

## The Hydrolysis of Metal Ions. Part 9.<sup>1</sup> Iron(III) in Perchlorate, Nitrate, and Chloride Media (1 mol dm<sup>-3</sup>)

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The hydrolysis of iron(III) has been investigated at 25 °C in 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub>, KNO<sub>3</sub>, and KCl media. The high ionic strength was unavoidable because of the low pH values involved. The results ( $-\log \beta_{pq}$ ) obtained for  $[\text{Fe}_p(\text{OH})_q]^{(3p-q)+}$  are: NaClO<sub>4</sub>,  $-\log \beta_{11} = 2.73(0.006)$ ,  $-\log \beta_{12} = 6.29(0.009)$ ,  $-\log \beta_{22} = 3.20(0.004)$ ; KNO<sub>3</sub>,  $-\log \beta_{11} = 2.77(0.014)$ ,  $-\log \beta_{12} = 6.61(0.037)$ ,  $-\log \beta_{22} = 3.22(0.011)$ ,  $-\log \beta_{34} = 6.98(0.035)$ ; KCl,  $-\log \beta_{11} = 3.21(0.023)$ ,  $-\log \beta_{12} = 6.73(0.029)$ ,  $-\log \beta_{22} = 4.09(0.037)$ ,  $-\log \beta_{34} = 7.58(0.042)$ , the estimated standard deviations being given in parentheses. Some general principles involved in the study of hydrolytic equilibrium systems are discussed.

The hydrolytic reactions of iron(III) have been investigated to a greater extent, perhaps, than those of any other metal ion over a period of nearly one hundred years. Nevertheless, there have been relatively few studies of the equilibria (in solution) involved in these reactions and some of these have been at least partly dependent on earlier work. The study of these equilibria is known to be difficult because of the presence of slow reactions, even at low pH values, leading to the formation of monodisperse or polydisperse polymers, or precipitates, depending on the experimental conditions. The various equilibria that appear to be present were reviewed by Sylva<sup>2</sup> to 1971 and Flynn<sup>3</sup> has recently reviewed polymer and precipitate formation.

The potentiometric method, as might be expected, has provided the most reliable insight into this system. The excellent early study by Hedstrom,<sup>4</sup> using both glass and platinum (redox) electrodes, provided evidence for the formation of the species  $[\text{Fe}(\text{OH})]^{2+}$ ,  $[\text{Fe}(\text{OH})_2]^+$ , and  $[\text{Fe}_2(\text{OH})_2]^{4+}$ . It was proposed in an unpublished report<sup>5</sup> that  $[\text{Fe}_3(\text{OH})_4]^{5+}$  may also be produced. A recent investigation<sup>6</sup> suggests that the high-molecular-weight species  $[\text{Fe}_{12}(\text{OH})_{34}]^{2+}$  is also formed under suitable experimental conditions but the evidence for this is not very convincing.<sup>7</sup>

We feel that this system is of sufficient importance to warrant further investigation, using our advanced experimental and computational techniques; this paper reports on a detailed study carried out at 25 °C in 1.0 mol dm<sup>-3</sup> sodium perchlorate, potassium nitrate, and potassium chloride media.

### Experimental

**Reagents.**—The source of iron was iron(III) nitrate 9-hydrate, iron(III) chloride 6-hydrate, or iron(III) perchlorate 9-hydrate (Fluka Garantie). The base was potassium hydrogencarbonate (Fluka Garantie). The sodium perchlorate was Merck GR grade, and the potassium nitrate, potassium chloride, and all their corresponding acids were Merck Suprapur grade. The water was purified by ultrafiltration and ion exchange, followed by distillation. Iron analyses were carried out using atomic absorption spectrophotometry.

