Indian Journal of Chemistry
Vol. 14A, June 1976, pp. 413-417

Studies on Some N-Acyl-N-phenylhydroxylamines as Metal Complexing Ligands: Part X — Formation Constants of Fe(III) Complexes of Some N-Hydroxysuccinamic Acids

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Received 15 *April* 1975; *accepted* 21 *August* 1975

The first step formation constants of Fe(III) complexes of some N-hydroxysuccinamic acids, viz. N-phenyl N-hydroxysuccinamic acid (R_pH_2), N-*o*-tolyl N-hydroxysuccinamic acid ($R_t^oH_2$) and N-*m*-tolyl N-hydroxysuccinamic acid ($R_t^mH_2$) have been determined spectrophotometrically. Stabilities are in the ligand order $R_t^oH_2 > R_t^mH_2 > R_pH_2$. The hydrolysis constant *k′* of Fe(III) ion (first step only) has been determined spectrophotometrically and found to be *pk′* = 2·24 at a constant ionic strength ($\mu = 0{\cdot}5$) at 30°±0·5°.

THE hydroxamic acids — N-phenyl-N-hydroxysuccinamic acid (R_pH_2)[1], N-*o*-tolyl-N-hydroxysuccinamic acid ($R_t^oH_2$)[2] and N-*m*-tolyl-N-hydroxysuccinamic acid ($R_t^mH_2$)[3], form brilliant purple-red colour with Fe(III) in aqueous solution. The existence of two different complexes of Fe(III), purple complex (1:1) at $p\text{H} \approx 2$ and the red complex (2:3) at $p\text{H} \approx 3$ with λ_{max} at 470 and 490 nm respectively have been found by Job's method of continuous variation[4]. The formation constants of only 1:1 chelates of Fe(III) with ligand R_pH_2, $R_t^oH_2$ or $R_t^mH_2$ have been determined following Budesinsky's method of proportional absorbance[5].

Theoretical

Determination of equilibrium constant — Let us consider a number of equimolecular solutions of $Fe(ClO_4)_3$ and RH_2 (ligand) at a constant ionic strength having different *p*H values. The reaction between the ligand (RH_2) and the ferric ion may be assumed to take place as

$$Fe^{3+} + RH_2 \rightleftharpoons FeRH_{2-n}^{(3-n)+} + nH^+ \qquad \ldots(1)$$

The equilibrium constant

$$K = \frac{M_1(H^+)^n}{M_0 . R_2} \qquad \ldots(2)$$

and the conditional stability constant Υ for (1:1) complex is given by

$$\Upsilon = \frac{M_1}{(M-M_1)(R-M_1)} \qquad \ldots(3)$$

Considering the first-step hydrolysis of ferric ion as $Fe^{3+} + H_2O \rightleftharpoons [Fe(OH)]^{2+} + H^+$ the hydrolysis constant

$$k' = \frac{M'}{M_0}[H^+] \qquad \ldots(4)$$

For the dissociation of RH_2,

$$RH_2 \rightleftharpoons RH^- + H^+$$
$$RH^- \rightleftharpoons R^{2-} + H^+$$

the dissociation constants

$$k_2^* = \frac{R_1}{R_2}[H^+] \qquad \ldots(5)$$

$$k_1^* k_2^* = \frac{R_0}{R_2}[H^+]^2 \qquad \ldots(6)$$

After attainment of equilibrium at any stage,

$$M = M_0 + M_1 + M' \qquad \ldots(7)$$

$$R = R_0 + R_1 + R_2 + M_1 \qquad \ldots(8)$$

where M and R are initial concentrations of ferric ion and ligand; M_0, M_1, M', R_0, R_1, R_2 are equilibrium concentrations of Fe^{3+}, $[FeRH_{2-n}]^{(3-n)+}$, $[Fe(OH)]^{2+}$, R^{2-}, RH^-, RH_2 respectively.

