rule suggested elsewhere,[22] $b(\text{pentamer}, NaClO_4) = (5/2)b(HL^-, Na^+) = 0.30$. We have concluded that $b(\text{pentamer}, NaClO_4) = 0.3 \pm 0.2$.

The extrapolation procedure ended with the $°\beta_{p,q,r}$ constants

$$\log °\beta_{1,-1,1} = 3.4_7 \pm 0.1, \log °\beta_{1,-2,2} = 4.1_7 \pm 0.1, \log °\beta_{1,-4,2} = -3.2 \pm 0.1, \log °\beta_{5,-13,5} = 7.1 \pm 0.3$$

Symbols

H_2L, salicylhydroxamic acid
b(i,k), interaction coefficient between species i and k
C_3, total concentration of Fe(III)
C_2, total concentration of Fe(II)
C_L, total concentration of H_2L
C_A, concentration of $HClO_4$
C_B, concentration of $NaHCO_3$
pH = −log [H^+]

$\beta_{p,q,r}$, equilibrium constant for $p\mathrm{Fe}^{3+} + q\mathrm{H_2O} + r\mathrm{H_2L} \rightleftarrows \mathrm{Fe}_p(\mathrm{OH})_q(\mathrm{H_2L})_r^{\,3p-q} + q\mathrm{H}^+$

$^\circ\beta_{p,q,r}$, the value of $\beta_{p,q,r}$ at the infinite dilution reference state

Z, average number of hydrogen ions split off per Fe^{3+} ion, $= ([\mathrm{H}^+] - [\mathrm{OH}^-] - C_\mathrm{A} + C_\mathrm{B})/C_3$.

Concentrations, otherwise stated, are expressed on the $\mathrm{mol \cdot dm^{-3}}$ scale

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