**pH Measurement and Interpretation.**—The pH measurements were carried out using a Radiometer PHM84 pH-meter.

Conversion to hydrogen-ion concentration was achieved via equation (1), where  $\lambda$  is a refinable parameter.<sup>1,8</sup>

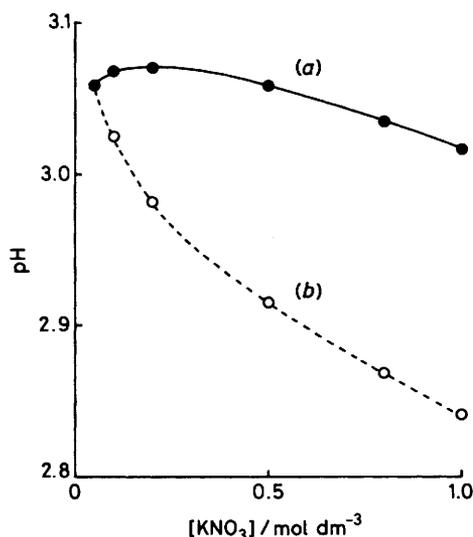
$$[\text{H}^+] = 10^{-\text{pH}/\lambda} \quad (1)$$

The titrations in NaClO<sub>4</sub> posed a problem since the electrode (Radiometer GK2401C) could not be used successfully in this medium because the precipitation of KClO<sub>4</sub> (derived from the filling solution of KCl) at the porous-pin interface would interfere with the electrolyte flow, causing unsteady pH readings.<sup>9</sup>

To circumvent this problem the filling solution was changed from saturated KCl to saturated NaCl and the electrode allowed to equilibrate with the new electrolyte for one month. As is to be expected, the behaviour of the NaCl electrode was quite different from that of the normal KCl-filled electrode. This is the result of the imbalance of ionic mobilities between Na<sup>+</sup> and Cl<sup>-</sup> (being 50.1 and 76.4 S cm mol equiv.<sup>-1</sup> dm<sup>-3</sup> respectively) compared with KCl (K<sup>+</sup>, 73.5).<sup>10</sup> This has the effect of increasing the liquid junction potential and hence decreasing the pH readings as was verified experimentally by measuring the pH of 10<sup>-3</sup> mol dm<sup>-3</sup> solutions of hydrochloric acid at various ionic strengths (KNO<sub>3</sub>) using both KCl and NaCl electrodes. Figure 1 illustrates these results.

The veracity of the NaCl electrode was demonstrated by the measurement of the pK<sub>a</sub> of benzoic acid (25 °C, 0.10 mol dm<sup>-3</sup> NaNO<sub>3</sub>) using both the NaCl and KCl electrodes. The results obtained are 4.0054(0.0008) and 4.0024(0.0007), respectively, the estimated standard deviations (e.s.d.) being given in parentheses. These values compare excellently with those recently obtained.<sup>11</sup> Clearly, the NaCl electrode can be employed successfully if the approach defined by equation (1) is used since the refinement of  $\lambda$  makes a uniform displacement on the pH scale inconsequential; the meter readings will not, of course, correspond to conventional pH values.

For the iron(III) titrations, the refined values of  $\lambda$  for the perchlorate, nitrate, and chloride systems are 1.970, 0.983, and 0.964, respectively. The high value for the perchlorate system is a result of using the NaCl electrode and is the means by which the increased junction potential, and hence the displacement on the pH scale, is accommodated.



**Figure 1.** pH Meter readings of 1 mmol dm<sup>-3</sup> HCl solutions of different KNO<sub>3</sub> concentration: (a) saturated KCl solution-filled glass electrode and (b) saturated NaCl solution-filled glass electrode

**Table 1.** Summary of titrations of iron(III) at 25 °C

Total (initial) iron(III) concentration (10 <sup>-3</sup> mol dm <sup>-3</sup> )	-log[H <sup>+</sup> ]	Number of points
(a) In 1.0 mol dm <sup>-3</sup> NaClO <sub>4</sub>		
0.214	1.764—3.301	123
0.539	1.760—3.084	215
1.000	1.785—2.957	175
2.017	1.786—2.830	175
5.085	1.781—2.679	185
10.518	1.759—2.597	216
20.357	1.708—2.512	260
(b) In 1.0 mol dm <sup>-3</sup> KNO <sub>3</sub>		
0.199	1.694—3.302	110
0.503	1.693—3.187	157
1.001	1.694—2.971	155
1.989	1.693—2.894	158
4.992	1.695—2.760	166
10.034	1.694—2.624	165
19.776	1.694—2.526	160
(c) In 1.0 mol dm <sup>-3</sup> KCl		
0.182	1.886—3.440	109
0.468	1.885—3.193	107
0.870	1.887—3.102	107
1.882	1.885—2.970	93
4.180	1.884—2.772	93
8.570	1.888—2.611	85
17.984	1.885—2.462	77

**Procedure.**—For each titration the appropriate iron(III) solution was prepared at a pH of *ca.* 1.5 and used immediately. Checks made of the pH stability of these solutions showed negligible drift ( $\pm 0.004$  units) over a period of 24 h.

