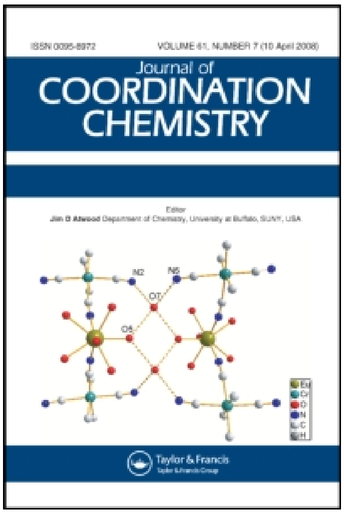

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THE IRON(III) AND IRON(II) COMPLEXES OF NITRILOTRIACETIC ACID

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Because of conflicting and incomplete reports of the ferric and ferrous nitrilotriacetate (NTA, H_3L) equilibria in the literature, and uncertainties about the metal complex species present under various conditions, the system was investigated by potentiometric and spectrometric measurements, and the data were analyzed by simultaneous consideration of all species present. The new constants for the ferric complexes at 25.0°C and $\mu = 0.100$ (KCl) are the stepwise formation constant log $K_{ML_2} = 8.07$, and the successive hydrolysis constants, log $K_{M(OH)L} = -4.36$, log $K_{M(OH)_2L} = -7.58$, and log $K_{M(OH)_3L} = -10.72$. The first stepwise formation constant, log $K_{ML} = 15.9$, was not determined in the present work since the value of 15.9 was considered accurate. For the ferrous complexes under the same conditions, the constants reported are: log $K_{ML} = 8.90$, log $K_{ML_2} = 3.08$, and log $K_{M(OH)L} = -10.82$. The log protonation constants of the ligand under these conditions are reported as 9.59, 2.52, and 1.47.

KEYWORDS: NTA (nitrilotriacetic acid), iron(II,III) complexes, stability constants, potentiometry, spectrophotometry, equilibrium data.

INTRODUCTION

Nitrilotriacetic acid (NTA) is one of the most widely investigated and used of the organic chelating agents. Its main use is as a detergent additive or builder, but a rapidly-developing application is formation of complexes of transition metal ions that may be used as redox catalysts. An interesting example is the Fe(III)-NTA chelate system for the oxidation of H_2S to elemental sulfur.[1] A difficulty arises in defining the iron(II) and iron(III) chelate systems because of several conflicting stability constants in the literature.[2] In order to resolve these conflicts, appropriate equilibrium studies involving iron(II) and iron(III) NTA at 1:1 and 1:2 molar ratios of metal ion to ligand were performed and analyzed both potentiometrically and spectrophotometrically.

EXPERIMENTAL

Materials

The ferric chloride and ferrous sulfate ($FeSO_4.7H_2O$) employed were of analytical grade and were obtained from Fisher Scientific Company. Standard HCl was

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prepared from reagent grade 12 M HCl and determined by phenolphthalein end-point titration with standard potassium KOH which was in turn prepared from DILUT-IT ampoules and standardized by titration against potassium acid phthalate. Ferric chloride solution was prepared by the addition of crystalline $FeCl_3.6H_2O$ to a volumetric flask containing an aliquot of standard HCl. The exact concentration was determined from the amount of acid released on a column of DOWEX 50W X-8 H^+, whereby an alliquot of ferric chloride is quantitatively placed on the resin and eluted with distilled water. After subtraction of the excess HCl originally present, the released hydrogen ion represent three times the ferric ion present, since one iron exchanges three protons on the resin. The result obtained was also checked and found to be correct in the ferric-NTA titrations. The NTA, obtained from the Hampshire Chemical Company, was recrystallized from boiling water before use and was weighed out directly for each experiment. A 1.00 M potassium chloride solution was prepared directly from reagent grade KCl obtained from Baker Chemical Company. Each test solution was adjusted to be 0.100 M in KCl initially, so that essential ionic strength control could be maintained.

Potentiometric Titrations

Throughout this report the symbol p[H] is used to emphasize its meaning: $-\log_{10}[H^+]$. The pH meter is calibrated to read the concentration of hydrogen ion at a given ionic strength with an aliquot of standard HCl above p[H] 2 and these values are then directly used in quantitative stoichiometric calculations. The details of the calibration and potentiometric method used have been described.[3] The ligand titration was done once. The Fe(III)-NTA systems were titrated for orientation first; then the final titrations on which the calculations are based are reported. Each Fe(III)-NTA titration was done once.

