Iron(III) Acetate Complexes in Aqueous 3 M (Na⁺)ClO₄⁻ Medium

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The equilibria of iron(III) and acetate ions in aqueous 3 M $(Na^+)ClO_4^-$ have been investigated at 25°C by potentiometric methods, using glass and redox (Fe^{2+}, Fe^{3+}) electrodes. The experimental data have been examined, first by a graphical approach and then using the generalized least squares program LETAGROP. The results agreed satisfactorily. The emf data may be explained by assuming the formation of FeA^{2+}, FeA_2^{2+}, $Fe_3(OH)_2A_6^+$, $Fe_3(OH)_3A_2^{4+}$, and $Fe_7(OH)_9A_6^{6+}$, with the equilibrium constants given in Table 3. Since all possible formulas were not tested systematically the last formula should be understood only as an indication of complexes with more than 3 Fe.
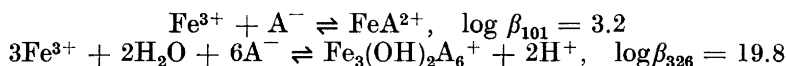
Symbols

a = $[A^-]$, concentration of free acetate ions

A = total concentration of acetate in A^-, HA, or complexes

b = $[Fe^{3+}]$, concentration of free iron(III) ion

B = total Fe(III) concentration

$F_{ps} = \sum_r K_{psr} H^r$ (13b)

h = $[H^+]$ at equilibrium

H = analytical excess of hydrogen ions, counting H_2O, Fe^{3+}, Fe^{2+}, and A^- as zero level.

K = equilibrium constant for $Fe^{2+} + A^- \rightleftharpoons FeA^+$

K_H = equilibrium constant for $H^+ + A^- \rightleftharpoons HA$

K_{psr} = equilibrium constant for $pFe^3{}^+ + rHA \rightleftharpoons Fe_pH_{-s}(HA)_r^{(3p-s)+} + sH^+$

p,q,r = coefficients in formula of complex

$s = q + r$ (5)

β_{pqr} = equilibrium constant for

$pFe^{3+} + qH_2O + rA^- \rightleftharpoons Fe_p(OH)_qA_r^{(3p-q-r)+} + qH^+$

$\eta = \log(B/b)$

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* The experimental work and the preliminary graphical treatment were carried out by L. C. and G. N. in Napoli, the computer adjustment by G. N. and L. G. S. in Stockholm.

Acetate complexes of iron(III) in aqueous solution have been the subject of several investigations. In 1930 Treadwell and Fisch,[2] titrating Fe(III) chloride solutions containing some Fe(II) with sodium acetate, observed a sharp drop of the potential of redox electrodes when 8/3 acetate ions per Fe(III) had been added. From the amount of acetic acid that had formed at this end-point and could be extracted with diethyl ether, thay concluded that the complex ion $Fe_3(OH)_2A_6{}^+$ is formed. However, we may note that any species of the general formula $(Fe_3(OH)_2A_6)_n{}^{n+}$ would have given the same results.

Brintzinger and Jahn [3] by the dialysis method determined the molecular weight of the iron(III) acetate complex at the endpoint and concluded that it contains three Fe(III) and thus is $Fe_3(OH)_2A_6{}^+$.

Perrin [4] measured the equilibrium concentrations of H^+ and Fe^{3+} in solutions of various B, H, and A, at 25°C and unit ionic strength, using glass and redox electrodes. His data, for log B ranging from -1.3 to -4.3, log a from -1.53 to -4.16 and log h from -1.73 to -3.24, were explained by assuming the following equilibria:

$$Fe^{3+} + A^- \rightleftharpoons FeA^{2+}, \quad \log \beta_{101} = 3.2$$
$$3Fe^{3+} + 2H_2O + 6A^- \rightleftharpoons Fe_3(OH)_2A_6{}^+ + 2H^+, \quad \log \beta_{326} = 19.8$$

Sommer and Pliška [5] made spectrophotometric measurements at 0.1 ionic strength (temperature not stated). Assuming that in their dilute solutions ($B \approx 10^{-4}$M) the predominating species are mononuclear in Fe(III), they estimated the values log $\beta_{101} = 3.2$, log $\beta_{102} = 6.5$, and log $\beta_{103} = 8.3$.

METHOD OF MEASUREMENT

The free concentrations (=activities) $b = [Fe^{3+}]$ and $h = [H^+]$ were determined by emf methods in a series of perchlorate solutions of various total (analytical) concentrations of H^+ (H), iron(III) (B) and acetate (A). The measurements were carried out at 25°C as potentiometric titrations. In each titration, B and H were kept constant while A was gradually increased.

In order to minimize the variation of activity coefficients, all the solutions studied were made to contain 3 M $ClO_4{}^-$ by adding $NaClO_4$, and hence had the general composition

Solution S $= B$ M Fe(III), M M Fe(II), H M H^+, A M A^-, $(3-3B-2M-H+A)$M Na^+, 3 M $ClO_4{}^-$

Iron(II) was added to enable us to measure b with the redox electrode. M was either kept constant ("set I") or varied ("set II") during each run.

In our solutions, b and h were measured by means of cells

$$-RE \mid \text{solution S} \mid Au + \qquad\qquad (B)$$

$$-RE \mid \text{solution S} \mid GE + \qquad\qquad (H)$$
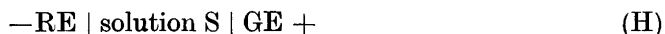
where GE is a glass electrode and RE is the reference half cell

$$RE = Ag,AgCl \mid 0.01 \text{ M } Cl^-, 2.99 \text{ M } ClO_4{}^-, 3 \text{ M } Na^+ \mid 3 \text{ M } NaClO_4$$
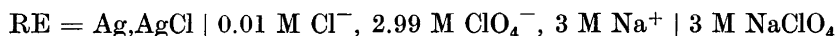
Assuming that we may set activities (on the medium scale)=molar concentrations,[6] the emf's of cells (B) and (H) at 25°C can be written, in mV units

$$E_B = E_B^\circ + 59.15 \log b - 59.15 \log [Fe^{2+}] + E_{jB} \tag{1}$$

$$E_H = E_H^\circ + 59.15 \log h + E_{jH} \tag{2}$$

Here E_B° and E_H° are constants, E_{jB} is the liquid junction potential between solution S and 3 M $NaClO_4$, and E_{jH} includes any deviations of the glass electrode from ideal behavior.

The concentration of free Fe^{2+} was calculated from the relationship

$$[Fe^{2+}] = M(1 + Ka)^{-1} \tag{3}$$

using values of a estimated from (7), and taking for log K, the equilibrium constant of $Fe^{2+} + A^- \rightleftharpoons FeA^+$, the value 0.54 ± 0.05 estimated in a separate study.[7] The hydrolysis of the Fe^{2+} ion [8] can be safely neglected in the acidity range investigated, log $h > -4.4$.