The titrations were carried out in the usual manner.<sup>8</sup> Potassium hydrogencarbonate was used as titrant, rather than potassium hydroxide, to avoid localised concentration effects; this approach was first used by Hedstrom.<sup>4</sup> A summary of the titrations is given in Table 1.

**Selection of pH Range.**—It is our practice to commence a

titration at as low a pH as practicable (without interfering with the ionic strength). Titrations are complete when the change in pH with time is greater than 0.002 units during the first 5 min after base addition. This change will always cause a decrease in pH since it occurs at the point of onset of precipitation when, for any species  $[\text{Fe}_p(\text{OH})_q]$  (charges are ignored) in solution,  $q/p$  is always less than the value of this ratio in the precipitate; thus, as the polymers are converted to precipitate, protons are released. The continued addition of base accelerates this process, producing the apparently paradoxical result of a decrease in pH.

The practice of commencing titrations at a very low pH often produces a large number of points, which may represent negligible hydrolysis, on the titration curve; these points have a deleterious effect on the overall data set which is reflected in the numerical refinement of the data. Therefore, some reduction of the pH range is usually necessary.

In our earlier work<sup>11,12</sup> where the least important species is still present at appreciable levels, it was sufficient simply to remove those points which represented less than *ca.* 5% hydrolysis. In this work there are two minor species which are present to only a small extent throughout the entire pH range but which, nevertheless, appear to need inclusion in the hydrolysis scheme. The selection procedure therefore needed to be more stringent (*ca.* 8%). To facilitate this selection procedure we modified the program MINQUAD<sup>13,14</sup> to process data at any point in a titration (see below).

**Computational Procedure.**—Numerical analysis of the data was carried out using the computer program MINQUAD.<sup>13,14</sup> Our version of MINQUAD is an augmented version of the original and has the following additional features.

(i) Two programmed model selection procedures are available whereby the experimental data can be examined systematically to find the most appropriate model.

(ii) Refinement of negative formation constants is possible; obviously such constants are chemically meaningless but in the numerical process of data refinement a formation constant can temporarily assume a negative value. In the original version of MINQUAD<sup>13,14</sup> such constants would often be prematurely rejected.

(iii) Numerical refinement of the analytical proton excess (which can be negative) is performed. This allows a titration to be commenced at any point, irrespective of the extent of hydrolysis. It can be seen that this procedure also accounts quantitatively for any free acid or base that may be present in the reagents.

(iv) Refinement of the parameter  $\lambda$  in equation (1) is possible when necessary. This parameter can be considered as a conversion factor incorporating such aspects as activity coefficient, liquid junction potential, asymmetry potential, and calibration errors.

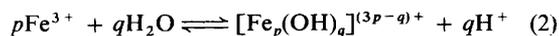
The use of the refinable parameter  $\lambda$  means that it is present in all the species terms in the mass-balance equations. Thus, the refinable formation constants of the species are functions of the (refinable) value of  $\lambda$ . Invariant (non-refinable) equilibrium constants, such as that referring to the ionisation of water, cannot be included, therefore, in an equilibrium system when  $\lambda$  is being refined with the other parameters. However, it is satisfactory initially to exclude the water ionisation reaction, determine the optimum value of  $\lambda$ , and then use this value as a constant when the water ionisation reaction is included. In practice, it has been found that this reaction is significant only at pH values close to neutrality, and its effect is to improve the estimated standard deviations of the formation constants without significantly altering their values or the goodness-of-fit parameter  $R$ .

(v) Optional scaling of the proton mass-balance equation to any desired extent such that species of high molecularity, for

example  $[\text{Fe}_{12}(\text{OH})_{34}]^{2+}$ , can be considered without invoking numerical problems associated with the magnitude of the variables involved.

