PROTON SPIN RELAXATION IN Fe(III)-EDTA AND Cr(III)-EDTA AQUEOUS SOLUTION

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PREFACE

Events conspired to broaden considerably the normal base of those who assisted in providing an opportunity to study. I would therefore like to express my appreciation for financial support to the following:

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CHAPTER I

INTRODUCTION

General

This thesis presents the results of an exploratory study on the magnetic proton spin relaxation properties of transition metal-chelate structures in water. Two chelates were studied, Chromium(III) and Iron (III) ethylenedinitrilotetraacetate ion $(EDTA^{4-})$. The observational tool was earth's field free precession NMR (low field NMR). The independent variables were temperature and PH dependence, and for Fe(III), concentration dependence. For both chelates it was possible to relate the collected data with general structural and chemical properties. With respect to Fe(III) correlation was sufficient to permit development of a specific analytic model. From the model, the constants describing hydrolysis, and the individual species proton spin relaxtion rates were obtained. Also a diamagnetic species was identified.

Metal Ion and Chelate Selection

For an introductory effort, ion and chelate needed to satisfy preestablished criteria. These were,

(a) Ion-chelate formation constants would have to be large.

(b) Chelated ion should be non-labile.

(c) Chelated ion would have to be stable over a wide temperature and PH range.

(d) The chelate and chelated ion would have to be soluble at the required concentration.

(e) Since bulk water is being excluded from the primary hydration sphere, a large spin appeared desirable.

(f) A "spin only" magnetic moment was necessary.

(g) Information already available on the system must be sufficient to establish a "base-line".

The selected ions and chelate satisfied these requirements[1,2,3,4,5,6,7]. Other ions and chelates did also. However, EDTA has been one of the most extensively studied sequestering agents and was assumed to completely surround the ion (simplifying the problem of determining water coordination number). Previous experience with Cr(III) and the biological importance of Fe(III) were considerations also.

Background

Fe(III)

Although first prepared in 1943 and studied extensively since, considerable uncertainty exists on the hydrolysis and solution properties of aqueous $FeEDTA^-$. The solution coordination[2] number is in doubt and reported constants for hydrolysis with[8] and without[9] a dimeric form have been determined. Protonation of the complex has been observed, but not consistently. The formation constant is the largest reported for $EDTA^{4-}$, PK = 25.1[4].

Cr(III)

Hydrolysis and protonation are reported for $CrEDTA^-$.[4] In an intermediate PH range (5-9) an equilibrium with bulk water is assumed to exist.[1] In crystalline $CrEDTA^-$ one water molecule is tightly bound. A feature of interest is the very slow rate with which the chelated ion forms. The formation constant is PK = 23.

Thesis Organization

The presentation and development of the experimental data is preceeded by chapters on proton spin relaxation and experimental procedure. The goal of the chapter on proton spin relaxation is to provide a basis for interpreting the observed data in terms of the known functional dependencies. The Fe(III) and Cr(III) data are presented in separate chapters. A summary containing recommendations for future work concludes the presentation.

FOOTNOTES

[1] F. Dwyer and D. Meller, Chelating Agents and Metal Chelates, Academic Press, New York, N. Y. (1964), p. 306.

[2] S. Kerschner, Advances in the Chemistry of the Coordination Compounds, The Macmillan Co., New York (1961), p. 296.

[3] W. Klamm, Z. Anorg. Chem. 252, 225 (1944).

[4] J. Bjerrum, et al., Stability Constants Part I, Organic Ligands, The Chemical Society, London (1957).

[5] R. Hamm, J. Am. Chem. Soc. 75, 5970 (1953).

[6] C. Furlani, Z. Anog. Allg. Chem. 303, 1 (1960).

[7] M. Beck and S. Goeroeg, Chem. Anal. 48, 90 (1959).

[8] R. Gustafson and A. Martell, J. Phys. Chem. 67, 576 (1963).

[9] G. Schwarzenbach and J. Heller, Helv. Chim. Acta. 65, 576 (1951).

CHAPTER II

PROTON SPIN RELAXATION

General

Addition of paramagnetic ions to water drastically shortens the characteristic time describing the exponential polarization of the water protons in an external magnetic field. The cause is the coupling of the proton nuclear magnetic moment with the intense magnetic field of the ion. This coupling is via the spectral densities of processes causing time varying fields at the proton. It is the intent of this chapter to provide background on the factors affecting these processes.

First Coordination Sphere[1]

For protons which are associated with the ion via coordinated water, the characteristic time T_{1c} is given by[2,3]

$$\frac{1}{T_{1c}} = \frac{1}{30} \frac{S(S+1)\, g^2\beta^2\gamma_I^2}{r^6} \left(3\,\tau_c + \frac{7\,\tau_c}{1+\omega_s^2\tau_c^2}\right)$$

$$+ \frac{2}{3} S(S+1) \frac{A}{\hbar^2} \left(\frac{\tau_s}{1+\omega_s^2\tau_s^2}\right) \qquad \text{(II-1)}$$

with $\frac{1}{\tau_c} = \frac{1}{\tau_r} + \frac{1}{\tau_h} + \frac{1}{\tau_e}$ and

$$\frac{1}{\tau_s} = \frac{1}{\tau_h} + \frac{1}{\tau_e} .$$

τ_r ≡ rotational correlation time

τ_e ≡ electron spin correlation time

τ_h ≡ exchange lifetime, chemical.

Also,

S ≡ spin

r ≡ ion to proton distance

$\frac{A}{\hbar^2}$ ≡ scalar coupling constant

ω_s ≡ electron spin precession frequency.

The τ's are assumed to be exponential functions of temperature (activation energy) and represent process which produce time varying fields at the proton, for protons which move with the ion. Typical values are $\tau_r \approx 10^{-11}$ sec, $\tau_e \approx 10^{-10}$ sec, $\tau_h > 10^{-10}$ sec. τ_r becomes shorter with increasing temperature and τ_e becomes longer.

In dilute solution the magnetization of the protons associated with the ion is not detectable, the magnetization of bulk water is. In order for the presence of the ions to be noted there must be a rapid exchange of coordinated protons and bulk water protons. For sufficiently rapid exchange the measured relaxation time of the solution is given by weighting the two relaxation times[4]

$$\frac{1}{T_1} = \frac{N_w}{N_w + N_c} \frac{1}{T_{1w}} + \frac{N_B}{N_w + N_c} \frac{1}{T_{1c}} \qquad \text{(II-2)}$$

N_w ≡ number of bulk water protons

N_B ≡ number of protons associated with the ion

T_{1w} ≡ relaxation time of bulk water (results from proton-proton coupling).

If, $N_B << N_w$ this reduces to

$$\frac{1}{T_1} - \frac{1}{T_{1w}} = \frac{N_B}{N_w} \frac{1}{T_{1c}} \equiv \text{RATE}$$

There are also processes which are effective outside the first coordinate sphere.

Extra First Coordination Sphere[1]

An elegant development identifies relative translational diffusion of ion and bulk water molecules as the primary processes causing proton spin relaxation outside the first coordination sphere[5]. In this development a new correlation time is defined

$$\tau_d = \frac{a^2}{3(D + D_I)}$$

a ≡ distance of closest approach

D ≡ diffusion rate for water

D_I ≡ diffusion rate for the ion.

For $(\omega \tau_s)^2 << 1$ and $\tau_d << \tau_s$

$$\frac{1}{T_{1T}} = \frac{32}{15} \frac{S(S+1)\, g^2 \beta^2 \gamma_I^{\,2} \tau_1 N_1 \tau_d}{a^3} \left(1 - \frac{5}{6}\sqrt{\frac{3\tau_d}{\tau_s}} + \frac{9\tau_d}{7\tau_s}\right). \quad \text{(II-3)}$$

$$N_I = \text{particles/cm}^3 \text{ (paramagnetic ion)}$$

Note: In water, $\approx 4 \times 10^{-12} < \tau_d < \approx 4 \times 10^{-11}$.

This equation predicts a near linear dependence on τ_d and little dependence on the correlation times unique to a particular ion.

An idea of the relative magnitude of the rate $\frac{1}{T_{1T}}$ can be obtained by dividing Eq. II-3 by II-1

$$\frac{\frac{1}{T_{1T}}}{\frac{1}{T_{1c}}} = \frac{8}{5} \pi N_w \frac{\tau_d}{\tau_c} \frac{N_I}{N_B} \frac{r^6}{a^3}$$

$$N_I = \frac{N_B}{12} \frac{6.0 \times 10^{23}}{10^3} \frac{\text{particles/mole}}{\text{cm}^3/\ell}$$

$$\frac{\frac{1}{T_{1T}}}{\frac{1}{T_{1c}}} = \frac{8}{5} \pi (1. \times 10^2 \text{ mole}/\ell)\ 5 \times 10^{19} \frac{\ell}{\text{cm}^3\text{-mole}} \frac{\tau_d}{\tau_c} \frac{r^6}{a^3}$$

With $a = r = 2.7 \times 10^{-8}$ cm, $\frac{\frac{1}{T_{1T}}}{\frac{1}{T_{1c}}} = .05 \frac{\tau_d}{\tau_c}$. If $a > r$ the factor will be smaller. If the relation between D and τ_c is approximated by the Debye Equation and the Stokes-Einstein Equation, this ratio would remain constant. For Cr^{3+} the ratio is approximately 0.1.[6]

Second coordination sphere relaxation could also account for extra-coordination sphere relaxation. Reduced scalar interaction would require rate representation by the τ_c term in Eq. II-1 only. The temperature dependence would be a straight line on a semi-log plot. Eq. II-3 is a more complex function and could have a characteristic and unique shape, especially if $3\tau_d \approx \tau_s$ for a portion of the curve. It is believed that the minimum rate curve for $CrEDTA^-$ (S - shaped curve of Fig. 5) is more adequately represented by a translational diffusion model rather than second coordination sphere processes. The difficulties associated with second sphere coordination numbers and ion to proton distance preclude useful discrimination between the two models.

Chemical Exchange

As previously mentioned, protons in the first coordination sphere must exchange with bulk water in order to affect T_1. When the exchange is not fast, the measured T_1 is exchange limited and given by[4]

$$\frac{1}{T_1} - \frac{1}{T_{1w}} = \frac{N_c}{N_w}\,\frac{1}{\tau_h + T_{1c}} \qquad \text{(II-4)}$$

with $\tau_h \equiv$ proton lifetime.

In a previous effort an exchange was uncovered in which τ_h represented a reaction whose product exchanged protons very rapidly[7]. A small amount of product became a magnetization bridge between the ion and bulk water. The result is a very involved relationship for measured T_1 as a function of τ_h, T_{1c}, and the reaction equilibrium constant and a non-linear dependence of observed relaxation rate with respect to the concentration of relaxing species. However, this complex T_1 dependency provides a tool for investigating reactions with rates $\approx 10^5$ sec^{-1} and which are associated with proton exchange.

Summary

Interpreting correctly functional dependences of proton spin relaxation rates requires both knowledge of the NMR characteristics and chemical proton exchange. This background material provides a basis for selecting phenomenological models in explaining experimental data.

FOOTNOTES

[1] The expressions for the characteristic times are based on 1st order perturbation theory.

[2] I. Solomon, Phys. Rev. 99, 559 (1955).

[3] N. Bloembergen, J. Chem. Phys. 27, 572 (1957).

[4] N. Bloembergen and L. Morgan, J. Chem. Phys. 34, 842 (1961).

[5] H. Pfeifer, Ann. Phys. 8, 1 (1961).

[6] B. Melton, private communication, Oklahoma State University, 1968.

[7] C. Manley, M.S. Thesis, Oklahoma State University, 1966 (unpublished).

CHAPTER III

EXPERIMENTAL

Proton Spin Relaxation Rates

Longitudinal proton spin relaxation times (T_1) were determined using earth's field free precession technique. The sample is placed inside a solenoid which is at right angles to the earth's field, and a polarizing current is applied for a specific time. At the end of this time the AC voltage produced in the coil by the precessing nuclear spins is amplified and displayed on an oscilloscope. Since $E = E_\infty (1 - e^{-\frac{t}{T_1}})$ a plot of $E - E_\infty$ vs t on semi-log paper yields T_1. In order to maintain signal strength, the dependence of T_1 on polarizing field strength is determined using current pedestals. The sample is polarized at full current, and then the magnetization is allowed to decay in a reduced field for a specific time. A semi-log plot of E vs t yields T_1, in the reduced field.