E_j was at first estimated with the equation $E_j = -17\,h$ mV, as determined by Biedermann and Sillén.[6]

Each series of experiments, with B and H constant, consists of two parts. In the first, emf is determined in the absence of acetate ions and at high acidities, $H \geq 0.025$ M, where $[Fe^{2+}] = M$, and b and h can be obtained from B and H after a small correction for the hydrolysis of the Fe^{3+} ion;[9,10] E_B° and E_H° can then be calculated from (1) and (2). In the second part, NaA is added, and complex formation sets in. Since E_H° is known, h can be calculated from (2) and then a from (7), $[Fe^{2+}]$ from (3), and finally b from (1).

Choice of the B and H ranges

Exploratory experiments indicated that η is a function of all of B, h^{-1} and a, so that one or more complexes of the most general formula are probably formed; it will prove convenient to write the general formula for the species in alternative ways, either more traditionally as

$$Fe_p(OH)_q A_r^{(3p-q-r)+} = Fe_p H_{-q} A_r^{(3p-q-r)+} \tag{4a}$$

or as

$$Fe_p H_{-s}(HA)_r^{(3p-s)+} \tag{4b}$$

where

$$s = q + r \tag{5}$$

In addition the species may, as usual, contain water molecules and ions of the medium, which, however, do not appear in the equilibrium conditions.

We shall usually denote the species by (pqr) or (psr). When (psr) is meant, we give a subscript s, hence e.g.

$$(326) = (38_s 6), \quad (101) = (11_s 1)$$

The equilibrium condition may then be written in two ways

$$p Fe^{3+} + q H_2O + r A^- \rightleftharpoons Fe_p(OH)_q A_r^{(3p-q-r)+} + q H^+$$
$$[\text{complex}] = \beta_{pqr} b^p h^{-q} a^r \tag{6a}$$

$$pFe^{3+} + rHA \rightleftharpoons Fe_pH_{-s}(HA)_r^{(3p-s)+} + sH^+$$
$$[\text{complex}] = K_{psr}b^p h^{-s}c^r \tag{6b}$$
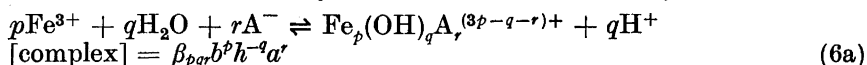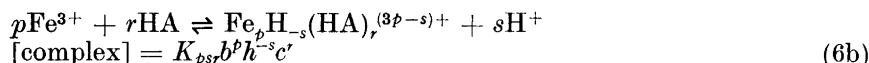
If K_H is the equilibrium constant for $H^+ + A^- \rightleftharpoons HA$ then

$$c = [\text{HA}] = K_H ha, \text{ or } a = cK_H^{-1}h^{-1} \tag{7}$$

From (6a), (6b), and (7) we see that

$$\beta_{pqr} = K_{psr}K_H^r \tag{8}$$

Assuming that we may neglect all other species than those mentioned, the total (analytical) concentrations of Fe(III), H^+, and A^- are given by (H always counted as excess over Fe^{3+}, A^-, and H_2O):

$$B = b + \sum p\beta_{pqr}b^p h^{-q}a^r = b + \sum pK_{psr}b^p h^{-s}c^r \tag{9a,b}$$

$$H = h + K_H ha - \sum q\beta_{pqr}b^p h^{-q}a^r = h + c - \sum(s-r)K_{psr}b^p h^{-s}c^r \tag{10a,b}$$

$$A = a + K_H ha + \sum r\beta_{pqr}b^p h^{-q}a^r = cK_H^{-1}h^{-1} + c + \sum rK_{psr}b^p h^{-s}c^r \tag{11a,b}$$

The sums are taken over all species (pqr) or (psr). Hydrolytic Fe(III) species without acetate will have coefficients ($pq0$) or ($ps0$).

The data give sets of four variables, say ($B/b,h,b,A$), or ($B/b,h,b,a$), since the free concentration of A^- can, in principle, be obtained by integration methods.[11] The data hence correspond to a curved surface in four-dimensional space. In order to deduce the formulas of the dominating species one would like to reduce the problem to one of three variables, which might conveniently be attacked by approaches proposed by Sillén.[12]

If all complexes were mononuclear in Fe^{3+}, then η (h,a) would be independent of b. If all complexes were mononuclear in H^+, then H h^{-1} (b,a) would be independent of h. In either case, one could reduce the data by a simple transformation. However, neither condition proved to be fulfilled.

On the other hand we could reduce the number of variables by working at constant H levels with $A > H \gg B$. Under these conditions, $H \gg h$ and

$$H \approx c = [\text{HA}] \tag{12}$$

Introducing (12) into (9b) we find

$$\eta = \log(B/b) = \log\ (1 + \sum pK_{psr}b^{p-1}h^{-s}H^r) \tag{13}$$

or $\qquad\qquad \eta = \log(1 + \sum pF_{ps}b^{p-1}h^{-s}) \tag{13a}$

where $\qquad\qquad F_{ps} = \sum K_{psr}H^r \tag{13b}$

Hence, as far as the approximation (12) holds, and H is kept constant, η in (13a) should be a function of b and h only.

From measurements at a single value of H one may deduce the most important values of p and s, using (13a), and the corresponding F_{ps}. From the variation of F_{ps} with H we may then deduce the important r values, using (13b).

This is the approach we decided to use in the present study. The values of H ranged from 0.025 to 0.15 M. For each H, values of B up to 0.04 H were investigated. The available range of B is limited by the decreasing accuracy

at the lowest values, and by the deviations from the condition $B \ll H$ at the highest values for B.

Alternatively we might have made experiments at constant A levels, with $H > A \gg B$ so that $c \approx [HA] \approx A$ and $h \approx H - c$. We would then have had, from (9b), $\eta = \log(1 + \sum p K_{psr} A' b^p h^{-s})$, which is a function of b and h only, at a constant A. Again the data could have been analysed to give the formulas of the dominant species and their formation constants.

EXPERIMENTAL

Reagents and analyses. Iron(III) perchlorate stock solutions were prepared from $Fe(NO_3)_3(H_2O)_9$ Merck *p.a.*, which was purified by double crystallization from 1:1 HNO_3. This preparation was added to a large excess of 70 % $HClO_4$, and HNO_3 and a large part of the excess $HClO_4$ were expelled by heating with an infrared lamp. In the final product, no NO_3^-, Cl^-, or SO_4^{2-} could be detected.

In the stock solutions, $B = [Fe(III)]_{tot}$ was determined iodometrically by Mohr's method,[13] and by reduction of $Fe(III)$ to $Fe(II)$ by hydrogen gas in presence of platinum black and subsequent titration with standard $KMnO_4$. The results obtained by these methods agreed within ± 0.1 %.

The hydrogen ion excess in the $Fe(III)$ perchlorate stock solutions was determined as follows. Through a portion of stock solution hydrogen gas was bubbled in the presence of platinum black until all $Fe(III)$ has been converted into $Fe(II)$. The hydrogen ion concentration of the solution, which was equal to $[ClO_4^-] - 2B$, was determined by potentiometric titration with standard $NaOH$ using a glass electrode, and the end-point was established by Gran's method.[14] Since $Fe(II)$ ion does not hydrolyse [8] appreciably at $\log h > -5$, linear plots could be obtained from which the end-point was calculated by linear extrapolation. The excess of hydrogen ions in the original stock solution was equal to $[ClO_4^-] - 3B$.

