

185. *Complexes involving Tervalent Iron and Orthophosphoric Acid. Part IV.* Evidence for the Formation of Polynuclear Complexes from Ion-exchange Experiments.*

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Cation-exchange studies of ferric sulphate-phosphoric acid solutions have provided evidence for the formation therein of polynuclear phosphato-ferric cations and, possibly, when much free sulphuric acid is present, of polynuclear complex ions containing both phosphato- and sulphato-groups. Anion-exchange studies have also indicated the formation of mixed phosphato-sulphato-complexes.

The results of cation-exchange experiments with ferric chloride-phosphoric acid solutions are consistent with the sorption of polynuclear phosphato-ferric cations from solutions containing little free hydrochloric acid and of the monomeric FeHPO_4^+ ion from solutions containing higher concentrations of free acid.

PREVIOUS papers in this series contained evidence of the formation of a cationic complex FeHPO_4^+ in solutions containing approximately equimolecular amounts of ferric chloride and phosphoric acid¹ and of anionic complexes such as $[\text{Fe}(\text{HPO}_4)_3]^{3-}$ or $[\text{Fe}(\text{PO}_4)_3]^{6-}$ in solutions of ferric phosphate in phosphoric acid.² Amongst the experimental facts quoted in support of the formation of the FeHPO_4^+ ion were the results of pH-titrations of ferric chloride solutions with phosphoric acid. However, recent studies³ indicated that the release of hydrogen ions during the pH-titration is much less when ferric sulphate is substituted for ferric chloride. This might arise because the chloro-complexes of iron(III) are more labile than sulphato-complexes, and the chloro-groups are more easily displaced by phosphate than are the sulphate groups. A further cause might be found in the buffering action of the sulphate complexes, which would remove some of the hydrogen ions liberated: $\text{FeSO}_4^+ + \text{H}^+ \rightleftharpoons \text{FeHSO}_4^{2+}$. Nevertheless the difference between the two systems seemed sufficiently great to warrant examination of the ferric sulphate-phosphoric acid system by use of the ion-exchange methods described before.¹ In view of the unexpected results obtained, the previous work on the ferric chloride-phosphoric acid system was extended.

EXPERIMENTAL

Procedure.—The batch technique described by Salmon⁴ was employed, with 50 ml. of solution and either 0.500 g. of cation exchange resin (Zeo-Karb 225) or 1.000 g. of anion exchange resin (I.R.A. 400). Hydrochloric acid or, in some cases, nitric acid (2*N*, ca. 300 ml.) was used to elute the species sorbed on the resin. The combined eluate and washings were made up to 500 ml. and aliquot portions used for analysis. As a check, aliquot samples of the solution in equilibrium with the resin were also analysed in most experiments. Equilibrium was reached in 3–4 days if frequent and prolonged agitation was employed, but generally at least a week was allowed.

Analysis.—Iron was determined by titration with potassium dichromate, after elimination of nitric acid, phosphate as phosphomolybdate, after elimination of hydrochloric acid (if present), and sulphate as barium sulphate, after removal of iron by sorption on a column of cation exchange resin. The capacity of the resin was determined as previously described.¹

Reagents.—All reagents, apart from the ferric sulphate whose purity was checked, were of analytical grade.

* Part III, *J.*, 1954, 28.

¹ Salmon, *J.*, 1953, 2644.

² Jameson and Salmon, *J.*, 1954, 28.

³ Holroyd and Salmon, *J.*, 1956, 269.

⁴ Salmon, *Rev. Pure Appl. Chem.*, 1956, 6, 24.

RESULTS AND DISCUSSION

The results of the cation-exchange experiments with mixtures in various proportions of ferric sulphate (0.1M in Fe) and phosphoric acid (0.3M) solutions are shown in Table 1, together with those of further experiments in which the pH of the ferric sulphate solution was

TABLE 1. Sorption of iron and phosphate by Zeo-Karb 225 (H-form, 0.500 g.) from solutions (50 ml.) containing ferric sulphate and phosphoric acid.

