The Complexation of Iron(III) with Sulphate, Phosphate, or Arsenate Ion in Sodium Nitrate Medium at 25 °C

Ging H. Khoe *
Australian Nuclear Science and Technology Organisation, Lucas Heights Research Laboratories, Private Mail Bag 1, Menai, NSW 2234, Australia
Robert G. Robins
Department of Mineral Processing and Extractive Metallurgy, University of New South Wales, P.O. Box 1, Kensington, NSW 2033, Australia

---

The complexation and hydrolysis of iron(III) has been investigated potentiometrically using a glass electrode at 25 °C in the presence of sulphate ion in 1.0 mol dm^{-3} sodium nitrate. The formation constants of the species which are defined as $[\mathrm{Fe}_p(\mathrm{OH})_{q-r}(\mathrm{SO}_4)_r] = \beta_{\mathrm{species}}[\mathrm{Fe}]^p[\mathrm{H}]^{-q}[\mathrm{HSO}_4]^r$ (charges ignored for brevity), expressed as log β_{species}, are: log $\beta_{\mathrm{Fe(OH)}} = -3.01$ (0.01), log $\beta_{\mathrm{Fe_2(OH)_2}} = -3.09$ (0.01), log $\beta_{\mathrm{Fe_3(OH)_4}} = -6.92$ (0.03), log $\beta_{\mathrm{Fe(SO_4)}} = 0.41$ (0.01), and log $\beta_{\mathrm{Fe_3(OH)_4(SO_4)}} = -5.44$ (0.02). These results required the independent determination of the second dissociation constant of sulphuric acid (pK_2), which was found to be 1.104 (0.005). The complexation of iron(III) with phosphate and arsenate ion has also been investigated in the same manner at 25 °C in 3.0 mol dm^{-3} $\mathrm{NaNO_3}$. No significant hydrolysis was observed because of the low pH values (<2.0) involved. The formation constants of the species which are defined as $[\mathrm{Fe}_p\mathrm{H}_{3r-q}(\mathrm{PO}_4)_r] = \beta_{\mathrm{species}}[\mathrm{Fe}]^p[\mathrm{H}]^{-q}[\mathrm{H_3PO_4}]^r$, are: log $\beta_{\mathrm{Fe(HPO_4)}} = 1.28$ (0.03) and log $\beta_{\mathrm{Fe(PO_4)}} = 0.78$ (0.01). The corresponding results for the iron(III)–arsenate system are: log $\beta_{\mathrm{Fe(HAsO_4)}} = 0.11$ (0.02) and log $\beta_{\mathrm{Fe(AsO_4)}} = -1.34$ (0.03). The first dissociation constants of phosphorus(V) and arsenic(V) acids were found to be 1.763 (0.002) and 2.128 (0.002) respectively.

Although the iron(III)–sulphate system has been investigated numerous times[1–4] the equilibria involving the *ternary* system iron(III)–water–sulphate in *solution*[5] has received little attention. The system has been investigated at 25 °C in 1.0 mol dm^{-3} sodium nitrate. The measurements were extended to include both phosphate(V) and arsenate(V) also at 25 °C, but in these systems the accessible pH ranges were severely limited by precipitation reactions. This necessitated measurements at such low pH values that, to preserve ionic strength constancy, a medium of 3.0 mol dm^{-3} sodium nitrate was used; the low pH values precluded hydrolysis reactions.

The second dissociation constant of sulphuric acid and the first dissociation constants of phosphorus(V) and arsenic(V) acids were determined independently in the appropriate ionic media.

Experimental

Reagents.—The source of iron was iron(III) nitrate 9-hydrate (Fluka Garantie). The arsenic(V) acid was Merck Extra Pure, and the sulphuric acid, phosphorus(V) acid, sodium sulphate, and sodium nitrate 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. The Merck Suprapur anhydrous sodium sulphate was used as a primary standard after checking that it did not contain absorbed moisture. The acids were standardised by a sodium hydroxide solution which was in turn analysed using sodium tetrahydroborate as a primary standard.[6]

pH *Measurement and Interpretation.*—The pH measurements were carried out using a Radiometer PHM84 pH meter and a GK2401C combined glass electrode. Hydrogen-ion concentrations were determined using $[\mathrm{H^+}] = 10^{-\mathrm{pH}}/\lambda$, where λ is a refinable parameter.[7–9] This approach is nearly identical to that used in the program SUPERQUAD except that in the latter the Nernst equation is addressed directly.[9,10]

The refined values of λ for the different sets of titrations were as follows: iron–sulphate system, 1.171; sulphuric acid, 1.211; iron–phosphate system, 2.358; phosphoric acid, 2.409; iron–arsenate system, 2.462; and arsenic(V) acid, 2.407. In the work of Sylva and co-workers,[9,11–17] 0.1 mol dm^{-3} sodium or potassium nitrate medium could be used since higher initial pH values were involved; here, λ was in the range 0.701—0.914. λ is dependent on experimental conditions such as temperature, ionic medium and strength, and the individual characteristics of the electrode such as the liquid-junction and asymmetry potentials. Since the investigations pertaining to the various equilibrium systems were not performed using the same electrode, a proper comparison of λ obtained for the various equilibrium systems cannot be carried out. The $-\log [\mathrm{H^+}]$ values shown in Tables 1—3 have been calculated from the pH *meter readings* using the above λ values.

Procedure.—For titrations of the iron(III)–sulphate system, the iron(III) solution was prepared with a variable concentration of sulphate (see Table 1) from the sodium sulphate stock solution, at a pH of *ca.* 1.5, and used immediately. For titrations in the presence of the phosphate and arsenate ions, the iron(III) solution was prepared at a pH of *ca.* 0.8 from the stock of acidified iron nitrate solution (pH *ca.* 0.6).

