723. *Ionic Association and Reaction Rates. Part I. A Spectrophotometric Study of the Hydrolysis of Iron*(III).

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The hydrolysis of Fe^{3+} to $FeOH^{2+}$ has been studied by spectrophotometry over the wavelength range 290—330 mμ in perchlorate solutions of ionic strength 0·025—0·15 at 18·2—35·5°. The conventional hydrolysis constant is expressed in terms of equilibria for free and associated ions, and evaluated without any assumptions about the extent of perchlorate association or its effect on extinction coefficients. Values found for the hydrolysis constant at zero ionic strength, its temperature coefficient, and its variation with ionic strength, agree with Milburn and Vosburgh's results obtained at 340 mμ. Extinction coefficients for Fe^{3+} and $FeOH^{2+}$ are given. The effect on the hydrolysis constant of substituting barium for sodium perchlorate is consistent with the estimate of ferric–perchlorate association derived from Olson and Simonson's data. The structure of $FeOH^{2+}$ is discussed in terms of the view that the spectrophotometric method detects all associated species irrespective of their interionic separation.

The effect of anions on the rate of the ferric–iodide reaction has been attributed to the formation of associated species which are unreactive compared with free ferric ions.[1] However, the kinetic work on which this suggestion was based was purely exploratory, no close correlation was established between the kinetic and associating effects of a given anion, and the structures of the associated species were not elucidated. Nevertheless, the principle seemed likely to be of significance for ionic reactions in general if it were substantiated, so a wider investigation of the thermodynamic, structural, and kinetic factors was begun. Anion–ferric association was studied by spectrophotometry of its electron-transfer spectrum in order to provide independent evidence for the existence of the species postulated and to determine their concentrations,* while the effect of the anion on the individual rate constants of the ferric–iodide reaction was measured accurately under the same conditions. More rigorous interpretations of both types of experiment for the anions hydroxide, sulphate, and nitrate were developed in the light of advances in the concept of ionic association, and changes of solvent were made to illustrate the important rôle of water in these ionic interactions.

An essential first step, described in this paper, was to establish the spectrophotometry of ferric hydrolysis in aqueous solution over the range 290—330 mμ. Hydroxide is itself an important ligand, and knowledge of its effect is essential for the study of the other systems, since ferric ions are appreciably hydrolysed in solutions of sufficiently low acidity for the influence of sulphate and bisulphate ions to be separated or for low ionic strengths to be used. This wavelength range includes the band maxima for the Fe^{3+}–OH^-, Fe^{3+}–$SO_4^=$, and Fe^{3+}–NO_3^- interactions, and so should be the most sensitive and reliable region for spectrophotometric study of these species.

Measurement of Hydrolysis Constant.—If perchlorate association, which may be appreciable,[2] is not neglected, the possible equilibria in a dilute solution of ferric perchlorate in aqueous perchloric acid–sodium perchlorate are

$$Fe^{3+} + H_2O = FeOH^{2+} + H^+ \qquad K_{10} \qquad (1)$$

$$Fe^{3+} + kClO_4^- = Fe(ClO_4)_k^{(3-k)+} \qquad K_{0k}\ k = 1,2\ldots n \qquad (2)$$

$$FeOH^{2+} + jClO_4^- = FeOH(ClO_4)_j^{(2-j)+} \qquad K_{1j}\ j = 1,2\ldots m \qquad (3)$$

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* A preliminary account of some of this work appeared in *Chem. Soc. Spec. Publ.*, **1954**, No. 1, p. 64.

[1] Sykes, *J.*, 1952, 124.

[2] Sykes, *J.*, 1959, 2473.

Further hydrolysis products are neglected at this stage, but the validity of this assumption is examined later. If separate extinction coefficients are assigned to each of the $n + m + 2$ different species, ε_{00} for Fe^{3+}, ε_{10} for $FeOH^{2+}$, ε_{0k} for $Fe(ClO_4)_k^{(3-k)+}$, and ε_{1j} for $FeOH(ClO_4)_j^{(2-j)+}$, the mean molar extinction coefficient of the ferric ion, $\bar{\varepsilon}$, becomes