The error estimate for each constant (except the third protonation constant of NTA) determined in this work is at worst 0.01 log units. In refining the overall equilibrium constants, the calculated p[H] was matched to the observed p[H] throughout the titration from near p[H] 2 to about p[H] 10.5 (9.1 for 1:1 Fe(III)/NTA): $\sigma_{fit} = 0.006$ for NTA alone, $\sigma_{fit} = 0.004$ for NTA-Fe(III), and $\sigma_{fit} = 0.010$ for NTA-Fe(II) systems. Since all the p[H] values were reproducible to within $<<|0.005|$ for ligand, and for Fe(III) and ligand, and $<<|0.010|$ for Fe(II) and ligand, all the concentration constants determined herein have a low error. However, each constant was rounded to 2 decimal places.

NTA alone

In a 100 mL jacketed-thermostated titration cell, equipped with p[H] and reference electrodes, fitted with inert gas (Argon) inlet-outlet and a precision piston buret, were placed 5.000 mL of 1.00 M KCl to maintain the ionic strength, 20.50 mg of nitrilotriacetic acid and 45.00 mL distilled water. This makes 50.00 mL of a test solution containing 0.1073 mmoles NTA, which was then carefully titrated through its complete neutralization, while 40 pairs of p[H] vs. mL 0.1067 M KOH added were recorded at equally spaced intervals at every 0.100 mL base. The equilibrium data obtained constitutes the p[H] profile (potentiometric titration curve) which was interpreted in terms of its three protonation constants.

NTA-iron(III)

A 1:1 NTA iron(III) solution was prepared using 23.73 mg NTA, 4.40 mL of 0.02790 M $FeCl_3$ in 0.02498 M HCl, 5.00 mL of 1.00 M KCl and 40.60 mL water. For the 2:1 NTA iron(III) titration, the quantity of NTA was approximately doubled to 45.90 mg while the iron solution added had the same volume. Equally spaced 0.100 mL volume increments of 0.1067 M KOH were added while recording p[H] readings in each case. The titration was slowed down as equilibration rates required. Both 1:1 and 2:1 solutions became markedly slow just after the neutralization of the initial excess acid and the titratable NTA protons present. Waiting periods of the order of 10 min. were required for equilibrium readings. Upon reaching p[H] 9.3, the 1:1 solution became unstable and the p[H] readings drifted downward until $Fe(OH)_3$ was eventually formed. Sixtynine data points were collected. Data for the 2:1 solution were similarly obtained, but 112 equilibrium data points were obtained up to p[H] 10.77 before drifting occurred (loss of supersaturation with respect to $Fe(OH)_3$ precipitation). After correction for excess acid present, the final volume of base added amounted to almost 9 *m*-values (moles of base added per mole of metal ion present).

As the value of K_{sp} for $Fe(OH)_3$ indicates, the solutions obtained in the potentiometric measurements at pH 8 and higher are metastable in that they are supersaturated with respect to $Fe(OH)_3$, and that a precipitate of ferric hydroxide can be expected by waiting a sufficient length of time. It should be noted that in commercial practice of the oxidation process,[1] ferric hydroxide precipitation is avoided throughout the alkaline pH range by the inclusion of a supplementary chelating agent.

NTA-iron(II)

The potentiometric ferrous sulfate-NTA study required special precautions to prevent the oxidation of the ferrous chelate. The general method was described previously.[4] In the present work an approximate 1:1 system was prepared under argon. In the present work the dry, weighed solid $FeSO_4.7H_2O$ was kept separated for 12 hours from the gently-stirred NTA solution by placing the salt on a small boat kept afloat over the prepurified, Ar-purged, sealed titration cell. The quantities employed were 24.10 mg NTA (0.1262 millimoles) for the approximate "1:1" system and 42.65 mg (0.2233 millimoles) NTA for the 2:1 system. Exactly 26.55 mg $FeSO_4.7H_2O$ (0.0955 millimoles) was used in each case. The standard alkali was 0.0999 M KOH. At the end of 12 hours the ferrous boat was tipped through agitation induced when the sirrer speed was increased. The ferrous salt was considered dissolved after the pH meter reading stabilized. The 1:1 solution was incrementally titrated to pH 10.79 (50 points) whereupon a precipitate appeared. The 2:1 solution was incrementally titrated to pH 10.9 (80 points) with no precipitate forming. All Fe(II) solutions were colorless, but quickly became visibly oxidized upon exposure to air, giving assurance that Fe(II) was still present even at high pH after a long incubation and titration time.

Calculations were performed with 1:1 systems for 1:1 constants and 2:1 systems for 2:1 constants. In addition, ferrous systems were analyzed separately at low and high pH values.

Electronic Spectra

UV-VIS spectra were measured in two ways. When spot checks were desired, a sample was prepared or taken from the bench and placed into a 1.00 cm quartz cell and measured generally from 600–300 nm with a PE Model 553 Spectrophotometer equipped with a constant temperature cell compartment. The instrument was first balanced using cells containing the reference electrolyte alone.