Iron(II) perchlorate solutions were obtained by reduction of $Fe(III)$ perchlorate with hydrogen gas in the presence of platinum black: $Fe^{3+} + \frac{1}{2}H_2 \xrightarrow{Pt} Fe^{2+} + H^+$ as described elsewhere.[15] By this procedure one avoids the preservation and manipulation of $Fe(II)$ solutions, which are easily oxidized by air.

Sodium acetate stock solutions were made from C. Erba $NaOCOCH_3(H_2O)_3$, which was crystallized twice from water. $A = [CH_3CO_2^-]_{tot}$ was determined using an ion exchange resin. As a check, known portions of stock solution were treated repeatedly with hot concentrated HCl, and the solid then ignited at 360°C and weighed as $NaCl$. The results agreed within ± 0.2 %.

Sodium perchlorate and perchloric acid stock solutions were prepared and analysed as described previously.[15]

Experimental details of the emf measurements. All emf measurements were made at $25.00 \pm 0.05°C$. The cell arrangement was similar to that described by Forsling, Hietanen and Sillén.[16] The emf's of cell (B) were measured with a Leeds and Northrup potentiometer type K3. The emf's of cell (H) were measured with a valve potentiometer Radiometer PHM4, which was calibrated against the Leeds and Northrup potentiometer.

The Ag,AgCl electrodes were prepared according to Brown.[17]

Glass electrodes, Beckman type 40498 were employed. They gave constant and reproducible potentials within ± 0.2 mV. Two or three bright gold foils were used for redox electrodes. Their potentials were constant to within ± 0.05 mV or better, $10-15$ min after each addition of reagents. Pt electrodes were somewhat slower to attain equilibrium.

A vigorous stream of nitrogen gas was passed through the solutions during the measurements. Nitrogen from a cylinder was purified by passing it through activated copper, 10 % H_2SO_4, 10 % $NaOH$, and water, after which it was finally presaturated with a solution containing 3 M ClO_4^- and having the same H and A values as solution S in the cell.

Table 1. Composition of solutions in "series I". The experiment started with 25 ml of solution S_0 (H_0 mM H^+), to which V_T (0—25) ml of T_1 (H_0 mM H^+, B_1 mM Fe^{3+}, M_1 mM Fe^{2+}) was added. After that, V_T (0—25) ml was added of each of T_1 and T_2 (H_2 mM H^+, C_2 mM HA). At the end of titrations 8 and 9, a second T_2 was added ($H_2' = -200$, $C_2' = 350$).

Titration	H_0 mM	B_1 mM	M_1 mM	H_2 mM	C_2 mM
1	25	0.125	0.125	−100	125
2	25	0.25	0.25	−100	125
3	25	1.0	1.0	−100	125
4	50	0.25	0.25	−200	250
5	50	0.125	0.125	−200	250
6	100	2.0	1.0	−400	500
7	100	4.0	1.0	−400	500
8	150	0.125	0.125	−600	750
9	150	0.25	0.25	−600	750
10	150	8.0	8.0	−600	750
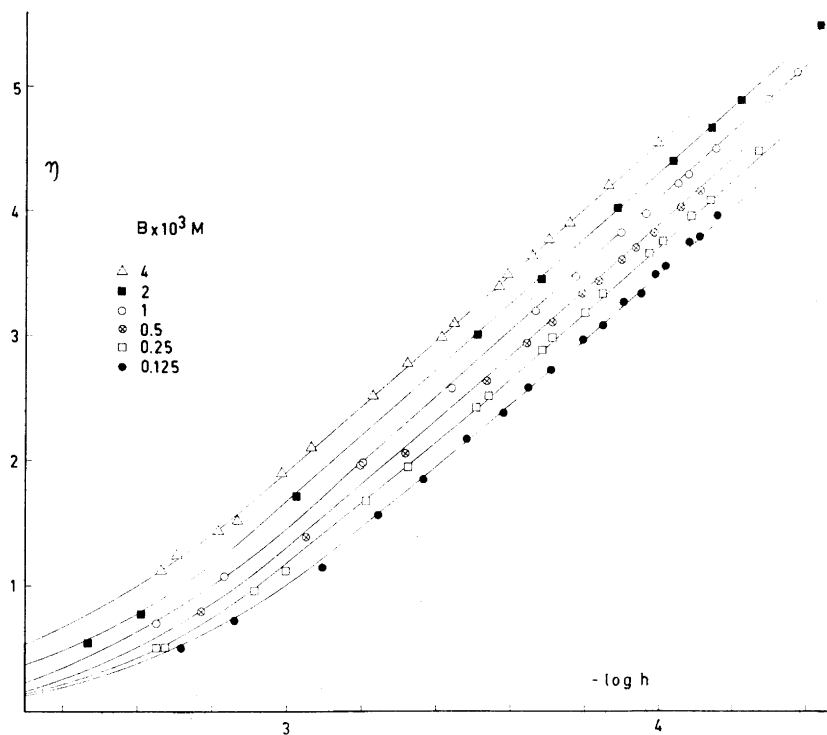
Fig. 1. Data at $H = 0.1$ M. $\eta = \log([Fe(III)]/[Fe^{3+}])$ as a function of $\log h$. Curves calculated assuming the equilibrium constants given in Table 3 as well as the hydrolytic reactions eqn. (18).

PRELIMINARY TREATMENT OF DATA AND RESULTS

Table 1 gives the composition of the solutions used in the ten titrations of "set I" and Table 2 gives those primary data used in the computer treatment, and also some derived quantities, and deviations from the calculated values, with the final model chosen (see the text to Table 2). Fig. 1 and Fig. 2 show the families of data $\eta(\log h)_B$ for $H=0.1$ and 0.025.

The experimental data were treated as follows. First the most important sets (p,s) and the values for F_{ps} (eqn. 13b) were deduced by applying graphical
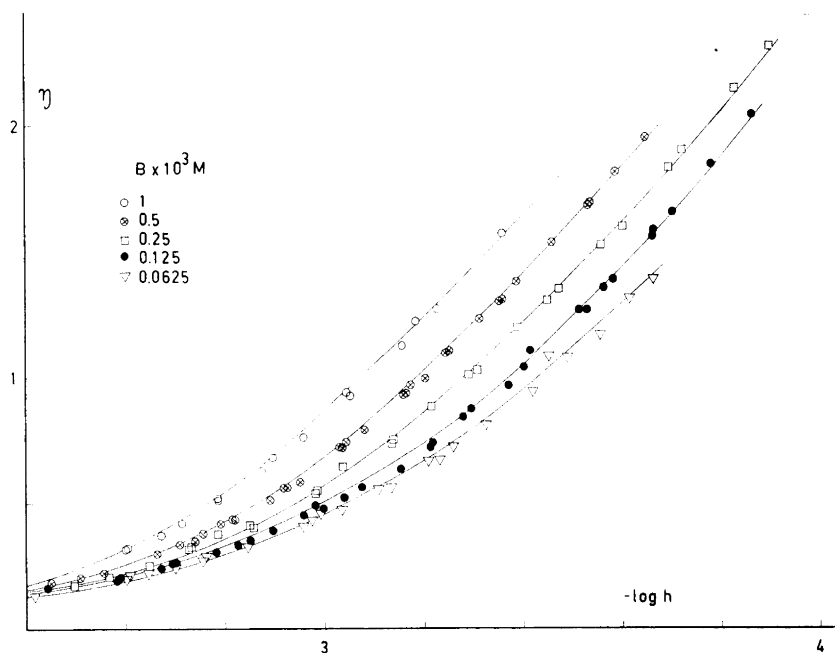
Fig. 2. Data at $H=0.025$ M. $\eta=\log\ ([Fe(III)]/[Fe^{3+}])$ as a function of $\log h$. Curves calculated as in Fig. 1.