The titrations were carried out in the previously described manner; sodium hydrogencarbonate was used as titrant, rather than sodium hydroxide, to avoid localised concentration effects.[18]

Titrations were commenced at as low a pH as practicable without significantly interfering with the ionic strength. In our initial work with the iron(III) system,[18] it was possible to reduce the compositional changes to *ca.* 2% or less of the ionic strength. In the present work, even with an ionic strength of 1.0 or 3.0 mol dm^{-3} the sum of the initial concentrations of reactants was as

Table 1. Summary of titrations of iron(III) in the presence of sulphate ions in 1.0 mol dm^{-3} NaNO$_3$ at 25 °C

Total (initial) concentration (10^{-3} mol dm^{-3})			
Fe^{III}	SO$_4^{2-}$	$-\log[H^+]$	Number of points
19.77	20.0	1.769—2.390	147
19.51	10.0	1.771—2.372	137
19.79	4.0	1.771—2.385	145
4.96	10.0	1.770—2.647	159
5.30	5.0	1.769—2.652	127
4.98	2.5	1.771—2.652	153
4.92	1.0	1.769—2.650	151
0.99	2.0	1.770—2.910	214
0.99	1.0	1.770—2.922	169
0.99	0.5	1.769—2.929	213
0.20	0.4	1.771—3.253	174
0.20	0.2	1.771—3.306	172

Table 2. Summary of titrations of iron(III) in the presence of phosphate ions in 3.0 mol dm^{-3} NaNO$_3$ at 25 °C

Total (initial) concentration (10^{-3} mol dm^{-3})			
Fe^{III}	H$_3$PO$_4$	$-\log[H^+]$	Number of points
19.80	20.60	0.924—1.248	161
19.80	41.20	0.922—1.228	126
19.80	10.30	0.922—1.618	193
9.90	5.15	0.923—1.763	179
4.95	5.15	0.923—1.384	177
4.95	10.30	0.922—1.354	185
0.99	1.03	0.922—1.620	148
0.99	2.06	0.924—1.580	174
0.20	0.21	0.923—1.960	213

Table 3. Summary of titrations of iron(III) in the presence of arsenate ions in 3.0 mol dm^{-3} NaNO$_3$ at 25 °C

Total (initial) concentration (10^{-3} mol dm^{-3})			
Fe^{III}	H$_3$AsO$_4$	$-\log[H^+]$	Number of points
19.8	9.70	0.968—1.287	141
9.85	9.70	0.973—1.329	151
4.93	4.85	1.045—1.364	107
1.98	1.94	1.070—1.519	122
0.49	0.49	1.105—1.749	116
0.20	1.94	1.089—1.849	138
0.20	0.19	1.170—1.991	209

high as 6% of the ionic strength. This should be considered in the light of Sillen's statement (an arbitrary approximation) that it is reasonable for the reactants to represent up to 10% of the ionic strength.[19]

In the iron(III)–sulphate system, titrations were considered to be complete when the change in pH with time was greater than 0.002 units during the first 5 min after base addition. However, in the iron(III)–phosphate and –arsenate systems, no such pH relaxation was observed even though precipitation did occur; this was taken to indicate that the precipitation reactions do not involve hydroxo-species,[18] an assumption that was confirmed by the results of the numerical analyses (the experimental pH values in these systems were too low for hydroxo-species to form in appreciable quantities). Accordingly, for these systems, tyndallimetry was used to indicate precipitation and hence completion of a titration. Since this technique is unavoidably subjective, the last 20 titration points were excluded from the data sets in order to ensure that only equilibrium points were used.

Selection of pH *Range*.—The practice of commencing titrations at very low pH values can produce a large number of points, some of which do not make a meaningful contribution to the data because of the negligible extent of complex formation. Indeed, such points can have an adverse effect on the data set, as is indicated by the results of the numerical refinement of the data. Therefore, some truncation of the pH range at the low values was necessary, as in our earlier work.[18] It is important here to note that our augmented version of the computer program MINIQUAD[20–22] allows a titration to be commenced at any point, irrespective of the extent of complexation, dissociation, or hydrolysis. It also accounts quantitatively for any free acid or base that may be present in the reagents.

Results

At each point of the titrations, the complexation reactions of the metal ion (M) and the concomitant deprotonation reactions of water and the protonated ligand (H$_a$L) can be hypothetically represented by equations (1) and (2) (charges omitted for brevity).

$$pM + qH_2O + rH_aL \rightleftharpoons M_p(OH)_q(H_aL)_r + qH \qquad (1)$$

$$pM + qH_2O + rH_aL \rightleftharpoons M_p(OH)_{(q-ar)}L_r + qH + arH_2O \qquad (2)$$

$$\beta_{p,q,r} = \frac{[M_p(OH)_{(q-ar)}L_r][H]^q}{[M]^p[H_aL]^r} \qquad (3)$$

If pH of the solution is sufficiently low such that the extent of hydroxo-species formation is negligible, the complexation reaction and the corresponding formation constant can be expressed by equations (4) and (5). In this case q, which can be considered as the number of OH$^-$ supplied by the titrant or the number of water molecules deprotonated, is less than or equal to ar. Here the formation constants of the species are expressed as the overall stoicheiometric equilibrium constants.

$$pM + rH_aL \rightleftharpoons M_pH_{(ar-q)}L_r + qH \qquad (4)$$

$$\beta_{p,q,r} = \frac{[M_pH_{(ar-q)}L_r][H]^q}{[M]^p[H_aL]^r} \qquad (5)$$

Each species is represented by its formula or by (p,q,r) notation; it should be noted that the convention is adopted that the hydroxide ion ($OH^- = -H^+$) will be written as H_{-1} and it will have a formation constant $\beta_{0,-1,0} = K_w$.[21,23] Accordingly, for reactions involving OH$^-$ ion as a reactant, or H$^+$ as a product, q is negative. Thus in the formation of hydrolysed species or in complexation reactions in which the deprotonation of a ligand is involved, q is negative.