Proton spin relaxation rate is defined as

$$\frac{1}{(T_1)\text{measured}} - \frac{1}{(T_1)\text{pure water}}, \text{ Eq. II-3.}$$

All of the experimental data presented in this thesis has been corrected for the rate of pure water. This isolates the rate due to the addition of the paramagnetic ion. Fig. 1 provided the correction. For unsealed

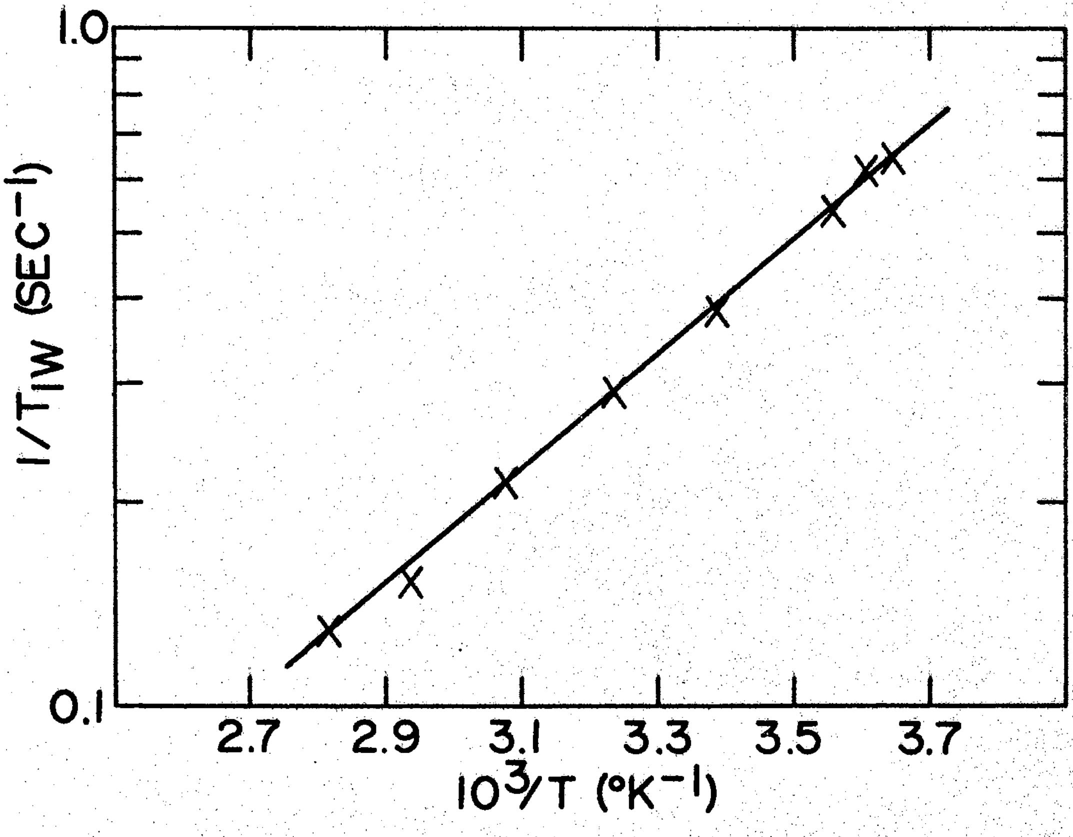

Figure 1. Bulk Water Correction Rates

samples there is a small hysterisis (< 10%) due to the change in concentration of dissolved 0_2 (weakly paramagnetic).

The reproducibility of data points is better than ± 2%. The primary limitation on the technique is that the concentration of paramagnetic ion must be low enough so that $T_1 > \approx 100$ msec. Otherwise the transverse relaxations time (T_2, a measure of the rate at which signal coherence is lost) is so short that the signal disappears before it can be measured.

Data were corrected for coil rise time (≈ 10 msec). Stated temperatures are accurate to ± 1°C.

Reagents

Fe(III)

One liter of 1.14 molar $Fe(NO_3)_3$ was used as a master solution. Sample concentrations were obtained by diluting volumetrically. Baker Analyzed Reagent Grade Chemical was used. The solution was made 0.1 molar in $HClO_4$ to prevent irreversible hydrolysis[1,2,3] either in the master solution and during dilution. Concentration was determined by weighing and by titrating Fe SCN^{2+} with EDTA. The results were within 1% of each other. In preparing Fe $EDTA^-$ at high pH it is necessary to avoid locally high concentrations of base, otherwise some irreversible hydrolysis takes place.

Cr(III)

A master solution of $Cr(NO_3)_3$ was also prepared. Concentration was determined by weighing and by comparing the molar relaxation rate with that of a standardized Cr^{3+} sample[4]. Since the formation of the complex is very slow, it is necessary to elevate the temperature of a Cr^{3+} - $EDTA^{4-}$ water mixture. Solutions prepared at room temperature had proton spin relaxation rates which were still drifting two weeks later. For Cr $EDTA^{-}$ solutions properly prepared no thermal hysteresis was apparent at any pH studied.

EDTA

Two master solutions of dihydrogen disodium ethylenedinitrilotetraacetic acid were prepared. 37.29 gms of H_2Na_2EDTA/liter was used for a 0.1 molar solution[5]. After 8 months it was discovered that the original EDTA master was short the stated number of protons, although the base stock was advertised as a reagent grade. The second master was prepared from Baker Analyzed Reagent. A titration for neutralization obtained the correct number of protons.

Ionic Strength

Unless specifically excepted all solutions used in obtaining data were 0.3 molar in $NaClO_4$. $NaNO_3$ would have been a better choice. Potentiometric titrations with a KCl salt bridge in $NaClO_4$ proved to be difficult.

FOOTNOTES

[1] J. Butler, Ionic Equilibrium, Addison-Wesley Publishing Co., Reading, Massachusetts, 1964, p. 369.

[2] B. Hedstrom, Arkiv Kemi 6, 1 (1952).

[3] H. Lengweiler et al., Helv. Chim. Acta. 91, 796 (1961).

[4] B. Melton, private communication, Oklahoma State University, 1968.

[5] H. Flaschka, EDTA Titrations, Pergammon Press, New York, 1959, p. 61.

CHAPTER IV

Fe(III) OH_2 $EDTA^-$

Introduction

This chapter presents data on the proton spin relaxation rates of aqueous Fe $EDTA^-$ ion, and describes a quantitative data analysis. The data primarily concern the temperature, pH, and ion concentration dependence of the relaxation rates. Some miscellaneous observations are also presented. The bases of the data analysis are the development of a phenomenological model and the least squares fit of the data to this model. The results of this effort are:

(a) A self-consistent set of constants representing the hydrolysis of Fe $EDTA^-$ and of H_2 $EDTA^{2-}$.

(b) Confirmation of the existence of $(\text{Fe OH EDTA})_2^{4-}$.

(c) Addition of $(\text{Fe OH EDTA})_2^{4-}$ to the small group of iron compounds[1,2,3,4] which, contrary to predictions[5], are diamagnetic.

(d) Placement of a molecule of water in the coordination sphere of the Fe $EDTA^-$ ion.

(e) The presentation of evidence for the existence of a seven coordinated structure for Fe OH_2 $EDTA^-$.

The chapter is organized around the data analysis, with experimental data presented when appropriate. Chapter sub-headings in the order encountered are Model Development, Data Fit, Results and Discussion, Miscellaneous Observations, and Summary.

Model Development

General

When compactness of form or interpolation is the goal of a data analysis, sequential multiple regression analysis is satisfactory. However, the equation parameters have no meaning. Alternatively, an equation representing the experimental data, in which the parameters have meaning, may be formulated. It then becomes the goal of the analysis to determine these parameters. In this section meaningful parameters describing the system are developed from the observed characteristics of the experimental data.

Analysis

The important features of the proton spin relaxation rate as a function of base added (Figure 2) are,[5]

(a) Rapid reduction in rate from the point where 2 equivalents of base have been added.

(b) A minimum in the rate at the point where approximately 3 equivalents of base have been added, followed by a rate increase.

(c) A decrease in the molar rate minimum as the Fe $EDTA^-$ concentration is increased.

The onset in the rate reduction is accompanied by the characteristic change in solution color from light yellow to orange, associated

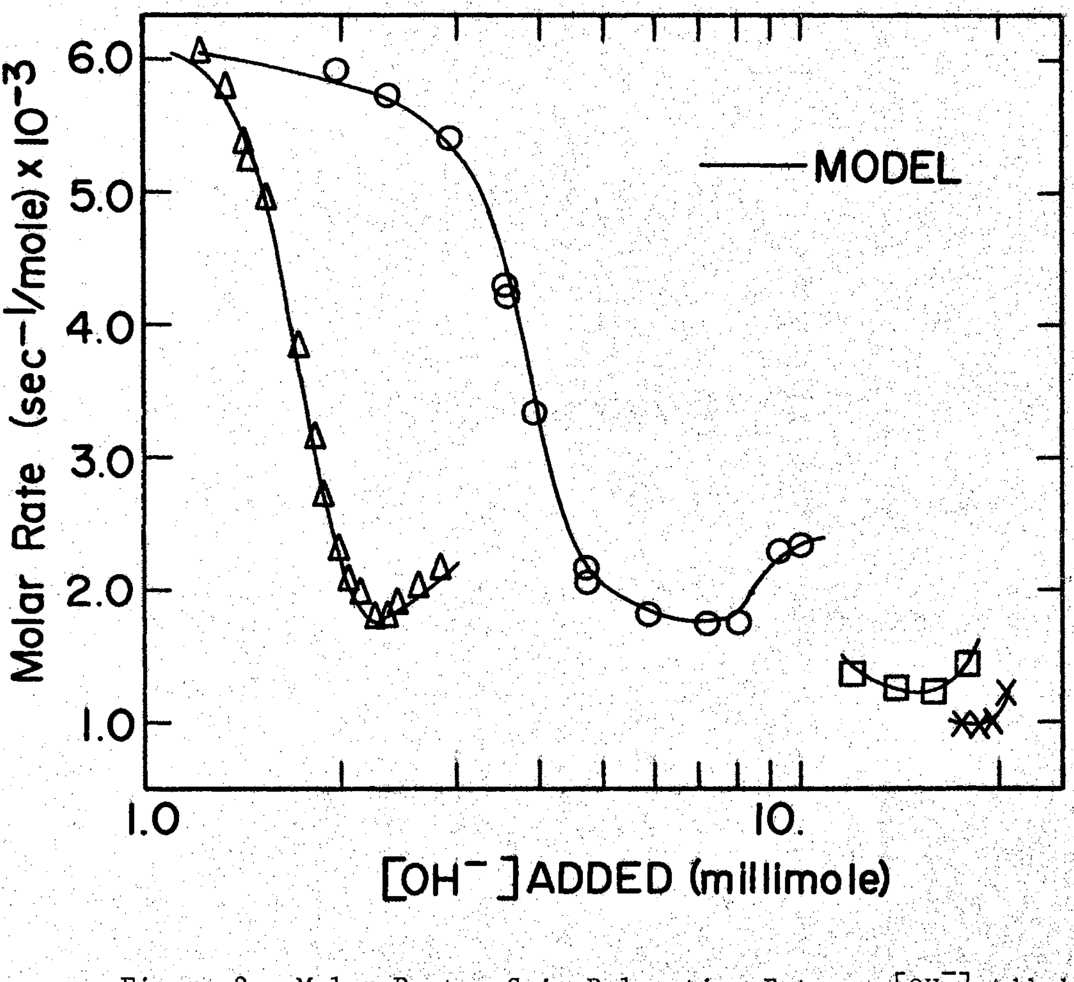

Figure 2. Molar Proton Spin Relaxation Rate vs $[OH^-]$ Added for Fe OH_2 $EDTA^-$ as a Function of Fe^{3+} Concentration at 1.5°C. Series I ($H_{1.5}Na_{2.5}EDTA$.) $[NaClO_4] = 0.3m$. Δ,$[Fe^{3+}] = 6.87 \times 10^{-4}m$, $[EDTA^{4-}] = 1.00 \times 10^{-3}m$. O, $[Fe^{3+}] = 6.87m$, $[EDTA^{4-}] = 5.00 \times 10^{-3}m$. □ $[Fe^{3+}] = 2.29 \times 10^{-3}$ m, $[EDTA^{4-}] = 1.00 \times 10^{-2}m$. X,$[Fe^{3+}] = 4.58 \times 10^{-3}m$, $[EDTA^{4-}] = 1.00 \times 10^{-2}m$.

with Iron-EDTA hydrolysis[6,7]. It is therefore simple and logical to accept as a working hypothesis the association of the hydrolysis products with the changes in the relaxation rate. Fe OH $EDTA^{2-}$, Fe $(OH)_2$ $EDTA^{3-}$, and Fe $(OH)_3$ $EDTA^{4-}$,[7] and Fe OH $EDTA^{2-}$ and $(Fe\ OH\ EDTA)_2^{4-}$[8] have all been reported in solution. The occurrence of Fe $(OH)_3$ EDTA is associated with the onset of precipitation. Therefore, the changes in observed rate may be associated with variations in the concentrations of