For detailed study of solution spectra as a function of p[H], the spectrophotometer was equipped with a 1.000 cm quartz spectrophotometric flow cell connected through a peristaltic pump to a thermostated titration cell equipped with a Gilmont 2.000 mL precision burette for delivery of titrant, glass and reference electrodes, argon protective gas inlet and outlet, and stirred by means of a magnetic stirring bar. This set-up was useful for the determination of solution changes with both p[H] and time.

RESULTS AND DISCUSSION

NTA Protonation Constants

The top curve shown in Figure 1 is a plot of the titration data for NTA alone obtained at 25.0°C and 0.100 M ionic strength (KCl). The neutral NTA molecule is an H_3L-type ligand, the subscript indicating the number of titratable protons present. The shape of the curve indicates two protons neutralized up to p[H] 4 and the remaining one neutralized in the p[H] region 9–10. The logarithms of the three protonation constants for NTA were calculated as 9.59, 2.52 and 1.5 corresponding to the first three equations

$$L^{3-} + H^{+} \leftrightarrows HL^{2-} \tag{1}$$

$$HL^{2-} + H^{+} \leftrightarrows H_2L^{-} \tag{2}$$

$$H_2L^{-} + H^{+} \leftrightarrows H_3L \tag{3}$$

$$H_3L + H^{+} \leftrightarrows H_4L^{+} \tag{4}$$

For comparison, the literature values obtained at 0.100 M ionic strength summarized in the Critical Stability Constants provide three values for the first protonation constant depending on the cation present in the supporting electrolyte: 9.49 (Na^+), 9.67 (K^+) and 9.84 (R_4N^+). The NTA concentration of these literature NTA determinations is not stated, but agreement of our work with these values is acceptable for the K^+ ion as background. The second protonation constant found in the literature is 2.52 while the third is listed as (1.9), where parentheses indicate uncertainty. When in the course of experimental determination a fouth protonation reaction is invoked, the third protonation value becomes higher. In this case literature lists the fourth constant (equation 4) as (1.0) log units. The variations found in the first protonation constant are largely the result of not taking into account the stability constant of the cation of the background electrolyte with NTA.

$$L^{3-} + K^{+} \leftrightarrows KL^{2-} \tag{5}$$

which is a reaction competing with protons for the deprotonated NTA molecule. Conventionally this is not done and the protonation constant is obtained under the

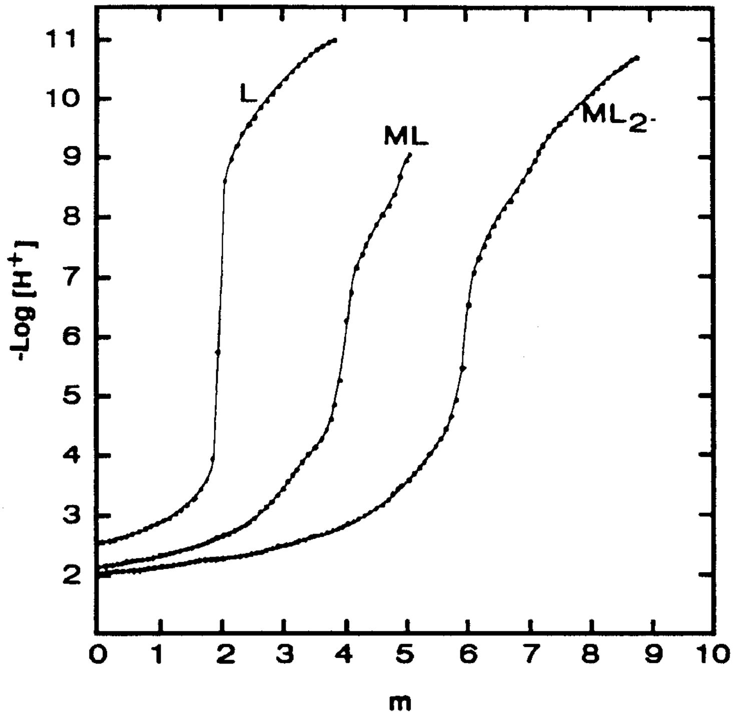

Figure 1 pH profiles at $\mu = 0.100$ (KNO_3) of NTA alone (L) and Fe(III)-NTA 1:1 (ML) and 1:2 (ML_2) plotted as p[H] readings as a function of m-values, where m is the moles of KOH added per mole of metal ion present. For NTA alone $a = m$ and is the moles of KOH added per mole of ligand added. $[NTA]_0 = 2.146 \times 10^{-3}$M. For metal titrations $[NTA]_0 = 2.48 \times 10^{-3}$M or 4.81×10^{-3}M. $[Fe(III)]_0 = 2.4 \times 10^{-3}$M. [KOH] = 0.1067 M.

conditions of the experiment, i.e. the tendency to complex an aklali cation is built into the value of the first protonation constant. EDTA also shows this kind of behavior.[10]

NTA-Iron(III) Interactions

Figure 1 shows the titration data obtained for 1:1 and 2:1 stoichiometries of NTA to iron(III).