## Results

For the (hypothetical) hydrolysis reactions of iron(III) the overall stoichiometric equilibrium constants,  $\beta_{pq}$ , are defined for equation (2) by equation (3). Each species is represented either by its formula or by  $(p,q)$  notation.



$$\beta_{pq} = \frac{[\text{Fe}_p(\text{OH})_q]^{(3p-q)+} [\text{H}^+]^q}{[\text{Fe}^{3+}]^p} \quad (3)$$

For the three experimental media, initial data analysis involved models containing in various combinations, the species (1,1), (1,2), (2,1), (2,2), (3,4), (3,5), and high-molecular-weight species  $[\text{Fe}_p(\text{OH})_q]^{(3p-q)+}$  with  $q/p$  ratios in the vicinity of 2.8. These numerical analyses demonstrated that the only species likely to be involved in this equilibrium system under the experimental conditions are (1,1), (1,2), (2,2), and (3,4). The species (1,3) and (1,4), which appear only in neutral and basic media,<sup>15</sup> are not relevant here because of the low pH values involved in the experiments ( $\text{pH} < 3.5$ ).

The criteria on which this decision is based have been outlined previously;<sup>8</sup> they are that the goodness-of-fit parameter,  $R$ , is less than 0.002, and the e.s.d. of the formation constants of the species are  $< 10\%$ . The arbitrariness of these criteria has been stressed<sup>8</sup> but not adequately explained.

The mass-balance equation for the metal ion in a hydrolytic equilibrium system is given by equation (4) (charges are omitted). The summation in equation (4) is taken for all species

$$M(\text{total}) = M(\text{free}) + \sum_{p,q} p\beta_{pq} [\text{M}]^p [\text{H}]^{-q} \quad (4)$$

$(p,q)$ . Conceptually equation (4) can be expressed as equation (5), where  $M(\text{tot})$  is the total metal-ion concentration,  $M(\text{free})$  is

$$M(\text{tot}) = M(\text{free}) + M(\text{sp } 1) + M(\text{sp } 2) + \dots + M(\text{sp } n) + M(\text{m sp } 1) + M(\text{m sp } 2) + \dots + M(\text{m sp } n) + M(\text{error}) \quad (5)$$

the unreacted or free metal-ion concentration,  $M(\text{sp } 1-n)$  is the contribution to the metal ion mass-balance equation by 'major' species 1— $n$ ,  $M(\text{m sp } 1-n)$  is the contribution by detectable minor species 1— $n$ , and  $M(\text{error})$  the errors which affect the metal ion mass-balance equation. Examples of the last term are spurious (non-existent) species, numerically missed (detectably present) species, and/or species present at concentrations too low to be detected reliably but high enough to interfere, and any other errors which affect the metal ion mass-balance equation.

Data analysis consists of the minimisation of the quantity (6)

$$U = [M(\text{total,calculated}) - M(\text{total,known})]^2 \quad (6)$$

so that  $R$ , as defined by equation (7), is minimised, where  $U$  is

$$R = [U/\Sigma(M_i^2 + B_i^2)]^{\frac{1}{2}} \quad (7)$$

the error square sum,  $M_i$  is the total metal-ion concentration, and  $B_i$  is the total base concentration added. It should be noted that MINQUAD also minimises  $[H(\text{total,calculated}) - H(\text{total,observed})]^2$  both separately, and independently of the metal mass-balance equation.

The overall  $R$ ,<sup>8</sup> which is a property of experimentally

observed quantities and not functions thereof, is normalised by equation (7) in terms of both the number of titration points and the total concentration of reactants. It was 'borrowed' from the field of X-ray crystallography and first introduced into solution chemistry by Vacca *et al.*<sup>16</sup> We have arbitrarily chosen that  $R < 0.002$  be a necessary (but not sufficient) condition for model acceptance.

The precision of the detection of the individual species (1— $n$ ) is expressed by the values of the e.s.d.s of the formation constants of the individual species. Any species is considered 'real' if this value is  $< 10\%$ . Where one or more species is dominant, the e.s.d. can often be  $< 5\%$  and the value of the formation constant can be relatively independent of the other terms (other models) in equation (5).<sup>11,12</sup>

The application of both of these criteria simultaneously is a stringent model selection procedure since, *inter alia*, they will often act in opposition. Thus, the overall goodness-of-fit can be improved by the inclusion of a spurious species (high e.s.d.) or, alternatively, the inclusion of a 'real' species (of acceptable e.s.d.) may have a deleterious effect on  $R$ . The effect of the simultaneous application of both criteria therefore invalidates the criticism that, with enough parameters, any number of models can be accommodated.