$$\bar{\varepsilon} = \frac{\varepsilon_{00} + \sum_{k=1}^{n} \varepsilon_{0k}K_{0k}c_2^{\,k} + \frac{K_{10}}{c_1}(\varepsilon_{10} + \sum_{j=1}^{m} \varepsilon_{1j}K_{1j}c_2^{\,j})}{1 + \sum_{k=1}^{n} K_{0k}c_2^{\,k} + \frac{K_{10}}{c_1}(1 + \sum_{j=1}^{m} K_{1j}c_2^{\,j})} \quad . \quad . \quad . \quad (4)$$

where c_1 and c_2 are the concentrations of hydrogen ions and free perchlorate ions respectively. Eqn. (4) reduces to the conventional form

$$\bar{\varepsilon} = [\varepsilon_0 + \varepsilon_1({}^*K_1/c_1)]/[1 + ({}^*K_1/c_1)] \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$${}^*K_1 = K_{10}(1 + \sum_{j=1}^{m} K_{1j}c_2^{\,j})/(1 + \sum_{k=1}^{n} K_{0k}c_2^{\,k}) \quad . \quad . \quad . \quad . \quad (6)$$

$$\varepsilon_0 = (\varepsilon_{00} + \sum_{k=1}^{n} \varepsilon_{0k}K_{0k}c_2^{\,k})/(1 + \sum_{k=1}^{n} K_{0k}c_2^{\,k}) \quad . \quad . \quad . \quad . \quad (7)$$

$$\varepsilon_1 = (\varepsilon_{10} + \sum_{j=1}^{m} \varepsilon_{1j}K_{1j}c_2^{\,j})/(1 + \sum_{j=1}^{m} K_{1j}c_2^{\,j}) \quad . \quad . \quad . \quad . \quad (8)$$

Equilibrium constants and extinction coefficients for individual species will, as a working hypothesis, be assumed constant at a given ionic strength in dilute solution; eqns. (6)—(8) imply that ${}^*K_1$, ε_0, and ε_1 should only be assumed constant if both perchlorate concentration and ionic strength are fixed. For two solutions of given perchlorate concentration and ionic strength, one of which is denoted by primed symbols,

$$\frac{c_1' - c_1}{\bar{\varepsilon} - \bar{\varepsilon}'} = \frac{\Delta c_1}{\Delta\bar{\varepsilon}} = \frac{({}^*K_1 + c_1')({}^*K_1 + c_1)}{{}^*K_1(\varepsilon_1 - \varepsilon_0)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If c_1' is a fixed hydrogen-ion concentration and c_1 is varied, $\Delta c_1/\Delta\bar{\varepsilon}$ depends linearly on c_1 and the ratio of intercept at $c_1 = 0$ to slope is ${}^*K_1$. Eqn. (9) thus enables ${}^*K_1$ to be evaluated without the extent to which perchlorate associates with Fe^{3+} or $FeOH^{2+}$ or affects their extinction coefficients being assumed. The standard elimination [3] of ε_0 and ε_1 from eqn. (5) applied to three acidities is a special case of this procedure in which only two points on the $\Delta c_1/\Delta\bar{\varepsilon}$–$c_1$ graph are used. The standard method is therefore independent of assumptions about perchlorate, but there is no justification for supposing, without experimental proof, that ε_0 or ε_1 is independent of ionic strength [4] or temperature.[5,6] In the present work, ${}^*K_1$ is evaluated as a function of ionic strength and of temperature by determining the relation between $\Delta c_1/\Delta\bar{\varepsilon}$ and c_1 for each set of conditions.

Fig. 1 shows that eqn. (9) is obeyed at a given wavelength by 3×10^{-4}M-ferric perchlorate in $HClO_4$–$NaClO_4$ solutions of ionic strength 0·025—0·15 and perchloric acid concentrations ($c_1^{\,0}$) 0·002—0·120M. Measurements at $c_1^{\,0} = 0{\cdot}001$M lie consistently above the line through the other points with an average deviation of 7%; they are probably influenced by further stages of hydrolysis and are neglected. Table 1 gives the values of ${}^*K_1$ calculated for all wavelengths in the range 290—320 mμ, the line being assumed to pass through the point at $c_1^{\,0} = 0{\cdot}002$M, corresponding to the highest optical density, and the centre of gravity of the other two. To allow for hydrogen ions produced by the

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[3] Olson and Simonson, *J. Chem. Phys.*, 1949, **17**, 1322.

[4] Siddall and Vosburgh, *J. Amer. Chem. Soc.*, 1951, **73**, 4270.