The 1:1 ML curve features a strong acid titration curve up to $m = 3$, the number of titratable protons initially present. This neutralization is followed by an additional deprotonation reaction between $m = 3$ and $m = 4$, which can only be explained by the formation of $M(OH)L^-$. As base is added a further neutralization takes place from $m = 4$ to $m = 5$ while $M(OH)_2L^{2-}$ is forming near p[H] 8. Shortly thereafter above p[H] 9 the pH started drifting down steadily and eventually led to a precipitate of $Fe(OH)_3$.

The 2:1 solution contains 6 titratable protons per iron(III) and hence there is a break in the curve at $m = 6$ indicating a net neutralization of 6 protons per iron(III) present. It is important to note that six protons are released by either the formation of ML_2 from two NTA molecules or the formation of $M(OH)L^-$ (4-protons) in the presence of 1 mole of free NTA (2-protons). In fact, both processes were found to take place. The 2:1 solution behaves "similarly" to the 1:1 system through p[H] 9, but was found to possess an additional neutralization between $m = 8$ and $m = 9$ as $M(OH)_3L^{3-}$ forms. The stoichiometry of this species is derived from proton inventory: 6 to form the hydroxo complex and 3 to neutralize the second NTA. Thus the buffer between $m = 7$ and $m = 8$ essentially is the neutralization of separated NTA.

Prior to this work, Volume 1 of *Critical Stability Constants*[2] summarized the NTA-Iron(III) interactions with the following sketchy report:

at 25.0°C, $\mu = 0.100$

$$M^{3+} + L^{3-} \leftrightarrows ML \quad \log K = 15.9 \tag{6}$$

at 20.0°C, $\mu = 0.100$

$$M^{3+} + L^{3-} \leftrightarrows ML \quad \log K = 15.9 \tag{7}$$

$$M^{3+} + 2L^{3-} \leftrightarrows ML_2{}^{3-} \quad \log K = 24.3 \tag{8}$$

$$ML \leftrightarrows M(OH)L^- + H^+ \quad \log K = (-4.1) \tag{9}$$

$$M(OH)L^- \leftrightarrows M(OH)_2L^{2-} + H^+ \quad \log K = (-7.8) \tag{10}$$

at 20.0°C, $\mu = 0.100$

$$ML \leftrightarrows M(OH)L^- + H^+ \quad \log K = (-5.0) \tag{11}$$

$$2M(OH)L^- \leftrightarrows M_2(OH)_2L_2{}^{2-} \quad \log K_D = (4.0) \tag{12}$$

In a more recent paper by Andregg[5] the log K_{ML} was remeasured as 16.0 in 1.00 M $NaClO_4$ at 20.0°C. In addition, the species MHL was also proposed, with a pKa of 0.9. Thus it is clear that different workers had not reached agreement on the constitution of the Fe-NTA species as a function of p[H]. They do agree, however, that the stability constant for the 1:1 complex is sufficiently large that iron is 100% complexed at p[H] 2, even at the beginning of the titration. Furthermore, the published constants seem to indicate that even in solutions slightly above neutral the solubility product of $Fe(OH)_3$ is sufficiently small to indicate that this hydroxide should appear as a solid phase. Practically speaking, this does not occur rapidly and consequently perfectly good titration curves and hence stability constants can be obtained at high p[H] up to the point of precipitation.

Analysis of the 1:1 and 2:1 NTA-iron(III) titration curves obtained in this work supports the formation of ML, $ML_2{}^{3-}$, $ML(OH)^-$, $ML(OH)_2{}^{2-}$, and $ML(OH)_3{}^{3-}$ species:

at 25.0°C, $\mu = 0.100$ (KCl)

$$M^{3+} + L^{3-} \leftrightarrows ML \quad \log K = 15.9 \tag{13}$$

$$ML + L^{3-} \leftrightarrows ML_2{}^{3-} \quad \log K = 8.07 \tag{14}$$

$$ML \leftrightarrows M(OH)L^- + H^+ \quad \log K = -4.36 \tag{15}$$

$$M(OH)L^- \leftrightarrows M(OH)_2L^{2-} + H^+ \quad \log K = -7.58 \tag{16}$$

$$M(OH)_2L^{2-} \leftrightarrows M(OH)_3L^{3-} + H^+ \quad \log K = -10.72 \tag{17}$$