The above approach has been consistently successful in our earlier work involving the hydrolysis of  $\text{Cu}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Th}^{4+}$ ,  $\text{Sc}^{3+}$ ,  $\text{Be}^{2+}$ , and  $\text{Al}^{3+}$ .<sup>1,8,11,12,17-19</sup> Examination of Table 2, however, indicates that for  $\text{Fe}^{3+}$  an unambiguous result is not always obtained when the species (1,1), (1,2), (2,2), and (3,4) are considered using these criteria. Hence the most satisfactory procedure for model selection must be determined. Three different approaches can be considered.

(i) Vacca *et al.*<sup>16</sup> discuss this problem in some detail and conclude that the application of the Hamilton ratio test<sup>20</sup> on the  $R$  factors of the various models is appropriate. They observe that this approach does not necessarily remove all ambiguity but that it may clearly favour one model at the expense of others. We believe, however, that this approach is of indeterminate value since a statistical test involving parameters subject more significantly to systematic rather than to random errors can only lead to an uncertain result.<sup>21</sup> Indeed, it is feasible that systematic errors,  $M(\text{error})$  in equation (5), can mimic an  $M(\text{sp } n)$  or  $M(\text{m sp } n)$  term, leading to the inclusion of a spurious species. Jaskolski and Lomozik<sup>22</sup> also recommend that the selection of chemical models should not be based on the  $R$  factor alone. The latter should always be regarded as an auxiliary tool and used in conjunction with other tests.

(ii) Baes and Mesmer<sup>15</sup> discuss but do not use numerical acceptance criteria and merely accept the model for which  $\sigma_n$  (e.s.d. of the average ligand number) is least. In addition, they repeatedly stress the importance of accepting a model which contains the least number of species, again without defining any acceptance criteria. The Occam's razor principle<sup>15</sup> notwithstanding, it does not follow that the simplest model is necessarily the most realistic (correct) one, so this is an arbitrary method which could yield a misleading result.

(iii) The application of quantitatively consistent criteria (the e.s.d. and the  $R$  factor), and, if ambiguity remains, chemical reasoning or judgement, would seem to be the wisest approach. This latter aspect has not, until recently, been exploited and deserves attention. The work of Brown *et al.*<sup>23</sup> showed the possibility of reducing what might seem to be a bewildering array of possible stoichiometries of hydrolysis products to four distinct groups of which the last is trivial since it refers only to (2,1) species. The first three groups are as follows.<sup>23</sup>

Group 1. Metal ions which may be six-co-ordinate and octahedral in the purely aquated form but which form polynuclear hydrolysis products which are four-co-ordinate.

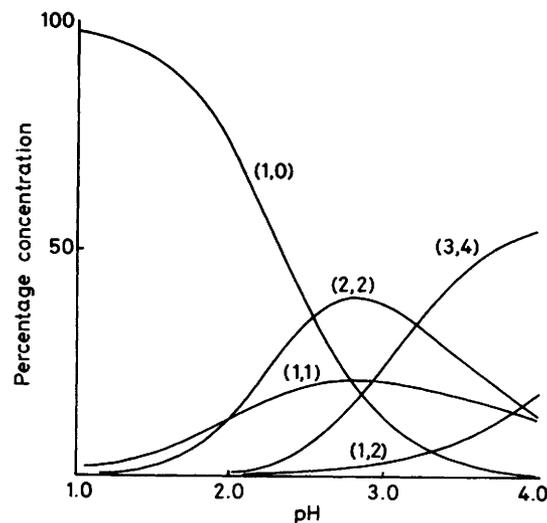
**Table 2.** Comparison of models of the hydrolysis of iron(III)