[5] Rabinowitch and Stockmayer, *J. Amer. Chem. Soc.*, 1942, **64**, 335.

[6] Milburn, *J. Amer. Chem. Soc.*, 1957, **79**, 537.

TABLE 1. *Values of* $10^3{}^*K_1$ *(mole l.*$^{-1}$*).*

Temp.	18·2°	18·7°	20·0°	20·1°	20·3°	20·3°	35·5°
Ionic strength...	0·15	0·10	0·08	0·06	0·04	0·025	0·15
290 mμ	1·75	2·02	2·04	2·49	(3·27)	3·03	4·68
295 mμ	1·86	2·02	2·04	2·58	2·91	3·02	4·73
300 mμ	1·87	2·03	2·15	2·57	2·90	3·03	4·85
305 mμ	1·87	2·01	2·11	2·57	2·88	3·05	4·85
310 mμ	1·84	2·04	2·15	2·52	2·83	3·02	4·79
315 mμ	1·81	1·96	2·10	2·46	2·76	3·04	4·80
320 mμ	1·88	1·92	2·06	2·44	2·79	3·07	4·85
Average	1·84	2·00	2·09	2·52	2·85	3·04	4·79
Obs. error	±0·05	±0·04	±0·05	±0·06	±0·06	±0·02	±0·07
Calc. error	±0·09	±0·09	±0·09	±0·11	±0·12	±0·13	±0·20
Milburn and Vosburgh [7]	1·75 ±0·10	1·99 ±0·12	2·27 ±0·14	2·44 ±0·15	2·70 ±0·16	2·97 ±0·18	4·72 ±0·28

hydrolysis of ferric ions of total concentration c_0, small corrections not exceeding 2×10^{-4}M were made by successive approximation according to the relation

$$c_1 = c_1^0 + \left(\frac{{}^*K_1 + c_1^0}{2}\right)\left[\left\{1 + \frac{4{}^*K_1 c_0}{({}^*K_1 + c_1^0)^2}\right\}^{\frac{1}{2}} - 1\right] \quad . \; . \; . \quad (10)$$

The results do not vary systematically with wavelength in the range 290—320 mμ, so the average is taken, with the exception of the single inconsistent value in parentheses, and the observed error expressed as the standard deviation of the mean. If the optical densities (0·112—0·820) are accurate to ±1%, the calculated error, σ_K, in $^*K_1$ is given by

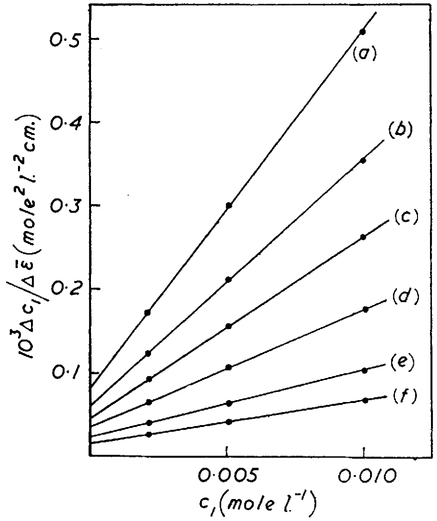

FIG. 1. *Test of eqn* (9) *at* 305 *mμ. Ionic strength*: (*a*) 0·15, (*b*) 0·10, (*c*) 0·08, (*d*) 0·06, (*e*) 0·04, (*f*) 0·025. *Values of* c_1' (*mole l.*$^{-1}$): (*a*) 0·12, (*b*) 0·09, (*c*) 0·07, (*d*) 0·05, (*e*) 0·03, (*f*) 0·02.

$$\sigma_K = \frac{0{\cdot}01414 y_2(x_5 + x_{10} - 2x_2)(y_5^2 + y_{10}^2 + y_5 y_{10})^{\frac{1}{2}}}{(y_5 + y_{10} - 2y_2)^2} \quad . \; . \quad (11)$$

where $x = c_1$, $y = \Delta c_1/\Delta\bar{\varepsilon}$, and the subscripts denote the value of $10^3 c_1^0$. Since the observed errors all fall within the calculated ones, eqn. (9) adequately represents the results over the wavelength range 290—320 mμ. Variation of $^*K_1$ with ionic strength [†] can be expressed in the form

$$\log ({}^*K_1^0/{}^*K_1) = 4AI^{\frac{1}{2}}/(1 + BI^{\frac{1}{2}}) \quad . \; . \; . \; . \; . \; . \quad (12)$$

