

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

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**ABSTRACT:** The complex formation between the  $\text{Fe}^{3+}$  ion and 2-hydroxybenzoic acid (salicylic acid,  $\text{H}_2\text{L}$ ) has been studied at 298.15 K in  $1.05 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$  medium by both potentiometric titrations with glass electrodes and spectrophotometric measurements in the range of wavelengths between (410 and 600) nm. The concentrations of ligand ( $C_L$ ) and metal ion ( $C_M$ ) were varied between  $(0.105 \times 10^{-3}$  and  $21 \times 10^{-3}) \text{ mol} \cdot \text{kg}^{-1}$ , and the ligand-to-metal ratio was varied between (1 and 1000) ( $1 \leq C_L/C_M \leq 1000$ ). The hydrogen ion concentration was decreased stepwise to the incipient precipitation of a basic salt of metal. The experimental data have been explained with the formation of the complexes  $\text{FeL}^+$ ,  $\text{FeL}_2^-$ ,  $\text{FeL}_3^{3-}$ ,  $\text{Fe}(\text{HL})\text{L}$ , and  $\text{Fe}_2(\text{OH})_2(\text{HL})\text{L}^+$ . Stability constants for their formation in  $1.05 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$  as well as in dilute solution are reported.

### INTRODUCTION

The therapy for metal overload pathologies usually involves the administration of suitable chelating agents to selectively remove the metal from the body. Hexadentate ligands possess very high selectivity toward  $\text{Fe}(\text{III})$ , but usually they have a poor oral bioavailability,<sup>1</sup> whereas bidentate ligands have the opposite behavior, i.e., lesser selectivity but higher oral bioavailability. In 1966 Park<sup>2</sup> studied the complexation equilibria  $\text{Fe}^{3+} + \text{H}_2\text{L} \rightleftharpoons \text{FeL}^+ + 2 \text{H}^+$ ,  $\text{Fe}^{3+} + 2 \text{H}_2\text{L} \rightleftharpoons \text{FeL}_2^- + 4 \text{H}^+$ , and  $\text{Fe}^{3+} + 3 \text{H}_2\text{L} \rightleftharpoons \text{FeL}_3^{3-} + 6 \text{H}^+$  ( $\text{H}_2\text{L}$  stands for 2-hydroxybenzoic acid) in  $0.1007 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$  by potentiometric titrations with a glass electrode. The author proposed at 298.15 K the equilibrium constants  $\beta_1 = 10^{-0.11}$ ,  $\beta_2 = 10^{-1.94}$  and  $\beta_3 = 10^{-9.17}$ . In 1970 McBride et al.<sup>3</sup> in a spectrophotometric investigation at 298.15 K in  $0.513 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$  found evidence for the formation of the complex  $\text{FeL}^+$  with a value of the constant  $\beta_1 = 10^{0.03}$ . In 1973, Ramamoorthy and Manning<sup>4</sup> using potentiometric titrations with a glass electrode in  $0.1007 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$  at 298.15 K found evidence for the formation of  $\text{FeL}^+$  and  $\text{FeL}_2^-$  with equilibrium constants  $\beta_1 = 10^{-0.29}$  and  $\beta_2 = 10^{-3.38}$ , respectively.

In 1982, Chattopadhyaya<sup>5</sup> investigated the system at 298.15 K in perchlorate media of ionic strength  $0.1007 \text{ mol} \cdot \text{kg}^{-1}$  by spectrophotometric method finding evidence for the formation of the complex  $\text{FeL}^+$  with a value of the constant  $\beta_1 = 10^{-0.46}$ . Although these reactions have, as indicated, been examined already by a number of investigators, concordance among the different published stability constants is not very good. Taking into account the discrepancy of the results of previous works and in consideration of the numerous biological and medical applications of 2-hydroxybenzoic acid, it seems important reconsider the system in order to determine the composition of the reaction products. In this work the complex formation between the  $\text{Fe}^{3+}$  ion and 2-hydroxybenzoic acid (salicylic acid,  $\text{H}_2\text{L}$ ) has been studied at 298.15 K in  $1.05 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$  medium by spectrophotometric measurements in a range of wavelengths between (410 and 600) nm taking into account low concentrations of metal ion and high concentration of ligand, in which mononuclear species are predominant. Moreover, the composition of the solutions was

determined by potentiometric titrations with glass electrodes when the concentration of the  $\text{Fe}^{3+}$  ion and salicylic acid were in comparable amount. In these conditions, in particular for high concentration of metal ion, it was possible to determine the stability constant for a polynuclear complex.