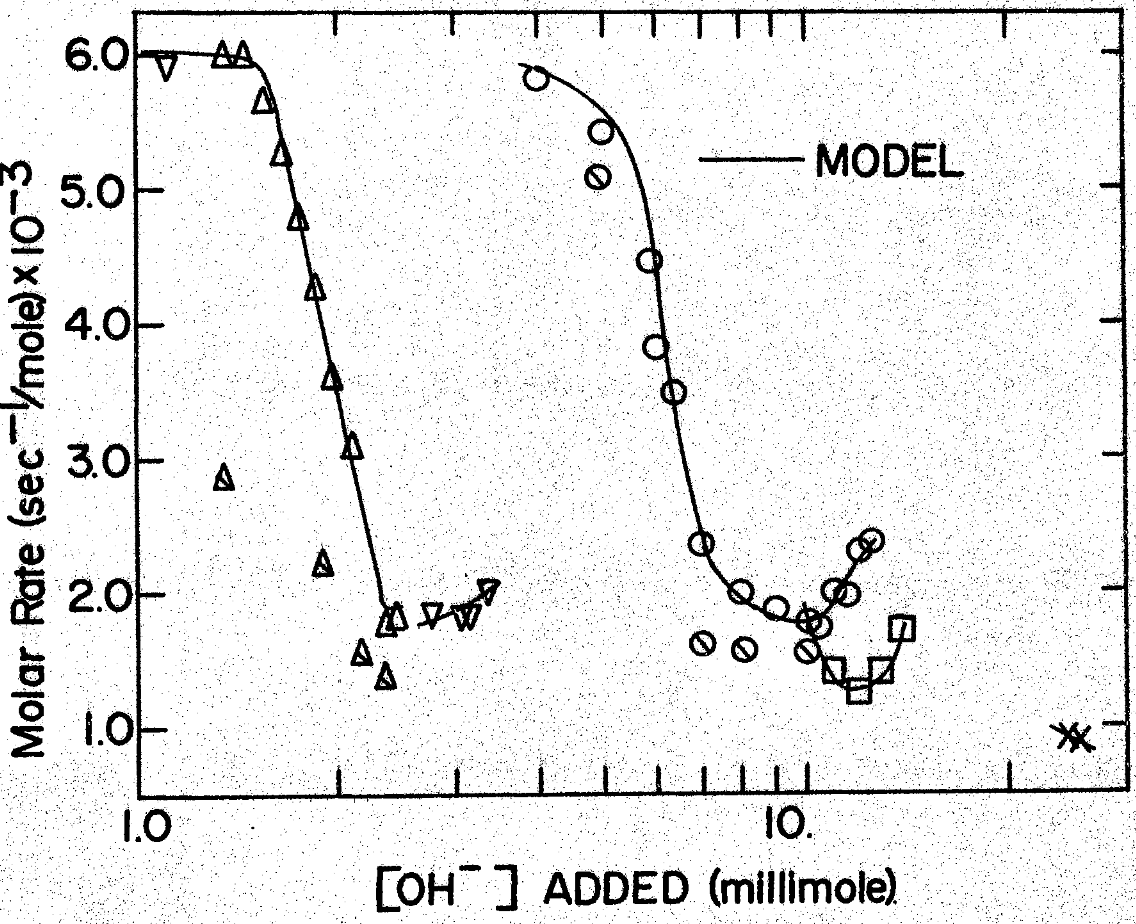

Figure 3. Molar Proton Spin Relaxation Rate vs $[OH^-]$ Added for Fe OH_2 $EDTA^-$ as a Function of Fe^{3+} Concentration at 1.5°C. Series II (H_2Na_2EDTA). $[NaClO_4] = 0.3m$. ▽, $[Fe^{3+}] = 6.87 \times 10^{-4}m$, $[EDTA^{4-}] = 1.00 \times 10^{-3}$. △, $[Fe^{3+}] = 6.87 \times 10^{-4}m$,

$[EDTA^{4-}] = 7.20 \times 10^{-4}$m. 0, $[Fe^{3+}] = 6.87 \times 10^{-4}$m, $[EDTA^{4-}] = 5.00 \times 10^{-3}$m. □, $[Fe^{3+}] = 2.29 \times 10^{-3}$m, $[EDTA^{4-}] = 5.00 \times 10^{-3}$m. X, $[Fe^{3+}] = 5.73 \times 10^{-3}$m, $[EDTA^{4-}] = 1.00 \times 10^{-3}$m. Δ, $[Fe^{3+}] = 6.87 \times 10^{-4}$m, $[EDTA^{4-}] = 7.20 \times 10^{-4}$m, T = 30°C. Ø, $[Fe^{3+}] = 6.87 \times 10^{-4}$, $[EDTA^{4-}] = 5.00 \times 10^{-3}$m, [KCl] = .3m.

the following species:

(a) $Fe\ EDTA^{-}$ (possibly $Fe\ OH_2\ EDTA^{-}$)

(b) $Fe\ OH\ EDTA^{2-}$

(c) $(Fe\ OH\ EDTA)_2^{4-}$

(d) $Fe\ (OH)_2\ EDTA^{3-}$

At this point it is necessary to determine whether the observed rate is the sum of the individual rates or a non-linear function of the respective concentrations (Chapter II). This in turn requires identifying the probable mechanisms for hydrolysis and proton exchange, and assigning a structure to the solution species. In Figure 4 the near-linear portion of the rate curve starting at the first data point after the rate reduction starts has been extended by a straight line. Reading the rate at an abscissa value corresponding to the addition of 1 equivalent of base (approximately corrected for H_2EDTA^{2-} hydrolysis) provides an approximate expected value for the molar relaxation rate of $Fe\ OH\ EDTA^{2-}$. This rate

$$R_{Fe} \approx 2.6 \times 10^{3}\ \text{sec}^{-1}/\text{mole}$$

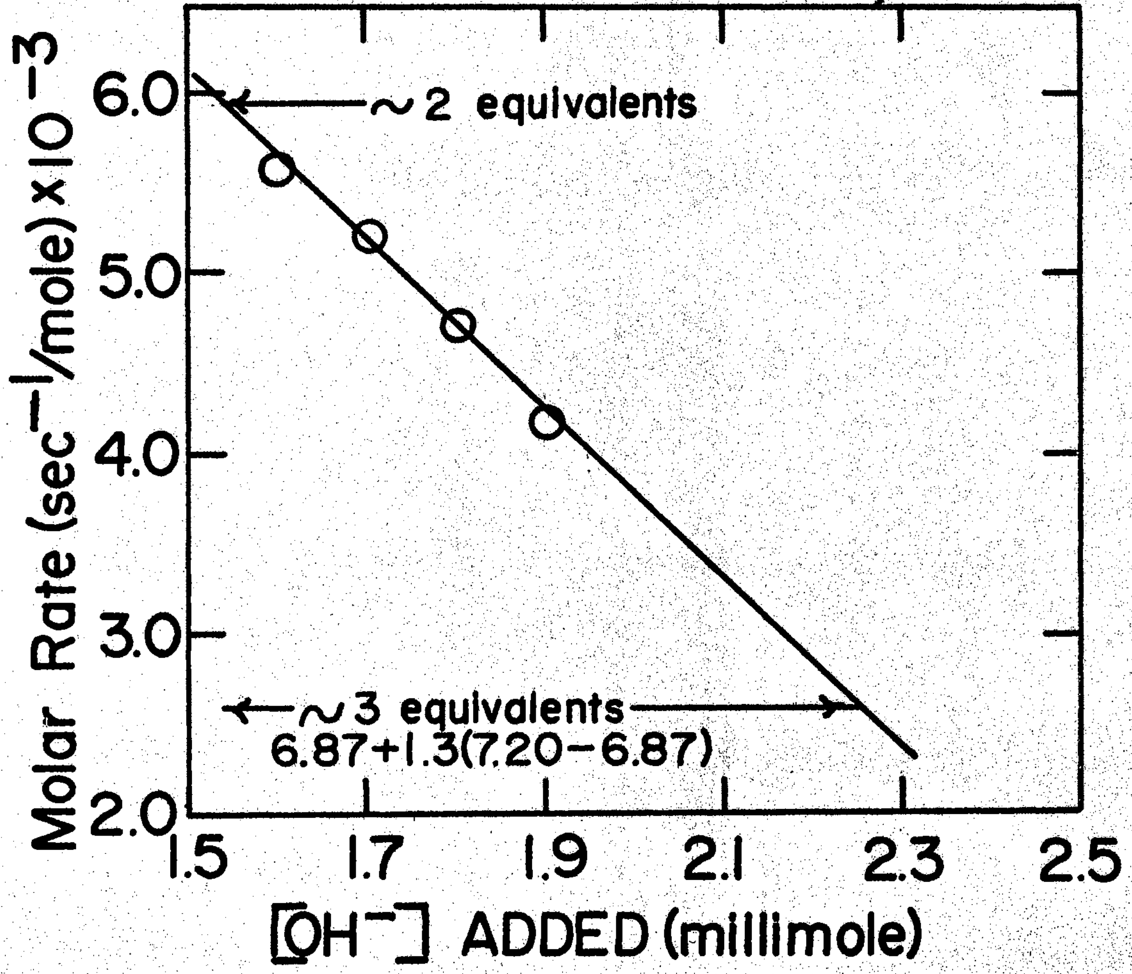

Figure 4. Calculation of Approximate Molar Rate for Fe OH EDTA^{2-} at 1.5°C. [Fe^{3+}] = 6.87 x 10^{-4}m, [H_2 Na_2 EDTA] = 7.20 x 10^{-4}m and [$NaClO_4$] = 0.3m.

is comparable with the extra 1st coordination sphere relaxation as determined by other investigators[9,10]. In addition, assuming that

$$\mu^2_{\text{eff}} \; \alpha \; S(S + 1), \mu_{\text{eff}} \equiv \text{ magnetic moment of the ion, and}$$

taking the molar rate for a non-exchanging Cr EDTA$^-$ species, Chapter V,

$$R_{CR} = 1.1 \times 10^3 \text{ sec}^{-1}/\text{mole}$$

then

$$\frac{(1.1 \times 10^3 \text{ sec}^{-1}/\text{mole})[\frac{5}{2} (\frac{5}{2} + 1)]}{\frac{3}{2} (\frac{3}{2} + 1)}$$

$$\simeq 2.6 \times 10^3 \text{ sec}^{-1}/\text{mole}.$$

the appropriate rate for Fe OH EDTA^{2-}. Although a fortuitous circumstance, some correlation is expected if the rates of the two species are determined by extra 1st coordination sphere interactions. In Pfeiffer's Model", Chapter II, the rate is primarily determined by the translational diffusion of bulk water molecules. There is no reason for the diffusion constants to be noticeably different in the two solutions. Unless contrary evidence is encountered, it is assumed that the first hydrolysis product does not exchange protons with bulk water. Further insight into the interrelationships of relaxation rates among the solution species is gained by considering the precursor to Fe OH EDTA^{2-}. The temperature data, Figure 5, is characteristic of the dipole-dipole interaction of a proton rotating with the complex. The change in the logarithm of the rate with respect to 1/K^o is near linear

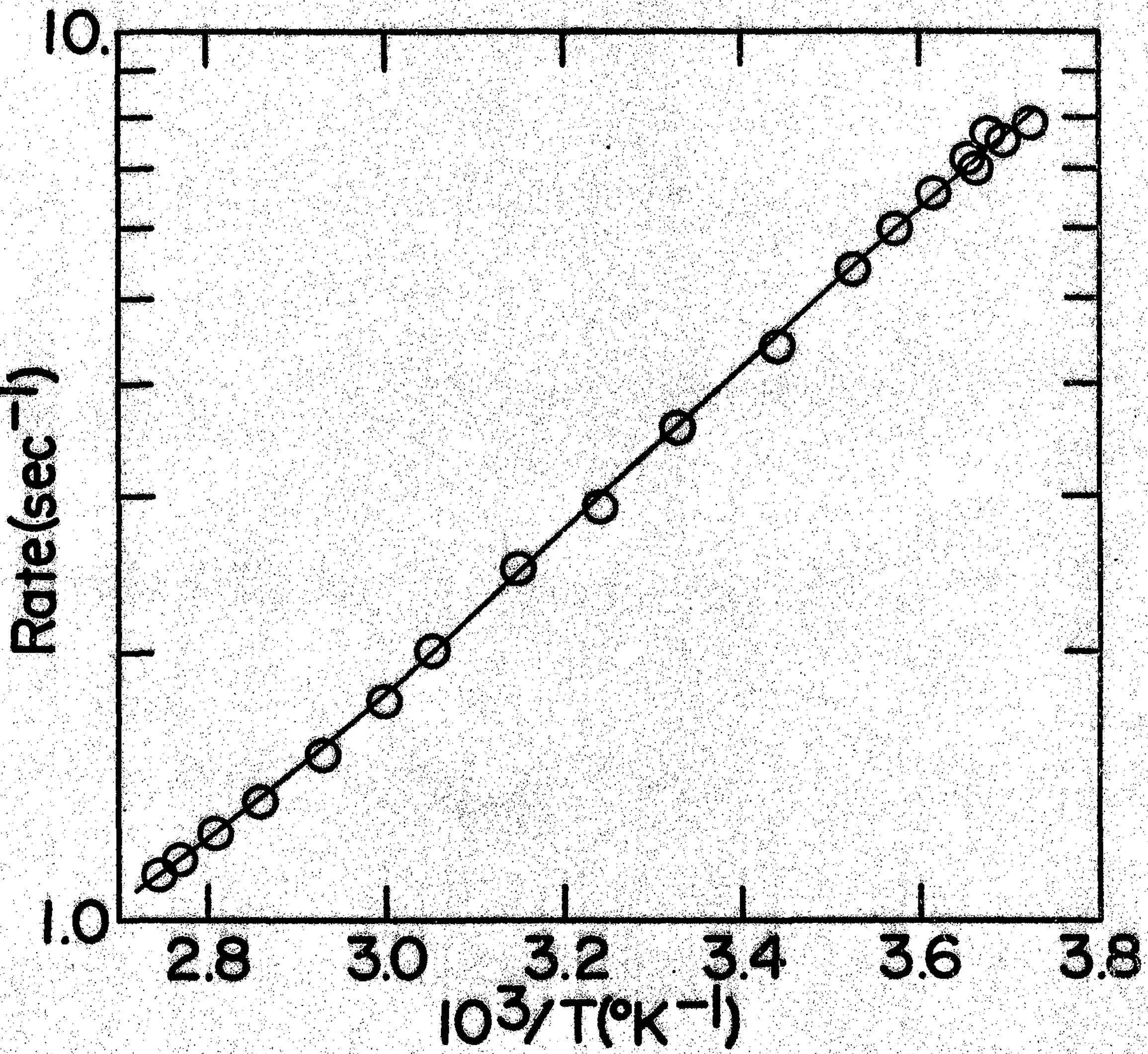

Figure 5. Proton Spin Relaxation Rate vs 1/°K for [Fe] = 1.14 x 10^{-3}m, [H_2 Na_2 EDTA] = 1.6 x 10^{-3}m, [H] Added = 1.00 x 10^{-1}m, and $NaClO_4$ = .3m. No Field Dependence 2 to 500 Gauss and No Acid Concentration Dependence [H] 1.0 x 10^{-3} < [H] < 1.0m.

and constantly decreasing. This indicates that the rate is not proton chemical exchange controlled. Further, since,

$$\frac{1}{NT_1} = \frac{1}{111.\text{mole}} \; \frac{1}{T_{1c} + \tau_h}$$

$$\tau_h \equiv \text{proton lifetime}$$

and $$\frac{1}{NT_1} \text{ due to dipole-dipole interaction}$$

$$\approx 3.4 \times 10^3 \text{ sec}^{-1}/\text{mole}$$

then $\tau_h << 3 \times 10^{-6}$ sec, for the proton lifetime in the Iron-EDTA complex in the acid range. (an identical calculation leads to the conclusion that τ_h, for the proton in Fe OH $EDTA^{2-}$, >> 3×10^{-5} sec.)