[†] In ref. 2 the left sides of eqns. (11) and (12) should read $\log\{{}^*K_1(b)/{}^*K_1(a)\}$ and $\log\{K_2(b)/K_2(a)\}$ respectively, and the right side of eqn. (14) ${}^*K_1(a)\{1 + K_2(a) \,.\, c_2(a)\}K_1(b)/\{1 + K_2(b) \,.\, c_2(b)\}K_1(a)$; all the calculations were made with the correct forms.

with $B = 2{\cdot}44$ ($\pm 0{\cdot}3$) as calculated from the values of $^*K_1$ at ionic strengths of 0·15 and 0·025, corrected to 20° with the heat content change given below and $A = 0{\cdot}505$. Extrapolation with this function of the values at all ionic strengths, after correction to 20°, gives for the mean value of $10^3{}^*K_1{}^0$ and its standard deviation $5{\cdot}01 \pm 0{\cdot}25$, in good agreement with $4{\cdot}96 \pm 0{\cdot}30$ calculated from Milburn and Vosburgh's results [7] ($10^3{}^*K_1{}^0 = 6{\cdot}7 \times 0{\cdot}4$ at 25°, $\Delta^*H_1{}^0 = 10{\cdot}4 \pm 0{\cdot}2$ kcal., $B = 2{\cdot}40$) obtained by a different method from data for 340 mμ. As shown in the last row of Table 1, Milburn and Vosburgh's results are consistent with the present ones, to within the experimental errors, under all conditions. Earlier determinations of $^*K_1$ have already been reviewed.[7] Turner and Miles's more recent value [8] is not strictly comparable since it is calculated from hydrogen-ion activity. These authors [9] give their result for $10^3{}^*K_1$ in terms of hydrogen-ion concentration as $3{\cdot}85 \pm 0{\cdot}30$, for the range 320—350 mμ at $I = 0{\cdot}01$ at 25°, compared with $4{\cdot}6 \pm 0{\cdot}3$ derived from the value of $^*K_1{}^0$ given above.

Effect of $Fe_2(OH)_2{}^{4+}$.—Small but appreciable deviations at 325—330 mμ (Table 3 below) suggest that $Fe_2(OH)_2{}^{4+}$, which absorbs strongly at 340 mμ,[7] may be important in this region. If the formation of this species is written

$$2FeOH^{2+} = Fe_2(OH)_2{}^{4+} \qquad K_d \quad \ldots \ldots \quad (13)$$

its concentration c_d is equal to

$$c_d = {}^*K_1{}^2 K_d w^2 \quad \ldots \ldots \quad (14)$$

where

$$w = \frac{\{(c_1 + {}^*K_1)^2 + 8{}^*K_1 K_d c_0\}^{\frac{1}{2}} - (c_1 + {}^*K_1)}{4{}^*K_1{}^2 K_d} \quad \ldots \quad (15)$$

and

$$c_1 = c_1{}^0 + {}^*K_1 w + 2{}^*K_1{}^2 K_d w^2 \quad \ldots \ldots \quad (16)$$

K_d is interpolated at the appropriate temperatures and ionic strengths from Milburn's results [6] for perchlorate solution, so the effect of any perchlorate association is included. Since the dimer changes the hydrogen-ion concentration by less than 0·5%, c_d is calculated from eqns. (14) and (15) with the previous values of c_1; its largest value is $6{\cdot}4 \times 10^{-6}$M at $c_1{}^0 = 0{\cdot}002$M, $I = 0{\cdot}15$, 35·5°. The hypothetical extinction coefficient of ferric solutions without dimer, $\bar{\varepsilon}$(corr.), is related to the observed value, $\bar{\varepsilon}$, by the equation

$$\bar{\varepsilon}c_0 = \bar{\varepsilon}(\text{corr.})(c_0 - 2c_d) + \varepsilon_d c_d \quad \ldots \ldots \quad (17)$$

where ε_d is the extinction coefficient of the dimer, so the effect of the dimer on the determination of $^*K_1$ can be calculated by replacing $\bar{\varepsilon}$ by $\bar{\varepsilon}$(corr.) in eqn. (9).