Equilibrium (13) was taken from the literature since there is general agreement on its magnitude. Examination of the literature[6–9] shows that Cl^- binding to Fe^{3+} possesses a stability constant of magnitude less than one log unit while the magnitude of the SO_4^{2-} constant is just above two log units. However none of these binding constants are really pertinent since there is virtually no free Fe^{3+} present in our test solutions. All the Fe^{3+} is complexed by NTA. The relative extents to which equilibria (13)–(17) participate in the Fe(III)-NTA system is not only dependent on the stoichiometry, and p[H] but also on the concentration. These interesting features can be appreciated only by the examination of species distribution diagrams shown in Figure 2 for the 1 millimolar solution and Figure 3 for the 10 millimolar solution of 2 NTA:1 Fe(III) as a function of p[H]. At both concentrations ML predominates below p[H] 3, $M(OH)_2L^{2-}$ maximizes at p[H] 9 and the ultimate species is $M(OH)_3L^{3-}$ at high p[H]. However, at p[H] 6 for the 1 millimolar solution there is found twice as much $M(OH)L^-$ as ML_2^{3-}. This situation reverses at 10 millimolar in that now ML_2^{3-} exceeds $M(OH)L^-$ by a factor of two, indicating a large concentration dependence induced by a small second stability constant.

The characteristics of the Fe(III)-NTA titrations are such that equilibrium is achieved essentially instantaneously below pH ~3 and above ~6. However in the intervening pH region where the species Fe(OH)L and FeL_2^{3-} form, equilibrium is reached within 10 minutes. Apparently one or the other forms quickly; then their equilibrium distribution is slowly achieved with a concommitant stabilization of p[H].

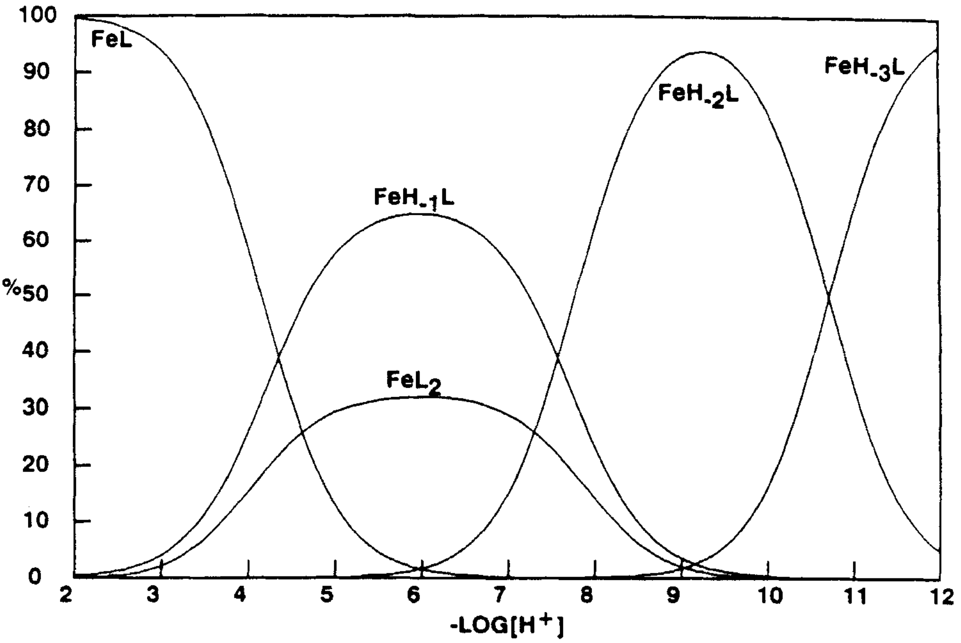

Figure 2 One millimolar $[Fe(III)]_0$ and two millimolar $[NTA]_0$ species as a function of p[H] with % based on total Fe(III) present. Only metal ion containing species are plotted. H_{-n} represents $(OH)_n$.