### MATERIALS AND METHODS

**Instrumentation.** The cell arrangement was similar to that described by Forsling et al.<sup>6</sup>  $\text{Ag}/\text{AgCl}$  electrodes were prepared according to Brown.<sup>7</sup> Glass electrodes, manufactured by Metrohm, were of the 6.0133.100 type. They acquired a constant potential within 10 min after the addition of the reagents and remained unchanged within  $\pm 0.1$  mV for several hours. The titrations were carried out with a programmable computer controlled data acquisition switch unit 34970 A supplied by Hewlett-Packard. The EMF values were measured with a precision of  $\pm 10^{-5}$  V using an OPA 111 low-noise precision DIFET operational amplifier. A slow stream of nitrogen gas was passed through four bottles (a–d) containing (a)  $0.96 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaOH}$ , (b)  $0.94 \text{ mol} \cdot \text{kg}^{-1}$   $\text{H}_2\text{SO}_4$ , (c) twice distilled water, and (d)  $1.05 \text{ mol} \cdot \text{kg}^{-1}$   $\text{NaClO}_4$ , and then into the test solutions, stirred during titrations, through the gas inlet tube. During the EMF measurements, the cell assembly was placed in a thermostat kept at  $(298.15 \pm 0.1)$  K. The spectrophotometric measurements have been conducted with a Varian Cary 50 Scan UV–visible Spectrophotometer. Absorbance values between (350 and 800) nm were measured each 2 nm. The spectra were recorded 120 s after mixing metal and ligand with strong base. This time was considered sufficiently short to avoid the photochemical decomposition. The temperature of the cell holder was kept at  $(298.15 \pm 0.3)$  K by a Grant circulating water bath. Matched quartz cells of thickness 1 cm were employed. The absorbance,  $A_\lambda$ , was recorded to  $\pm 0.001$  units. The formulations of the parameters and the acquisition of

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the data have been managed with the aid of a computer connected to the tool.

**Reagents and Analysis.** A perchloric acid stock solution was prepared and standardized as described previously.<sup>8</sup> A sodium perchlorate stock solution was prepared and standardized according to Biedermann.<sup>9</sup> Sodium hydroxide titrant solutions were prepared and standardized as described previously.<sup>10</sup> Sodium hydrogen salicylate stock solutions were prepared from the commercial product Aldrich p.a.; it was kept in a desiccator over silica gel. The salt purity was determined gravimetrically as NaCl. A known amount of the commercial product was put in a porcelain crucible and dissolved in the minimum quantity of methanol. A large excess of a 10 mol·kg<sup>-1</sup> HCl solution (Merck p.a.) was added dropwise at the warm solution and successively evaporated to dryness. The sample was held at 473.15 K, the temperature recommended for the sublimation of salicylic acid, to constant weight. As a check NaCl was determined by titration with AgNO<sub>3</sub> according to Mohr method. The results of gravimetric and volumetric determinations agreed within 0.1 %. The mole fraction purity of the salt was (0.965 ± 0.003). Iron(III) perchlorate was prepared and standardized as reported by Ciavatta et al.<sup>11</sup>

All solutions were prepared with twice distilled water.

**Spectrophotometric Measurements.** Absorption spectra in the visible region were recorded on a series of iron(III) and salicylate solutions, in which the concentration of the metal was lower than that of the ligand, which was varied over a wide range. In this way it was possible to stabilize the complexes mononuclear in the metal and polynuclear in the ligand. The metal concentration,  $C_M$ , was ranged from (0.105 × 10<sup>-3</sup> to 1.05 × 10<sup>-3</sup>) mol·kg<sup>-1</sup> and the acidic concentration,  $C_A$ , was varied from (0.105 × 10<sup>-3</sup> to 0.105) mol·kg<sup>-1</sup>. The ligand-to-metal ratio was varied between (1 and 1000) (1 ≤  $C_L/C_M$  ≤ 1000). During each titration, conducted at analytical concentrations of acidity and Fe(III) constants, increasing quantities of HL<sup>-</sup> have been added until we observed a significant variation of spectral absorbance.

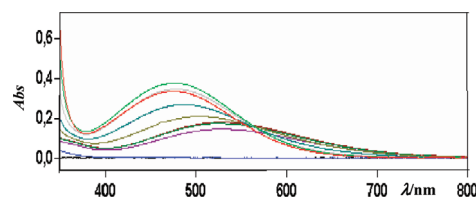
The absorbance values of test solutions, intensely colored, were recorded every two nanometers in a wavelength range between (350 and 800) nm. For the numerical treatment of experimental data the wavelength range was restricted between (410 and 600) nm where the additions of salicylate ion was associated to significant changes in the absorbance values. A typical spectrum is given in Figure 1.