Milburn and Vosburgh [7] evaluated ε_d only for 340 mμ, but it may be estimated for 325—330 mμ from their data for 0·05M-$Fe(ClO_4)_3$ in 0·25–1·0M-$HClO_4$ at $I = 1{\cdot}55$ at 25°. If α, β, and 2γ are the fractions of iron present as Fe^{3+}, $FeOH^{2+}$, and $Fe_2(OH)_2{}^{4+}$ in such solutions, and the subscripts *a* and *b* denote different acid concentrations

$$\varepsilon_d = \frac{\bar{\varepsilon}_b\beta_a - \bar{\varepsilon}_a\beta_b + \varepsilon_0(\alpha_a\beta_b - \alpha_b\beta_a)}{\beta_a\gamma_b - \beta_b\gamma_a} \quad \ldots \ldots \quad (18)$$

Table 2 gives α, β, and γ as calculated from Milburn and Vosburgh's equilibrium constants,[7] $\bar{\varepsilon}$ as obtained by photographic enlargement of their Fig. 1, and the results for ε_d. The value

TABLE 2. *Calculation of* ε_d *from Milburn and Vosburgh's data.*

				$\bar{\varepsilon}$			$10^{-3}\varepsilon_d$		
c_1	α	$10^3\beta$	$10^3\gamma$	325 mμ	330 mμ	340 mμ	325 mμ	330 mμ	340 mμ
1·00M	0·998	1·50	0·11	14·5	9·5	4·6	2·6	2·4	2·4
0·25M	0·991	5·93	1·69	24·5	19·0	12·8			

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[7] Milburn and Vosburgh, *J. Amer. Chem. Soc.*, 1955, **77**, 1352.

[8] Turner and Miles, *Canad. J. Chem.*, 1957, **35**, 1002.

[9] Turner and Miles, personal communication.

of 2·4 × 10^3 for ε_d at 340 mμ, which is included to test the method, agrees reasonably with Milburn and Vosburgh's estimate of 3(±1) × 10^3 derived from other data, so an average of 2·5 × 10^3 is assumed for 325—330 mμ. The corrections (Table 3) make $^*K_1$ approximate more closely to the average for 290—320 mμ at all ionic strengths except 0·025, where the change is small but of the wrong sign, so the deviations at 325—330 mμ are substantially explained. It also follows that the effect of the dimer at 290—320 mμ must be within the experimental error, presumably because at each wavelength in this range ε_d approximates to $2\bar{\varepsilon}$ at the lowest acidity where the dimer concentration is greatest.

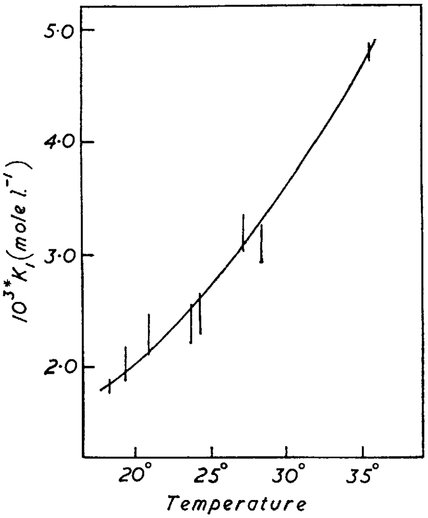

FIG. 2. *Variation of $^*K_1$ with temperature at I = 0·15. Vertical lines: standard deviation of average for* 290—320 mμ. *Curve:* Δ^*H_1 = +9·9 *kcal.*

Heat Content Change.—The results in Table 1 for 18·2° and 35·5° at I = 0·15 give Δ^*H_1 = +9·9 ± 0·4 kcal. This is useful confirmation of Milburn's estimate[6] of +10·4 ± 0·2 kcal., since it does not depend on the assumption that ε_1 is independent of temperature.

TABLE 3. *Effect of* $Fe_2(OH)_2^{4+}$ *on values of* $10^3{}^*K_1$ (*mole l.*$^{-1}$).