methods outlined by Sillén.[18],[19] Then probable values of r and preliminary values of K_{psr} were found from the variation of F_{ps} with H, using (13b).

All these conclusions were based on the hypothesis that (12) is a good approximation. The data were finally treated—without this approximation—by the generalized least squares program LETAGROP.[1] By this approach the existence of some minor species was tested, and the values of the equilibrium constants were refined.

For the calculations we needed the value for $\log K_H$, which was determined by separate acid-base titrations in the medium 3 M $(Na)ClO_4$ using a glass electrode. We found

$$\log K_{\mathrm{H}} = 5.017 \pm 0.010 \tag{14}$$

Range $\eta > 2$. As seen from Fig. 1 the curves η (log $h)_B$ for $H = 0.1$ and $\eta > 2$ are nearly parallel, with a spacing $(\partial \log B/\partial \log h)_\eta = 4$ which indicates species of the "core+links" formula $\mathrm{Fe(FeH_{-4}(HA)_z)_n}$. Similar conclusions could be drawn from the data at $H = 0.05$ and 0.15 M, whereas no constant spacing was observed for $H = 0.025$; the data for the low H will hence not be considered in this section.

Comparison of the graphs $\eta(\log Bh^{-4})_H$ with families of curves representing various reaction mechanisms gave satisfactory agreement with curves calculated assuming a single complex ("hypothesis II" in Ref. 19) with $n = 2$, which would correspond to $\mathrm{Fe(FeH_{-4}(HA)_r)_2}$. From the positions in the best fit, the following values for log F_{33} were calculated

H M	0.150	0.100	0.050	
log F_{38}	-13.1 ± 0.1	-14.15 ± 0.1	-15.9 ± 0.1	(15)

A plot of log F_{38} *versus* log H may be well approximated by a straight line of slope 6, indicating (see eqn. 13b) $r = 6$, hence the formula $\mathrm{Fe_3H_{-8}(HA)_6}^+$ or $\mathrm{Fe_3(OH)_2A_6}^+$. For its formation constant we estimated the approximate value

$$\log K_{386} = -8.1 \pm 0.2 \tag{15a}$$

Range $\eta > 2$. In the preliminary treatment of the data in the range $\eta < 2$ we calculated the quantities

$$B' = B - 3[\mathrm{Fe_3(OH)_2A_6}^+] - [\mathrm{FeOH^{2+}}] - [\mathrm{Fe(OH)_2}^+] - 2[\mathrm{Fe_2(OH)_2}^{4+}] - \\ [3\ \mathrm{Fe_3(OH)_4}^{5+}] \tag{16}$$

and

$$\eta' = \log(B'/b) \tag{17}$$

We assumed the value for K_{386} deduced above and the equilibrium constants of Biedermann (quoted in Ref. 10) valid in 3 M $(\mathrm{Na}^+)\mathrm{ClO_4}^-$ at 25°C:

$$
\begin{array}{lll}
\mathrm{Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+} & \log K_{110} = -3.05 \pm 0.05 & \\
\mathrm{Fe^{3+} + 2H_2O \rightleftharpoons Fe(OH)_2^+ + 2H^+} & \log K_{120} = -6.31 \pm 0.10 & (18) \\
\mathrm{2Fe^{3+} + 2H_2O \rightleftharpoons Fe_2(OH)_2^{4+} + 2H^+} & \log K_{220} = -2.96 \pm 0.01 & \\
\mathrm{3Fe^{3+} + 4H_2O \rightleftharpoons Fe_3(OH)_4^{5+} + 4H^+} & \log K_{340} = -5.77 \pm 0.05 &
\end{array}
$$
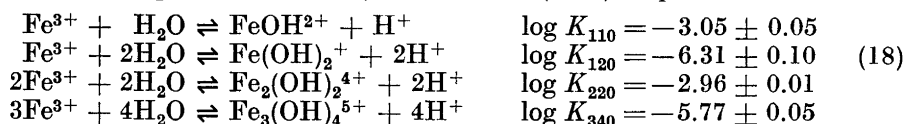
When $\eta'(\log h)_{B'}$ was plotted for $H = 0.15$ M, the points obtained with $B \leq 0.00025$ M fell on a single curve within the limits of experimental error, indicating the predominance of species mononuclear in Fe. With increasing B, and decreasing H, η' was found to become a function of both h and B, indicating that also other polynuclear products become important than those eliminated in (16).

It is seen from Fig. 3 that the points $\eta'(\log a)$ for $H = 0.15$ and $B \leq 0.00025$, those for $H = 0.05$ and $B \leq 0.000125$ all fall on a single curve, independent of H, which indicates species with the formula FeA_r, or $\mathrm{FeH_{-r}(HA)_r}$. Since the data in Fig. 3 could be fitted with the normalised curve [20]

$$y = \log(1 + lw + w^2) \tag{19}$$
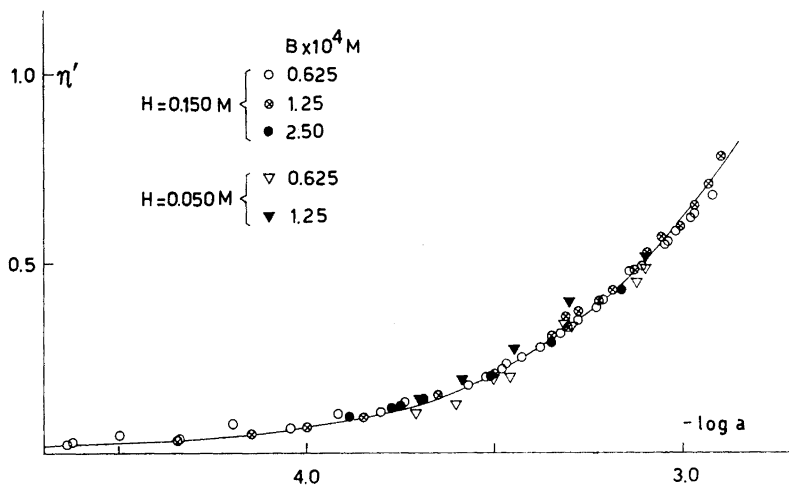
Fig. 3. Determination of mononuclear species. η' (eqn. (17)) as a function of log a. Curves calculated with log $\beta_{101}=3.20$ and log $\beta_{102}=6.22$.

it was concluded that FeA^{2+} and FeA_2^+ exist, and using the relationship

$$w_2 = \beta_{102}a^2, \qquad l^2 = \beta_{101}{}^2\beta_{102}{}^{-1} \qquad (19a)$$

we estimated the formation constants

$$\log \beta_{101} = 3.1 \pm 0.2, \qquad \log \beta_{102} = 6.3 \pm 0.2$$

These values of β_{101} and β_{102} were used to subtract the species and calculate the "corrected" functions

$$B_c = B' - [FeA^{2+}] - [FeA_2^+] = b + \sum p'[Fe_{p'}(OH)_{q'}A_{r'}] \qquad (20)$$

$$\eta_c = \log(B_c/b) \qquad (21)$$

which formed the basis for our calculations to estimate the remaining sets $(p'q'r')$.