The different curves reported in Figure 1 are obtained for analytical concentrations of acidity and Fe(III) constants and increasing concentration of HL<sup>-</sup> until we observed a significant variation of spectral absorbance. The absorbance values and the analytical concentrations of the reactants are the basis of calculations for the determination of the complex formation constants.

**Potentiometric Measurements.** The complexation equilibria have been studied, at 298.15 K and in 1.05 mol·kg<sup>-1</sup> NaClO<sub>4</sub>, by measuring with a glass electrode the competition of the salicylic acid, H<sub>2</sub>L, for the iron(III) and H<sup>+</sup> ions. The potentiometric measurements, conducted as titrations, were performed with cell G



where RE, reference electrode, = Ag/AgCl/0.0105 mol·kg<sup>-1</sup> AgClO<sub>4</sub>, 1.0395 mol·kg<sup>-1</sup> NaClO<sub>4</sub>/1.05 mol·kg<sup>-1</sup> NaClO<sub>4</sub> and test solution =  $C_M$  mol·kg<sup>-1</sup> Fe(ClO<sub>4</sub>)<sub>3</sub>,  $C_L$  mol·kg<sup>-1</sup> NaHL,  $C_A$  mol·kg<sup>-1</sup> HClO<sub>4</sub>,  $C_B$  mol·kg<sup>-1</sup> NaOH, (1.05–3 $C_M$ – $C_L$ – $C_A$ – $C_B$ ) mol·kg<sup>-1</sup> NaClO<sub>4</sub>. The metal and the ligand concentrations,  $C_M$  and  $C_L$ , respectively, were ranged from



**Figure 1.** Measurements of absorbance (Abs) at different wavelengths ( $\lambda/\text{nm}$ ), carried out on a solution with the following composition: 0.105 × 10<sup>-3</sup> mol·kg<sup>-1</sup> Fe<sup>3+</sup>, 1.05 × 10<sup>-3</sup> mol·kg<sup>-1</sup> H<sup>+</sup>, 10.5 × 10<sup>-3</sup> mol·kg<sup>-1</sup> HL<sup>-</sup>. Blank: 1.05 mol·kg<sup>-1</sup> NaClO<sub>4</sub>. The different curves are obtained for analytical concentrations of acidity and Fe(III) constants and increasing concentration of HL<sup>-</sup> until we observed a significant variation of spectral absorbance.

(5.25 × 10<sup>-3</sup> to 21 × 10<sup>-3</sup>) mol·kg<sup>-1</sup> and the ligand-to-metal ratio was varied between (1 and 3) (1 ≤  $C_L/C_M$  ≤ 3). The hydrogen ion concentration was varied from 1.05 × 10<sup>-3</sup> mol·kg<sup>-1</sup> to incipient precipitation of basic salts which takes place in the range  $[\text{H}^+] = 1.05 \times 10^{-4} - 1.05 \times 10^{-5}$  mol·kg<sup>-1</sup> depending on the specific ligand-to-metal ratio.

Since the effects of composition changes on activity coefficients can be considered negligible, the EMF of cell (G) can be written, in mV, at the temperature of 298.15 K, as eq 1:

$$E = E^\circ + 59.16 \log [\text{H}^+] + E_j \quad (1)$$

where  $E^\circ$  is constant in each series of measurements,  $E_j$  is the liquid junction potential which is a function of  $[\text{H}^+]$  only.<sup>12</sup> In a previous study we have found<sup>8</sup>  $E_j = -58 [\text{H}^+]$  in 1.05 mol·kg<sup>-1</sup> NaClO<sub>4</sub>. Each titration was divided in two parts. In the first part,  $E^\circ$  was determined in the absence of Fe<sup>3+</sup> ion and the acidity was decreased stepwise by coulometric generation of OH<sup>-</sup> ions with the circuit C:

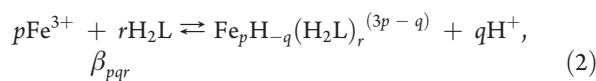


where AE, auxiliary electrode, = 1.05 mol·kg<sup>-1</sup> NaClO<sub>4</sub>/0.105 mol/dm<sup>3</sup> NaCl, 0.945 M NaClO<sub>4</sub>/Hg<sub>2</sub>Cl<sub>2</sub>/Hg. Assuming that the only reactions occurring at the cathode are  $\text{H}^+ + \text{e}^- \rightarrow 1/2 \text{H}_2$  and  $\text{H}_2\text{O} + \text{e}^- \rightarrow 1/2 \text{H}_2 + \text{OH}^-$ , then in the test solution the molal concentration of OH<sup>-</sup> is  $C_B = \text{mol} \cdot \text{kg}^{-1}$ , where moles are related to microfaradays passing through the cell, according to Faraday's law. In the second part for the investigation of Fe(III) complexes, alkalification was achieved by adding NaOH.