From Eqs. (4), (5), (6), (7) and (8)

$$M_0 = \frac{M-M_1}{1+k/[H^+]} \qquad \ldots(9)$$

and

$$R_2 = \frac{R-M_1}{1+k_1^*/[H^+]+k_1^*k_2^*/[H^+]^2} \qquad \ldots(10)$$

And from Eqs. (2), (9) and (10)

$$K = \frac{M_1\left(1+\frac{k'}{[H^+]}\right)\left(1+\frac{k_1^*}{[H^+]}+\frac{k_1^*k_2^*}{[H^+]^2}\right)[H^+]^n}{(M-M_1)(R-M_1)}$$
$$= \Upsilon\left(1+\frac{k'}{[H^+]}\right)\left(1+\frac{k_1^*}{[H^+]}+\frac{k_1^*k_2^*}{[H^+]^2}\right)[H^+]^n \qquad \ldots(11)$$

Thus

$$\log \Upsilon + \log\left(1+\frac{k'}{[H^+]}\right) + \log\left(1+\frac{k_1^*}{[H^+]}+\frac{k_1^*k_2^*}{[H^+]^2}\right) = np\text{H} + \log K \qquad \ldots(12)$$

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Plot of $\log \Upsilon + \log\left(1+\frac{k'}{[\mathrm{H}^+]}\right) + \log\left(1+\frac{k_1^*}{[\mathrm{H}^+]}+\frac{k_1^* k_2^*}{[\mathrm{H}^+]^2}\right)$ against pH would be linear. From the intercept log K and from the slope the value n can be found out.

Thus determination of equilibrium constant K requires: (i) determination of conditional stability constant (Υ), (ii) determination of hydrolysis constant of the metal ion, and (iii) knowledge of dissociation constants of the ligands.

Conditional stability constant (Υ) — Let us consider three equimolecular solutions of ferric perchlorate and the ligand (RH_2) at different dilutions having a constant ionic strength and the same pH value. Let $C_M = C_R$, $C'_M = C'_R$ and $C''_M = C''_R$ are the concentrations of the ferric ion and the ligand in the three solutions whose concentrations are related with each other by the relation $C''_M = 0{\cdot}8\, C'_M = 0{\cdot}64\, C_M$. Let C_1, C_2, C_3 are the concentrations of the complex at the three different dilutions whose optical densities are A_1, A_2, A_3 respectively.

Now for the particular pH, the conditional stability constant may be given by Eq. (13)

$$\Upsilon = \frac{C_1}{(C_M - C_1)^2} = \frac{C_2}{(C'_M - C_2)^2} = \frac{C_3}{(C''_M - C_3)^2} \qquad \ldots(13)$$

Again, $\frac{C_1}{C_2} = \frac{A_1}{A_2}$, $\frac{C_1}{C_3} = \frac{A_1}{A_3}$ and $\frac{C_2}{C_3} = \frac{A_2}{A_3}$

$$\text{then } C_2 = \frac{A_2}{A_3}.C_3 \text{ and } C_1 = \frac{A_1}{A_3}.C_3 \qquad \ldots(14)$$

Substituting C_1 and C_2 in Eq. (13)

$$\frac{C_3}{\frac{A_3}{A_1}\left(C_M - \frac{A_1}{A_3}.C_3\right)^2} = \frac{C_3}{\frac{A_3}{A_2}\left(C'_M - \frac{A_2}{A_3}.C_3\right)^2} = \frac{C_3}{(C''_M - C_3)^2} \ldots(15)$$

On solving Eq. (15) three values of C_3 may be obtained:

$$\text{(a) } C_3 = \frac{\left[\sqrt{\frac{A_3}{A_1}} - 0{\cdot}64\right] C_M}{\left[\sqrt{\frac{A_1}{A_3}} - 1\right]} \qquad \ldots(16)$$

$$\text{(b) } C_3 = \frac{\left[\sqrt{\frac{A_3}{A_2}} - 0{\cdot}8\right] C'_M}{\left[\sqrt{\frac{A_2}{A_3}} - 1\right]} \qquad \ldots(17)$$

$$\text{(c) } C_3 = \frac{\left[\sqrt{\frac{A_2}{A_1}} - 0{\cdot}8\right] C_M}{\left[\sqrt{\frac{A_2}{A_1}.\frac{A_1}{A_3}} - \frac{A_2}{A_3}\right]} \qquad \ldots(18)$$

$[\because C''_M = 0{\cdot}8 C'_M = 0{\cdot}64 C_M]$

The average of the three values may be used to calculate Υ from Eq. (13). Similarly determing C_1 and C_2 from Eq. (14), Υ may be calculated.