Iron(III)*-Sulphate Equilibrium*.—The solution equilibria in this system can be represented (hypothetically) by equations (6) and (7). The formation equation is presented such that the most protonated form of the ligand which is present in a significant quantity is shown on the left side of the equation. Thus HSO$_4^-$

is used instead of H_2SO_4 (since the titrations were carried out in the pH range 1.7—3.3, and the predicted pK_1 value for sulphuric acid is in the range −1.7 to −3.6,[24] H_2SO_4 is taken as already fully dissociated to HSO_4^- and SO_4^{2-} at the commencement of the experiments). The *overall* stoicheiometric formation constants, $\beta_{p,q,r}$, are defined for equation (7) by equation (8).

$$HSO_4^- \overset{K_2}{\rightleftharpoons} SO_4^{2-} + H^+ \qquad (6)$$

$$p\mathrm{Fe}^{3+} + (q - r)H_2O + rHSO_4^- \rightleftharpoons [\mathrm{Fe}_p(OH)_{(q-r)}(SO_4)_r]^{(3p-q-r)+} + qH^+ \qquad (7)$$

$$\beta_{p,q,r} = \frac{[\mathrm{Fe}_p(OH)_{(q-r)}(SO_4)_r{}^{(3p-q-r)+}][H^+]^q}{[\mathrm{Fe}^{3+}]^p[HSO_4^-]^r} \qquad (8)$$

If the formation constant is defined as $\beta' = [\mathrm{Fe}_p(OH)_q(SO_4)_r][H]^q/[\mathrm{Fe}]^p[SO_4]^r$ (charges omitted), then the relationship between β' and $\beta_{p,q,r}$ is $\beta' = \beta_{p,q,r}/K_2{}^r$, where K_2 is the second dissociation constant of H_2SO_4.

The investigation of these equilibria ideally requires an independent determination of the dissociation constant (pK_2) of HSO_4^- which was carried out [pK_2 = 1.104, estimated standard deviation (e.s.d.) = 0.005]. This value was used as a guide (for comparison with the refined pK_2 value) when the iron(III)–sulphate equilibria, pK_2, and λ were simultaneously refined.

If various ternary species $[\mathrm{Fe}_p(OH)_q(SO_4)_r]$ (charges omitted) are considered with *p* 1—3, and *q* and *r* 0—3, for example, the total number of possible species is 48, and the total number of possible combinations of species (models) will be very large even if the majority of the species can be excluded on the grounds of chemical sense. Hence, the model selection procedure adopted for numerical analysis has to be more discriminating than in the case of the binary system. The selection procedure, which in principle is somewhat similar to the 'decision-tree pathway analysis,' was as follows.

(*i*) The first base model (B.M.1) consisted of the major hydrolytic species [Fe(OH)] and $[\mathrm{Fe}_2(OH)_2]$ (charges omitted), and the second dissociation constant reaction of sulphuric acid (K_2). To B.M.1 was then added, singly, the following species: $[\mathrm{Fe}(HSO_4)]$, $[\mathrm{Fe}(SO_4)]$, $[\mathrm{Fe}(SO_4)_2]$, $[\mathrm{Fe}(OH)(SO_4)]$, $[\mathrm{Fe}_2(OH)_2(SO_4)]$, $[\mathrm{Fe}(OH)_2]$, and $[\mathrm{Fe}_3(OH)_4]$. The results of numerical analysis showed that B.M.1 + $[\mathrm{Fe}_3(OH)_4]$ was the only model which gave satisfactory results (the others resulted in negative values for one or more of the formation constants). This model was therefore taken as the updated base model 2 (B.M.2).

(*ii*) To B.M.2 was then added, singly, the following species: $[\mathrm{Fe}(SO_4)]$, $[\mathrm{Fe}(SO_4)_2]$, $[\mathrm{Fe}(HSO_4)]$, $[\mathrm{Fe}(OH)(SO_4)]$, $[\mathrm{Fe}_2(OH)_2(SO_4)]$, and $[\mathrm{Fe}_3(OH)_4(SO_4)]$. Of these six models, only the first two models produced satisfactory numerical results. Since it is chemically not sensible to have the species $[\mathrm{Fe}(SO_4)_2]$ in an equilibrium model in the absence of $[\mathrm{Fe}(SO_4)]$ species, both species were tried together. The results were unsatisfactory (high e.s.d.), consequently B.M.2 + $[\mathrm{Fe}(SO_4)]$ was taken to be the updated base model (B.M.3).

(*iii*) It has been observed in the present work that models with more than five species can be sensitive to poor initial estimates of the formation constants. Thus in order to ensure that species are not injudiciously rejected because of poor initial estimates of β, in the following model-testing step, the species belonging to B.M.3 and λ were held invariant at the previously determined refined β values, with the following species tried one at a time: $[\mathrm{Fe}(HSO_4)]$, $[\mathrm{Fe}(SO_4)_2]$, $[\mathrm{Fe}(OH)(SO_4)]$, $[\mathrm{Fe}(HSO_4)(SO_4)]$, $[\mathrm{Fe}_2(OH)_2(SO_4)]$, $[\mathrm{Fe}_3(OH)_4(SO_4)]$, and $[\mathrm{Fe}(OH)_2]$. The seven models tested were therefore, in effect, one-species models which were not so sensitive to poor initial estimates of β. Computational analyses showed that only the last two species returned reasonable results, namely, a satisfactory *R* factor and e.s.d. values of less than 20%. These two species were then tried, singly or in combination, with B.M.3, using their previously refined β values as the initial estimates.