The primary  $C_M$ ,  $C_L$ ,  $C_A$ ,  $C_B$  and  $[\text{H}^+]$  data represent the basis of the treatment to obtain the equilibrium constants.

## RESULTS

The general equilibrium can be written, schematically, as eq 2



that takes into account the formation of simple ( $q = r$ ), mixed ( $q \neq r$ ), mononuclear ( $p = 1$ ), and polynuclear ( $p > 1$ ) species.

The most probable  $p$ ,  $q$ ,  $r$  values and the corresponding constants  $\beta_{pqr}$  were calculated by a numerical treatment using the program HYPERQUAD<sup>13</sup> to elaborate the spectrophotometric data and by a computational approach based on the least-squares procedure using the program SUPERQUAD<sup>14</sup> to evaluate the potentiometric measurements.

In the numerical treatments the equilibrium constants concerning the species formed according to equilibria (eqs 3 and 4)

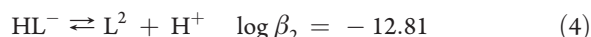
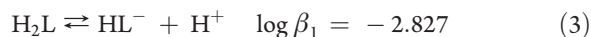
**Table 1.** Summary of the Relevant Data Taken in Six Spectrophotometric Titrations for the System 2-Hydroxybenzoic acid–Fe<sup>3+</sup>

$C_M/\text{mol}\cdot\text{kg}^{-1}$	$C_H/\text{mol}\cdot\text{kg}^{-1}$	$(C_L/\text{mol}\cdot\text{kg}^{-1})_{\text{range}}$
$1.05 \times 10^{-3}$	0.105	$(1.05 \text{ to } 26.2) \cdot 10^{-3}$
$0.105 \times 10^{-3}$	$1.05 \times 10^{-3}$	$(0.105 \text{ to } 105) \cdot 10^{-3}$
$0.21 \times 10^{-3}$	$10.5 \times 10^{-3}$	$(21 \text{ to } 105) \cdot 10^{-3}$
$0.52 \times 10^{-3}$	$1.05 \times 10^{-3}$	$(0.31 \text{ to } 0.73) \cdot 10^{-3}$
$0.21 \times 10^{-3}$	$1.05 \times 10^{-3}$	$(21 \text{ to } 105) \cdot 10^{-3}$

**Table 2.** Best Set of  $\log \beta_{pqr}(\sigma)$  for the System 2-Hydroxybenzoic acid–Fe<sup>3+</sup>, According to General Equilibrium  $p\text{Fe}^{3+} + r\text{H}_2\text{L} \rightleftharpoons \text{Fe}_p\text{H}_{-q}(\text{H}_2\text{L})_r^{(3p-q)} + q\text{H}^+$ 

$(pqr)$	M1	M2	M3	M4
$(1,2,1)^+$	$-0.31 \pm 0.03$	$-0.25 \pm 0.02$	$-0.233 \pm 0.009$	$-0.217 \pm 0.006$
$(1,4,2)^-$		$-2.89 \pm 0.06$	$-2.55 \pm 0.02$	$-2.25 \pm 0.06$
$(1,6,3)^{3-}$				$-6.48 \pm 0.06$
$(1,3,2)$			$0.194 \pm 0.01$	$0.216 \pm 0.009$
$\sigma$	0.1279	0.0558	0.028	0.015
$U$	11.10	2.052	0.5156	0.1434

and determined in previous works<sup>8,15</sup> have been maintained invariant



The principal cationic hydrolysis products of Fe<sup>3+</sup> have been established as FeOH<sup>2+</sup>, Fe(OH)<sub>2</sub><sup>+</sup>, and Fe<sub>2</sub>(OH)<sub>2</sub><sup>4+</sup> by several studies in 1.05 mol·kg<sup>-1</sup> perchlorate media.<sup>16</sup> In the present work, in the numerical treatment the equilibrium constants for these dominant hydrolysis products of the iron(III) ion were fixed because they are well-known from the literature.<sup>17</sup>