The points η_c (log $B_c - t$ log h) were found to form a single curve for $t = 2.5$ (Fig. 4) which indicates complexes close to the "core+links" formula $Fe(Fe_2H_{-5}(HA)_x)_n$. To get some information concerning the prevailing values of n, "direct analysis" was applied to the curves $\eta_c(B_c{}^2h^{-5})$. With the notation $u = b^2h^{-5}$ the function

$$g(u) = \sum F_{2n+1,5n}u^n \qquad (22)$$

was calculated from

$$1 + g = \frac{1}{u} \int_0^u \frac{B_c}{b} \, du \qquad (23)$$

This is eqn. (16) in Ref. 19. The results are shown in Fig. 5 for the data at $H = 0.025$ M. The average value of n, $\bar{n} = $ d log $g/$d log u, was found to
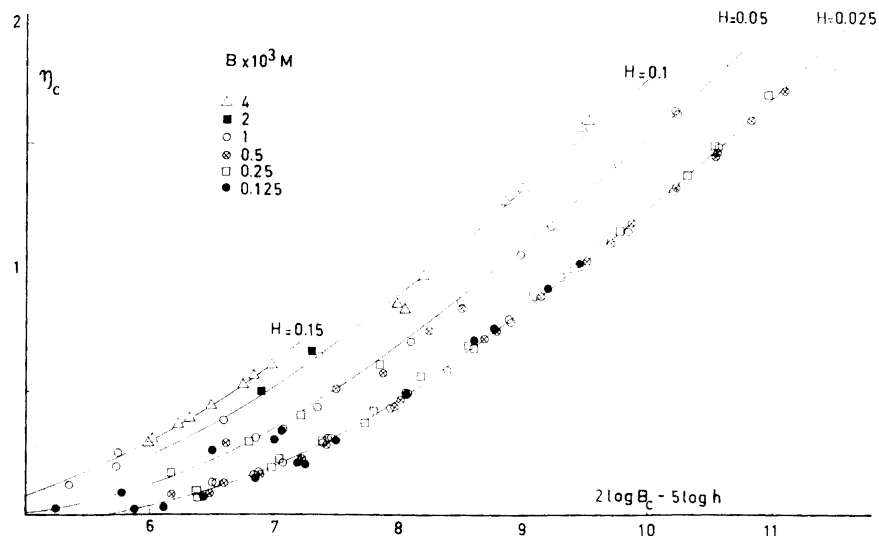
Fig. 4. η_c (eqn. (21)) as a function of log $B_c{}^2h^{-5}$. Curves calculated with the equilibrium constants of Table 3.
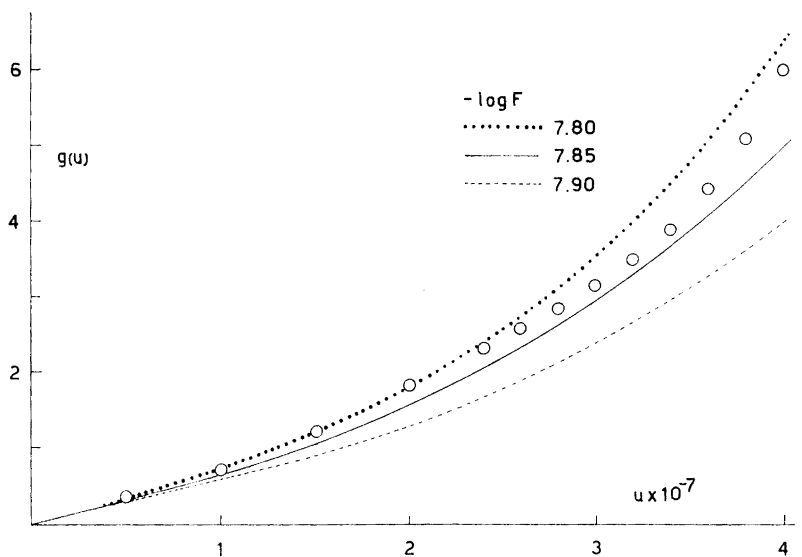
Fig. 5. Direct analysis of the $\eta_c(B_c{}^2h^{-5})$ curves for data at $H = 0.025$ M. $g(u)$ as a function of u. Curves calculated with "hypothesis IIIa", log $F_0 = 0.6$ and log $F = -7.80$, -7.85 and -7.90.

start at 1 and to increase continuously with u, finally attaining values higher than 2. This indicates that complexes with $n > 2$ may exist at the highest u values.

A reasonable agreement between experimental data and curves calculated with different models was obtained with "mechanism IIIa" which implies that the value of n is unlimited and that the formation constant of any complex $Fe(Fe_2H_{-5}(HA)_x)_n$ is given (cf. eqn. 13b) by $F_{2n+1,5n} = F_0 F^n$ where F_0 and F are constant at a given H. The following values for the parameters F_0 and F were estimated

$$
\begin{array}{lllll}
H\ M & 0.025 & 0.050 & 0.100 & 0.150 \\
\log F_0 & 0.6 \pm 0.1 & 0.6 \pm 0.1 & 0.5 \pm 0.1 & 0.5 \pm 0.2 \quad (24) \\
\log F & -7.85 \pm 0.05 & -7.2 \pm 0.1 & -6.5 \pm 0.1 & -6.2 \pm 0.2
\end{array}
$$

The plot of $\log F$ against $\log H$ was well approximated by a straight line of slope 2 which indicates $x = 2$ and consequently the species $Fe(Fe_2H_{-5}(HA)_2)_n \cdot F_0$, as it should, does not seem to vary with H. The formation constant of the nth complex would then be given by

$$
\log K_{2n+1,5n,2n} = \log F_0 + n(\log F - 2 \log H) = \log F_0 + n \log k \quad (25)
$$

From our data we estimate $\log k = -4.6 \pm 0.1$.

In these estimates less weight was ascribed to measurements at $H > 0.1$ M since the uncertainty of η_c increases with H.

This description is, of course, a crude approximation. At any rate it may indicate the existence of some additional species (at least one with $p \geq 3$) of composition not far from the "core and links" formula.