The only feasible structure for the Iron-EDTA complex ion is

$$\text{Fe } OH_2 \text{ } EDTA^-$$

with possible proton exchange mechanisms being:

(a) interaction with an OH^- ion,

(b) Loss of a proton, resulting in Fe OH $EDTA^{2-}$,

(c) whole water molecule exchange.

Mechanism (a) can be eliminated since it implies an absence of proton exchange at low pH values. The temperature data indicates that proton exchange does occur.

Mechanism (b) can also be eliminated. Consider the equilibrium rate equation,

$$k_1[\text{Fe } OH_2 \text{ } EDTA^-] - k_2[H_3{}^+O][\text{Fe OH } EDTA^{2-}] = 0$$

at the pH where [Fe OH_2 $EDTA^-$] = [Fe OH $EDTA^{2-}$], the observed molar rate is ≈ $4. \times 10^3$ sec^{-1}/mole. Using Eq. II-4

$$\tau_h + T_{1c} \approx 3. \times 10^{-6}.$$

Since a proton limited exchange region does not occur in the data,

$$\tau_h << 10^{-6}.$$

Also, since $k_1 = \tau_h^{-1}$, then

$$k_1 = k_2[H_3^+O] >> 10^6$$

At a pH ≈ 8, the PK for the 1st hydrolysis,

$$k_2[10^{-8}] >> 10^6$$

implies that $k_2 >> 10^{14}$/sec-mole, a rate much faster than the acid proton diffusion rate in water. Therefore, proton exchange in Fe OH_2 $EDTA^-$ occurs via whole water molecule exchange.

In considering the way in which proton spin magnetization is transferred from chelated ion to bulk water the possibility of non-linear effects must also be considered. Considering the assigned structure and mechanism there are two ways for this to occur. These are,

(a) At low concentration of Fe OH_2 $EDTA^-$ and high concentration of Fe OH EDTA, the rate at which Fe OH $EDTA^{2-}$ → Fe OH_2 $EDTA^-$ is comparable to the rate of whole water molecule exchange in Fe OH_2 $EDTA^-$.

(b) At high concentration of Fe OH $EDTA^{2-}$ and low concentration of Fe $(OH)_2$ $EDTA^{3-}$ the rate at which Fe $(OH)_2$ $EDTA^{3-}$ →

Fe OH EDTA is comparable to the relaxation rate of a proton in the 1st coordination sphere.

Considering again an equilibrium rate equation,

$$k_1[\text{Fe OH EDTA}^-] - k_2[\text{OH}][\text{Fe OH}_2\text{ EDTA}] = 0$$

and the equilibrium constant[8]

$$K = \frac{k_2}{k_1} \approx 10^7/\text{mole}$$

then for a pessimistically fast base reaction rate constant

$$k_2 \approx 10^8/\text{sec-mole}$$

then $$k_1 \approx 10^1/\text{sec}$$

This insures that each proton associated with Fe OH EDTA has relaxed before exchange. At the concentration of iron studied, this reaction exchanges

$$\approx 10^{-2} \text{ moles of protons/sec.}$$

With $\approx$ 55 moles to exchange, the effect is not observable. A comparable argument indicates that process b would exchange

$$\approx 10^2 \text{ moles of protons/sec if}$$

$k_2 \approx 10^8$/sec-mole, a rate which is fast enough. However, for non-linear effects to occur the two OH^- ions would have to be equivalent. This does not appear likely. Also if proton exchange effects are not noted,

$$k_2 < 10^6/\text{sec-mole.}$$

A final consideration concerns the coordination number of the ion. In Cr OH_2 $EDTA^-$ solution the protonation of the complex, which is associated with an uncoordinated acid group[5,13,14], at ≈ pH3 is accompanied by an increase in the proton spin relaxation rate, Fig. 4, Chapter V. At pH = 0 protonation of the Fe OH_2 $EDTA^-$ complex was not observed at any temperature. This implies non-protonation or a very long proton exchange time. Neither of these possibilities can be associated with an uncoordinated acid group. Reasonable proton reaction rates in water would preclude a long exchange time. It is therefore assumed that in Fe OH_2 $EDTA^-$, the EDTA is six coordinated, resulting in a seven coordinated structure for the Iron-EDTA ion in water.

To summarize, the key assumptions developed in the preceeding are

(a) The Iron-EDTA complex ion has the formula Fe (OH_2) $EDTA^-$ and is seven coordinated.

(b) Exchange of protons in Fe (OH_2) $EDTA^-$ is through whole water molecule exchange.

(c) The change in relaxation rate with addition of OH^- ion results from the appearance of hydrolysis products in the solution. The species to be considered are:

(1) $Fe(OH_2)EDTA^-$

(2) $Fe(OH)EDTA^{2-}$

(3) $(Fe\ OH\ EDTA)_2^{4-}$

(4) $Fe(OH)_2EDTA^{3-}$.

(d) Fe OH $EDTA^-$ does not exchange protons with bulk water. Its relaxation effects are due to extra first coordination sphere interactions.

(e) The solution proton spin relaxation rate will be equal to the linear sum of the individual species rates.

Parameters

Using (II-2), the equation corresponding to the data shown in Figs. 1 and 1(a) for the relaxation rate (R) is

$$R = r_1 x_1 + r_2 \frac{\alpha_1 x_1}{x_3} + r_3 \alpha_2 \frac{x_1}{x_3^2} + r_4 \alpha_3 \frac{x_1^2}{x_3^2} \qquad \text{(IV-2)}$$

with $r_i \equiv$ species molar relaxation rate (sec^{-1}/mole)

$x_1 \equiv [\mathrm{Fe\ OH_2\ EDTA^-}]$ $\qquad$ $[\mathrm{Fe\ OH\ EDTA^{2-}}] = \alpha_1 \dfrac{[\mathrm{Fe\ OH_2\ EDTA^-}]}{[\mathrm{H_3{}^+O}]}$

$x_3 \equiv [\mathrm{H_3{}^+O}]$ $\qquad$ $[\mathrm{Fe\ (OH)_2\ EDTA^{3-}}] = \alpha_2 \dfrac{[\mathrm{Fe\ OH_2\ EDTA^-}]}{[\mathrm{H_3{}^+O}]^2}$

$\alpha_i \equiv$ over all formation constant $\qquad$ $[\mathrm{(Fe\ OH\ EDTA)_2^{4-}}] = \alpha_3 \dfrac{[\mathrm{Fe\ OH_2\ EDTA^-}]^2}{[\mathrm{H_3{}^+O}]^2}$

This equation identifies seven parameters, three formation constants and 4 molar relaxation rates constants, on which the observed rate depends. In addition other parameters must also be considered.

Since two $\mathrm{EDTA^{4-}}$ ion buffer regions occur in the acid ranges represented by the data, the third and fourth hydrolysis of this ion must be included in the development. In addition the amount of free acid in reagent $\mathrm{Fe(NO_3)_3}$ is unknown, and as was pointed out in Chapter III some of the iron data (Series I) was obtained for an $\mathrm{H_2Na_2EDTA}$ solution which was missing some protons. A possible twelfth parameter which might be considered accounts for a reported formation constant[15] for the reaction

$$Na^{+}\ EDTA^{4-} \rightleftharpoons NaEDTA^{3-}$$

This reaction does occur, Fig. 3, but turns out to be of negligible importance. The reactions which would occur in a EDTA$^-$Na solution during a titration are, letting Y ≡ EDTA^{4-} and ignoring charge signs,

$$H_2\,Y \rightleftharpoons H + HY:\ \beta_1$$

$$H\,Y \rightleftharpoons: H + Y \quad \beta_2$$

$$H\,Y + Na \rightleftharpoons HNaY:\ K_1$$

$$HNaY \rightleftharpoons NaY + H:\ \beta_3$$

$$Na + Y \rightleftharpoons NaY: \quad K_2$$

Considering the mass balances (ionization of water ignored),

$$[H^2Y] + [HY] + [Y] + [HNaY] + [NaY] - [Y_t] = 0$$

$$[HY] + [2Y] + [HNaY] + [2NaY] - [A] = [H]$$

with $[Y_t]$ ≡ total EDTA concentration

[A] ≡ concentration of base added

They may be solved in terms of the equilibrium constants, then

$$Y(\beta_1\beta_2[H]^2 + \beta_2[H] + \beta_3K_2[H][Na] + K_2[Na]) = Y_t$$

$$Y(\beta_2[H] + 2 + \beta_3K_2[H][Na] + 2\,K_2\,[Na]) = A$$

Dividing the second equation by the first and rearranging the result

$$\frac{A}{Y_t} = \frac{\dfrac{\beta_2 + \beta_3 K_2[\mathrm{Na}]}{K_2[\mathrm{Na}] + 1}[\mathrm{H}] + 2}{\dfrac{\beta_1\beta_2}{K_2[\mathrm{Na}] + 1}[\mathrm{H}]^2 + \dfrac{\beta_2 + K_2[\mathrm{Na}]}{K_2[\mathrm{Na}] + 1}[\mathrm{H}] + 1}$$

is obtained. If the [Na] is effectively a constant, which implies that $[\mathrm{Na}] \gg [Y_t]$, then this equation describes a normal titration curve for $H_2\ \mathrm{EDTA}^{2-}$ with modified acid formation constants. Therefore, this parameter need not be considered.

Without adequate consideration of the factors involved, a data fit with eleven adjustable parameters might appear indeterminate. However, one of these parameters, an EDTA hydrolysis constant, will be used to define H. Two parameters, free acid and EDTA Series I correction, are obviously determinate, at least 2 rates are determinate, and the nonlinear variation in molar rate with Fe concentration is determinate. This leaves 5 parameters to be extracted from the data. As a further agreement against singularity it is appropriate to mention that all prior attempts to fit the data failed until it was learned that the original EDTA solution (Series I Data) was missing hydrogen ions.

Data Fit

Differential Correction

The objective of a least squares fit is to minimize the function

$$S = \sum_{i=1}^{n} (R_i' - R_i)^2$$

where

R_i' = value of the experimental data point

R_i = value of the computed data point

n = number of data points for each adjustable parameter.

This implies

$$\frac{dS}{d\alpha_k} = 0 = \sum_{i=1}^{n} (R_i' - R_i) \frac{dR_i}{d\alpha_k}, \quad \alpha_k = k^{th} \text{ parameter}$$

Since

$$R_i = R_{oi} + \frac{dR_i}{d\alpha_1} \Delta\alpha_1 + \frac{dR_i}{d\alpha_2} \Delta\alpha_2 \cdots \frac{dR_i}{d\alpha_s} \Delta\alpha_s$$

Then

$$\sum_{i=1}^{n} e_i \frac{dR_i}{d\alpha_k} - \left(\frac{dR_i}{d\alpha_1} \frac{dR_i}{d\alpha_k}, \frac{dR_i}{d\alpha_2} \frac{dR_i}{d\alpha_k}, \cdots \frac{dR_i}{d\alpha_s} \frac{dR_i}{d\alpha_k}\right) \begin{pmatrix} \Delta\alpha_1 \\ \Delta\alpha_2 \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \Delta\alpha_s \end{pmatrix}$$

with $e_i = R'_i - R_i = 0$

Expanding to the full matrix and solving for the vector $\Delta\alpha$

$$(\Delta\alpha) = M^{-1} (E) \qquad \text{(IV-3)}$$

with

$$M = \sum_{i=1}^{n} \begin{pmatrix} \frac{dR_i}{d\alpha_1} \frac{dR_i}{d\alpha_1} & \cdots\cdots & \frac{dR_i}{d\alpha_1} \frac{dR_i}{d\alpha_s} \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \cdot & & \cdot \\ \frac{dR_i}{d\alpha_1} \frac{dR_i}{d\alpha_s} & \cdots\cdots & \frac{dR_i}{d\alpha_s} \frac{dR_i}{d\alpha_s} \end{pmatrix}$$

and

$$(E) = \sum_{i=1}^{n} e_i \begin{pmatrix} \dfrac{dR_i}{d\alpha_1} \\ \dfrac{dR_i}{d\alpha_2} \\ \cdot \\ \cdot \\ \cdot \\ \cdot \\ \dfrac{dR_i}{d\alpha_s} \end{pmatrix}$$

s = number of adjustable parameters.

The $\Delta\alpha_i$ provide the necessary corrections to the initial values assumed in a 1st trial. The correct values of α_k are obtained by iterating.

To use Eq. IV-3 it is necessary to know the values for

x_1 and x_3 used in Eq. IV-2.

Therefore, the system of equations describing the chemical system must be solved.