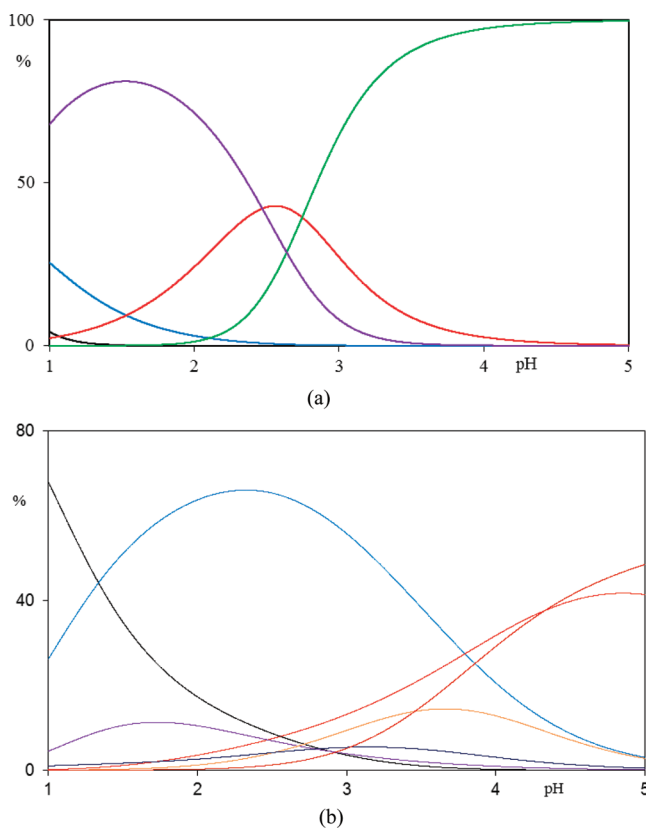
**Spectrophotometric Measurements.** The experimental data consists of 120 data points collected in five titrations. A summary of the relevant data taken in all titrations are reported in Table 1.

In the numerical estimation of the equilibrium formation constants of the complexes between salicylic acid and Fe<sup>3+</sup> by HYPERQUAD<sup>13</sup> the minimum of the function  $U = \sum_i \sum_k w_k (A_{ik} - A_{ik}^c)^2$  was sought. Results of the calculations are reported in Table 2.

The numerical evaluation started assuming the presence of only FeL<sup>+</sup> (model 1), but the standard deviation is higher than the experimental uncertainty. Various models were tested by adding one single species; the best agreement was obtained with the complex FeL<sub>2</sub><sup>-</sup> (model 2) with a consequent decrease of the function  $U$  equal to 81 %. An additional improvement was reached including in the previous model the species FeL<sub>3</sub><sup>3-</sup> (model 3); on the other hand, on adding the neutral complex Fe(HL)L (model 4), the fit is significantly improved. As no other species lowered the minimum, model 4 was assumed as the best describing the data, also in consideration that the standard deviation ( $\sigma$ ) is comparable with the experimental uncertainty.

**Table 3.** Summary of the Relevant Data Taken in Three Potentiometric Titrations for the System 2-Hydroxybenzoic acid–Fe<sup>3+</sup>

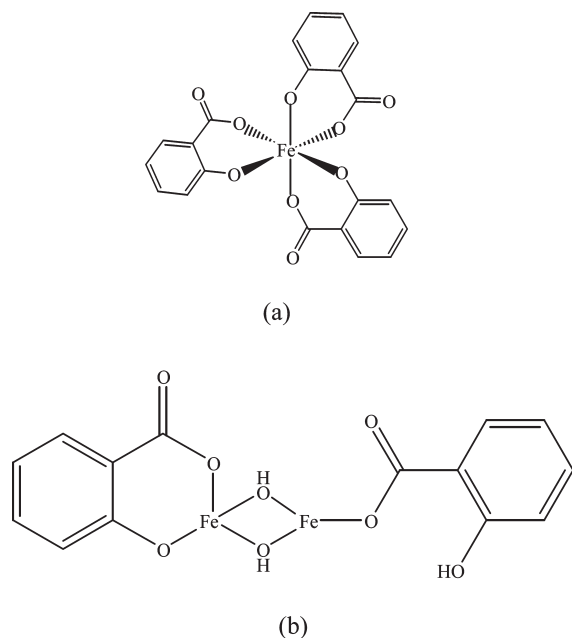
$C_M/\text{mol}\cdot\text{kg}^{-1}$	$C_L/\text{mol}\cdot\text{kg}^{-1}$	pH <sub>range</sub>
$5.2 \times 10^{-3}$	$15.7 \times 10^{-3}$	(3.8 to 4.5)
$10.5 \times 10^{-3}$	$10.5 \times 10^{-3}$	(3.2 to 5.0)
$10.5 \times 10^{-3}$	$21 \times 10^{-3}$	(3.0 to 4.1)