Hydrolysis of ferric ions (*only first step*) — The first-step hydrolysis constant of ferric ion has been determined following the spectrophotometric method of Irving *et al.*[6].

The observed absorbance (in 1 cm cell)

$$A = \frac{\mathrm{M}(\epsilon_o \mathrm{M}_o + \epsilon' \mathrm{M}')}{\mathrm{M}_o + \mathrm{M}'} \qquad \ldots(19)$$

where ϵ_o, ϵ' are molar absorptivities of Fe^{3+} and $Fe(OH)^{2+}$ respectively.

From Eqs. (4) and (19)

$$\frac{A}{\mathrm{M}} = \frac{\frac{\epsilon_o + \epsilon' k'}{[\mathrm{H}^+]}}{1 + k'/[\mathrm{H}^+]}$$

This may be represented as given in Eq. (20)

$$p\mathrm{H} = \log (A - \mathrm{M}\epsilon_o) - \log (\mathrm{M}\epsilon' - A) + pk' \qquad \ldots(20)$$

Differentiating Eq. (20) with respect to pH

$$\frac{dA}{d\,(p\mathrm{H})} = \frac{2{\cdot}303(A - \mathrm{M}\epsilon_o)(\mathrm{M}\epsilon' - A)}{(\mathrm{M}\epsilon' - \mathrm{M}\epsilon_o)}$$

and

$$\frac{d^2A}{d\,(p\mathrm{H})^2} = \frac{(2{\cdot}303)^2(A - \mathrm{M}\epsilon_o)(\mathrm{M}\epsilon' - A)(\mathrm{M}\epsilon' + \mathrm{M}\epsilon_o - 2A)}{(\mathrm{M}\epsilon' - \mathrm{M}\epsilon_o)^2}$$

At the stationary point of $\frac{dA}{d\,(p\mathrm{H})}$

$$\frac{d^2A}{d\,(p\mathrm{H})^2} = 0$$

A is either $\mathrm{M}\epsilon' = \mathrm{M}\epsilon_o/2$ or $\mathrm{M}\epsilon'$ or $\mathrm{M}\epsilon_o$.

$$\text{Again, } \frac{d^3A}{d\,(p\mathrm{H})^3} = \frac{(2{\cdot}303)^3}{(\mathrm{M}\epsilon' - \mathrm{M}\epsilon_o)^3}[(A - \mathrm{M}\epsilon_o)(\mathrm{M}\epsilon' - A)^2(\mathrm{M}\epsilon' + \mathrm{M}\epsilon - 2A) - (A - \mathrm{M}\epsilon_o)^2 (\mathrm{M}\epsilon' - A)(\mathrm{M}\epsilon' + \mathrm{M}\epsilon_o - 2A) - 2(A - \mathrm{M}\epsilon_o)^2(\mathrm{M}\epsilon' - A)^2]$$

when $A = (\mathrm{M}\epsilon' + \mathrm{M}\epsilon_o)2$, $d^3A/d(p\mathrm{H})^3 = -\mathrm{ve}$, a maximum on the plot of $dA/d(p\mathrm{H})$ against pH is indicated.

Substitution of $A = (\mathrm{M}\epsilon' + \mathrm{M}\epsilon_o)/2$ in Eq. (20), $p\mathrm{H} = pk'$.

Therefore the pH value corresponding to the maximum (where $A = (\mathrm{M}\epsilon' + \mathrm{M}\epsilon_o)/2$ of the curve $dA/d(p\mathrm{H})$ vs pH, gives pk'.

In practice, the ferric perchlorate solution showed no absorption at low pH, thus $\mathrm{M}\epsilon_o$ may be taken as zero.