Temp.	Ionic strength	325 mμ obs.	325 mμ corr.	330 mμ obs.	330 mμ corr.	290—320 mμ average
18·2°	0·15	1·71	1·83	1·61	1·78	1·84
35·5	0·15	4·71	4·74	4·63	4·72	4·79
18·7	0·10	1·70	1·78	1·68	1·81	2·00
20·0	0·08	2·00	2·06	1·91	2·01	2·09
20·1	0·06	2·33	2·40	2·27	2·38	2·52
20·3	0·04	2·76	2·83	2·67	2·78	2·85
20·3	0·025	3·18	3·24	3·20	3·27	3·04

To test the possibility that the present result might be influenced by other stages of hydrolysis becoming important at the higher temperature, further experiments are made at the same ionic strength and ferric concentration with $10^3c_1{}^0$ equal to 10, 20, and 30 instead of 2, 5, and 10. Larger random deviations occur because the optical densities are smaller at the higher acid concentrations, but the results are consistent with the others (Fig. 2).

Perchlorate Association.—According to eqn. (6), measurement of $^*K_1$ as a function of c_2 at a given ionic strength should give the dependence on perchlorate concentration of the quantity:

$$(1 + \sum_{j=1}^{m} K_{ij}c_2{}^j)/(1 + \sum_{k=1}^{n} K_{0k}c_2{}^k),$$

which is the ratio of the fractions of Fe^{3+} and $FeOH^{2+}$ not associated with perchlorate.

Replacement of sodium perchlorate by barium perchlorate provides the necessary variation of c_2, if the concentration is small enough for the principle of ionic strength to be significant. Repetition of the determination at $I = 0{\cdot}15$, except for adding 0·0333M-barium perchlorate and decreasing the highest perchloric acid concentration to 0·0482M, makes $10^3{*}K_1$ for 290—320 mμ 2·10 ± 0·08 at $c_2 = 0{\cdot}1158$M at 19·8°, whereas the value in Table 1 for the same ionic strength at $c_2 = 0{\cdot}1491$M becomes 2·02 ± 0·06 at 19·8°. These values should be more reliable than the preliminary ones,[10] which involved the use of Rabinowitch and Stockmayer's value [5] of 12·3 kcal. for $\Delta{*}H_1$ and less comparable ranges of acidity for the sodium and barium solutions. Clearly, the effect of perchlorate is small; if the whole change is attributed to $FeClO_4^{2+}$ according to the relation

$$K_{01} = \frac{{*}K_1(a) - {*}K_1(b)}{{*}K_1(b)c_2(b) - {*}K_1(a)c_2(a)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where a and b denote the barium and sodium solutions respectively, K_{01} is put in the range 0—5·5 by the extreme values of ${*}K_1$. Though K_{01} is not accurately determined, these limits are useful because they do not depend on the assumption that the extinction coefficients are unaffected by change of perchlorate concentration. Sykes's estimate [2] of K_{01} (7·0—14·9 at $I = 0$) from Olson and Simonson's date [3] for more dilute solutions becomes 2·2—4·7 when extrapolated to an ionic strength of 0·15 by the equation

$$\log\,(K_{01}{}^0/K_{01}) = 6AI^{\frac{1}{2}}/(1 + 3{\cdot}52I^{\frac{1}{2}}) \quad . \quad . \quad . \quad . \quad . \quad (20)$$

The suggestion [2] that ferric and perchlorate ions in dilute solution have at least two water molecules between them at their distance of closest approach thus appears to hold at an ionic strength of 0·15. This is consistent with the view that perchlorate concentrations of about 6M are needed to dehydrate ferric ions appreciably,[11] or to alter significantly the visible absorption spectrum of neodymium,[12] a similar tri-positive ion; this spectral shift is presumably due to changes in the first hydration shell, since f electrons are involved.

Extinction Coefficients.—The intercept of the $(\Delta c_1/\Delta\bar{\varepsilon})$–$c_1$ graph leads directly to $\varepsilon_1 - \varepsilon_0$, since from eqn. (9)

$$\Delta\varepsilon = \varepsilon_1 - \varepsilon_0 = (c_1' + {*}K_1)/(\Delta c_1/\Delta\bar{\varepsilon})_{c_1=0} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Table 4 shows that $\Delta\varepsilon$, at the essentially constant temperature of 18·2—20·3°, is independent of ionic strength from 0·025 to 0·15 to within about ±5%. Corrections as described above are made for $Fe_2(OH)_2^{4+}$ at 325—330 mμ. The observed error, which is the standard deviation of the average over the various ionic strengths, is comparable with the calculated error, $\sigma_{\Delta\varepsilon}$, caused by an uncertainty of ±1% in the optical densities and obtained from the following expression in the notation of eqn. (11)

TABLE 4. *Values of* $\Delta\varepsilon$.