**Figure 2.** Distribution of the Fe(III) species, expressed as percentages (%) versus pH, in (a)  $C_L = 0.105 \text{ mol}\cdot\text{kg}^{-1}$ ,  $C_M = 0.105 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ ; (b)  $C_L = 10.5 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ ,  $C_M = 10.5 \times 10^{-3} \text{ mol}\cdot\text{kg}^{-1}$ . The colors in the figure are referred to the following species: black, Fe<sup>3+</sup>; blue, FeL<sup>+</sup>; red, FeL<sub>2</sub><sup>-</sup>; green, FeL<sub>3</sub><sup>3-</sup>; violet, Fe(HL)L; orange, Fe<sub>2</sub>(OH)<sub>2</sub>(HL)L<sup>+</sup>; dark blue, Fe(OH)<sub>2</sub><sup>2+</sup>; and dark red, Fe(OH)<sub>2</sub><sup>2+</sup>.

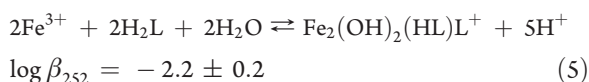
**Potentiometric Measurements.** The data comprise three titrations with 67 data points. A summary of the relevant data taken in all titrations are reported in Table 3.

The most probable  $p$ ,  $q$ , and  $r$  values and the corresponding constants  $\beta_{pqr}$ , according to equilibrium 2, were computed by a numerical approach based on the least-squares procedure using the program SUPERQUAD<sup>14</sup> in which the minimum of the function  $U' = \sum w_i (E_{\text{exp}} - E_{\text{calc}})$  was required. In the numerical treatment, the equilibrium constants concerning the formation of the species FeL<sup>+</sup>, FeL<sub>2</sub><sup>-</sup>, FeL<sub>3</sub><sup>3-</sup>, and Fe(HL)L, refined by evaluation of spectrophotometric data, have been maintained invariant. In the computational evaluation of potentiometric data the only complex which significantly lowered the minimum of the square error sum and the standard deviation ( $\sigma$ ) was the polynuclear complex Fe<sub>2</sub>(OH)<sub>2</sub>(HL)L<sup>+</sup> formed according to



**Figure 3.** Plausible structures of the complexes  $\text{FeL}_3^{3-}$  (a) and  $\text{Fe}_2(\text{OH})_2(\text{HL})\text{L}^+$  (b).

equilibrium 5



The uncertainties on the formation constant represents  $3\sigma$ .

## DISCUSSION

The refined equilibrium constants concerning the complexation of salicylic acid,  $\text{H}_2\text{L}$ , with the  $\text{Fe}^{3+}$  ion, determined by spectrophotometric as well as by potentiometric methods, are used to represent the distribution of the metal in the different species (Figure 2).

As can be seen all of the proposed species are formed in an appreciable amount, before the precipitation of basic salts. In particular when the analytical concentrations of ligand are greater than those of the metal, e.g.,  $C_L = 0.105 \text{ mol} \cdot \text{kg}^{-1}$ ,  $C_M = 0.105 \times 10^{-3} \text{ mol} \cdot \text{kg}^{-1}$  (Figure 2 a)  $\text{FeL}^+$ ,  $\text{FeL}_2^-$ ,  $\text{FeL}_3^{3-}$ , and  $\text{Fe}(\text{HL})\text{L}$  reach significant percentages and are predominant over the hydrolysis product.

When the analytical concentrations of ligand and metal are comparable, in addition to the mononuclear complexes, the species  $\text{Fe}_2(\text{OH})_2(\text{HL})\text{L}^+$  as well as the hydrolytic complexes  $\text{FeOH}^{2+}$  and  $\text{Fe}(\text{OH})_2^+$  are in considerable amounts (Figure 2b).