From Eqs. (4) and (19)

$$\log A\left(1 + \frac{k'}{[\mathrm{H}^+]}\right) = p\mathrm{H} - pk' + \log \mathrm{M}\epsilon \qquad \ldots(21)$$

Thus a plot of $\log A\left(1 + \frac{k'}{[\mathrm{H}^+]}\right)$ against pH should be linear with a slope of unity and the intercept gives $(-pk' + \log \mathrm{M}\epsilon')$. From the experimental value of pk', $\mathrm{M}\epsilon'$ may be calculated. Eq (21) may be arranged as

$$\log A - \log (\mathrm{M}\epsilon' - A) = p\mathrm{H} - pk' \qquad \ldots(22)$$

Using the calculated value of ϵ', pk' may be again found out from the plot of $\log A - \log (\mathrm{M}\epsilon' - A)$ against pH. Thus by the method of successive approximation the refined value of the hydrolysis constant may be found out.

Dissociation constants of the ligands — The acid dissociation constants of the ligands have been determined[7] employing Bjerrum's method[8] with appropriate modifications[9,10]. The formation curves are obtained by plotting $\bar{n}_H$ vs pH and the acid dissociation constants are evaluated by Bjerrum's half-$\bar{n}$ method.

Formation constants of Fe(III) complexes — The formation constant β of the complex $[FeRH_{2-n}]^{3-n+}$ may be evaluated from the relations

$$\beta = \frac{M_1}{[Fe^{3+}][R^{2-}][H^+]^{(2-n)}}$$

$$= \frac{M_1}{M_0R_0[H^+]^{(2-n)}}$$

$$= \frac{M_1[H^+]^2}{M_0R_2(k_2^*)\,(k_1^*)\,[H^+]^{2-n}} \text{[From Eq. (6)]}$$

$$= \frac{M_1[H^+]^n}{M_0 \cdot R_2} \cdot \frac{1}{k_1^*\,k_2^*} = \frac{K}{k_1^*\,k_2^*}$$

Hence $\log\beta = \log K + pk_1^* + pk_2^*$.(23)

Materials and Methods

All the chemicals used were of either AR quality or properly purified. Solutions were made with doubly distilled water. Freshly prepared recrystallized R_pH_2, $R_t^oH_2$ and $R_t^mH_2$ were used. Ferric perchlorate solution was standardized with a standard method. Free acid in this solution was determined by passing the ferric perchlorate solution through cation exchanger, (H-form). Absorbances were measured with a Uvispek spectrophotometer using 1 cm quartz cell against water as blank. *p*H values were adjusted with a Cambridge *p*H-meter (portable type).

Results

Conditional stability constants — A number of equimolecular solutions of ferric perchlorate and the ligand R_pH_2, $R_t^oH_2$ or $R_t^mH_2$ at a constant ionic strength ($\mu = 0{\cdot}5$) having different *p*H values were made up to 25 ml ($7{\cdot}56\times10^{-4}M$). Absorbances of the solutions were measured against water at 480 and 520 nm. 20 ml of each of the solution were diluted with $0{\cdot}5M$ $NaClO_4$ solution to 25 ml ($6.048\times10^{-4}M$) and absorbances of these solutions measured at 480 and 520 nm against water after recording *p*H values. 20 ml of the diluted solutions were further diluted with $0{\cdot}5M$ $NaClO_4$ solution to 25 ml ($4{\cdot}838\times10^{-4}M$), *p*H values and absorbances against water at 480 and 520 nm were measured. Absorbances of the solutions at the three different dilutions containing the ligand R_pH_2, were plotted against corresponding *p*H values (Fig. 1). Similar curves were also plotted with other tow ligands, $R_t^oH_2$ and $R_t^mH_2$. Absorbances at the different dilutions at a particular *p*H were obtained from the curves. Concentrations of the complexes at different dilutions were then calculated using relations (14) and (15). Conditional stability constants were obtained from the relations given in Eq. (13). The average of the three values were taken. Data for the system Fe(III)-R_pH_2 at $\lambda = 520$ nm as a representative one, are given in Table 1.