Table 4. Comparison of models of the hydrolysis and complexation of iron(III) in the presence of sulphate

Model	Species	log $\beta_{p,q,r}$	E.s.d. of log $\beta_{p,q,r}$	E.s.d. (%) of $\beta_{p,q,r}$	*R*
1	(1, − 1,0)	−2.82	0.01	3.3	0.001 009
	(2, − 2,0)	−3.35	0.01	2.9	
	(3, − 4,0)	−6.66	0.01	2.5	
	(0, − 1,1)	−0.93	0.008	1.8	
	(1, − 1,1)	−0.34	0.04	9.3	
	(1, − 2,0)	−6.60	0.03	6.6	
2	(1, − 1,0)	−2.92	0.02	4.2	0.000 933
	(2, − 2,0)	−3.14	0.01	2.2	
	(3, − 4,0)	−6.78	0.03	5.8	
	(0, − 1,1)	−1.022	0.006	1.5	
	(1, − 1,1)	0.35	0.01	3.2	
	(3, − 5,1)	−5.48	0.02	5.5	
3	(1, − 1,0)	−2.90	0.02	3.8	0.000 898
	(2, − 2,0)	−3.17	0.01	2.3	
	(3, − 4,0)	−6.81	0.02	5.7	
	(0, − 1,1)	−0.987	0.007	1.6	
	(1, − 1,1)	0.30	0.02	3.7	
	(1, − 2,0)	−6.74	0.04	8.1	
	(3, − 5,1)	−5.53	0.02	5.7	
4	(1, − 1,0)	−3.07	0.02	3.9	0.001 173
	(2, − 2,0)	−3.21	0.01	1.7	
	(3, − 4,0)	−6.62	0.01	2.9	
	(0, − 1,1)	−1.104	Held invariant		
	(1, − 1,1)	0.02	0.01	2.0	
	(1, − 2,0)	−7.03	0.07	15.4	
	(0, − 1,0)	−13.75	Held invariant		
5	(1, − 1,0)	−3.01	0.01	2.6	0.000 978
	(2, − 2,0)	−3.092	0.007	1.5	
	(3, − 4,0)	−6.92	0.03	6.7	
	(0, − 1,1)	−1.104	Held invariant		
	(1, − 1,1)	0.41	0.01	2.5	
	(3, − 5,1)	−5.44	0.02	4.9	
	(0, − 1,0)	−13.75	Held invariant		
6	(1, − 1,0)	−3.07	0.02	3.6	0.001 173
	(2, − 2,0)	−3.084	0.007	1.5	
	(3, − 4,0)	−7.03	0.04	9.3	
	(0, − 1,1)	−1.104	Held invariant		
	(1, − 1,1)	0.40	0.01	2.5	
	(1, − 2,0)	−7.08	0.07	15.4	
	(3, − 5,1)	−5.47	0.02	5.0	
	(0, − 1,0)	−13.75	Held invariant		

(*iv*) Table 4 shows the results of updating B.M.3 with the species $[\mathrm{Fe}(OH)_2]$ (model 1), $[\mathrm{Fe}_3(OH)_4(SO_4)]$ (model 2), and both species together (model 3). Models 1—3 satisfy the acceptance criteria,[18] *i.e.* $\beta > 0$, e.s.d. < 10%, and *R* factor < 0.002; it may be noted that model 2 gives a refined pK_2 value which is the closest to the independently determined constant. Models 4—6 in Table 4 show the results of computation for models 1—3 with the independently determined pK_2 value (1.104) and pK_w (13.75 at 25 °C, I = 1.0 mol dm^{-3})[25] included but held invariant. Model 5 is the only model which satisfies the acceptance criteria.

(*v*) Further attempts, which are not detailed here, to include in model 2 (Table 4) the species $[\mathrm{Fe}(OH)(SO_4)]$, $[\mathrm{Fe}_2(OH)_2(SO_4)]$, $[\mathrm{Fe}(SO_4)_2]$, and $[\mathrm{Fe}(HSO_4)]$ (for confirmation of previous model testing steps), and other trimer species

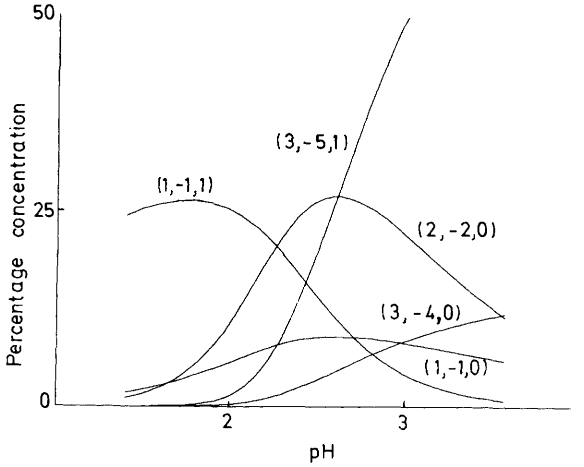

Figure 1. Percentage distribution of iron(III) complexation products at a total (initial) iron(III) concentration of 0.020 mol dm^{-3} and a sulphate concentration of 0.020 mol dm^{-3} in 1.0 mol dm^{-3} $NaNO_3$ at 25 °C

$[Fe_3(OH)_4(SO_4)_2]$, $[Fe_3(OH)_3(SO_4)]$, $[Fe_3(OH)_5(SO_4)]$, and $[Fe_3(OH)_6(SO_4)]$ (charges ignored) resulted in model failures caused by negative formation constants, ill-conditioned matrices, non-convergence, or species with high e.s.d.s.

Figure 1 illustrates the distribution of iron(III) complexed species according to model 5 (Table 4) as a function of pH. For clarity, the percentage of free Fe^{3+} [uncomplexed iron(III)] in solution is not shown.