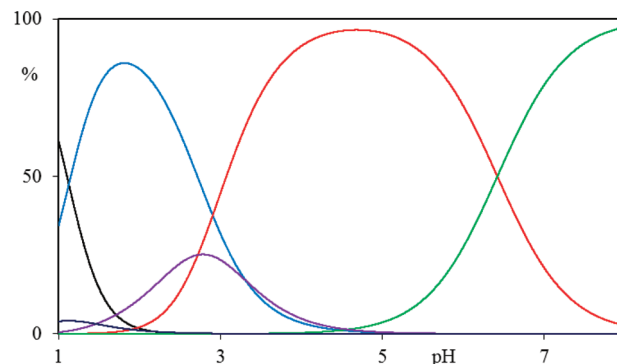
**Extrapolation to Infinite Dilution Reference State.** Some practical applications, i.e., modeling in natural systems, require the knowledge of the formation constants valid in the infinite dilution reference state. Extrapolation to zero ionic strength was carried out by assuming the validity of the SIT.<sup>18,19</sup> According to the theory, the activity coefficient,  $\gamma_i$  of the species  $i$  with charge  $z_i$  can be expressed at 298.15 K in aqueous solutions as

$$\log \gamma_i = -z_i^2 D + \sum b(i, k) m_k \quad (6)$$

where  $D = 0.51 (\sqrt{1.05}) / (1 + 1.5(\sqrt{1.05}))$ ,  $b$  is the specific interaction coefficient of  $i$  with species  $k$  of molality  $m_k$ . Interaction coefficients depend on the ionic strength but the variation in

**Table 4.** Survey of the Formation Constants of the  $\text{Fe}^{3+} - \text{H}_2\text{L}$  System at 298.15 K at the Infinite Dilution Reference State

$\log \beta_{121}^\circ$	$\log \beta_{142}^\circ$	$\log \beta_{163}^\circ$	$\log \beta_{132}^\circ$	$\log \beta_{252}^\circ$
$1.06 \pm 0.05$	$-1.2 \pm 0.1$	$-7.3 \pm 0.2$	$1.53 \pm 0.05$	$0.4 \pm 0.2$



**Figure 4.** Distribution of the Fe(III) species, expressed as percentages (%) versus pH, using the constants valid to infinite dilution:  $C_L = 5.25 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1}$ ,  $C_M = 1.05 \times 10^{-5} \text{ mol} \cdot \text{kg}^{-1}$ . The colors in the figure are referred to the following species: black,  $\text{Fe}^{3+}$ ; blue,  $\text{FeL}^+$ ; red,  $\text{FeL}_2^-$ ; green,  $\text{FeL}_3^{3-}$ ; violet,  $\text{Fe}(\text{HL})\text{L}$ ; and dark blue,  $\text{Fe}(\text{OH})_2^{2+}$ .

the range  $0.5 \leq I \leq 3.5 \text{ m}$  is sufficiently low that they may be assumed as constants. As a further simplification, interaction coefficients of ions with the same charge type are nearly zero. According to equilibrium 2 and indicating with  ${}^\circ\beta_{pqr}$  the constant at zero ionic strength, the variation of the various equilibrium constants determined in this work can be expressed as

$$\log {}^\circ\beta_{121} = \log \beta_{121} + 6D - \log \gamma_{\text{H}_2\text{L}} + [b(\text{FeL}^+, \text{ClO}_4^-) + 2b(\text{H}^+, \text{ClO}_4^-) - b(\text{Fe}^{3+}, \text{ClO}_4^-)] \cdot 1.05 \quad (7)$$

$$\log {}^\circ\beta_{142} = \log \beta_{142} + 4D - 2\log \gamma_{\text{H}_2\text{L}} + [b(\text{FeL}_2^-, \text{Na}^+) + 4b(\text{H}^+, \text{ClO}_4^-) - b(\text{Fe}^{3+}, \text{ClO}_4^-)] \cdot 1.05 \quad (8)$$

$$\log {}^\circ\beta_{163} = \log \beta_{163} - 6D - 3\log \gamma_{\text{H}_2\text{L}} + [b(\text{FeL}_3^{3-}, \text{Na}^+) + 6b(\text{H}^+, \text{ClO}_4^-) - b(\text{Fe}^{3+}, \text{ClO}_4^-)] \cdot 1.05 \quad (9)$$

$$\log {}^\circ\beta_{132} = \log \beta_{132} + 6D - 2\log \gamma_{\text{H}_2\text{L}} + [b(\text{Fe}(\text{HL})\text{L}, \text{NaClO}_4) + 3b(\text{H}^+, \text{ClO}_4^-) - b(\text{Fe}^{3+}, \text{ClO}_4^-)] \cdot 1.05 \quad (10)$$

$$\log {}^\circ\beta_{252} = \log \beta_{252} + 12D + [b(\text{Fe}_2(\text{OH})_2(\text{HL})\text{L}^+, \text{ClO}_4^-) + 5b(\text{H}^+, \text{ClO}_4^-) - 2b(\text{Fe}^{3+}, \text{ClO}_4^-)] \cdot 1.05 - 2\log \gamma_{\text{H}_2\text{L}} - 2\log a_w \quad (11)$$