Chemical System

The equilibrium concentrations of the species in solution are obtained by solving simultaneously the three non-linear equations describing the mass balances for Iron-EDTA, EDTA, and hydrogen ion. The three equations are

Fe:

The iron species to be considered are $Fe\ OH_2\ EDTA^-$, $Fe\ OH\ EDTA^{2-}$,

$Fe\ (OH)_2\ EDTA^{3-}$, and $(Fe\ OH\ EDTA)_2^{4-}$. Since the formation constant for Fe^{3+} and $EDTA^{4-}$ is very large, and an excess of EDTA is always used, free Iron will not be present. Letting

$$x_1 = [Fe\ OH_2\ EDTA^-]$$

$$x_3 = [H_3^+O]$$

$$x_{1t} = [\text{total iron in solution}]$$

then in terms of the overall formation constant α,

$$[Fe\ OH\ EDTA^{2-}] = \alpha_1 \frac{x_1}{x_3}$$

$$[Fe\ (OH)_2\ EDTA^{3-}] = \alpha_2 \frac{x_1}{x_3^2}$$

$$[(Fe\ OH\ EDTA)_2^{4-}] = \alpha_3 \frac{x_1^2}{x_3^2}$$

the equation which is to be solved is

$$f = 0 = x_1 + \alpha_1 \frac{x_1}{x_3} + \alpha_2 \frac{x_1}{x_3^2} + 2\alpha_3 \frac{x_1^2}{x_3^2} - x_{1t}$$

EDTA:

Letting $x_2 \equiv [EDTA^{4-}]$

$x_{2t} \equiv [Na_2\ H_2\ EDTA]_{TOTAL}$

then $[HEDTA^{3-}] = \alpha_5 x_2 x_3$

$$[H_2\ EDTA^{2-}] = \alpha_4 [H\ EDTA^{3-}] x_3$$

$$= \alpha_4 \alpha_5\ x_2 x_3^2$$

and

$$g = 0 = x_2 \, (1 + \alpha_5 x_3 + \alpha_4 \alpha_5 x_3^{\,2}) - (D x_{2t} - x_{1t})$$

H_3^+O:

$$h = 0 = (A - x_3 + \frac{kw}{x_3})$$

:Base added plus base due to ionization

$$+ \alpha_1 \frac{x_1}{x_3} + 2\alpha_2 \frac{x_1}{x_3^{\,2}} + 2\alpha_3 \frac{x_1^{\,2}}{x_3^{\,2}}$$

:hydrolysis of Fe OH_2 $EDTA^-$

$$+ (1 + \alpha_6) \, x_{1t}$$

:reaction of Fe^{3+} and Na_2 H_2 EDTA. $0 < \alpha_6 < 1$. α_6 corrects for shortage of protons in Series I EDTA.

$$+ x_2 (1 - \alpha_4 \alpha_5 \, x_3^{\,2}) + \alpha_6 D x_{2t} - x_{1t}$$

:hydrolysis of H_2 $EDTA^{2-}$. D corrects for shift in molecular weight for Series I EDTA[16].

$D = 1$ Series II

$D = \dfrac{372.2}{415.2 - 43\,\alpha_6}$ Series I

$$+ \alpha_7 x_{1t}$$

:free acid in $Fe(NO_3)_3$

This set of equations is solved using the Newton-Raphson Method. That is, since

$$f = f_o + \frac{\partial f}{\partial x_1} \Delta x_1 + \frac{\partial f}{\partial x_2} \Delta x_2 + \frac{\partial f}{\partial x_3} \Delta x_3$$

$$g = g_o + \frac{\partial g}{\partial x_1} \Delta x_1 + \frac{\partial g}{\partial x_2} \Delta x_2 + \frac{\partial g}{\partial x_3} \Delta x_3$$

$$h = h_o + \frac{\partial h}{\partial x_1}\Delta x_1 + \frac{\partial h}{\partial x_2}\Delta x_2 + \frac{\partial h}{\partial x_3}\Delta x_3$$

then

$$\begin{pmatrix} \Delta x_1 \\ \Delta x_2 \\ \Delta x_3 \end{pmatrix} = - V^{-1} \begin{pmatrix} f_o \\ g_o \\ h_o \end{pmatrix}$$

with

$$V = \begin{pmatrix} \frac{\partial f}{\partial x_1} & \frac{\partial f}{\partial x_2} & \frac{\partial f}{\partial x_3} \\ \frac{\partial g}{\partial x_1} & \frac{\partial g}{\partial x_2} & \frac{\partial g}{\partial x_3} \\ \frac{\partial h}{\partial x_1} & \frac{\partial h}{\partial x_2} & \frac{\partial h}{\partial x_3} \end{pmatrix} .$$

The V^{-1} matrix is also useful for another task. Since the rate, Eq. IV-2, is a function of the concentrations of x_1 and x_3, themselves a function of parameters, this matrix is necessary for the computation of the derivatives:

$$\frac{dR_i}{d\alpha_k} = \frac{dR}{dx_1}\frac{dx_1}{d\alpha_k} + \frac{dR_i}{dx_3}\frac{dx_3}{d\alpha_k} + \frac{dR}{d\alpha_k}$$

The $\frac{dx_i}{d\alpha_k}$ are computed using the Jacobian (V) of the functions f, g, and h. Since

$$\left.\begin{matrix} f \\ g \\ h \end{matrix}\right\} = 0 \text{ when the equations have been solved}$$

$$\begin{pmatrix} \frac{f}{\partial x_1} & \frac{f}{\partial x_2} & \frac{f}{\partial x_3} \\ \frac{\partial g}{\partial x_1} & \frac{\partial g}{\partial x_2} & \frac{\partial g}{\partial x_3} \\ \frac{\partial h}{\partial x_1} & \frac{\partial h}{\partial x_2} & \frac{\partial h}{\partial x_3} \end{pmatrix} \begin{pmatrix} \frac{\partial x_1}{\partial \alpha_k} \\ \frac{\partial x_2}{\partial \alpha_k} \\ \frac{\partial x_3}{\partial \alpha_k} \end{pmatrix} = - \begin{pmatrix} \frac{\partial f}{\partial \alpha_k} \\ \frac{\partial g}{\partial \alpha_k} \\ \frac{\partial h}{\partial \alpha_k} \end{pmatrix}$$

or

$$\begin{pmatrix} \frac{\partial x_1}{\partial \alpha_k} \\ \frac{\partial x_2}{\partial \alpha_k} \\ \frac{\partial x_3}{\partial \alpha_k} \end{pmatrix} = - V^{-1} \begin{pmatrix} \frac{\partial f}{\partial \alpha_k} \\ \frac{\partial g}{\partial \alpha_k} \\ \frac{\partial h}{\partial \alpha_k} \end{pmatrix}$$

At this point the solution is complete. One additional refinement was incorporated into the procedure. Since the values of $\frac{\partial R_i}{\partial \alpha_k}$ are widely divergent, they were normalized by multiplying them by α_k. This was accomplished in the following way: From Eq. IV-3,

$$M\ (\Delta\alpha) \quad = \quad (E) \qquad \text{and}$$

$$\alpha M \alpha\alpha^{-1}\ (\Delta\alpha) \quad = \quad \alpha(E) \qquad \text{with}$$

$$\alpha \quad \begin{pmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & \\ 0 & & \alpha_s \end{pmatrix}$$

and

$\alpha^{-1}\ (\Delta\alpha) = (\alpha M \alpha)^{-1}\ \alpha(E)$. Since $\alpha^{-1} = \begin{pmatrix} \frac{1}{\alpha_1} & 0 & 0 & 0 \\ 0 & \frac{1}{\alpha_2} & & \\ & & & \\ 0 & & & \frac{1}{\alpha_s} \end{pmatrix}$ and

$\alpha^{-1}(\Delta\alpha)$ = P = fractional modification in α, then

α_{new} = α_{old} (I - P')

I = identity matrix

P' = square form of P.

The program developed with this procedure contained about 200 steps and would iterate the fit approximately 35 times in ten minuts for 85 data points. In starting the program it was necessary to determine approximate initial values using a closed interval search, Appendix A.

Results and Discussion

pH Dependence

In the procedure developed in the preceeding section, x_3 remains undefined. To define x_3, one of the equilibrium constants must be determined. The value $\frac{K_w}{x_3}$ is so small over a major portion of the pH range considered, that it is inadequate for this purpose. Thus, the reaction

$$\text{HEDTA} \longrightarrow \text{EDTA} + \text{H}: \qquad K_4$$

was used. There are two reasons for using this reaction. One, the equilibrium constant is closer to the Fe OH_2 EDTA hydrolysis equilibrium constants. And two, the PK is close to that of a standard buffer for which data exists at the required temperature. The PK was determined potentiometrically. The results of measurements made in a "cold" room at 1.5° C are summarized in Table I.

TABLE I

PK_3 AND PK_4 FOR EDTA AT 1.5°C

Reaction	PK		
	Calculated[19] $[K^+] = .1m$	$[K^+] = .3m$	$[Na^+] = .3m$
$H_2EDTA \longrightarrow HEDTA$	6.51	6.43	6.27
$H\ EDTA \longrightarrow EDTA$	10.63	9.94	9.33

Note: Sodium Borate (pH = 9.43 and Phthalate pH = 4.01) were used as standards[18].

With the equilibrium constant for the hydrolysis of $HEDTA^-$ as a standard, TABLES II and III list the results of the fit of the phenomenological equation to the experimental data. Published data are shown for comparison. With the exception of the constant for K_2, differences are attributable to variations in ionic strength. With reference to K_2, the published value was determined potentiometrically for a solution with $[Fe\ EDTA] = 1.53 \times 10^{-3}$ molar. The existence of a dimer was not accounted for. At the concentration used some of the complex undoubtedly appeared in dimeric form.

The molar rates provide some definitive data on the complex ion.

Noteworthy is the rate for $(\mathrm{Fe\ OH\ EDTA})_2$. In this case zero requires that the calculated rate be at least 100 times smaller than the expected rate. A low field NMR experiment is unable to distinguish between diamagnetism and a short τ_s, electron spin correlation time. The results of other investigators[1,3] with $(\mathrm{Fe\ OH})_2$, and the small probability of a $\tau_s = 10^{-13}$ sec, indicate that the complex is diamagnetic.

Of interest also is the molar rate for $\mathrm{Fe(OH)_2EDTA}$. This rate, associated with extra - 1st coordination sphere relaxation, implies a slow proton exchange. For the equilibrium rate condition

$$k_1\ [\mathrm{Fe\ (OH)_2\ EDTA}] - k_2\ [\mathrm{OH}][\mathrm{Fe\ OH\ EDTA}] = 0$$

$$k_1 \ll 10^4\ (\frac{1}{t_h};\ t_h \text{ lifetime for effective exchange})$$

which implies $k_2 \ll 10^7$.

Accuracy

With respect to the fit of the predicted value to experimental one, the average root mean square deviation per data point is 2.9%. This compares well with a day to day expected variation of 3% in data point reproducability.

Variation in K_1 and K_{22} are nearly linear with respect to a change in the value used for the hydrolysis of HEDTA^{3-}. The estimated error in this value is 5%. The variation in K_2 is almost linear with respect to a change in K_w, the ionization constant of water. The accuracy of K_w is related to the accuracy of the procedure used in calculating the activity coefficients. This accuracy is approximately 8%.

TABLE II

EQUILIBRIUM CONSTANTS AT 1.5°C

Reaction	K	d
	Published	Curve Fit $[Na^+]$ = .3m
$FeOH_2EDTA$ —— FeOHEDTA + H: K_1	1.1×10^{-8}[a]	1.5×10^{-8}
FeOHEDTA —— $Fe(OH)_2EDTA$ + H: K_2	3.9×10^{-10}[b]	3.5×10^{-12}
2(FeOHEDTA) —— $(FeOHEDTA)_2$: K_{22}	1.7×10^{3}[a]	5.2×10^{2}
H_2EDTA —— HEDTA	5.37×10^{-7}[c]	4.7×10^{-7}

Notes: a - 1.0M KCl[8]

b - .1M KCl and 20°C.[7]

c - Measured. See Table I

d - Free acid concentration in the $Fe(NO_3)_3$ master solution is 7.78×10^{-2} molar and the formula for SERIES I EDTA is $H_{1.54}Na_{2.46}$ EDTA.

TABLE III

MOLAR RATES AT 1.5°C

Species	Rate x 10^{-3} (sec^{-1}/mole)
Fe OH_2 EDTA	6.0
Fe OH EDTA	2.6
Fe $(OH)_2$ EDTA	2.5
$(Fe\ OH\ EDTA)_2$	0

The molar rates are within 3% of the true values.

The ultimate validity of the parameters is synonomous with the validity of the phenomenological model. In this case, the test is the usual. The proposed mechanism is the simplest which explains the known data. Steps which are unidentifiable by the experimental technique used are unaccountable.