LETAGROP TREATMENT OF THE DATA

The graphical treatment has thus furnished some evidence for species FeA^{2+}, FeA_2^+, and $Fe_3(OH)_2A_6^+$ and in addition for some species of composition not far from $Fe(Fe_2(OH)_3A_2)_n^{(3+n)+}$. However, to simplify the calculations we had used approximations, especially $[HA] \approx H$ and $B \ll H$. Since more than four equilibrium constants had to be considered, it seemed necessary to use an electronic high-speed computer in order to check our conclusions in a more rigorous way and to refine the equilibrium constants. The experimental data were hence examined using the general minimizing program LETAGROP, provided with the special blocks needed for the present case of two-ligand equilibria.

The program is so constructed that the computer searches for the "best" set of values for a number of unknown parameters $k_1 \cdots k_N$, which is defined as the set which gives the minimum value to the error square sum

$$
U = \sum w(y_{calc} - y_{exp})^2 \quad (26)
$$

In this equation, w is a weight factor, y_{exp} is an experimental quantity and y_{calc} is the value for y calculated from an assumed functional relationship

$$
y_{calc} = f(k_1 \cdots k_N; \ a_1 \cdots a_{Na}) \quad (26a)
$$

where $a_1 \cdots a_{Na}$ are quantities assumed to be exactly known.

In the present case, it was assumed that E_H and the total concentrations M, B, and A were known exactly in each point. As adjustable common parameters we used — besides the equilibrium constants K_{psr}, K, and K_H — also the ratios $j_g = E_{jH}/h$ and $j_r = E_{jB}/h$. As adjustable parameters for each "group" (in this case for each titration) we could use E_H°, E_B° and the fraction α of our Fe(II) solution that had been oxidized to Fe(III).

Assuming a certain set of values for all these parameters, the computer could calculate h from (2), and $[Fe^{2+}]$, b, and a from (3), (9), and (11), by successive approximations. The program as written gives two choices for the quantity y in U (eqn. 26): either the deviation in E_B as calculated from (1) or the deviation in H, as calculated from (10) can be used. For several reasons we preferred to use $y=E_B$ in the final calculations. Since we saw no *a priori* method of weighting the data we used the same weight ($w=1$) for all points.

Many of the parameters were taken from separate experiments: K and K_H were taken from our own experiments, the K_{ps0} for the hydroxo complexes (18) were taken from Biedermann's work, and separate experiments indicated that we could safely neglect the amount of Fe(III) in our Fe(II) stock solution, hence $\alpha=0$. For the liquid junction potentials we found by separate experiments, as already mentioned, $E_{jH}=E_{jB}=-17\ h$.

Since all these parameters represent relatively minor effects in the present data—where the main effect is due to the Fe(III) acetate complexes — there would have been no point in trying to "adjust" them together with the K_{psr}.

Even the E_H° and E_B° values were calculated from the first part of each titration, and adjusted only in the final calculations.

Two sets of data were treated. Set I contains 10 titrations, during each of which M was kept constant. The H levels are 0.025, 0.050, 0.100, and 0.150, and there are altogether 166 points. Set II contains 12 titrations, during each of which M decreased. Most of the data — together 169 points — are at the lower H levels, and hence species like FeA^{2+} and FeA_2^+ get little weight in these data. In addition, we consider set II less accurate than set I.

The two sets were treated independently by LETAGROP, assuming the species indicated by the graphical treatment and searching for the set of K_{psr} that gave the lowest value of U.

With both sets, $K_{5,10,4}$ came out less than its standard deviation, and hence was finally rejected by the computer. When an attempt was made to add the species $(1\ 2_s\ 1)=FeOHA^+$, it was also rejected in the same way, both for set I and II.

The values for log K_{psr} found for the minimum are given in Table 3a, and compared with the results of the graphical treatment. We consider the results with set I as the most reliable ones. The deviations of K_{111} and K_{122} with set II are easily explained by the low concentrations of the corresponding species in most points of set II. It is satisfactory that the agreement is in general so good between set I, set II, and the graphical treatment. Even for set I, the standard deviation $\sigma(E_B)\approx0.38$ mV, still leaves something to be desired. It seems likely that a considerably better agreement could be obtained if one tries to add systematically species of other conceivable formulas, and also to use the information contained in the H values. At present this would be somewhat costly, but computer calculations are getting less and less ex-

Table 2. Experimental data (Set I). Computer output for 10 titrations. After each titration ("sats") are given the "final" values for E_{0H} and E_{0B}, and then for each point the added value V_T (for composition of solutions, see Table 1), the measured E_H and E_B, the calculated η and log h, and the difference "D(ER)" between the calculated and experimental values for E_B.

SATS 1   EOH= 400.78 EOB= 413.47

VT	EH	EB	ETA	LCGH	D(ER)
10.00	306.70	412.25	0.0131	=1.5829	-0.11
15.00	306.80	412.36	0.0112	=1.5812	-0.22
20.50	306.80	412.50	0.0089	=1.5812	-0.36
25.00	306.80	412.50	0.0089	=1.5812	-0.37
10.00	274.60	409.00	0.0735	=2.1309	0.26
11.00	269.50	407.85	0.0933	=2.2175	0.47
11.50	266.60	407.24	0.1038	=2.2667	0.46
14.00	247.80	401.25	0.2060	=2.5854	0.39
14.80	238.60	396.75	0.2823	=2.7421	0.19
15.60	226.00	398.35	0.4246	=2.9543	-0.39
16.40	209.20	371.00	0.7184	=3.2385	-0.67
17.00	195.60	320.19	1.0707	=3.4684	0.04
17.40	188.10	305.94	1.3120	=3.5953	0.43

SATS 2   EOH= 402.29 EOB= 413.24

VT	EH	EB	ETA	LCGH	D(ER)
10.00	307.20	411.91	0.0153	=1.6003	-0.03
15.00	307.20	411.95	0.0146	=1.6003	-0.07
20.00	307.20	412.00	0.0137	=1.6003	-0.12
25.00	307.20	411.95	0.0146	=1.6003	-0.07
5.00	293.40	410.61	0.0403	=1.8366	0.48
10.00	275.10	408.48	0.0785	=2.1481	0.34
14.00	249.40	401.10	0.2046	=2.5858	0.08
14.50	242.70	397.75	0.2614	=2.6973	0.01
15.20	235.00	392.93	0.3431	=2.8276	-0.24
15.70	227.40	386.71	0.4485	=2.9562	-0.39
16.20	217.30	375.91	0.6313	=3.1270	-0.51
16.70	207.50	361.75	0.8710	=3.2967	-0.01
17.30	194.60	398.10	1.2713	=3.5109	0.48
17.80	185.70	319.56	1.5852	=3.6614	0.08
18.30	179.00	303.95	1.8496	=3.7747	0.23
18.70	174.00	292.35	2.0462	=3.8592	-0.17