The activity coefficient,  $\gamma_{\text{H}_2\text{L}}$ , of salicylic acid has been obtained as the ratio (solubility in water)/(solubility in 1.05 m  $\text{NaClO}_4$ ) from literature.<sup>20</sup> Some  $b(i, k)$  values, needed for the calculations, have been deduced from various sources. From ref 18  $b(\text{H}^+, \text{ClO}_4^-) = 0.14$  and  $b(\text{Na}^+, \text{OH}^-) = 0.04$ ; from ref 21  $b(\text{Fe}^{3+}, \text{ClO}_4^-) = 0.56$ ; from ref 15  $b(\text{L}^{2-}, \text{Na}^+) = 0.02$ ; and from ref 8  $b(\text{HL}^-, \text{Na}^+) = 0.06$ . The  $b(i, k)$  values for the complexes of stoichiometry (1,2,1), (1,4,2), and (1,3,2) can be estimated on the basis of empirical rules, suggested by Ciavatta.<sup>19</sup> For the complexes  $\text{FeL}_3^{3-}$  and  $\text{Fe}_2(\text{OH})_2(\text{HL})\text{L}^+$  the probable specific ion interaction

**Table 5. Comparison between the Formation Constants at Zero Ionic Strength of the Fe<sup>3+</sup>–H<sub>2</sub>L System at 298.15 K Proposed Here and Those Previously Reported**

this work	ref 2	ref 3	ref 4	ref 5
$\log \beta_{121}^{\circ} = 1.06 \pm 0.05$	$0.55 \pm 0.05$	$1.10 \pm 0.05$	$0.37 \pm 0.05$	$0.20 \pm 0.05$
$\log \beta_{142}^{\circ} = -1.2 \pm 0.1$	$-1.5 \pm 0.1$		$-2.9 \pm 0.2$	
$\log \beta_{163}^{\circ} = -7.3 \pm 0.2$	$-9.8 \pm 0.2$			

coefficients are deduced from empirical rules derived from plausible structures of the species (Figure 3).

The short-range interaction of the complexes with medium ions takes place in reduced amounts according to the accessible contact area. From the collected coefficient values, the interaction of the complexes with medium ions, accounting that the coordination of metal cation is six, should be

$$\begin{aligned}
 b[\text{FeL}_3^{3-}, \text{Na}^+] &= 3/2b(\text{Na}^+, \text{HL}^-) = 0.09 \\
 b[\text{Fe}_2(\text{OH})_2(\text{HL})\text{L}^+, \text{ClO}_4^-] &= 5/6b(\text{Fe}^{3+}, \text{ClO}_4^-) \\
 &+ 2 \cdot (1/2)b(\text{Na}^+, \text{OH}^-) + \\
 &+ 2 \cdot (1/2)b(\text{Na}^+, \text{HL}^-) = 0.57
 \end{aligned}$$

The results of extrapolation are collected in Table 4.

The uncertainties assigned to the constants stem primarily from interaction coefficients of complexes, which are estimated as probable within  $\pm 0.05$  or  $\pm 0.1 \text{ kg mol}^{-1}$ .

The constants given in Table 4 have been used to construct the distribution diagram reported in Figure 4; in this way one can evaluate the predominant species present in the natural system.

The figure shows that complexes with salicylate ion can achieve a significant amount in the condition that resembles real natural systems and the prevalent species in neutral solution for Fe(III) ion is  $\text{FeL}_3^{3-}$ . It is well-known from literature<sup>16</sup> that ferric ion hydrolyzes to high acidity ( $-\log[\text{H}_3\text{O}^+] \approx 1$ ), but as is evident by the distribution diagram (Figure 4), the speciation with salicylic acid reduces the percentage of hydrolytical complex  $\text{FeOH}^{2+}$  which is minor of 5 %.

**Comparison with Literature Data.** Due to the difference of the ionic strength, the comparison of data of this manuscript with previously reported data has been made on the basis of extrapolated values of the equilibrium constant, for the common species, at the infinite dilution reference state (see Table 5).

As can be seen, the difference between the values of the equilibrium constants is remarkable. This difference was expected since there was also discrepancy in the values from different works obtained at the same ionic strength. Moreover, literature data were attained by spectrophotometric or potentiometric methods separately. In this work, we have studied the interactions between  $\text{Fe}^{3+}$  and salicylic acid by coupling both methods. This approach allowed us to obtain more reliable results and to identify some complexes never detected before.

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