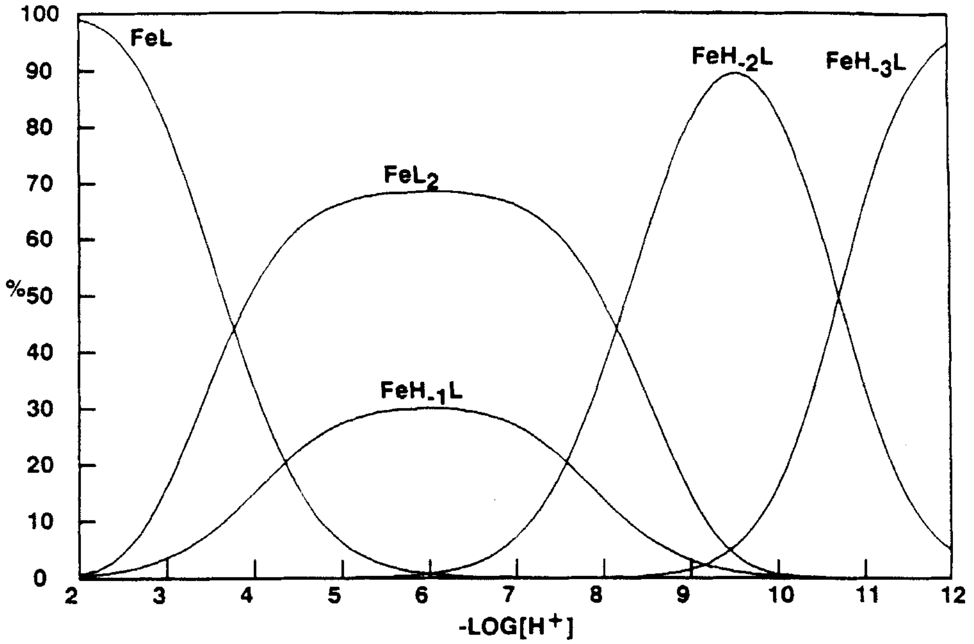

Figure 3 Ten millimolar $[Fe(III)]_0$ and twenty millimolar $[NTA]_0$ species as a function of p[H] with % based on total Fe(III) present. Only metal ion containing species are plotted. H_{-n} represents $(OH)_n$.

The UV-VIS spectra of a 2:1 NTA-Fe(III) solution shown in Figure 4 and in Figure 5 are of interest in that they confirm the potentiometric results and the conclusions pictured in the species distribution diagrams of Figure 2 and Figure 3. Starting at p[H] 1.9, as the p[H] is raised, the successive spectra shift progressively toward the visible, maximize their rate of shift near p[H] 3.4 then stay constant in the region p[H] 5–7 (see both Figure 4 and Figure 5). Then as $M(OH)_2L^{2-}$ forms in the region of p[H] 7–9, the spectra shown in Figure 5 shift toward violet. Recalling that ML_2^{3-} possesses two coordinated nitrogens, while both ML and $M(OH)L^-$ possess only one, these spectra constitute proof that at this concentration, at p[H] 8 considerable ML_2^{3-} converts to $M(OH)_2L^{2-}$. Qualitatively the visual observation, both in the potentiometric titration and in the spectrophoptometric titration, is that the pale solution gradually turns yellow when reaching p[H]5, and stays yellow through the break, and finally goes back to the initial pale solution by p[H] 9.0. While the normal chelate and the dihydroxy chelate do not possess an identical spectrum, their characteristic absorption spectra are in the same region, below 400 nm.

The Critical Stability Constant compilation[2] does not give the stability constants of Fe(II)-NTA complexes under our conditions. Our potentiometric studies gave the following results at 25.0°C and $\mu = 0.100$ M (KCl): log $\beta_{ML} = 8.90$, log $\beta_{ML_2} = 11.98$, log $K_{M(OH)L} = -10.82$. No protonated metal chelate was observed at the lowest accurately measurable p[H]. The binding constant of sulfate to Fe(II) is