Model	$-\log \beta_{pq}$	E.s.d. of $-\log \beta_{pq}$	E.s.d. (%) of $\beta_{pq}$	$R$
<b>(a) 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub></b>				
(1,1)	2.94	0.011	2.6	0.002 66
(2,2)	3.09	0.002	0.5	
(1,1)	2.73	0.006	1.3	0.001 91
(1,2)	6.29	0.009	2.1	
(2,2)	3.20	0.004	0.9	0.002 54
(1,1)	2.76	0.018	4.1	
(2,2)	3.17	0.009	2.1	
(3,4)	7.23	0.045	10.4	
(1,1)				
(1,2)				
(2,2)	model fails: $\beta_{3,4}$ negative			
(3,4)				
<b>(b) 1.0 mol dm<sup>-3</sup> KNO<sub>3</sub></b>				
(1,1)	3.25	0.032	7.3	0.002 20
(2,2)	3.03	0.003	0.8	
(1,1)	3.00	0.020	4.7	0.001 97
(1,2)	6.45	0.026	6.0	
(2,2)	3.11	0.006	1.4	0.001 92
(1,1)	2.77	0.020	4.7	
(2,2)	3.21	0.014	3.2	
(3,4)	6.83	0.028	6.3	
(1,1)	2.77	0.014	3.3	0.001 83
(1,2)	6.61	0.037	8.6	
(2,2)	3.22	0.011	2.6	0.001 83
(3,4)	6.98	0.035	8.2	
<b>(c) 1.0 mol dm<sup>-3</sup> KCl</b>				
(1,1)	3.16	0.016	3.6	0.001 77
(2,2)	3.81	0.011	2.5	
(1,1)	3.45	0.025	5.8	0.001 30
(1,2)	6.59	0.018	4.1	
(2,2)	3.82	0.007	1.7	0.001 38
(1,1)	3.00	0.011	2.6	
(2,2)	4.68	0.151	34.8	
(3,4)	7.29	0.021	4.8	
(1,1)	3.21	0.023	5.2	0.001 20
(1,2)	6.73	0.029	6.7	
(2,2)	4.09	0.037	8.5	0.001 20
(3,4)	7.58	0.042	9.6	

Examples of such ions are  $\text{Al}^{3+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Be}^{2+}$  and the stoichiometries of the polynuclear hydrolysis products are typically (3,3), (3,4), (3,5), (4,4), and (6,8). It is particularly noteworthy that this Group does not form the (2,2) dimer. For tripositive cations, any trimer that is produced will be (3,4) only, unlike bivalent cations where both (3,4) and (3,5) may form.

**Group 2.** Metal ions which are most commonly six-coordinate and octahedral and remain so in their polynuclear hydrolysis products. Examples are  $\text{Cu}^{2+}$ ,  $\text{Sc}^{3+}$ , and  $\text{Cr}^{3+}$ . The stoichiometries of the polynuclear hydrolysis products are (2,2), usually a dominant species, and the trimers (3,4) and (3,5). For the tripositive cations, our earlier experience<sup>1,8,11,12,16-18,23</sup> has shown that the following empirical rules concerning the formation of trimers apply: when  $-\log \beta_{11} > 4.3$  (at zero ionic strength) for the cation, then the trimer will be (3,5), and when  $-\log \beta_{11} < 4.3$ , the trimer will be (3,4).

**Group 3.** Metal ions of cationic charge of at least +3, such as  $\text{Th}^{4+}$ ,  $\text{Bi}^{3+}$ , and  $\text{Zr}^{4+}$ , whose polynuclear hydrolysis products are of high molecularity and of complex, unknown structure. There is no trimer formed (results for  $\text{Zr}^{4+}$  are



**Figure 2.** Percentage distribution of iron(III) hydrolysis products at a total (initial) iron(III) concentration of  $19.776 \text{ mmol dm}^{-3}$  in  $1 \text{ mol dm}^{-3}$   $\text{KNO}_3$  at  $25^\circ\text{C}$

considered to be unreliable because of attendant experimental difficulties).

Irrespective of the Group to which a metal ion belongs, it can always be assumed that a (1,1) species will be produced. It should be noted, however, that this species is not always detected because of the relative dominance of a polynuclear species and/or poor experimental design. Similar arguments apply to the (1,2) species except that it is usually very difficult to detect because of the intervention of precipitation before its formation becomes appreciable; this is not always the case, particularly for trivalent metal ions. In the general case it is readily argued that  $\log \beta_{1q} < q \log \beta_{11}$  ( $q > 1$ )<sup>23</sup> but that for  $q > 2$  the species are not usually detectable using potentiometric titration techniques.

Classification into Groups 1, 2, or 3 will be completed when, as a last step, any special cases, indicated by prior knowledge, intuition, or trial and error, are considered, for example, (2,1) for  $\text{Be}^{2+}$ <sup>11</sup> or '(13,32)' [more correctly, (p,q) with  $q/p = 2.46$ ] for  $\text{Al}^{3+}$ .<sup>1</sup>

Since, in the hydrolysis of iron(III), the present results, together with the earlier work of Hedstrom,<sup>4</sup> provide strong evidence for the detectable existence of the (2,2) dimer, we can confidently place  $\text{Fe}^{3+}$  in Group 2. It is the chemical reasoning alone which leads to the species list as stated, together with the special case of the high-molecular-weight species with a  $q/p$  ratio of 2.8.