Solution		Resin						
$\frac{[\text{PO}_4]}{[\text{Fe}]}$	pH *	N_{Fe}	$N_{\text{phosphate}}$	$q \uparrow$	Possible complexes ‡	q for complexes	q (average)	$\frac{pN_{\text{Fe}} - qN_{\text{phosphate}}}{q}$
(1) Ferric sulphate solution, pH 1.34, $p = 3$.								
0.00	1.18	0.333	—	—	—	—	—	1.00
0.33	1.03	0.535	0.203	2.98	<i>a</i>	3	3	1.00
0.75	0.99	0.566	0.269	2.60	<i>a</i> or <i>d</i>	3 or 2	2.5	1.03
1.29	0.97	0.584	0.313	2.40	<i>a</i> or <i>d</i>	3 or 2	2.5	0.97
1.69	0.93	0.581	0.271	2.74	<i>a</i> or <i>d</i>	3 or 2	2.5	1.06
2.78	0.95	0.553	0.219	3.05	<i>a</i>	3	3	1.00
4.51	0.98	0.510	0.159	3.24	<i>a</i>	3	3	1.05
(2) Ferric sulphate solution, pH 1.15, $p = 3$ (assumed).								
0.41	0.98	0.480	0.163	2.70	<i>a</i> or <i>d</i>	3 or 2	2.5	1.03
0.75	0.95	0.498	0.193	2.56	<i>a</i> or <i>d</i>	3 or 2	2.5	1.01
0.95	0.94	0.507	0.215	2.42	<i>a</i> or <i>d</i>	3 or 2	2.5	0.98
1.69	0.96	0.518	0.232	2.39	<i>a</i> or <i>d</i>	3 or 2	2.5	0.98
(3) Ferric sulphate solution, pH 0.98, $p = 3$ (assumed).								
0.00	0.94	0.319	—	—	—	—	—	0.96
0.40	0.81	0.461	0.106	3.62	<i>a</i> or <i>e</i>	3 or 4	3.5	1.01
0.74	0.80	0.477	0.124	3.48	<i>a</i> or <i>e</i>	3 or 4	3.5	1.00
0.93	0.80	0.484	0.133	3.40	<i>a</i> or <i>e</i>	3 or 4	3.5	0.99
1.66	0.83	0.487	0.156	2.95	<i>a</i>	3	3	0.99

* Of solution in equilibrium with resin.

† $q = (pN_{\text{Fe}} - 1)/N_{\text{phosphate}}$.

‡ $a = \text{Fe}_2(\text{PO}_4)^{3+}$; $b = \text{Fe}_2(\text{PO}_4)(\text{OH})^{2+}$; $c = \text{Fe}_2(\text{PO}_4)(\text{OH})_2^+$; $d = \text{FeHPO}_4^+$; $e = \text{Fe}_2(\text{PO}_4)(\text{HSO}_4)^{2+}$.

first lowered by addition of sulphuric acid (to pH 1.15 and 0.98 respectively). It is evident that, as in the experiments with ferric chloride,¹ the sorption of both phosphate and iron occurs and that the sorption of each again passes through a maximum at a mole ratio of $\text{PO}_4 : \text{Fe}$ of 1 : 1 or slightly greater. However, the amounts of phosphate and iron sorbed are not consistent with the sorption of FeHPO_4^+ ions together with Fe^{3+} ions.

It has been pointed out⁴ that for the sorption of a complex ion of the type $\text{FeH}_x\text{PO}_4^{x+}$ together with that of Fe^{3+} , the following equation will apply

$$3N_{\text{Fe}} - N_{\text{phosphate}}(3 - x) = 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where N_{Fe} and $N_{\text{phosphate}}$ represent the total number of moles of iron and phosphate sorbed respectively per equivalent of resin. This equation can be generalised for sorption of any one cationic complex together with free metal cations:

$$pN_{\text{Fe}} - qN_{\text{phosphate}} = 1 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Now p is dependent on the charge on the free metal cations only (and is thus 3 for Fe^{3+}), but q depends on the charge on the complex ion and on the free ion, as can be seen from equation (1) [for which $q = (3 - x)$]. The value of q can be obtained by rearranging equation (2), and the values thus deduced are shown in Table 1. It can be seen that in every case $q > 2$, whilst from equations (1) and (2) it is apparent that for sorption of FeHPO_4^+ $x = 1$ and $q = 2$, and for sorption of $\text{FeH}_2\text{PO}_4^{2+}$ $x = 2$ and $q = 1$. Thus sorption of these ions, at least singly, is not indicated.