Temperature Dependence

The small change in molar rate with respect to a change in pH, precluded determining the parameter values at 30°C. There is one exception not involving a curve fit. It is possible to determine the formation constant at 30°C for the reaction.

$$2\ \text{Fe OH EDTA}^{2-} \rightleftharpoons (\text{Fe OH EDTA})_2^{4-} : K_{22}$$

Accepting the validity of the calculation represented by Eq. IV-1, the molar rate of Fe OH EDTA^{-2} at 30°C must be given by the expression,

$$\left(\frac{1.47\ \text{sec}^{-1}}{2.23 \times 10^{-3}\ \text{molar}}\right) \frac{\frac{5}{2}\left(\frac{5}{2}+1\right)}{\frac{3}{2}\left(\frac{3}{2}+1\right)},$$

$$= 1.54 \times 10^{3}\ \text{sec}^{-1}/\text{mole}$$

The measured rate at 30°C, Figure 3, is 1.40 x 10^{3} sec^{-1}/mole. In keeping with previous assumptions, the difference between calculated and measured rate is due to the formation of diamagnetic (Fe OH EDTA)$_2^{4-}$. (The formation constant for Fe(OH)$_2$ EDTA^{3-} is small.) Then

$$\frac{1.40}{1.54} = 1-2f = .91$$

where f is the fraction of Fe OH EDTA^{-2} present as (Fe OH EDTA)$_2^{4-}$. Since

$$K_{22} = \frac{[(\mathrm{Fe\ OH\ EDTA})_2^{4-}]}{[\mathrm{Fe\ OH\ EDTA}^{2-}]^2}$$

then $K_{22} = \dfrac{f\, x_{1t}}{[(1-2f)x_{1t}]^2} = \dfrac{f}{(1-2f)^2}\,\dfrac{1}{x_{1t}} = \dfrac{0.054}{x_{1t}} = 7.9 \times 10^1/\text{molar}$

At 1.5°C

$$K_{22} = 5.2 \times 10^2/\text{molar} = \frac{0.36}{x_{1t}}\ .$$

Assuming the validity of the Arhenius Equation then

$$V = \left(\frac{1}{275^\circ K} - \frac{1}{303^\circ K}\right)\left(2.00\ \frac{\text{kilocal.}}{\text{mole}} - {}^\circ K\right)$$

$$\ln\left(\frac{\frac{0.36}{x_{1t}}}{\frac{0.054}{x_{1t}}}\right)$$

$$= 11 \text{ kilocalories/mole} \pm 2 \text{ kilocalories/mole}$$

Applying Equation II-1 and II-2, the temperature dependence, Fig. 3, was also approximated. The least squares criteria and a minimax search strategy, Appendix A, were used. The results are shown in Table IV.

TABLE IV

TEMPERATURE DEPENDENCE

Parameter	Value
τ_r (rotational correlation time)	1.8×10^{-11} sec$^{(a)}$
V_r (activation energy for rotation)	5.1 kilocalories
a (distance of nearest approach)	3.7 Å

Notes: a - The proton-ion distance = 2.7 Å[20]
b - It was assumed that D_I = .4Dw

The average mean square deviation per data point was 2.3%.

It is of interest that the activation energy for rotation is identical in magnitude to the activation energy for water diffusion between 0°C and 80°C.[21] This result would be expected if the Debye and Stokes-Einstein equations are valid.

$$\tau(\text{Debye}) = \frac{4\pi r_a^3}{3kT} \quad \text{and } D = \frac{kT}{6\pi r_a}$$

from which τD = Const.

The absence of any measureable field dependence (2 - 420 g) precluded developing information on the electron spin correlation times.

Miscellaneous Observations

Background Salt Effect

Fig. 3 includes some data for solutions in which KCl was used instead of $NaClO_4$ as a background salt. It appears that KCl enhances the formation of $(Fe\ OH\ EDTA)_2^{4-}$ and makes $H^3\ EDTA^{3-}$ a weaker acid. For KCl solutions the absolute rate minima is smaller and the rate has a smaller value for the identical solution in $NaClO_4$. On the basis of negative hydration the change in the formation constant of $(Fe\ OH\ EDTA)_2^{4-}$ can be explained. The structure breaking affect on water of K^+ ion increases the ability of two negative ions to approach and interact.[22] Except on the basis of a non zero formation constant for an interaction with Na^+, a qualitative explanation of the change in the acid strength of EDTA is less easy to formulate. The data were obtained only to determine if a salt effect existed. Further amplification requires more data.

Fe(III) - EDTA Photoreduction

Out of an early development of background knowledge on Fe(III)-EDTA come one of the more interesting observations. As reported[6], direct sunlight reduces Fe(III)-EDTA to Fe(II)-EDTA. As observed via the change in proton spin relaxation, approximately one hour of direct sunlight completely reduced a 1.13×10^{-2} molar solution. This reduction made it easy to obtain free Fe(II) ion in solution. The formation constants of Fe(II) and Fe(III) with EDTA are 10^{14} and 10^{25} respectively[23]. In a .1 molar acid solution H^+ ion completes successfully with Fe(II) for EDTA. The result is that EDTA coordinates with Fe(III), the complex is reduced, and free Fe(II) appears. A crystal which appears to be H_4EDTA also appears as a result of the reaction. Free 0_2 in solution is scavanged. Excess EDTA insures that the resultant Fe(III) is again reduced. For Fe(II), a molar rate

$$= 3.95 \times 10^2 \ \text{sec}^{-1}/\text{mole} \ (20^\circ\text{C})$$

was obtained. This rate is 15 times smaller than that for Fe(III)-EDTA, and 50 times smaller than that for Fe(III)^{3+} ion.

There are interesting properties[24,25] associated with Fe^{2+} ion in solution. The difficulty associated with preparing and keeping Fe(II) in water have prevented extensive study.

Summary

Using the experimental data and the known characteristics of proton spin relaxation rates in solution, a phenomenological model was developed. The least squares fit of the experimental data to this model resulted in the constants describing the hydrolysis and formation of Iron-EDTA species. The analysis resulted also in information concerning the structure and exchange properties of the complex ion.

The termination of the curves on the basic side represents the point at which the solutions became metastable (in some cases with one month lifetimes) or at which the onset of precipitation was evident. Excess EDTA extended the base region. The relationship between Fe^{3+} $EDTA^{4-}$ and OH^{-} at the point of precipitation was not investigated. For an approximately one to one Fe^{3+} - $EDTA^{4-}$ solution the rate minima could not be obtained[8].

FOOTNOTES

[1] T. Mulay and P. Selwood, J. Am. Chem. Soc. 77, 2693 (1955).

[2] P. Selwood, Magnetochemistry, Interscience Publisher, New York, N. Y., 1956, p. 233.

[3] S. Broersma, J. Chem. Phys. 26, 1405 (1957).

[4] S. Berkman and H. Zacker, Z. Physik. Chem. 124, 318 (1926).

[5] A. Earnshaw and J. Lewis, J. Chem. Soc. 1961, 396 (1961).

[6] S. Jones and F. Long, J. Phys. Chem. 56, 25 (1952).

[7] G. Schwarzenback, et al., Helv. Chim. Acta. 34, 576 (1951).

[8] R. Gustafson and A. Martell, J. Phys. Chem. 67, 576 (1963).

[9] H. Pfeifer, Z. Naturforsh. 17a, 279 (1962).

[10] B. Melton, private communication, Oklahoma State University, Stillwater, Oklahoma (1968).

[11] H. Pfeiffer, Ann. Phys. 8, 1 (1961).

[12] G. Porter, Progress in Reaction Rate Kinetics, Vol. 2, Pergammon Press, New York, N. Y., 1964, p. 297.

[13] G. Schwarzenbach and W. Biedermann, Helv. Chim. Acta. XXXI, 460 (1948).

[14] C. Furlani, et al., Z. Anog. u. allgem. Chem. 303, 1 (1960).

[15] G. Schwarzenbach and H. Ackerman, Helv. Chim. Acta. 30, 1798 (1947).

[16] The assumption was made that Na^+ would replace the missing H^+.

[17] C. Hodgeman, Handbook of Chemistry and Physics, The Chemical Rubber Publishing Company, Cleveland, Ohio, 1961, p. 80. Activities at 0°C were computed using the extended Debye-Huckel law. Kw was computed to be 2.24×10^{-15}.

[18] Ibid, p. D74.

[19] M. Tillotson and L. Staveley, J. Chem., Soc. 1958, 3613 (1958).

[20] J. Hoard, J. Am. Chem. Soc. 83, 2770 (1961).

[21] J. Simpson and H. Carr, Phys. Rev. 111, 1201 (1958).

[22] O. Samoilov, Structure of Aqueous Electrolyte Solutions and the Hydration of Ions, Consultants Bureau, New York, N. Y., 1965, Chapter 5.

[23] J. Bjerrum, G. Schwarzenbach, and L. Sillin, Stability Constants Part I, Organic Ligands, The Chemical Society, London (1957).

[24] R. Hausser and G. Laukien, Z. Physik. 153, 394 (1959).

[25] N. Bloembergen and L. Morgan, J. Chem. Phys. 34, 842 (1961).

CHAPTER V

Cr(III) EDTA

Ad viewed by NMR, the Chemistry of Cr(III) is always complex[1,2,3]. This character is continued in the chelated ion formed by Cr^{3+} and $EDTA^{4-}$. The data collected and presented here on the pH and temperature dependence of the proton spin relaxation properties of aqueous Cr $EDTA^{-}$ is difficult to interpret. In some cases it was not possible to definitely establish an adequate mechanism. As usual for Cr^{3+} in solution, explanation based on magnetic properties was insufficient. The chemical properties and proton exchange properties also had to be considered. On the crucial questions of solution coordination number and dentate number of the $EDTA^{4-}$ bond, conflicting data on apparently identical systems exist[4].

As the pH of a $CrEDTA^{-}$ solution is varied from acid to base the solution color changes from red to blue. The minimum relaxation rate occurs at the maximum pH where all of the $CrEDTA^{-}$ is in the red form. The maximum pH at which all of the $CrEDTA^{-}$ is red, and the minimum pH at which all of the ion is blue, were determined by titrating the solution potentiometrically. The $PK_H = 7.3$ determined, compares favorably with literature values of 7.41[5] and 7.5[6]. The species in solution at the maximum pH for the red form was assumed not to exchange protons. Thus, it represents a rate due only to the translation of bulk water molecules towards and away from the complex ion. This assumption is

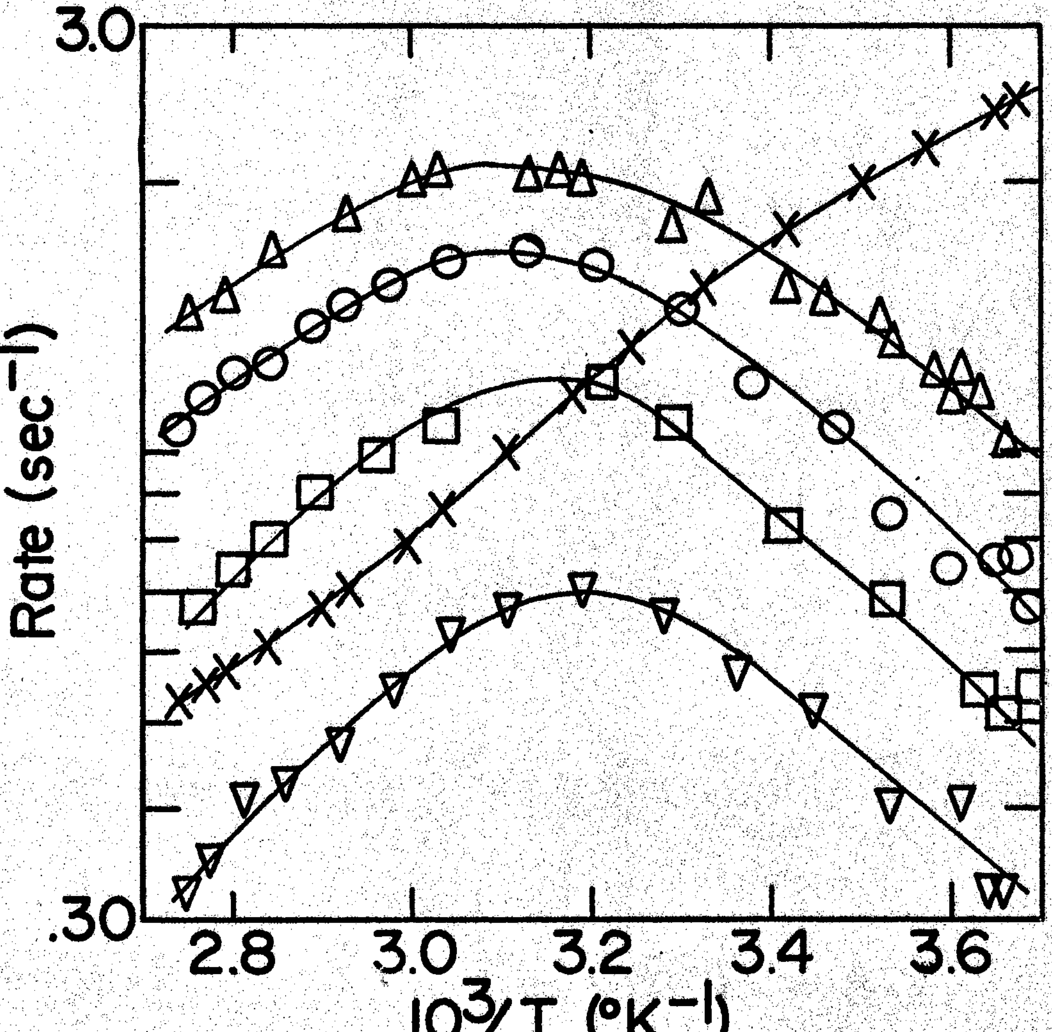

Figure 6. Proton Spin Relaxation Rate vs 1/°K as a Function of $[H^+]$ Added for Cr $EDTA^-$, $[NaClO_4]$ = .3m. [Cr] = 2.23 x 10^{-2}m, $[H_2\ Na_2\ EDTA]$ = 2.50 x 10^{-2}m. ▽, $[H^+]$ = 6.00 x 10^{-3}m. □, $[H^+]$ = 2.00 x 10^{-2}m. 0, $[H^+]$ = 5.00 x 10^{-2}m. Δ, [H] = 1.00 x 10^{-1}m. X, Minimum Rate.

based on the following:

1. The assumption makes the iron and chromium data compatable.

2. The rates and curve shape of plotted data compares well, mean square deviation $< 2\%$, with calculations based on Pfeiffers Model, Chapter II.