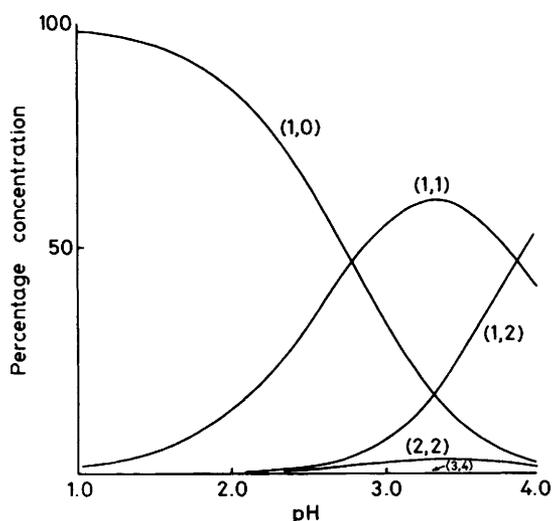
Table 2 contains the results of computations for four models for each of the three media, involving the species (1,1), (1,2), (2,2), and (3,4) (monomers plus Group 2 species). For the reasons outlined in the above discussion, we have chosen, for the nitrate and chloride systems, the model containing all four of these species and note that the  $R$  factors remain satisfactory (and indeed, decrease with this number of species) as do the e.s.d.s. In the perchlorate medium there is a departure with the (3,4) species not being detectable (as is usually the case for undetectable species, the  $\beta_{pq}$  value is negative for which the reasons are not apparent). We deduce that this is simply the result of the greater ease of precipitation in the presence of perchlorate ion as opposed to the nitrate or chloride ion; this is not a surprising result since precipitation reactions are well known to be strongly anion dependent.<sup>24</sup>

Figures 2 and 3 illustrate the percentage distribution of each species for the highest and lowest total initial iron(III) concentration in the nitrate medium.

**Table 3.** Survey of some results of the potentiometric investigation of the hydrolysis of iron(III)

Medium	Temp. (°C)	Total iron(III) concentration in (10 <sup>-3</sup> mol dm <sup>-3</sup> )	-log β <sub>pq</sub>					Ref.
			(1,1)	(1,2)	(2,1)	(2,2)	(3,4) (12,34)	
3 mol dm <sup>-3</sup> NaClO <sub>4</sub>	25	0.10—50.0	3.05	6.33		2.91		4
	25	not given	3.05	6.31		2.96	5.77	5
	25	1.25—40.0	3.10			2.80		6
2.67 mol dm <sup>-3</sup> NaClO <sub>4</sub>	25	0.5	2.92 <sup>a</sup>	5.70		3.22		b
	55	0.5	2.44 <sup>a</sup>	4.54		2.74		b
	80	0.5	2.06 <sup>a</sup>	3.20		2.45		b
0	25		2.60	7.30				c
0.1 mol dm <sup>-3</sup> NaClO <sub>4</sub>	20		2.97	6.98	0.98	3.00		d
1.0 mol dm <sup>-3</sup> NaClO <sub>4</sub>	20		2.73	6.05		2.85		25
1.0 mol dm <sup>-3</sup> NaClO <sub>4</sub>	25	0.20—20.4	2.73	6.29		3.20		This work
1.0 mol dm <sup>-3</sup> KNO <sub>3</sub>	25	0.20—19.8	2.77	6.61		3.22	6.98	This work
1.0 mol dm <sup>-3</sup> KCl	25	0.18—18.0	3.21	6.73		4.09	7.58	This work

<sup>a</sup> From spectrophotometric determinations. <sup>b</sup> R. S. Sapienszko, R. C. Patel, and E. Matijevic, *J. Phys. Chem.*, 1977, **81**, 1061. <sup>c</sup> A. B. Lamb and A. G. Jaques, *J. Am. Chem. Soc.*, 1938, **60**, 1215. <sup>d</sup> C. Ropars, M. Rougee, M. Momenau, and D. Lexa, *J. Chim. Phys. Phys. Chim. Biol.*, 1968, **65**, 816.