Iron(III)*-Phosphate Equilibrium.*—The experimental results, together with previous data for the hydrolysis of iron(III),[18] indicate that within the experimentally accessible pH range, the extent of hydroxo-complex formation of iron(III) or its phosphate complex is negligible. This was later confirmed by attempts to include in the equilibrium system, such hydroxo-species as $[Fe(OH)]^{2+}$, $[Fe_2(OH)_2]^{4+}$, $[Fe(OH)(PO_4)]^-$, and $[Fe_2(OH)_2(PO_4)]^+$ when unsatisfactory numerical results were obtained. Accordingly the system is defined by equations (9)—(13).

$$\mathrm{H_3PO_4} \underset{}{\overset{K_1}{\rightleftharpoons}} \mathrm{H_2PO_4}^- + \mathrm{H}^+ \qquad (9)$$

$$\mathrm{H_2PO_4}^- \overset{K_2}{\rightleftharpoons} \mathrm{HPO_4}^{2-} + \mathrm{H}^+ \qquad (10)$$

$$\mathrm{HPO_4}^{2-} \overset{K_3}{\rightleftharpoons} \mathrm{PO_4}^{3-} + \mathrm{H}^+ \qquad (11)$$

$$p\mathrm{Fe}^{3+} + r\mathrm{H_3PO_4} \rightleftharpoons [\mathrm{Fe}_p\mathrm{H}_{(3r-q)}(\mathrm{PO_4})_r]^{(3p-q)+} + q\mathrm{H}^+ \qquad (12)$$

$$\beta_{p,q,r} = \frac{[\mathrm{Fe}_p\mathrm{H}_{(3r-q)}(\mathrm{PO_4})_r{}^{(3p-q)+}][\mathrm{H}^+]^q}{[\mathrm{Fe}^{3+}]^p[\mathrm{H_3PO_4}]^r} \qquad (13)$$

Based on the convention adopted here, the species $[Fe(HPO_4)]^+$ is defined as $[Fe(HPO_4)] = \beta_{1,-2,1}[Fe]^1[H]^{-2}[H_3PO_4]^1$ (charges ignored); hence the notation for this species is (1, − 2,1). Sometimes the formation constant of this species is defined as $[Fe(HPO_4)] = \kappa[Fe][HPO_4]$, where κ is related to $\beta_{1,-2,1}$ by $\log \kappa = \log \beta_{1,-2,1} + pK_1 + pK_2$. Similarly, for the species $[Fe(PO_4)]$, which is defined as $[Fe(PO_4)] = \beta_{1,-3,1}[Fe]^1[H]^{-3}[H_3PO_4]^1$, the notation is (1, − 3,1). If this species is defined as $[Fe(PO_4)] = \kappa[Fe][PO_4]$, then $\log \kappa = \log \beta_{1,-3,1} + pK_1 + pK_2 + pK_3$.

Table 5. Comparison of models of the complexation of iron(III) with phosphate

Model	Species	log $\beta_{p,q,r}$	E.s.d. of log $\beta_{p,q,r}$	E.s.d. (%) of $\beta_{p,q,r}$	*R*
1	(0, − 1,1)	−1.30	0.03	7.1	0.001 497
	(1, − 3,1)	0.55	0.01	2.5	
2	(0, − 1,1)	−0.07	0.04	10.0	0.003 975
	(1,0,1)	2.44	0.07	15.5	
3	(0, − 1,1)	−1.81	0.03	6.1	0.001 336
	(1, − 2,1)	1.32	0.03	7.4	
	(1, − 3,1)	0.79	0.02	3.6	
3′*	(1, − 2,1)	1.28	0.03	7.1	0.001 326
	(1, − 3,1)	0.78	0.01	3.2	
4	(0, − 1,1)	−1.93	0.02	4.2	0.001 435
	(1, − 1.1)	2.02	0.01	2.1	
	(1, − 3,1)	1.134	0.002	0.6	

* $pK_1 = 1.76$, $pK_2 = 6.26$, $pK_3 = 10.79$, $pK_w = 14.20$, and $\lambda = 2.358$ (values held constant).

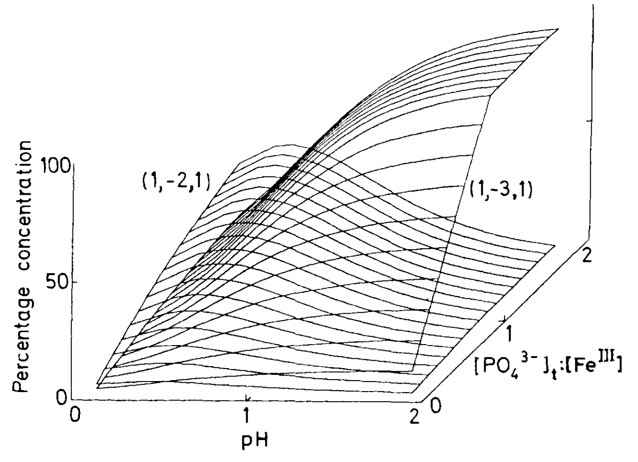

Figure 2. Percentage distribution of iron(III) complexation products at a total (initial) iron(III) concentration of 0.020 mol dm^{-3}, with varying ratio of total phosphate to iron(III) concentration, in 3.0 mol dm^{-3} $NaNO_3$ at 25 °C

The first dissociation constant of the phosphoric acid was determined independently [$pK_1 = 1.763$ (0.002)]. This is in good agreement with the value ($pK_1 = 1.81$) determined from the iron(III) titrations alone (Table 2) when pK_1, λ, together with the iron(III) equilibria were simultaneously determined (pK_2 and pK_3, whose values are much greater than the experimental pH values, cannot be sensibly refined; they were therefore excluded from this refinement procedure). These pK_1 values can be compared with a published value of 1.86 (25 °C, $I = 3$ mol dm^{-3}).[26] Finally, the refined value of λ, the independently determined pK_1, the values of pK_2 and pK_3 (6.26 and 10.79 at 25 °C, $I = 3$ mol dm^{-3}),[26] and pK_w (14.20 at 25 °C, $I = 3$ mol dm^{-3})[27] were all made invariant and the final values for the formation constants for the iron(III) complexes, $\beta_{p,q,r}$, determined.