3. If a water molecule is associated with the complex it does not exchange. If it did the rate would be higher.

4. Evidence exists for a solution species not coordinated with a water molecule[4]. (Evidence also exists for a species which is coordinated.)

5. No reasonable mechanism exists for individual proton exchange.

The experimental data on relaxation rates is organized into sections titled Acid Solution and Basic Solution. The data are presented as the difference between actual observed rate and the minimum red form rate at the same temperature.

Acid Solution

At pH~5, corresponding to two equivalents of OH^-, the relaxation rate for a $CrEDTA^-$ is a minimum. Addition of H^+ causes the rate to increase (see Fig. 6). This increase can only be due to the association of exchanging protons with the complex. Apparently at high temperature the rate is determined by the rotational correlation time and at low temperature the rate is exchange limited. At 70°C and pH 0 the rate is approximately 12 sec^{-1} and increases with decreasing temperature. Thermal hysteresis occurs also for this acid concentration. The data in Fig. 6 were independent of the direction the curve was traversed.

The most obvious cause-effect link is the protonation of the complex. This protonation occurs at about pH 2(PK = 3.37; M = 0.05[6], PK = 2.27; M = 0.15[5], PK = 1.95, M = 0.1[7]; M = molar concentration of background salt). It has been assumed that the relatively large PK is due to a quindentate nature of the $EDTA^{4-}$ bond in Cr $EDTA^{-}$[4,5,6,7,8]. A loose acetate group accepts the proton.

Other support for the existence of a quindentate structure is based on the observed small shift in absorption spectra when the proton is added[5,11]. The large shift in other quindentate transition metal-EDTA complexes has cast doubt on the validity of their assumed structure[9]. In crystals a sexadentate (no water) complex of Cr^{3+} and $EDTA^{4-}$ has been prepared. There is some feeling that at an intermediate PH, Cr OH_2 $EDTA^-$ and Cr OH $EDTA^{2-}$ are in equilibrium with Cr $EDTA^-$.[8] This possibility will not be considered.

Of the possible operative mechanisms, the most probable are listed in Table V., along with applicable comments.

Of these b and e are the most viable and with the aid of the McConnel-Bloch equation will be presented in more detail.

For mechanism b three additional assumptions are required. These are,

1. The complex must protonate prior to aquation.

2. Water exchange may not be fast.

3. Loss of the proton results in immediate water displacement of the acetate group.

With these in mind the magnetic polarization of the solution is represented by the following equation set:

$$\dot{M}_w = \frac{M_{ow} - M_w}{T_{1w}} - \frac{M_w}{\tau_{wy}} + \frac{M_y}{\tau_{yw}}$$

TABLE V

COMPARISON OF EXCHANGE MECHANISMS

Mechanism	Description	Against	For
a	Whole water molecule exchange	1. Doesn't explain pH dependence. 2. Non-lability of Cr^{3+} ligands ($k < 10^{-4}$ moles/sec). 3. Water molecule in $CrEDTA^-$ is known to be tightly bound.	1. Accounts for temperature dependence.
b	Seven coordinated structure in which the sixth EDTA ligand (acetate) alternates with a bulk water molecule.	1. Never observed	1. Accounts for pH dependence. 2. Accounts for temperature dependence.
c	Proton exchange, rate due the presence of the protonating H^+ in the coordination sphere.	1. Requires that the proton to ion distance be short, ~2.7 Å. 2. Implies a very high relaxation rate per proton (~10 times greater than in $Fe\ OH_2\ EDTA^-$ and ≈ 2 times greater than in free Cr^{3+}).	1. Explains pH dependence. 2. Explains temperature dependence.

TABLE V (Continued)

Mechanism	Description	Against	For
		3. Shift in absorption spectra is small on protonation.	
d	Acid activated $\left(\frac{1}{T_1} \alpha \frac{1}{\frac{1}{k[H]} + T_{1c}}\right)$	1. Temperature dependence is usually small, activation energy ≈ 0 for this reaction.	1. Qualitatively accounts for pH dependence.
		2. Rate at low temperature is relatively insensitive to $[H^+]$.	2. Explains temperature dependence.
e	Modified acid activated exchange.	1. Non simple mechanism	1. Accounts for pH dependence.
	Protonation results in a structure in which the added proton is hydrogen bonded to the coordinated water molecule. 2-3 exchanging protons.		2. Accounts for temperature dependence.

$$\dot{M}_y = \frac{M_{oy} - M_y}{T_{1y}} + \frac{M_w}{\tau_{wy}} - \frac{M_y}{\tau_{yw}}$$

with

M_w = magnetization in bulk water

M_y = magnetization in $Cr(OH_2)(OH_2)HEDTA^-$

τ_{yw} = proton lifetime (τ)

N = number of molecules

T_{1y}, T_{1w} = relaxation lifetime/proton

$\tau_{wy} = \frac{2Ny}{2Nw} \frac{1}{\tau}$ and assuming an exponential solution,

$$M \begin{pmatrix} C_w \\ C_y \end{pmatrix} e^{th} + M - \tau I \begin{pmatrix} C_{ow} \\ C_{oy} \end{pmatrix} = \begin{pmatrix} \frac{M_{ow}}{T_{1w}} \\ \frac{M_{oy}}{T_{1y}} \end{pmatrix}$$

and has a solution if

$|M| = 0$ Since

$$|M| = \begin{vmatrix} \tau + \frac{1}{T_{1w}} & -\frac{1}{\tau} \\ \frac{-2\,Ny}{2\,Nw} \frac{1}{\tau} & \frac{1}{T_{1y}} + \frac{1}{\tau} \end{vmatrix}$$

then

$$\tau + \frac{1}{T_{1w}} = - \frac{2N_y}{2N_w} \left(\frac{1}{T_{1y} + \tau}\right) \qquad \text{(V-1)}$$

The properties of this equation are

(a) At low temperatures the observed rate is proton lifetime limited. τ is the lifetime of the proton in the rotating complex and τ will be large compared to T_{1y}, the relaxation time of a proton rotating with the complex. T_{1y} is inversely proportional to τ_c, the rotational correlation time. At low temperature τ_c is large and T_{1y} small. The observed temperature dependence is that of τ.

(b) At high temperature the observed rate is determined by τ_c, the rotational correlation time. The inverse of the situation described in (a) is applicable. The observed temperature dependence is that of τ_c.

(c) At any temperature the observed rate is proportional to the concentration of protonated species.

(d) There are two exchanging protons.

For mechanism e, the set of exchange equations are more complex. The assumed mechanism is illustrated in Figure 7.

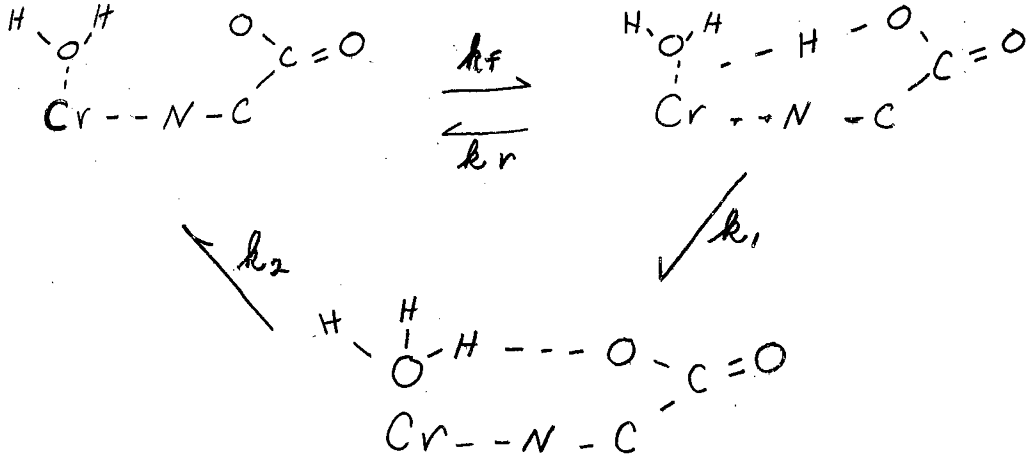

Figure 7. Modified Acid Activated Exchange

In the development which follows $k_r << k_1$, and k_1, k_2 will be represented by τ, the lifetime of a proton on the water molecule. k_r would have the effect of reducing the observed rate to a one proton value (Mechanism c) and should be more apparent at high temperatures.

Letting,

M_w = magnetization of bulk water

M_x = magnetization of Cr OH_2 EDTA

M_y = magnetization of Cr OH_2 HEDTA^o

M_z = magnetization of pseudo-species, protonating proton is not exchange equivalent with the two water protons.

Then,

$$\dot{M}_w = \frac{M_{ow} - M_w}{T_{1w}} - \frac{M_w}{\tau_{wz}} + \frac{M_y}{\tau_{yw}}$$

$$\dot{M}_x = \frac{M_{ox} - M_x}{T_{1x}} - \frac{M_x}{\tau_{xy}} + \frac{M_y}{\tau_{yx}} + \frac{M_z}{\tau_{zx}}$$

$$\dot{M}_y = \frac{M_{oy} - M_y}{T_{1t}} + \frac{M_x}{\tau_{xy}} - \frac{M_y}{\tau'_{yx}}$$

$$\dot{M}_z = \frac{M_{oz} - M_z}{T_{1z}} + \frac{M_w}{\tau_{wz}} - \frac{M_z}{\tau_{zx}}$$

Identifying τ'_{yx} with the lifetime of Cr OH_2 HEDTA^o

$$\frac{1}{\tau'_{xy}} = \frac{2}{\tau} \quad \text{and} \quad \frac{1}{\tau_{yx}} = \frac{1}{\tau_{yw}} = \frac{1}{\tau}$$

Detailed balance requires that

$$\frac{2N_w}{\tau_{wz}} = \frac{2N_y}{\tau_{yw}} \qquad \text{which results in} \qquad \frac{1}{\tau_{wz}} = \frac{2N_y}{2N_w}\,\frac{1}{\tau}$$

Also, $\frac{2N_w}{\tau_{wz}} = \frac{2N_z}{\tau_{zx}}$. Since $N_z = N_y$, $\frac{1}{\tau_{zx}} = \frac{2}{\tau}$. The last exchange rate

$$\frac{1}{\tau_{xy}} = \frac{N_y}{N_x}\,\frac{2}{\tau}$$

With these substitutions and rearranging, the solution is, letting

$$\frac{N_y}{N_x} = r$$

$$\lambda = -\frac{1}{T_{1w}} - \frac{2N_y}{2N_w}\,\frac{T_{1x}^{\,2}(6r+4) + T_{1x}\,\tau(2r+4) + \tau^2}{T_{1x}^{\,3}(4r) + T_{1x}^{\,2}\,\tau(6r+4) + T_{1x}\tau^2(2r+4)+\tau^3} \quad \text{(V-2)}$$

Comparing this solution with Eq. V-1, the following comments are appropriate:

1. Eq. V-1 predicts for all temperatures that at a given temperature, rate is proportional to the concentration of Cr OH_2 $HEDTA^o$,

2. For Eq. V-2 comment 1 is true only at low temperatures.

3. Eq. V-2 has an involved concentration dependence at high temperature. When the concentration of Cr OH_2 $HEDTA^o$ is small, the rate increases rapidly with increasing concentration. The rate of rate increase becomes smaller with increasing concentration. The smaller τh is, the faster the initial rate of increase.

4. The data indicate, but do not conclusively show, a shift downward in the maximum rate of change with respect to $[H^+]$ as the temperature increases. This would not be expected for Eq. V-1.

5. Eq. V-2 predicts a flatening of the curves at high temperature as the [Cr OH_2 $HEDTA^o$] increases.

To consider further the evidence for the respective mechanisms, the equilibrium constant will be computed. The equilibrium constant is given by

$$K = \frac{[\mathrm{Cr\ OH_2\ HEDTA^o}]}{[\mathrm{Cr\ OH_2\ EDTA^-}][\mathrm{H^+}]} \; .$$

Using the mass balance for H^+ and Cr^{3+} and identifying

R = observed rate

X = rate for $H^+ \rightarrow \infty$

the relationship between rate, equilibrium constant, and $[H^+]$ is

$$\frac{R}{X-R} = [H^+]K - [Cr_t]K\,\frac{R}{X} \qquad \text{(V-3)}$$

This equation may be used without modification to compute the equilibrium constant K and the value X at low temperature for both models. For mechanism e at high temperature a modification is required. Recognizing that

$$\frac{R}{X-R} = r \text{ in Eq. V-2,}$$

The expression $\frac{r}{r+1}\,\frac{6.67r + 4.44}{6.22r + 1.18} = \frac{R}{X}$

(Assuming the approximation $3\tau = T_{1x}$ is used to determine r and used in Eq. V-3). Also by identifying the slope tangents at the highest acid concentration studied, the activation energies, V_h and V_r may be computed.

These calculations are summarized in Table VI.

As descriminates between the two candidate mechanisms, the quantities of interest are V_r and ΔH. At low acid concentration the tangent slope should be nearly equal to $V_r + \Delta H$. The measured tangent slope is

TABLE VI

CALCULATION SUMMARY 0°C

Parameter	Mechanism b	Mechanism e
τ_h (sec) x 10^5	2.4	2.4
V_h (kcal)	3.5	3.5
T_{1c} (sec) x 10^5	7	6
V_r (kcal)	-2.8	-2.8
K(mole^{-1})	3.2 x 10^1	3.2 x 10^1
ΔH(kcal)	-1.5	-3.4

~4.5 kcal. The predicted slopes for b and e respectively are 4.3 and 6.2 kcal. It therefore appears that, even though the evidence is not conclusive, a water exchange in a seventh coordination site is favored. If the small required T_{1c} for mechanism c could be justified, this analytically identical solution would also account for the data. That the computed K is larger than previously reported is explained by the difference in background salt concentration.