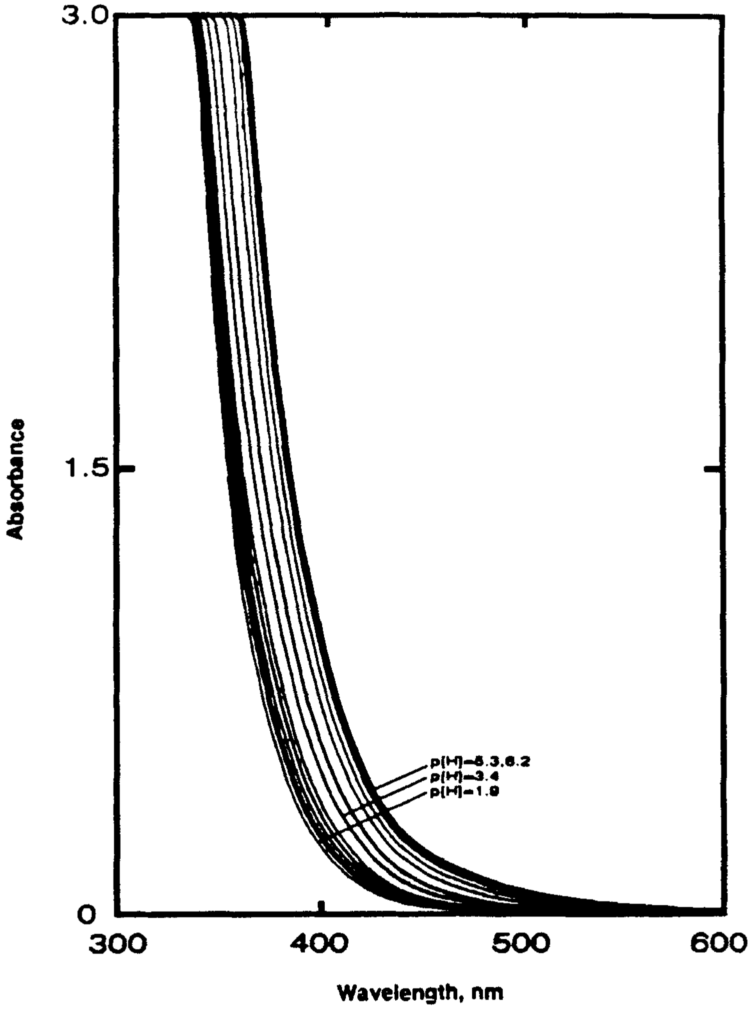

Figure 4 Absorbance vs wavelength UV-VIS spectra of 2:1 NTA-Fe(III) at 3.0×10^{-3} M $[\mathrm{Fe(III)}]_0$ as a function of p[H] from 1.9 to 6.2.

not listed in the Critical Stability Constant compilation[10] but based on its binding to other first row transition metal ions, was estimated to be < 10 and was therefore not used. With these equilibrium constants, the 1:1 species diagram was obtained and is illustrated in Figure 6a for the 1:1 system. It is seen that the 1:1 complex is formed at low p[H] and predominates between p[H]'s 4 and 10. At higher p[H] the hydroxo chelate is formed with a pK of 9.59. The corresponding 2:1 ligand to metal system illustrated in Figure 6b shows the partial formation at high p[H] of the 2:1 complex which is a relatively minor species. As the p[H] is increased the system is converted to the 1:1 monohydroxo complex, which predominates above p[H] 10.5.

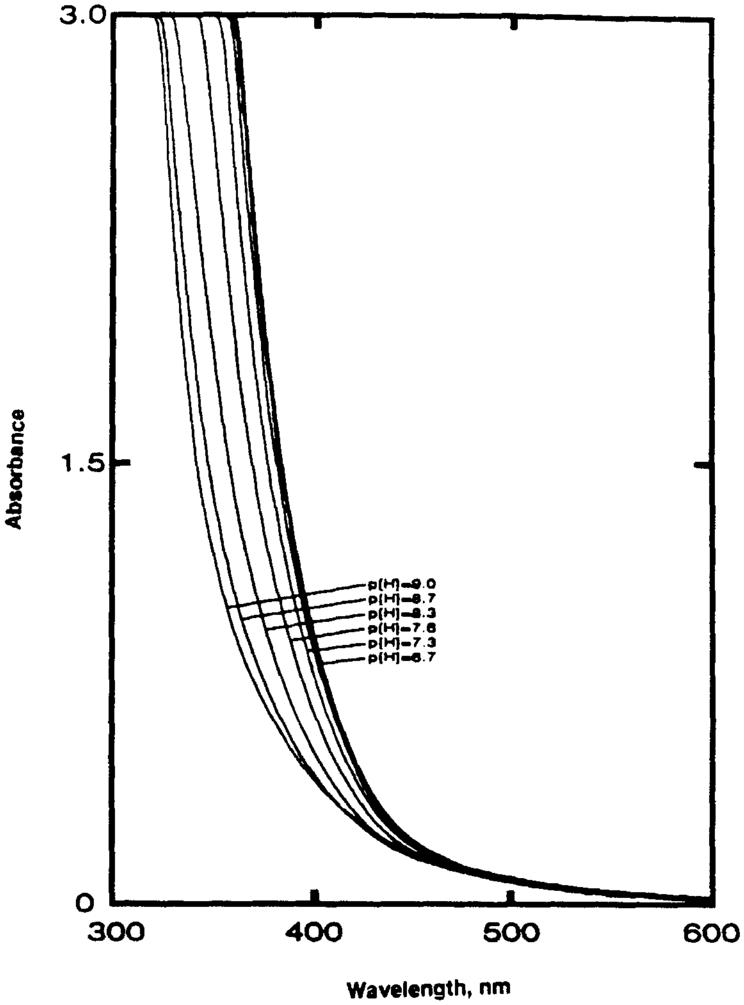

Figure 5 Absorbance vs wavelength UV-VIS spectra of 2:1 NTA-Fe(III) at 3.0×10^{-3} M $[\mathrm{Fe(III)}]_0$ as a function of p[H] from 6.7 to 9.0.

The crystal structure of ML_2^{3-} is known.[11] It is a seven coordinate pentagonal bipyramidal structure with one ligand binding in a tetradentate fashion and the other in the manner of iminodiacetic acid with one carboxylate uncoordinated and away from the metal center. In all probability the solution structure of the 2:1 complex is similar, with the uncoordinated carboxylate solvated.