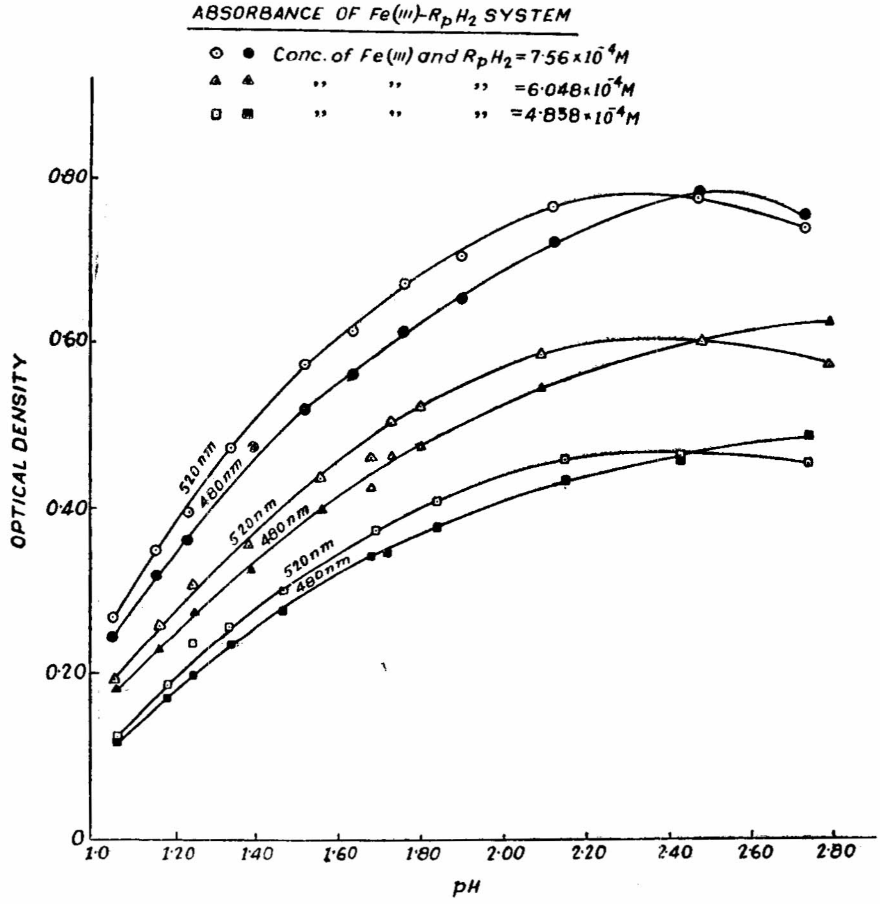

Fig. 1 — Plots of absorbance versus *p*H for Fe(III)-R_pH_2 system

TABLE 1 — CONDITIONAL STABILITY CONSTANTS (log γ) OF Fe(III)-R_pH_2 SYSTEM (1:1) AT $\lambda = 520$ nm

[Cell = 1 cm; $\mu = 0·5$; solvent, water; temp., 30° ± 0·5°]

pH	Absorbance* at			Conc. of (1:1) complex in			log γ (av. val.)
	$4·838\times10^{-4}M$ (A_3)	$6·048\times10^{-4}M$ (A_2)	$7·56\times10^{-4}M$ (A_1)	$4·838\times10^{-4}M$ (Av. val.) ($C_3\times10^4M$)	$6·048\times10^{-4}M$ ($C_2\times10^4M$)	$7·56\times10^{-4}M$ ($C_1\times10^4M$)	
1·20	0·190	0·272	0·378	1·271, 1·111, 1·423, (1·275)	1·825	2·478	3·00, 3·01, 2·98, (3·00)
1·40	0·275	0·375	0·510	1·965, 2·033, 1·903, (1·967)	2·682	3·649	3·38, 3·37, 3·28, (3·38)
1·60	0·345	0·455	0·607	2·642, 2·680, 2·574, (2·632)	3·496	4·634	3·73, 3·73, 3·73, (3·73)
1·80	0·403	0·525	0·685	3·158, 3·260, 3·089, (3·169)	4·129	5·387	4·06, 4·05, 4·06, (4·06)
2·00	0·446	0·570	0·738	3·627, 3·901, 3·385, (3·638)	4·650	6·022	4·40, 4·38, 4·40, (4·40)

*Absorbances evaluated from Fig. 1.