Table 5 shows the results of computation for several models of the system. The independently determined pK_1 was used as a guide for comparison with the pK_1 obtained from the refinement of the iron(III)-phosphate equilibria. Thus, model 1 which satisfies the acceptance criteria, *i.e.* $\beta > 0$, e.s.d. < 10%, and *R* factor < 0.002,[18] is not acceptable because the refined pK_1 is significantly different from the independently determined value. Of the two models which satisfy the acceptance criteria, model 4 which includes the species $[Fe(H_2PO_4)]^{2+}$ and $[Fe(PO_4)]^0$ but not $[Fe(HPO_4)]^+$ is considered to be unacceptable. Consequently, model 3 is the only model which

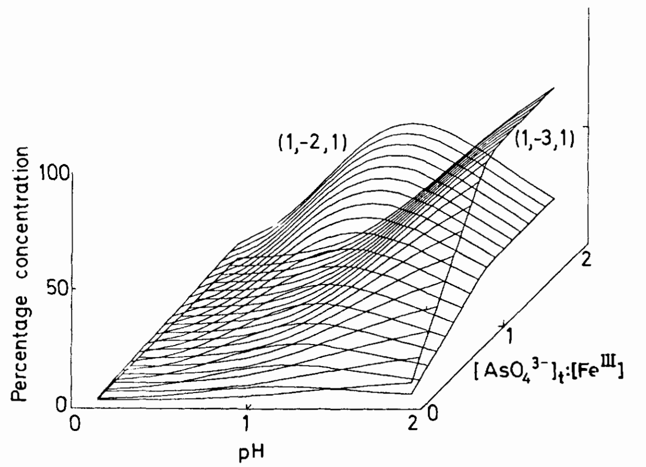

Figure 3. Percentage distribution of iron(III) complexation products at a total (initial) iron(III) concentration of 0.020 mol dm^{-3}, with varying ratio of total arsenate to iron(III) concentration, in 3.0 mol dm^{-3} $NaNO_3$ at 25 °C

can represent the iron(III)–phosphate equilibria under the present experimental conditions. Attempts to include polynuclear and bis(phosphato) species when added to model 3 resulted in either negative values for one or more of the formation constants, species with high e.s.d.s, or model failures caused by ill-conditioned data matrices or non-convergence. Model 3′ shows the results of numerical analysis of model 5 with the following parameters held invariant: the independently determined pK_1 (1.763), pK_2 (6.26), and pK_3 (10.79),[28] pK_w (14.20),[29] and the value of λ determined here (2.358).

Figure 2 shows the distribution of iron(III) complexes in solution with varying ratio of total phosphate to iron(III) concentration. For clarity, the percentage of free Fe^{3+} [the uncomplexed iron(III)] in solution is not shown.

Iron(III)–*Arsenate Equilibrium.*—The experimentally accessible pH range was also severely limited by precipitation reactions (Table 3). Therefore, as in the iron(III)–phosphate system, there was negligible formation of hydroxo-species of iron(III) or their arsenate complexes. Accordingly, the system can be represented by equations (9)—(13) if the notation As is substituted for every occurrence of P.

The numerical procedure was the same as that for the iron(III)–phosphate system and the best model obtained is analogous to that of the iron(III)–phosphate system, namely, log$\beta_{1,-2,1}$ = 0.11 (0.02) and log $\beta_{1,-3,1} = -1.34$ (0.03). The independently determined first dissociation constant of arsenic acid, log, $\beta_{0,-1,1} = -2.128$ (0.002).

Figure 3 illustrates the distribution of iron(III) complex species in solution with varying ratio of total arsenate to iron(III) concentration, according to the best model. For clarity, the percentage of free Fe^{3+} [the uncomplexed iron(III) in the solution] is not shown.

Discussion

Table 6 compares the results of earlier investigations on the Fe^{III}–SO_4 system with those of the present work. It should be noted that β' is used instead of $\beta_{p,q,r}$ because most of the published data are expressed as β'. The determined value for the second dissociation constant of sulphuric acid is in good agreement with the literature values when the effect of the different ionic strengths is taken into consideration.

The results of our earlier work on the hydrolysis of iron(III) in three different ionic media[18] are included in Table 6. The determined values for the formation constants of the hydrolytic species are in excellent agreement with our earlier work. This confirms the presence of the minor species $[Fe_3(OH)_4]^{5+}$ in the iron(III) hydrolytic scheme in a nitrate medium under the present experimental conditions. In our earlier work, the effect of the three different ionic media on the formation constant of hydrolytic species is log $\beta_{p,q,0}$ (ClO_4^-) ~ log $\beta_{p,q,0}$(NO_3^-) > log $\beta_{p,q,0}$(Cl^-).[18] The effect is greater for polynuclear complexes.

By comparing the results of this work with those of our earlier work in 1 mol dm^{-3} KNO_3,[18] it is apparent that the presence of sulphate slightly increases the formation constants of the polynuclear hydrolytic species. At the same time, it decreases the formation constants of the mononuclear hydrolytic species to such an extent that the minor species $[Fe(OH)_2]^+$ cannot be detected reliably.

The formation constants of the hydrolytic species do not vary very much from model to model. This kind of robustness however, is not displayed by the $[Fe(SO_4)]^+$ species. The experimentally determined parameters in this work are the pH and titrant volume. These are directly relevant to the hydrolysis reactions. The sulphate concentration, on the other hand, is determined *indirectly* from the proton concentration through the second-dissociation constant reaction of sulphuric acid.