Ionic strength	0·15	0·10	0·08	0·06	0·04	0·025	Average	Obs. error	Calc. error
290 mμ	1390	1350	1410	1310	(1150)	1290	1350	50	40
295 mμ	1480	1490	1560	1420	1380	1440	1460	60	40
300 mμ	1530	1550	1570	1480	1440	1490	1510	50	50
305 mμ	1520	1550	1580	1470	1440	1480	1510	50	50
310 mμ	1480	1480	1490	1440	1400	1430	1450	30	50
315 mμ	1400	1420	1430	1360	1320	1340	1380	40	40
320 mμ	1240	1320	1330	1250	1210	1230	1260	50	40
325 mμ	1100	1180	1150	1100	1040	1040	1100	60	40
330 mμ	980	1050	1020	970	920	910	980	60	30

$$\sigma_{\Delta\varepsilon} = \frac{0{\cdot}01\ \Delta\varepsilon\{x_2{}^2(y_5{}^2 + y_{10}{}^2) + (x_5 + x_{10})^2 y_2{}^2\}^{\frac{1}{2}}}{(x_5 + x_{10})y_2 - x_2(y_5 + y_{10})} \quad . \quad . \quad . \quad (22)$$

[10] Sykes, *Chem. Soc. Spec. Publ.*, 1954, No. 1, p. 64.

[11] Coll, Nauman, and West, *J. Amer. Chem. Soc.*, 1959, **81**, 1284.

[12] Krumholtz, *J. Phys. Chem.*, 1959, **63**, 1313.

This insensitiveness of the extinction coefficients to change in perchlorate concentration, for which there is other evidence for ε_0 up to 4·7M,[3] and for ε_1 up to 1·07M,[7] is understandable if hydration prevents any close approach of ClO_4^- to Fe^{3+} or $FeOH^{2+}$. Rather wider limits must be assigned to any possible variation of $\Delta\varepsilon$ with temperature. In three separate experiments the average change in $\Delta\varepsilon$ for all wavelengths from 290 to 320 mμ was: (*a*) −10·1% from 18·2° to 35·5°, (*b*) −0·3% from 19·4° to 28·3°, (*c*) +4·7% from 20·8° to 27·1°. Similarly, Lister and Rivington[13] found that the extinction coefficient of $FeCNS^{2+}$ changes by less than 2% at 450—520 mμ over the ionic strength range 0·2—1·2 and decreases by −4·5% at 460 mμ, the wavelength of maximum absorption, when the temperature rises from 5° to 45°.

Table 5 gives ε_0 and ε_1 calculated from the relations

$$\varepsilon_0 = \bar{\varepsilon}' - {}^*K_1\Delta\varepsilon/({}^*K_1 + c_1') \qquad \varepsilon_1 = \bar{\varepsilon}' + c_1'\Delta\varepsilon/({}^*K_1 + c_1') \quad . \quad . \quad (23)$$

where $\Delta\varepsilon$ is the average in Table 4 and $\bar{\varepsilon}'$ is measured directly for 3×10^{-4}M-$Fe(ClO_4)_3$ at $c_1' = 0{\cdot}120$M, $I = 0{\cdot}15$, 20·1°, for which conditions $10^{3*}K_1$ is 2·03. The probable errors are ±60 for ε_1 and ±3 for ε_0. Although these extinction coefficients are similar in general form to those of other authors, there are unexplained discrepancies in absolute magnitude as illustrated by the following values for ε_1 at 300 mμ: present work 1610; Olson and Simonson[3] 1950; Turner and Miles[8] 2250; Whiteker and Davidson[14] 2470.

TABLE 5. *Values of* ε_0 *and* ε_1.