Hydrolysis constant of Fe(III) (only first step) — To determine the hydrolysis by spectrophotometric method[6], first spectral curves at two different pH values were drawn by plotting optical densities against corresponding wevelengths. From the absorption curves wavelengths 370 and 400 nm were chosen for further studies.

Ferric perchlorate $0.0454M$ (1.10 ml) solution was taken in euch of a number of 25 ml flasks, nfter maintaining constant ionic strengths and adjusting to different pH values. Volumes were made up to the mark. The absorbances of the solutions were measured at 370 and 400 nm against water. From the absorbancy data $\Delta A/\Delta(pH)$ were plotted against the mean of the two respective pH values i.e. $\frac{1}{2}(pH'+pH'')$ (Fig. 2).

In the curve the peak at the $pH = 2·22$ corresponding to pk' — the hydrolysis constant of ferric ion for the first step of hydrolysis. By the method of successive approximation using Eqs. (21) and (22) the refined values of ϵ' and pk' were found to be 263 and 2·24 respectively.

Discussion

The formation constants of Fe(III) complexes have been determined following spectrophotometric technique of Budesinsky's proportional absorbance. Results are given in Table 2. Equilibrium constants of the complex formation reactions of the metal ions and the ligand molecules at $\lambda = 520$ nm have been determined by the linear plot method (Fig. 3). Similar linear plots have also been obtained by plotting data obtained at $\lambda = 480$ nm. From the slope of the linear plots the number of protons liberated in the complex formation has been found to be 2. Hence it may be predicted that the first-step complex formation reactions proceeds as

$$Fe^{3+}+RH_2\rightleftharpoons(FeR)^{+}+2H^{+}$$

The stabilities of the Fe(III) chelates are in the ligand order $R_t^oH_2>R_t^mH_2>R_pH_2$. The trends, the more basic are the ligands the more stable are their chelates, have been observed in many cases[11,12].

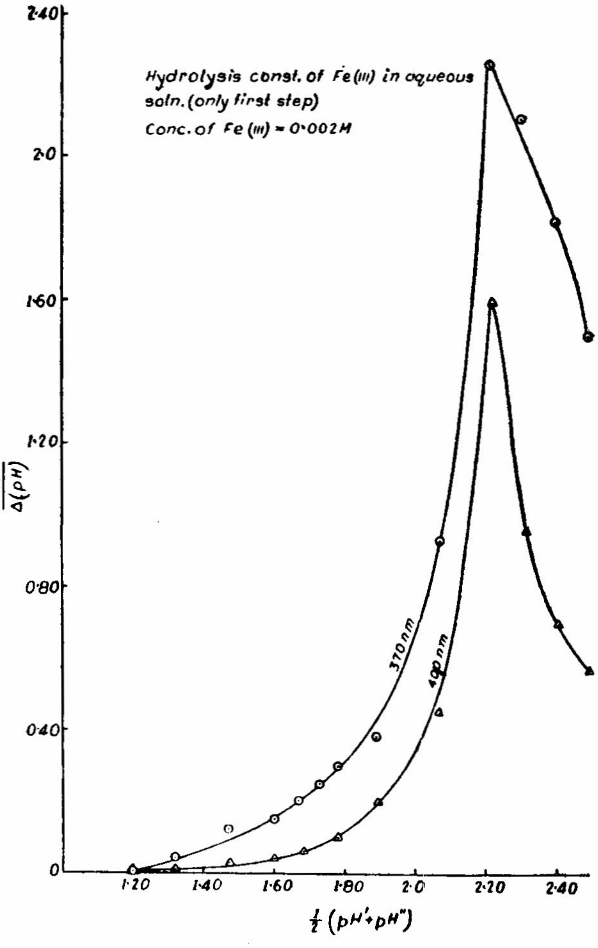

Fig. 2 — Plots of $\Delta A/\Delta(pH)$ versus $\frac{1}{2}(pH'+pH'')$ for evaluating hydrolysis constant (first step) of Fe(III) solution

The ligands $R_t^mH_2$ and R_pH_2 follow the trends but $R_t^oH_2$ showed anomalous behaviour.