SATS 3   EOH= 400.96 EOB= 413.57

VT	EH	EB	ETA	LCGH	D(ER)
4.95	305.30	412.04	0.0186	=1.5998	0.17
10.00	305.40	412.30	0.0142	=1.5960	-0.10
15.00	305.40	412.30	0.0142	=1.5960	-0.11
25.00	305.40	412.35	0.0134	=1.5960	-0.17
10.00	273.40	408.95	0.0761	=2.1493	-0.12
13.50	252.20	401.65	0.2007	=2.5037	0.37
14.50	243.10	396.11	0.2947	=2.6578	0.19
15.30	234.00	388.00	0.4320	=2.8118	-0.09
15.80	228.00	380.75	0.5548	=2.9134	-0.02
16.30	221.30	371.05	0.7189	=3.0267	-0.01
16.80	213.80	358.25	0.9355	=3.1536	-0.07
17.10	208.80	348.82	1.0950	=3.2381	-0.10
17.60	200.40	332.05	1.3788	=3.3802	-0.27
18.10	191.90	313.95	1.6852	=3.5259	-0.16
18.60	185.10	298.07	1.9540	=3.6389	0.77

SATS 4   EOH= 401.86 EOB= 413.59

VT	EH	EB	ETA	LCGH	D(ER)
10.00	325.30	412.44	0.0043	=1.2791	-0.19
15.00	325.20	412.58	0.0020	=1.2809	-0.32
20.00	325.20	412.65	0.0008	=1.2809	-0.39
25.00	325.10	412.55	0.0026	=1.2826	-0.29
15.80	247.00	396.92	0.2814	=2.6172	0.32
16.10	240.40	392.21	0.3613	=2.7269	0.53
16.40	232.90	385.68	0.4719	=2.8558	0.39
16.70	224.30	375.05	0.6520	=3.0013	0.54
17.10	212.10	353.55	1.0160	=3.2077	0.63
17.40	203.60	334.96	1.3307	=3.3514	0.49
17.70	196.50	318.15	1.6155	=3.4719	0.20
18.00	189.80	302.05	1.8883	=3.5848	-0.47
18.30	184.40	288.50	2.1180	=3.6761	-0.73
18.60	179.90	276.90	2.3148	=3.7522	-0.76

SATS 5   EOH= 400.07 EOB= 412.74

VT	EH	EB	ETA	LCGH	D(ER)
10.50	323.80	411.43	0.0069	=1.2741	-0.03
15.00	323.60	411.45	0.0066	=1.2776	-0.05
20.00	323.60	411.28	0.0095	=1.2776	0.12
25.00	323.60	411.60	0.0041	=1.2776	-0.20
16.00	234.70	389.84	0.3871	=2.7951	0.09
16.40	222.90	378.69	0.5760	=2.9947	0.09
16.80	210.60	360.57	0.8829	=3.2028	0.43
17.20	198.20	336.00	1.2990	=3.4125	-0.32

SATS 6   EOH= 402.95 EOB= 411.46

VT	EH	EB	ETA	LCGH	D(ER)
5.00	273.00	427.22	0.0043	=0.9763	0.03
10.00	272.90	427.45	0.0005	=0.9782	-0.19
15.00	273.10	427.34	0.0021	=0.9745	-0.10
25.00	273.00	427.39	0.0014	=0.9763	-0.14
15.00	204.60	419.09	0.1703	=2.1610	0.16
16.50	177.00	387.57	0.7048	=2.6289	0.73
17.50	144.50	342.34	1.9786	=3.1768	-0.22
18.50	116.80	299.97	3.2064	=3.6472	-0.88
19.50	103.30	262.65	3.8417	=3.8754	0.71
20.50	94.00	179.85	4.2318	=4.0366	-0.92
21.50	87.90	163.15	4.5182	=4.1358	-0.28
23.50	79.40	140.13	4.9149	=4.2795	0.42
25.00	74.80	127.57	5.1324	=4.3572	0.94

SATS 7   EOH= 431.50 EOB= 410.35

VT	EH	EB	ETA	LCGH	D(ER)
10.00	272.00	443.86	0.0052	=0.9754	0.08
15.00	272.00	443.95	0.0036	=0.9754	-0.01
20.00	272.00	443.99	0.0030	=0.9754	-0.05
25.00	272.00	444.04	0.0021	=0.9754	-0.10
16.50	187.00	413.49	0.5483	=2.4417	0.74
17.00	178.50	399.54	0.7846	=2.5857	-0.35
18.00	153.70	344.10	1.7232	=3.0054	-0.99
19.00	125.00	207.15	3.0273	=3.4908	0.86
19.50	114.90	241.26	3.4672	=3.6616	-0.02
20.50	102.80	207.65	4.0394	=3.8661	1.46
21.50	93.80	185.48	4.4186	=4.0183	-0.03
22.50	87.30	170.00	4.6845	=4.1282	-1.55
23.50	83.00	157.30	4.9027	=4.2008	-0.23
28.00	69.90	142.47	5.5063	=4.4243	0.36

SATS 8   EOH= 398.92 EOB= 413.96

VT	EH	EB	ETA	LCGH	D(ER)
10.00	349.00	411.30	-0.0016	=0.7906	-0.24
14.00	348.70	411.24	0.0000	=0.7963	-0.14
17.00	348.80	411.13	0.0017	=0.7944	-0.04
20.00	348.90	411.29	-0.0006	=0.7962	-0.18
8.00	319.20	411.32	0.0311	=1.3274	0.42
10.00	305.00	410.62	0.0485	=1.5560	0.23
11.50	291.10	408.50	0.0880	=1.8115	0.20
12.30	277.90	405.22	0.1453	=2.0364	0.14
12.80	264.80	400.20	0.2314	=2.2589	-0.13
0.50	262.20	398.68	0.2573	=2.3030	0.04
1.00	259.40	397.21	0.2824	=2.3505	-0.08
1.50	256.60	395.26	0.3155	=2.3980	0.13
2.00	253.90	393.55	0.3446	=2.4437	0.00
2.50	250.90	391.16	0.3852	=2.4946	0.14
3.00	248.10	388.93	0.4231	=2.5420	0.01
3.50	244.40	385.50	0.4813	=2.6047	-0.10
4.00	241.00	381.65	0.5466	=2.6662	-0.08
4.50	237.80	377.25	0.6212	=2.7164	0.11
5.00	234.30	371.66	0.7159	=2.7756	0.34
5.20	232.50	368.57	0.7683	=2.8061	0.37

SATS 9   EOH= 398.03 EOB= 413.24

VT	EH	EB	ETA	LCGH	D(ER)
9.00	348.10	410.26	0.0058	=0.8097	0.20
13.00	348.20	410.35	0.0041	=0.8078	0.09
16.00	348.20	410.32	0.0046	=0.8078	0.12
19.00	348.40	410.40	0.0033	=0.8078	0.04
9.50	305.40	409.95	0.0479	=1.5683	0.11
10.50	295.00	408.50	0.0751	=1.7468	0.18
11.00	288.50	407.35	0.0957	=1.8578	0.09
11.50	277.00	405.25	0.1324	=2.0026	0.01
12.00	267.70	400.84	0.2082	=2.2116	-0.20
12.20	260.30	397.75	0.2728	=2.3371	-0.34
12.40	251.60	390.71	0.3806	=2.4846	-0.41
0.40	248.50	387.36	0.4374	=2.5371	-0.09
0.60	247.80	386.65	0.4495	=2.5489	-0.15
1.00	244.50	382.41	0.5213	=2.6048	0.10
1.30	242.60	379.71	0.5671	=2.6370	0.14
1.70	239.40	374.61	0.6535	=2.6912	0.20
2.00	237.60	371.36	0.7086	=2.7216	0.28
2.30	234.90	366.43	0.7921	=2.7673	0.11
2.60	232.40	361.69	0.8724	=2.8096	-0.23
2.90	230.00	356.16	0.9661	=2.8503	0.15
3.20	227.50	350.66	1.0592	=2.8926	0.86
3.50	225.50	345.81	1.1414	=2.9264	0.29