Recently the μ-oxo dimer of NTA Fe(III) was reported as a barium salt and its crystal structure was determined,[12] but it was found to be formed in rather concentrated solutions.

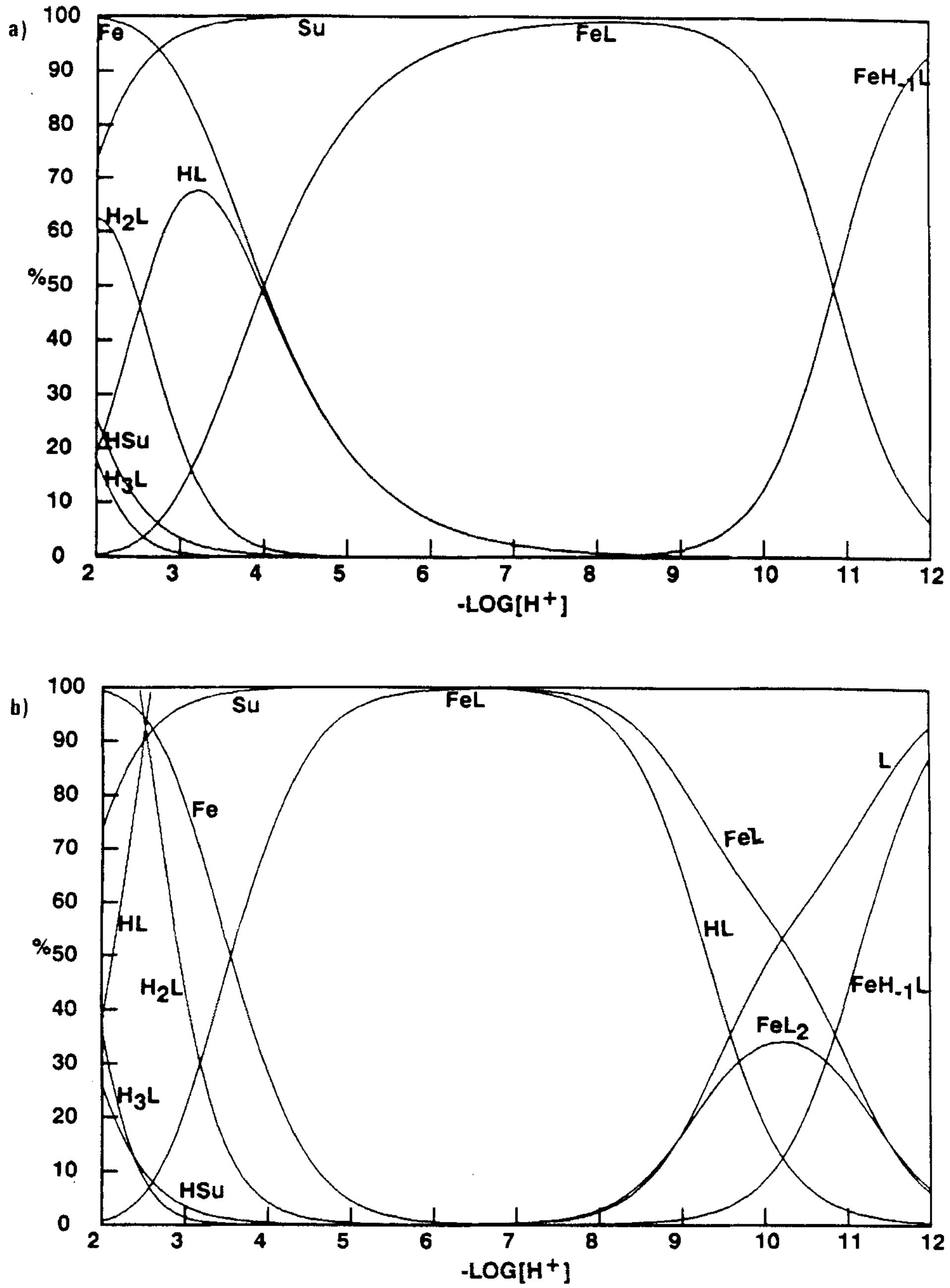

Figure 6 a) Species distribution curves for the 1:1:1 molar ratios of Fe(II), SO_4^{2-} and NTA at 1.00×10^{-3} molar, 25.0°C, and $\mu = 0.100$ M (KCl) with % based on total concentrations of species present; b) shows the species distribution curves for 1:1:2 molar ratios under the same conditions. For both 6a and 6b, L = NTA^{3-} and Su is SO_4^{2-}. H_{-n} represents $(OH)_n$.

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