Basic Solution

At pH 9 and room temperature all of the Cr EDTA$^-$ has coordinated with an OH$^-$. Addition of more base does not change the proton spin relaxation rate. (pH > 11.4 was not checked.) The data are displayed in Fig. 8. A conservative approach leaves the data inexplicable. Neither ordinary chemical mechanisms or NMR functional dependences are adequate. For example, the usual explanation for a relaxation rate which first decreases and then increases with respect to increasing temperature is

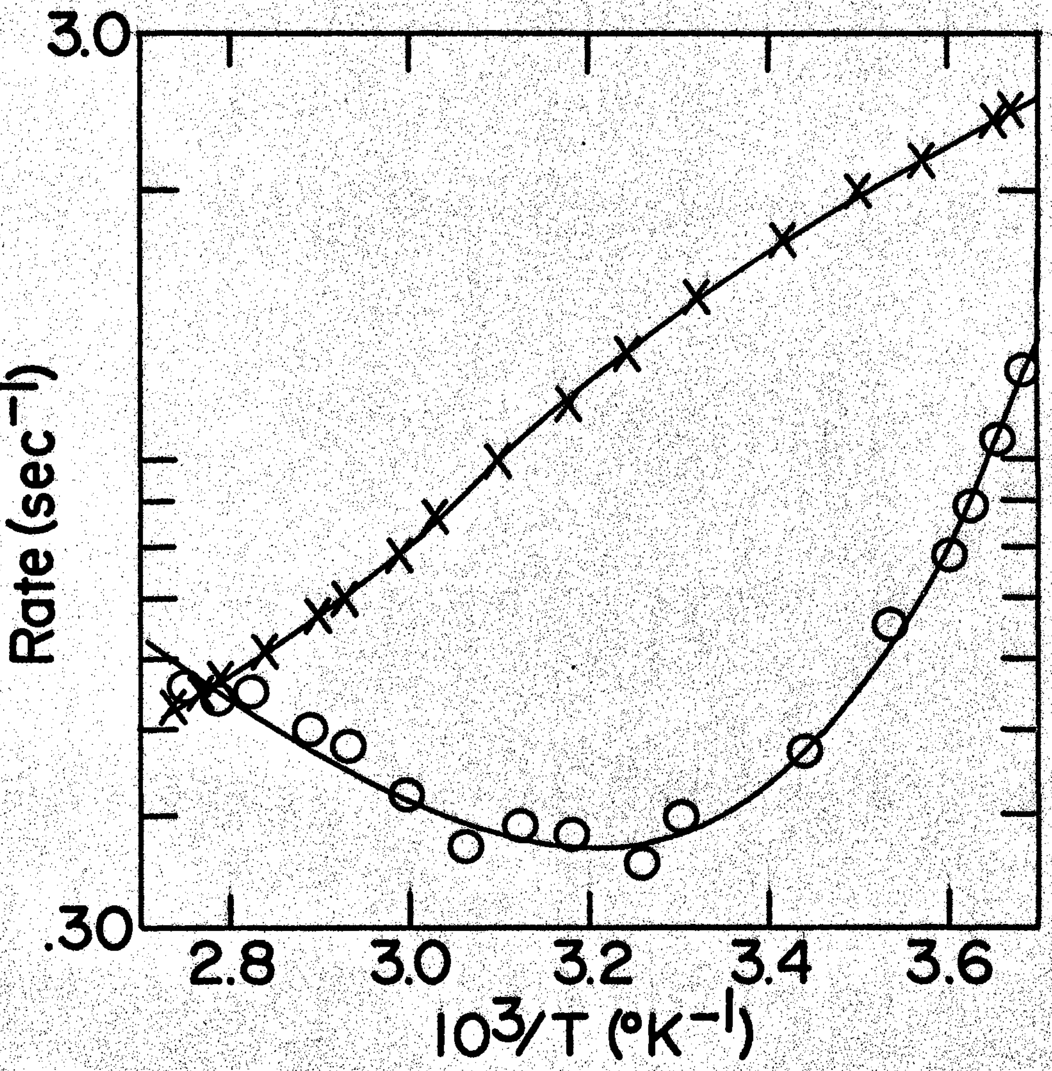

Figure 8. Proton Spin Relaxation Rate vs 1/°K as a Function of [OH^-] Added for $CrEDTA^-$. [$NaC2O_4$] = .3m. [Cr] = 2.23 x 10^{-2}m, [H_2 Na_2 EDTA] = 2.50 x 10^{-2}m. 0,[OH] = 4.45 x 10^{-3} and 9.60 x 10^{-3}m. X, Minimum Rate.

provided by Eq. 2-1. That is

$$\frac{1}{NT_1} = p\ (c\ \tau_c + C'\ \frac{\tau_s}{1 + \omega_2\tau_2{}^2})$$

since

$$\tau_c = \tau_{or}\ e^{-\frac{Vn}{RT}} \quad (\tau e;\ \tau_h > \tau_r)$$

and

$$\tau_s = \tau_{oe}\ e^{-\frac{Ve}{RT}} \quad \begin{array}{l}(\tau_h > \tau e)\\(Ve > 0)\end{array}$$

an explantion is provided.

However, V_r is normally on the order of -4 kilocalories/mole and an increasing τ_s implies a field dependence for the high temperature portion of the curve. A field dependence is not observed[12] and the decreasing portion of the data has an initial slope of approximately -12 kilocalories/mole.

A weak coordination with H_2O and an attack by H_2O are indicated for the low and high temperature portions of the curve respectively. Participation by OH^- seems a remote possibility due to the observed pH independence and a required $k_f > 10^9\ sec^{-1}$ for OH^- interaction.

For the low temperature portion of the data

$$\frac{1}{T_1} = C\ \frac{K}{K+1}\ e^{-\frac{Vr}{RT}} \qquad \text{and}$$

assuming that K + 1 = 1 (small rate, therefore, concentration of coordinated species is small), then

$$\frac{1}{T_1} = CK_o\ e^{-\frac{\Delta H}{RT}}\ e^{-\frac{Vr}{RT}} \quad \text{and} \quad \ln\frac{1}{T_1} = -\ \frac{\Delta H + Vr}{RT} + \ln CK_o$$

For a V_r = 3 kcal, Table VI,

$$\Delta H \approx -9 \text{ kcal/mole}$$
$$K \approx -0.2 \text{ at } 0^{o}C$$

For the high temperature portion of the data and the assuming reaction

$$Cr\ Ac^{-} + H_2O \rightleftharpoons Cr\ OH_2 + Ac^{-}$$

the mechanism can be represented by

$$\frac{1}{T_1} = C \frac{k_1}{k_1 + k_2} \frac{1}{\frac{1}{k_2} + T_{1c}} ; \frac{K}{K+1} = \frac{k_1}{k_1 + k_2}$$

It can be assumed that $k_2 > k$, but no conclusion concerning the value of k_2, except that $k_2 < 10^4$, can be reached. Any calculation of activation energies or equilibrium constant is uncertain. A calculation of activation energy also requires knowledge of the completely coordinated rate. A small molar rate/proton requires activation energies on the order of 18 kcal/mole and a large molar rate/proton yields molar rates of $\approx$2 kcal/mole. The uncertainty is a reflection of the uncertainty surrounding the anamolous proton rates in acidified solutions.

Summary

The aqueous chemistry of Cr OH_2 $EDTA^{-}$ is certainly more involved than reported in the literature. The experimental data presented here provides indirect evidence for more than one weak acetate bond for acidified and high pH solutions. It also appears that the chelated ion exhibits the properties of a seven coordinated structure. Thus, supporting the statement of other investigators[9], "that seven coordinated hexadentate chelates may be more common than previously supposed".

FOOTNOTES

[1] C. E. Manley, MS thesis, Oklahoma State University, 1966 (unpublished).

[2] Marvin J. Udy, Chemistry of Chromium and its Compounds, Rheinholdt Publishing Corp., New York, N. Y., 1956, p. 188.

[3] R. Hausser and F. Noach, Z. Physik. 182, 93 (1964).

[4] F. Dwyer and D. Mellor, Chelating Agents and Metal Chelates, Academic Press, New York, N. Y. (1964), p. 306.

[5] C. Furlani, et al., Z. Ancy. u. allgem. chem. 303, 1 (1960).

[6] T. Swift and R. Connick, J. Chem. Phys. 37, 307 (1962).

[7] G. Schwarzenbach u J. Heller, Heh. Chin. Acta. 65, 576 (1951).

[8] F. Dwyer and F. Garron, J. Am. Chem. Soc. 82, 4823 (1960).

[9] S. Kerschner, Advances in the Chemistry of the Coordination Compounds, The Macmillan Co., New York 1961, p. 296.

[10] T. Bhat and M. Krishnamurthy, J. Inorg. Nucl. Chem. 25, 1147 (1963).

[11] R. Hamm and R. Davis, J. Am. Chem. Soc. 75, 3085 (1953).

[12] If the scalar coupling constant were large, an increasing field dependence could be observed for a small τ_s. For Cr(III) this would imply a 10 fold increase in the scalar coupling constant[6].

CHAPTER VI

SUMMARY AND CONCLUSIONS

By appropriately considering the phenomenology of low field NMR, it has been possible to relate the experimental data to specific ion-solvent interactions. For Iron(III)-EDTA the description was complete enough for calculation of the hydrolysis constants and identification of a diamagnetic dimer. Also an exchanging water molecule was placed in the coordination sphere of the ion. Cr(III)-EDTA experimental results were more complex. More questions were generated than answered. A definitive self-consistent model was not realized. Coordination with at least one water molecule is indicated and proton exchange takes place over a surprising pH range. For both ions a near exact correlation between the Iron and Chromium chelate molar relaxation rates occurs for non proton exchanging species, supporting a supposition that extra first coordination sphere coordination does not take place.

An expected synergistic data response provides suggestions for future work. The relaxation rates of other transition metal-EDTA complexes should exhibit enough common features so that a comprehensive picture could be constructed. Copper (II) would be of special interest. It is assumed to have a quadridentate structure and OH^- bridges between metal ions are formed for a large group of copper compounds.

Variation of the chelating molecule would also provide useful information. The quindentate Hydroxyethlenedinitrilotriaacetate ion is similar enough to EDTA^{-} so that the effect of the last acetate bond could be investigated. On the other end of the scale, the monodentates could also be used to prescribe contents.

A logical goal of a series of chelate-ion investigations would be to investigate the properties of catalytically active and biologically important chelates.

APPENDIX A

FIBONACHI SEARCH, LEAST SQUARES FIT

1. Legend

    N = number of data points

    M = number of parameters

    CL(I) = lower limit of Ith parameter

    CU(I) = upper limit of Ith parameter

    C(I) = starting value of Ith parameter

    K = index value

    NT = number of trials

2. Program

    a. Initialize

```
    NN = 0
    R(1) = 1.
    R(2) = 1.
    DO  21  I = 1, M
    READ (    ) K,C(I), CL(I), CU(I)
    DO  22  J = 2,K
22  R(J+1) = R(J) + R(J-1)
    FB(I) = R(K-1)/R(K+1)
21  L(I) = K-1
    READ (    ) DATA POINTS
```

    b. Output

```
12   WRITE (       ) (C(I), I = 1, M)
```

c. Terminate

```
     1F(NN GT NT) CALL EXIT
```

d. SEARCH

```
     DO   6   I-1,M
     E3 = 1.E+30
     X1 = CL(I)
     X4 = CU(I)
     X = X4-FB(I)*(X4-X1)
     X3 = X4
     J1 = 1
     JF = L(I)
     DO   7   J=1, JF
     E = 0
     C(I) = X
     DO   8   K=1,N
     COMPUTE DATA POINT
     V=DIFFERENCE BETWEEN COMPUTED AND EXPERIMENTAL VALUE
8    E=E + V*V
     DX = X3-X
     1F (E3 .LT. E)  J1=J1 + 2
     GO  TO  (1,2,3,4), J1
1    X4=X3
     X3=X
     E3=E
     X=X1 + DX
     GO  TO  7
```

```
  2    X1=X3
       X3=X
       E3=E
       X=X4 + DX
       GO  TO  7
  3    X1=X
       X=X4 - DX
       J1=2
       GO  TO  7
  4    X4=X
       X=X1 - DX
       J1=1
  7    CONTINUE
  6    C(I)=X
       GO  TO  12
       END
```

3 Comment. A multivariant search is time consuming (machine time) and slow to converge if it arrives at a function ridge. However, it is fast to program and always converges. The fibonachi search is a minimum step search and requires the same number of calculations irregardless of where in the search interval the optimum lies. The accuracy is ± 1/R(K+1).

VITA

3

Claude Edward Manley

Candidate for the Degree of Doctor of Philosophy

Thesis: PROTON SPIN RELAXATION IN Fe(III)-EDTA AND Cr(III)-EDTA AQUEOUS SOLUTION

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Professional Experience: Professional soldier and military engineer, U.S. Army Corps of Engineers 1954-1960 and 1965-1967; Teaching Assistant at Oklahoma State University 1962-1965 and 1966. Staff physicist, Booz-Allen Applied Research Inc., at Kansas City, Missouri, 1968.