A possible explanation lies in the sorption of polynuclear complex ions. Thus for sorption of $\text{Fe}_2(\text{PO}_4)^{3+}$ ions together with Fe^{3+} ions, we have for *one equivalent* of resin

$$\text{Moles of free } \text{Fe}^{3+} \text{ sorbed} = (\text{total Fe}) - (\text{Fe in complex}) = N_{\text{Fe}} - 2N_{\text{phosphate}}$$

$$\text{Equivs. of free } \text{Fe}^{3+} \text{ sorbed} = p(N_{\text{Fe}} - 2N_{\text{phosphate}})$$

$$\text{Equivs. of complex sorbed} = 3N_{\text{phosphate}}$$

Total equivs. sorbed = 1 = $pN_{\text{Fe}} - (2p - 3)N_{\text{phosphate}}$, whence $q = 2p - 3$, or $q = 3$ (since $p = 3$). The use of the value of $p = 3$ appears to be justified here since in the absence of phosphate ($[\text{PO}_4]/[\text{Fe}] = 0$), 0.333 mole of Fe is sorbed per equivalent of resin.

In Table 1, certain complexes having values for q close to those found experimentally are indicated. Others are possible but the polynuclear complexes given are such that (a) it is possible to assign them structures containing phosphato-bridges $\text{M}-\text{PO}_4-\text{M}$ (or $\text{M}-\text{HPO}_4-\text{M}$) and (b) the complexes contain the lowest possible number of such bridges. The first of these conditions was decided on the basis of some studies of the magnetic properties of these systems⁵ which have indicated that bridging occurs through phosphato-groups. The second condition appears reasonable when it is considered that a complex such as $\text{M}_3(\text{PO}_4)_2^{3+}$ (for example, for which $q = 3$, when $p = 3$) contains twice as many metal-oxygen bonds, which are subject to attack by a proton with consequent breakdown of the complex, as does $\text{M}_2(\text{PO}_4)^{3+}$, which ion is, therefore, likely to be the more stable in acid solution.

In the final column of Table 1 are given the values of $pN_{\text{Fe}} - qN_{\text{phosphate}}$, which from equation (2) should be unity, as is observed (± 0.03) in all but two instances. This is satisfactory when account is taken of the fact that, where two complexes are indicated as having q values close to the experimental one, the average of these values has been used in the calculations; this involves the arbitrary assumption that the phosphate sorbed is divided equally between the two complexes.

The effect of lowering the initial pH of the ferric sulphate solution from 1.86 to 1.46 (Table 1) leads to a more marked sorption of FeHPO_4^+ ions (q approaches more closely to 2), although polynuclear ions are still sorbed as well. The stability of the FeHPO_4^+ ion is likely to be greater in solutions of lower pH, for whilst, if the HPO_4 group is bidentate, it contains two metal-oxygen bonds, like $\text{Fe}_2(\text{PO}_4)^{3+}$, it differs from that complex in that rupture of one metal-oxygen bond does not break down the complex, but yields instead $\text{FeH}_2\text{PO}_4^{2+}$ which can subsequently lose a proton to re-form FeHPO_4^+ .

To lower the pH of the ferric sulphate solution still further (to 0.98, Table 1) required addition of an appreciable quantity of sulphuric acid, in accord with the inference already drawn that FeSO_4^+ ions exert a buffering effect. The formation of complete sulphato-ferric ions is apparent from the fact that in the absence of phosphate the resin is not saturated (less than 0.333 mole of Fe^{3+} sorbed per equiv.), in contrast to the experiments with ferric chloride solutions at the same pH (Table 2). It is difficult therefore to base many conclusions on the q values derived for this series, but the fact that they are higher than those for the two preceding experiments indicates that polynuclear, rather than FeHPO_4^+ , ions are sorbed. Although the values of q might seem to indicate the sorption of $\text{Fe}_2(\text{PO}_4)(\text{OH})^{2+}$ ($q = 4$), this seems unlikely at the pH (*ca.* 0.80) and sulphate concentrations concerned {cf. the solutions of higher pH [Table 1 (1) (2)] where there is no evidence for sorption of $\text{Fe}_2(\text{PO}_4)(\text{OH})^{2+}$ }. It is suggested that instead the ion $\text{Fe}_2(\text{PO}_4)(\text{HSO}_4)^{2+}$ is sorbed, but is converted into $\text{Fe}_2(\text{PO}_4)(\text{OH})^{2+}$ during the washing of the resin—no sulphate was found in the eluate.