The first step hydrolysis constant of Fe(III) has also been determined in $3M$ $NaClO_4$ solution[13,14]. These values along with that reported in this paper are given in Table 3. Although values are in the

TABLE 2 — EQUILIBRIUM CONSTANTS AND FORMATION CONSTANTS OF (1: 1) Fe(III) COMPLEXES

[λ = 520 and 480 nm; temp. 30 ± 0·5°C; pk' = 2·24]

Ligand	pH	log γ at		2nd R.H. term in Eq. (12) from Fig. 3	No. of protons (n) liberated	log K at		log β = log $K+pk_1^*+pk_2^*$
		520 nm	480 nm			520 nm	480 nm	
$R_t^oH_2$	1·20	3·59	3·58	0·04	2	1·22	1·22	(1·22+4·32+8·56) = 14·10
	1·40	3·96	3·97	0·06				
	1·60	4·33	4·33	0·09				
	1·80	4·66	4·66	0·13				
	2·00	5·05	5·05	0·20				
R_pH_2	1·20	3·00	2·98	0·04	2	0·62	0·62	(0·62+4·32+8·64) = 13·58
	1·40	3·38	3·36	0·06				
	1·60	3·73	3·73	0·09				
	1·80	4·06	4·06	0·13				
	2·00	4·40	4·40	0·20				
$R_t^mH_2$	1·20	2·92	2·93	0·04	2	0·55	0·56	(0·55+4·32+8·80) = 13·67
	1·40	3·29	3·30	0·06				
	1·60	3·66	3·67	0·09				
	1·80	4·02	4·02	0·13				
	2·00	4·37	4·35	0·20				

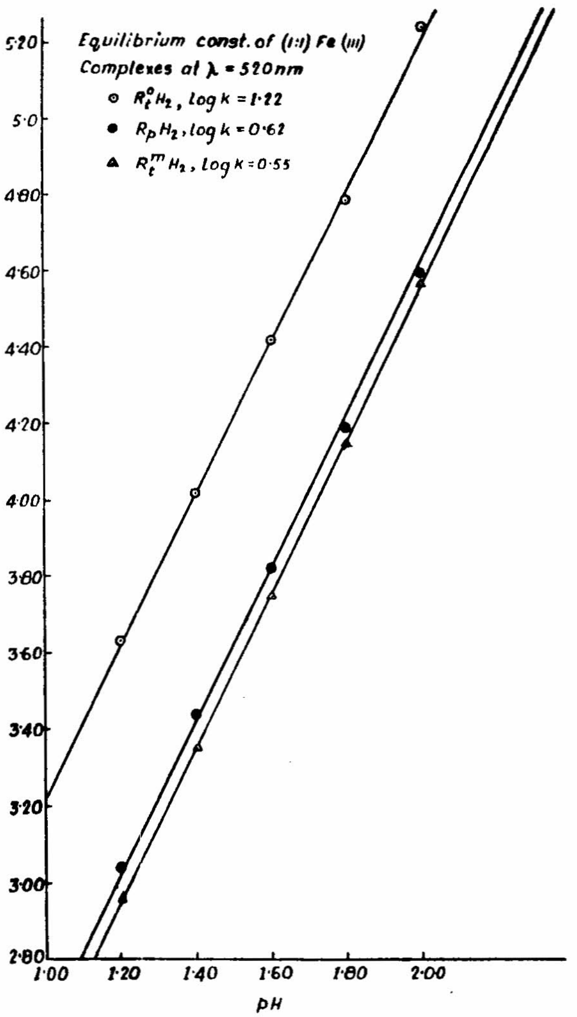

Fig. 3 — Plots of [log γ + log (1 + k'/[H$^+$]) + log (1 + k_1^*/[H$^+$] + $k_1^* k_2^*$/[H$^+$]^2)] versus pH at λ = 520 nm

TABLE 3 — FIRST-STEP HYDROLYSIS CONSTANT (k') OF Fe(III)

Temp. °C	Ionic strength (M) (NaClO$_4$)	pk'	Ref.
25	3·0	3·00	13
35	3·0	2·73	13
25	3·0	3·05	14
30	0·5	2·24	—

same order, but not in good agreement which may be due to appreciable differences in NaClO$_4$ concentrations[15].

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