SATS10   EOH= 399.40 EOB= 414.75

VT	EH	EB	ETA	LCGH	D(ER)
10.00	348.90	412.00	0.0019	=0.8041	-0.04
15.00	348.70	411.75	0.0065	=0.8129	0.23
20.00	348.70	411.86	0.0046	=0.8129	0.12
25.00	348.80	411.86	0.0044	=0.8110	0.10
16.50	267.30	385.35	0.4957	=2.2314	-0.33
16.70	264.70	380.90	0.5711	=2.2756	-0.18
17.00	260.70	374.02	0.6877	=2.3434	-0.55
17.30	256.40	365.40	0.8337	=2.4163	-0.44
17.60	251.60	355.16	1.0071	=2.4976	-0.42
17.90	246.20	342.15	1.2274	=2.5851	0.32
18.20	238.60	324.10	1.5330	=2.7144	0.53
18.40	232.30	307.55	1.8132	=2.8244	0.67
18.60	225.80	291.63	2.0829	=2.9343	-0.31
18.80	218.10	271.50	2.4239	=3.0646	-0.47
19.00	210.00	250.31	2.7832	=3.2016	-0.74
19.40	198.20	217.35	3.3425	=3.4011	0.83
19.90	186.80	187.58	3.8489	=3.5990	0.35
20.50	177.40	163.07	4.2670	=3.7529	-0.00
22.00	162.80	145.12	4.9178	=3.9997	-0.42

pensive so that (even with no essential change in the program) another attack may seem much more attractive within a few years.

In a new attack on this system with computer methods one should also add data over a broader range of total concentrations. When the present experiments were planned, the restrictions on the experimental conditions were set by the need to simplify the calculations. With the computer programs now available we are more free to choose the concentration range.

Even if the present results are to some extent preliminary, we would think that a further refinement of data and calculations will not change very much the formulas and equilibrium constants for the first four complexes in Table 3.

SUPERSATURATION OF THE SOLUTIONS

According to Biedermann and Schindler [21] freshly precipitated iron(III) hydroxide, FeOOH, is at equilibrium with solutions where $h^3b^{-1} = 10^{-3.96}$. One may, however, check from our experimental data that the product h^3b^{-1} is less than $10^{-3.96}$ for the majority of our experiments, which thus have been made in supersaturated solutions. Provided the amount of precipitate has been nil or negligible, our results may still give a true picture of the equilibria in clear solutions. In some cases, supersaturated solutions were back-titrated with acid, and the $\eta(\log h)$ points were found to fall, within the limits of

Table 3a. Calculated values for $\log K_{psr}$ for formation of $Fe_pH_{-s}(HA)_r$, by graphical methods and Letagrop. 3 σ given.

p s r	graphical methods	series I E_0 not adjusted	series I E_0 adjusted	series II
0 1 1	$-5.017(\pm0.010)$	-5.017	-5.02 ± 0.04	-5.017
1 1 1	-1.9 ± 0.2	-1.82 ± 0.04	-1.79 ± 0.03	-1.63 ± 0.14
1 2 2	-3.7 ± 0.2	-3.81 ± 0.08	-3.82 ± 0.07	$(-4.2(<-3.7))$
3 8 6	-8.1 ± 0.2	-8.068 ± 0.014	-8.068 ± 0.015	-8.07
3 5 2	-4.0 ± 0.2	-4.17 ± 0.06	-4.17 ± 0.05	$(-5.9(<-5.0))$
7 15 6	-13.2 ± 0.4	-12.86 ± 0.11	-12.86 ± 0.10	-12.84 ± 0.16
$\sigma(E)$		0.45	0.38	0.83

Table 3b. "Best set" of values for $\log \beta_{pqr}$ for formation of $Fe_pH_{-q}A_r$. From "series I, E_0 adjusted" in Table 3a, 3σ given as calculated from Letagrop (except for formation of HA where it was taken from earlier estimate).

p q r	Reaction	log equilibrium constant
0 $\bar{1}$ 1	$H^+ + A^- \rightleftharpoons HA$	5.02 ± 0.01
1 0 1	$Fe^{3+} + A^- \rightleftharpoons FeA^{2+}$	3.23 ± 0.03
1 0 2	$Fe^{3+} + 2A^- \rightleftharpoons FeA_2^+$	6.22 ± 0.07
3 2 6	$3Fe^{3+} + 2H_2O + 6A^- \rightleftharpoons Fe_3(OH)_2A_6^+ + 2H^+$	22.05 ± 0.05
3 3 2	$3Fe^{3+} + 3H_2O + 2A^- \rightleftharpoons Fe_3(OH)_3A_2^{4+} + 3H^+$	5.87 ± 0.05
7 9 6	$7Fe^{3+} + 9H_2O + 6A^- \rightleftharpoons Fe_7(OH)_9A_6^{6+} + 9H^+$	17.26 ± 0.10

experimental error, on the same curve as those measured (with the same H and B) in forward titrations. This again indicates that we have been measuring real equilibria in the solution.

TRINUCLEAR Fe(III) BASIC ACETATE COMPLEXES IN THE SOLID STATE

The iron(III) ion, as well as other trivalent ions like Cr^{3+} and Al^{3+}, forms a number of basic acetates which are supposed to contain complex ions of the type $Fe_3(OH)_2A_6^+$, although no X-ray evidence as yet seems to be available.[22]

Orgel,[23] on the basis of the strong magnetic interactions between metal ions measured in these salts, suggested for the complex ion $Fe_3(OH)_2A_6^+$ the structure shown in Fig. 6. Three metal atoms are arranged in an equilateral
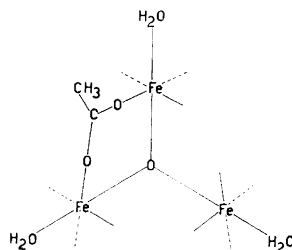
Fig. 6. Structure of the $Fe_3OA_6^+$ ion as proposed by Orgel.[23]

triangle around a central O^{2-} ion. The acetate groups and H_2O complete the octahedral coordination around the Fe ions, each acetate links a pair of Fe.

Figgis and Robertson[24] have determined the crystal structure of $Cr_3OA_6Cl(H_2O)_4$ and have found that these crystals contain discrete groups of three Cr atoms arranged around a central O^{2-} ion, essentially as postulated by Orgel.

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