In the corresponding experiments with ferric chloride solutions (0.1M) (Table 2) evidence is again found for the sorption of polynuclear complexes. The values of q are the highest for the ferric chloride solution of highest pH and correspond to the sorption of $\text{Fe}_2(\text{PO}_4)(\text{OH})_2^+$ or $\text{Fe}_2(\text{PO}_4)(\text{OH})^{2+}$ ions. With the solution of pH 1.46 (cf. the ferric

⁵ Holroyd, Jameson, Odell, and Salmon, Part V, in the press.

sulphate solution of pH 1.34) the $\text{Fe}_2(\text{PO}_4)^{3+}$ ions are sorbed in the main, whilst at the lowest pH values, which correspond to those used in the experiments reported in Part II,¹ the sorption of FeHPO_4^+ is indicated. The conditions in which the various ions are sorbed are consistent with the pH values at which they might be expected to be stable, and no complications arising from the formation of chloro-complexes are apparent. The values of $pN_{\text{Fe}} - qN_{\text{phosphate}}$ are close to unity (± 0.03) in most cases.

TABLE 2. *Sorption of iron and phosphate by Zeo-Karb 225 (H-form, 0.500 g.) from solutions (50 ml.) containing ferric chloride and phosphoric acid.*

Solution		Resin						
$[\text{PO}_4]$		N_{Fe}	$N_{\text{phosphate}}$	$q \uparrow$	Possible complexes ‡	q for complexes	q (average)	$pN_{\text{Fe}} - qN_{\text{phosphate}}$
$[\text{Fe}]$	pH *							
(1) Ferric chloride solution, pH 1.86; $p = 2.75$.								
0.00	1.40	0.365	—	—	—	—	—	1.00
0.33	1.02	0.442	0.047	4.60	<i>c</i>	4.50	4.50	1.00
0.48	0.95	0.450	0.056	4.25	<i>c</i>	4.50	4.50	0.99
0.74	0.90	0.480	0.058	5.52	<i>c</i>	4.50	4.50	1.06
0.94	0.90	0.504	0.138	2.80	<i>b</i> or <i>a</i>	3.50; 2.50	3.00	0.97
1.27	0.90	0.509	0.150	2.67	<i>a</i>	2.50	2.50	1.03
(2) Ferric chloride solution, pH 1.46; $p = 2.82$.								
0.00	1.20	0.355	—	—	—	—	—	1.00
0.33	0.92	0.530	0.165	3.00	<i>b</i> or <i>a</i>	3.64; 2.64	3.14	0.98
0.49	0.86	0.549	0.185	2.96	<i>b</i> or <i>a</i>	3.64; 2.64	3.14	0.97
0.75	0.84	0.585	0.238	2.73	α	2.64	2.64	1.02
0.94	0.84	0.598	0.252	2.72	<i>a</i>	2.64	2.64	1.02
1.28	0.84	0.604	0.317	2.22	<i>a</i> or <i>d</i>	2.64; 1.82	2.23	1.00
(3) Ferric chloride solution, pH 1.24; $p = 2.93$.								
0.00	0.99	0.341	—	—	—	—	—	1.00
0.19	0.88	0.499	0.165	2.80	<i>a</i>	2.86	2.86	0.99
0.41	0.78	0.509	0.213	2.31	<i>a</i> or <i>d</i>	2.86; 1.93	2.40	0.98
0.65	0.76	0.525	0.270	1.99	<i>d</i>	1.93	1.93	1.02
0.94	0.74	0.540	0.306	1.90	<i>d</i>	1.93	1.93	0.99
1.27	0.77	0.544	0.334	1.78	<i>d</i>	1.93	1.93	0.95
1.70	0.79	0.523	0.306	1.74	<i>d</i>	1.93	1.93	0.94

* † ‡ See Table 1.