Iron(III)–hydrogensulphate complexes have not been identified. This was expected because of the experimental pH values (1.7 < pH < 3.3) which were much greater than those used in the experiments in which the iron(III)–hydrogensulphate complexes were reported (0 < pH < 0.6[4] and 0.3 < pH < 1.7[2]). Lister and Rivington[2] stated that in addition to $[Fe(HSO_4)]^{2+}$ and $[Fe(SO_4)]^+$, $[Fe(SO_4)_2]^-$ is also formed when excess sulphate is present. However, their determined value for log $\beta_{Fe(SO_4)_2}$ varied from 4.22 (at 1.3 < pH < 1.7) to 4.50 (at pH 0.7). To account for this variation they postulated that $[Fe(SO_4)(HSO_4)]$ is also formed in the solution at pH 0.7; thus the significance of these results is questionable. The formation constant of $[Fe(SO_4)]^+$ differs from the published values. Given the differences in experimental conditions and differences in the equilibrium models, together with the paucity of additional data, not much significance can be attributed to the discrepancies.

Zvyagintsev *et al.*,[5] using the potentiometric titration method in a similar pH region as the present work, suggested two polynuclear mixed hydroxo-sulphato species, $[Fe_2(OH)_2(SO_4)]^{2+}$ and $[Fe_2(OH)_2(SO_4)_2]$, together with the hydrolytic species and the iron(III) sulphate complexes. Herein, only one ternary species, $[Fe_3(OH)_4(SO_4)]^{3+}$, has been proposed. The fact that this species is numerically detectable instead of $[Fe_2(OH)_2(SO_4)]^{2+}$ might indicate an enhanced stability of the trimeric unit which could act as a precursor to the formation of jarosite, $Na[Fe_3(OH)_6(SO_4)_2]$.

Table 7 compares the results of earlier investigations on the iron(III)–phosphate equilibria with those of the present work. It should be noted that κ is used instead of $\beta_{p,q,r}$ because most of the published data are expressed as $\kappa_{p,q,r}$ and the pK_a values for H_3PO_4 at different ionic strengths required for the conversion of κ to β are not available.

Although a rigorous comparison between the published values of the formation constants cannot be carried out because of the differences in the experimental conditions, there are discrepancies between the reported values of the constants. For example, Galal-Gorchev and Stumm[28] and Sidorenko *et al.*[29] gave similar results (assuming that the latter investigation was carried out at 25 °C), but the ionic strengths used in their respective experiments were quite different. Galal-Gorchev and Stumm[28] used very low concentrations of iron(III) and

Table 6. Comparison of results of the investigation of the hydrolysis and complexation of iron(III) in the presence of sulphate[a]

Medium (concentration/mol dm^{-3})	Temp./°C	Method[b]	Total concentration (10^{-3} mol dm^{-3})		pH	log β′						pK_2	Ref.
			Fe^{III}	SO_4^{2-}		$[Fe(OH)]$	$[Fe(OH)_2]$	$[Fe_2(OH)_2]$	$[Fe_3(OH)_4]$	$[Fe(HSO_4)]$	$[Fe(SO_4)]$		
$NaClO_4$ (1.0)	25—29	S,I	0.3	19—900	0—1.1						2.02		1
$NaClO_4$ (1.2)	25	S	1—30	1—50	0.3—1.3					0.78	2.21		2
$NaClO_4$ (0.5)	25	S	10—30	1	0.5—1.3						2.31	1.37	3
$NaClO_4$ (2.67)	25	S	3—20	2—3	0—0.6					0.60	1.92	1.14	4
$NaClO_4$ (3.0)	25	P	10—100	10—500	2—2.5	−3.0		−2.36			2.23	0.89	5
$NaNO_3$ (1.0)	25	P	0.2—20	0.2—20	1.8—3.3	−3.01		−3.09	−6.92		1.53	1.10	This work
KNO_3 (1.0)	25	P	0.2—20	0	1.7—3.3	−2.77	−6.61	−3.22	−6.98				18
$NaClO_4$ (1.0)	25	P	0.2—20	0	1.7—3.3	−2.73	−6.29	−3.20					18
KCl (1.0)	25	P	0.2—20	0	1.7—3.4	−3.21	−6.73	−4.09	−7.58				18

						log β′					pK_2	Ref.
						$[Fe(SO_4)_2]$	$[FeH(SO_4)_2]$	$[Fe_2(OH)_2(SO_4)]$	$[Fe_2(OH)_2(SO_4)_2]$	$[Fe_3(OH)_4(SO)_4)]$		
$NaClO_4$ (1.0)	25—29	S,I	0.3	19—900	0—1.1	3.00						1
$NaClO_4$ (1.2)	25	S	1—30	1—50	0.3—1.3	4.22	4.04					2
$NaClO_4$ (0.5)	25	S	10—30	1	0.5—1.3						1.37	3
$NaClO_4$ (2.67)	25	S	3—20	2—3	0—0.6						1.14	4
$NaClO_4$ (3.0)	25	P	10—100	10—500	2—2.5	5.26		0.15	0.68		0.89	5
$NaNO_3$ (1.0)	25	P	0.2—20	0.2—20	1.8—3.3					−4.34	1.10	This work
KNO_3 (1.0)	25	P	0.2—20	0	1.7—3.3							18
$NaClO_4$ (1.0)	25	P	0.2—20	0	1.7—3.3							18
KCl (1.0)	25	P	0.2—20	0	1.7—3.4							18

[a] Charges on species ignored for brevity. [b] S = Spectrophotometry, P = potentiometry, I = ion exchange.