**Figure 3.** Percentage distribution of iron(III) hydrolysis products at a total (initial) iron(III) concentration of 0.199 mmol dm<sup>-3</sup> in 1 mol dm<sup>-3</sup> KNO<sub>3</sub> at 25 °C

**Table 4.** Comparison of the hydrolytic speciation of some trivalent metal ions

Metal ion	Group	Ionic radius (Å)	Documented polynuclear species	Ref.
Fe <sup>3+</sup>	2	0.65	(2,2), (3,4)	This work
Al <sup>3+</sup>	1	0.51	(3,4), (13,32) <sup>a</sup>	1
Sc <sup>3+</sup>	2	0.73	(2,2), (3,5)	12
Tl <sup>3+</sup>	(2) <sup>b</sup>	0.88	None	c
In <sup>3+</sup>	2	0.81	(2,2)	d
Bi <sup>3+</sup>	3	1.02	(6,12), (9, q = 20, 21, or 22)	26

<sup>a</sup> More correctly, (p,q), q/p = 2.46. <sup>b</sup> No documented polynuclear species. <sup>c</sup> T. E. Rogers and G. M. Waind, *Trans. Faraday Soc.*, 1961, **57**, 1360. <sup>d</sup> Part 4, P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1982, 1911.

## Discussion

Table 3 compares the results of earlier investigations with our results. The model proposed by Hedstrom<sup>4</sup> (for 3.0 mol dm<sup>-3</sup> NaClO<sub>4</sub>) and that of the present work (1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub>) are in agreement but, overall, the agreement between the values

of the equilibrium constants can only be considered as satisfactory. Perrin<sup>25</sup> also used 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> as the medium and produced constants which agreed exactly with our results for the (1,1) species, and satisfactorily for the (1,2) and (2,2) species. Despite the quality of both Perrin's and Hedstrom's work, our advanced automated experiment method (which yields a very large amount of data) and computational techniques of analysis are more likely to yield the most reliable results. With the exception of the claims for the (2,1) and (12,34) species, the overall agreement of the numerous investigations shown in Table 3 is generally satisfactory considering some differences in the experimental conditions.

The complexing ability of the three anions in the present work is ClO<sub>4</sub><sup>-</sup> ~ NO<sub>3</sub><sup>-</sup> < Cl<sup>-</sup>, from which it would be expected that, for all species (as -log β<sub>pq</sub>), the order of the stability constants, β<sub>pq</sub>(anion), is β<sub>pq</sub>(Cl<sup>-</sup>) > β<sub>pq</sub>(NO<sub>3</sub><sup>-</sup>) ~ β<sub>pq</sub>(ClO<sub>4</sub><sup>-</sup>). This was indeed observed and is the result of the relatively strong complex formed between Fe<sup>3+</sup> and Cl<sup>-</sup> giving [FeCl]<sup>2+</sup> which, on simple charge arguments alone (which can be an oversimplification<sup>23</sup>) can be expected to hydrolyse far less than the parent cation. With polynuclear complexes, this effect is greater for reasons which are not apparent.

It is instructive to compare the hydrolytic speciation of a variety of tripositive cations, six of which are listed in Table 4. The variation in polynuclear speciation is remarkable, being both subtle (Al<sup>3+</sup> and Fe<sup>3+</sup>, or Sc<sup>3+</sup> and Fe<sup>3+</sup>) or dramatic (Bi<sup>3+</sup> and any other ion). These variations occur despite the apparent preference of all of the aquated ions for six-coordination (and presumably octahedral stereochemistry). The only significant differences between the ions are the ionic radii and the electronic structures; these differences must account for the variation in speciation.

In making such comparisons, however, it is important to temper the hypotheses with any experimental limitations which might be imposed by precipitation reactions or other considerations. Thus, to take one example, the surprising result that thallium(III) does not form polynuclear species may simply be the result of precipitation preventing the detection of such species. This limitation also applies to In<sup>3+</sup> where species 'beyond' (2,2) cannot be detected because of precipitation.<sup>26</sup>

Iron(III) clearly belongs to the Group 2 classification and chemical reasoning has enabled ambiguity in model selection to be resolved. The preferred model contains the two minor species (1,2) and (3,4) even though it is recognised that their existence

might be questioned. It remains to be seen how well the principles enunciated in the present work apply to other metal ion systems.

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