In connection with these experiments with the ferric chloride solution, it will be seen from Table 2 that the value of p used is always less than 3, although it approaches that value as the pH of the solution is lowered. This arises from the fact that in the absence of phosphate the amount of iron sorbed is always greater than 0.333 mole per equiv., indicating that the "free" iron is sorbed as a mixture of Fe^{3+} together with one or more of its hydrolysis products [such as, *e.g.*, $\text{Fe}(\text{OH})^{2+}$, for which $p = 2$]. The value of p used in each series of experiments has been determined from the value of $1/N_{\text{Fe}}$ obtained in the absence of phosphate. The trend towards $p = 3$ at the lower pH is to be expected from the accompanying repression of the hydrolyses.

The results of some anion-exchange studies of mixtures of ferric sulphate solutions (0.1M in Fe) with phosphoric acid solutions (0.3M) are given in Table 3. In this Table an attempt has been made, following a method previously described,^{1,2} to account for the capacity of the resin samples by assuming (*a*) the sorption of $[\text{Fe}(\text{PO}_4)_3]^{6-}$ (see ref. 2), $[\text{Fe}(\text{SO}_4)_2]^-$, and SO_4^{2-} ions and (*b*) the sorption of $[\text{Fe}(\text{PO}_4)(\text{SO}_4)]^{2-}$ and SO_4^{2-} ions. The choice of the second assumption was prompted by the observation that the iron and phosphate were sorbed in approximately equimolecular amounts, as required by this assumption. It has already been noted¹ that a similar sorption of iron and phosphate in equimolecular amounts occurs with ferric chloride-phosphoric acid solutions, but only in the presence of a marked excess of chloride.

TABLE 3. Sorption of iron, phosphate, and sulphate by I.R.A. 400 (phosphate form, 1.000 g.) from solutions (50 ml.) containing ferric sulphate and phosphoric acid.

Solution		Resin				
$\frac{[\text{PO}_4]}{[\text{Fe}]}$	pH *	N_{Fe}	$N_{\text{phosphate}}$	N_{SO_4}	Capacity accounted for (%) †	
					(a)	(b)
0.78	1.14	0.07 ₇	0.05 ₆	0.49 ₀	93	98
1.38	1.14	0.08 ₀	0.06 ₄	0.46 ₅	88	93
2.21	1.20	0.08 ₇	0.08 ₈	0.48 ₁	96	96
3.41	1.24	0.09 ₂	0.10 ₇	0.46 ₃	97	93
5.34	1.28	0.10 ₃	0.12 ₁	0.46 ₅	98	93

* Of solution in equilibrium with the resin.

† By assuming (a) that all the phosphate is sorbed as $[\text{Fe}(\text{PO}_4)_3]^{6-}$, that the remaining iron present is sorbed as $[\text{Fe}(\text{SO}_4)_2]^-$ and the remaining sulphate is sorbed as SO_4^{2-} ; (b) that within experimental error the iron and phosphate are present in equimolecular amounts ($N_{\text{Fe}} = N_{\text{phosphate}}$) in the $[\text{Fe}(\text{PO}_4)(\text{SO}_4)]^{2-}$ ion, with excess of sulphate present as SO_4^{2-} . For purposes of calculation it did not matter whether the value of N_{Fe} or $N_{\text{phosphate}}$ was taken as "correctly" representing both of them.

It can be seen from Table 3 that whilst the assumption of the sorption of $[\text{Fe}(\text{PO}_4)_3]^{6-}$, $[\text{Fe}(\text{SO}_4)_2]^-$, and SO_4^{2-} ions accounts more satisfactorily for the resin capacity at the higher ratio of $[\text{PO}_4]/[\text{Fe}]$ in solution, at the lower phosphate ion concentrations the sorption of the mixed complex ion $[\text{Fe}(\text{PO}_4)(\text{SO}_4)]^{2-}$ is indicated. This observation together with that made in the corresponding cation exchange experiments suggests that mixed sulphato-phosphato-ferric complexes may be formed more readily than mixed chloro-phosphato-ferric complexes.

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