	290 mμ	295 mμ	300 mμ	305 mμ	310 mμ	315 mμ	320 mμ	325 mμ	330 mμ
ε_0	260	163	100	63	37	21	13	9	7
ε_1	1610	1620	1610	1570	1490	1400	1270	1110	990

Structure of $FeOH^{2+}$.—It is not self-evident precisely what species, in molecular terms, are detected by the spectrophotometric method. The observation of spectral change does not necessarily imply that anion and cation are in contact, since anions in either the first or the second hydration shell of a cation can alter the ultraviolet spectrum, as Posey and Taube[15] have shown with SO_4^{2-} and $[Co(NH_3)_5H_2O]^{3+}$. Moreover, Bjerrum's theory[16] treats as associated all anions within a distance $q = z_1z_2e^2/2DkT$, which is 10·7 Å for Fe^{3+} and OH^-. Since the radii[17] of those ions are 0·6 Å and 1·4 Å and the diameter[18] of H_2O is 2·8 Å, species such as $Fe^{3+}(H_2O)_nOH^-$, in which the ionic centres are separated 10·4 Å by 3 water molecules and where there is probably no spectral interaction, may count as associated. Cohen[19] assumed that only species with a spectrum different from that of the free ions are detected, but, as King, Espenson, and Visco[20] have realised, the situation is analogous to that discussed by Orgel and Mulliken[21] for neutral molecules which interact to give a charge-transfer spectrum. All species which must be included in the thermodynamically correct description of the equilibria in solutions of constant ionic strength can be shown to contribute to the association constant determined by spectrophotometry. In the conventional treatment, an anion of concentration c contributes to the expression for the mean extinction coefficient of the cation a term εcK in the numerator and a term cK in the denominator. If configurations in which the associated ions are separated by various numbers of water molecules are distinguished by individual extinction coefficients ε_i and association constants K_i, the first term becomes $c\sum\varepsilon_iK_i$ and the second $c\sum K_i$. Consequently, the observed K is $\sum K_i$, the sum of the association constants of the individual

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configurations, and the observed ε is $\sum\varepsilon_i K_i/\sum K_i$, a mean value in which the individual extinction coefficients are weighted according to the fractional contribution of the corresponding configurations to the total association. These considerations are independent of the magnitudes of the ε_i, except that at least one ε_i must differ appreciably from the value for the free cation if there is to be any spectral change on which measurements can be based. The distance d over which the summation of associated pairs must be extended is, as Cohen [19] and Prue [22] have noted, not necessarily equal to q and is in general unknown.

If $^*K_1^0$ at 25° is combined with the ionization constant of water,[23] the equilibrium constant for the formation of $FeOH^{2+}$ from Fe^{3+} and OH^- becomes $6\cdot6 \times 10^{11}$. The predominant species of the type $Fe^{3+}(H_2O)_nOH^-$ is thus the one with $n = 0$, since those with one or more molecules of water between the ions cannot contribute more than a very small fraction of this large value. A good approximation to the ferric system $n \geqslant 1$ is provided by $Co(NH_3)_6{}^{3+}\ldots OH^-$, for which Caton and Prue [24] found an association constant of 71 at zero ionic strength at 25°.

EXPERIMENTAL

Water for all solutions was obtained from dilute alkaline permanganate in a Pyrex conductivity still. Sodium perchlorate was prepared by neutralising in solution a weighed amount of anhydrous sodium carbonate. Barium perchlorate was recrystallised and analysed for barium by precipitation as chromate.[25] To prepare ferric perchlorate, sufficient barium perchlorate to remove most of the sulphate was added to ferric ammonium sulphate. Ferric hydroxide was precipitated by ammonia from the hot solution, washed in suspension, and then digested with excess of perchloric acid. When all the sulphate had been removed by repetition of this procedure, evaporation under reduced pressure with a trace of hydrogen peroxide gave crystals of the composition $Fe(ClO_4)_3,\ 0\cdot58HClO_4,10H_2O$, as determined by analysis for iron with stannous chloride and dichromate [26] and for total perchlorate by Schumb and Sweetser's method.[27]

Ferric solutions were stored for 24 hr. before their optical densities were measured in 3 cm. silica cells on a Unicam S.P. 500 in a thermostatically controlled room. Solution temperatures determined with a calibrated thermocouple were usually constant to within $\pm 0\cdot1°$ in any set of measurements. Small corrections of up to 0·005 were made to the optical densities for differences in cell absorption by comparing the cells filled with distilled water. Comparison of the cells containing the same ferric solution showed that their lengths were identical within the experimental error. The ferric solution of hydrogen-ion concentration c_1' was used as the blank for the measurement of $\bar{\varepsilon} - \bar{\varepsilon}'$ in eqn. (9); its optical density was determined separately for use in eqn. (23).

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