Table 7. Comparison of some results of the investigation of the complexation of iron(III) with phosphate[a]

Medium (concentration/mol dm^{-3})	Temp./°C	Method	Total concentration (10^{-3} mol dm^{-3})		pH	log κ				Ref.
			Fe^{III}	PO_4^{3-}		$[Fe(H_2PO_4)]$	$[Fe(HPO_4)]$	$[Fe(PO_4)]$	$[Fe_2(HPO_4)]$	
$NaClO_4$ (0.4)	25	E.m.f., spectrophotometry	<0.05		0.8—2.2	3.47	8.30			28
$NaClO_4$ (3.0)	?	Amperometry	0.1	10—100	$0.18 < pH < 1.3$	3.61	8.13			29
$NaClO_4$ (0.1—0.2)	25	Spectrophotometry	10—20	5.7—20	pH < 2		10.62			*b*
$NaNO_3$ (0.665)	30	Spectrophotometry	4.1	3—10	pH < 2		9.35			*c*
KCl (0.1)	25	Spectrophotometry	0.005—0.1	0.01—5	pH ~ 1	3.60				*d*
$NaNO_3$ (0.1)	?	Spectrophotometry, I	<20	3.2	pH < 2				11.14	*e*
$NaNO_3$ (3.0)	25	Potentiometry	0.2—20	0.2—41	pH ~ 1		9.30	19.50		This work
(0)[f]	25				0.9—2.0	4.2	10.1			*g*
(0.5)[f]	25					3.47	8.30			26

[a] Charges on species ignored for brevity; I = ion exchange. [b] S. C. Lahiri, *J. Indian Chem. Soc.*, 1965, **42**, 10, 715. [c] O. E. Landford and S. J. Kiehl, *J. Am. Chem. Soc.*, 1942, **64**, 291. [d] H. L. Bohn and M. Peech, *Soil Sci. Soc. Amer. Proc.*, 1969, **33**, 873. [e] L. N. Filatova and M. L. Chepelevetskii, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1966, **11**, 7, 888. [f] Medium not known. [g] S. L. Philips, 'Hydrolysis and Formation Constants at 25°C,' LBL-14313, Lawrence Berkeley Laboratory, 1982.

phosphate in order to avoid the formation of polynuclear or bis(phosphato) complexed species.

Numerical analyses using our augmented MINIQUAD program have clearly shown that the same speciation model can be used to represent the iron(III)–phosphate and –arsenate equilibria under the present experimental conditions (although weaker complexes are found in the latter system). This covers a wide range of total (initial) iron(III) and phosphate concentrations (within the limit of accessibility of pH range and consideration of ionic strength constancy). Nevertheless, no acceptable model with polynuclear species could be found. Intercession by very early precipitation reactions prevent the detection of ternary hydroxo-phosphate complexes, whilst consideration for maintaining reasonable ionic strength constancy prevent the detection of dihydrogen or, possibly, trihydrogen iron(III)–phosphate complexes and bis(phosphato) complexes.

As there is no published information on the speciation in the iron(III)–arsenate equilibrium system, no comparison can be made.

Acknowledgements

We thank Dr. R. N. Sylva for many helpful discussions and Dr. P. L. Brown for assistance in the use of the computer program MINIQUAD.

References

1 R. A. Whiteker and N. Davidson, *J. Am. Chem. Soc.*, 1953, **75**, 3081.
2 M. W. Lister and D. E. Rivington, *Can. J. Chem.*, 1955, **33**, 1591.
3 G. G. Davis and W. M. Smith, *Can. J. Chem.*, 1962, **40**, 1836.
4 R. S. Sapieszko, R. C. Patel, and E. Matijevic, *J. Phys. Chem.*, 1977, **81**, 11, 1061.
5 O. E. Zvyagintsev and S. B. Lyakhmanov, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1969, **14**, 7, 956.
6 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1961, p. 238.
7 C. W. Childs and D. D. Perrin, *J. Chem. Soc. A*, 1969, 1039.
8 W. A. E. McBryde, *Analyst (London)*, 1970, **9**, 2465.
9 R. N. Sylva and M. R. Davidson, *J. Chem. Soc., Dalton Trans.*, 1978, 232.
10 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 1985, 1195.
11 R. N. Sylva and M. R. Davidson, *J. Chem. Soc., Dalton Trans.*, 1979, 465.
12 P. L. Brown and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1980, 1577.
13 P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1982, 1911.
14 P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 31.
15 P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 35.
16 P. L. Brown, J. Ellis, and R. N. Sylva, *J. Chem. Soc., Dalton Trans.*, 1983, 2001.
17 P. L. Brown, R. N. Sylva, G. E. Batley, and J. Ellis, *J. Chem. Soc., Dalton Trans.*, 1985, 1967.
18 G. H. Khoe, P. L. Brown, R. N. Sylva, and R. G. Robins, *J. Chem. Soc., Dalton Trans.*, 1986, 1901.
19 L. G. Sillen, 'Polynuclear Complexes in Solution,' in 'Coordination Chemistry,' ACS Monograph, ed. A. E. Martell, Van Nostrand, New York, 1971, vol. 1.
20 A. Vacca, A. Sabatini, and M. A. Gristina, *Coord. Chem. Rev.*, 1972, **8**, 47.
21 A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, 53.
22 P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.
23 A. Vacca, D. Arenare, and P. Paoletti, *Inorg. Chem.*, 1966, **5**, 1384.
24 D. D. Perrin, 'Ionisation Constants of Inorganic Acids and Bases in Aqueous Solution,' IUPAC Chem. Data Series No. 29, Pergamon Press, Oxford, 1982.
25 L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' Special Publication No. 17, The Chemical Society, London, 1964.
26 R. M. Smith and A. E. Martell, 'Critical Stability Constants,' Plenum Press, New York, 1976, vol. 4.
27 L. G. Sillen and A. E. Martell, 'Stability Constants of Metal-Ion Complexes,' Special Publication No. 25, The Chemical Society, London, 1971.
28 H. Galal-Gorchev and W. Stumm, *J. Inorg. Nucl. Chem.*, 1963, **25**, 567.
29 V. I. Sidorenko, E. F. Zhuravlev, V. I. Gordienko, and N. P. Grineva, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1973, **18**, 5, 670.

Received 2nd February 1987; *Paper* 7/178