539. *Complexes involving Tervalent Iron and Orthophosphoric Acid. Part II.* Ion-exchange Studies of Solutions containing Phosphate and Chloride.*

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The adsorption of iron, phosphate, and chloride by both cation- and anion-exchangers from ferric chloride–phosphoric acid solutions and from ferric phosphate–hydrochloric acid solutions has been studied. The results indicate that the complex, $[FeHPO_4]^+$, is adsorbed by the cation-exchanger from solutions containing equimolecular, or nearly equimolecular, amounts of ferric chloride and phosphoric acid, while the anion-exchanger adsorbs only chloride from such solutions.

Addition of hydrochloric acid to ferric phosphate solutions decreases the adsorption of iron and phosphate by the anion-exchanger. Although adsorption of chloride is simultaneously increased the iron is adsorbed as a ferric phosphate complex rather than as a chloroferriphosphate complex. The similarity of the results obtained when nitrate was substituted for chloride also suggests the absence of chloro-complexes. Only with solutions containing much chloride (Fe 0·1M, Cl 2·86M) was any evidence of such complexes obtained.

THE evidence for the existence of ferric phosphate complexes and the views of previous workers were summarised in Part I,* where it was shown that in pure phosphate solutions the complex, $[Fe(PO_4)_3]^{6-}$ or $[Fe(HPO_4)_3]^{3-}$, is probably present. Since several of the complexes previously described, namely $[Fe(HPO_4)_2]^-$, $[FeH_2PO_4]^{++}$, and $[Fe(PO_4)Cl_3]^{3-}$, were reported to be formed in solutions containing chloride, the investigation has now been extended to include such solutions. As before, Amberlite I.R.A.-400 (in chloride or phosphate form) and Zeo-Karb 225 (in hydrogen form) were used.

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* Part I, *J.*, 1952, 2316.

RESULTS

Experiments with Ferric Chloride–Phosphoric Acid Solutions.—The adsorption of ions from mixed solutions of ferric chloride (0·1M; pH 1·0—1·8) and phosphoric acid by both exchangers has been studied. With the anion-exchanger in the chloride form (Table 1*a*) little or no iron or phosphate was adsorbed until the ratio of phosphoric acid to iron in the solution was about 10 : 1. With a high chloride-ion concentration (2·86M) there was limited adsorption of iron and phosphate in approximately equimolecular amounts (Table 1*b*).

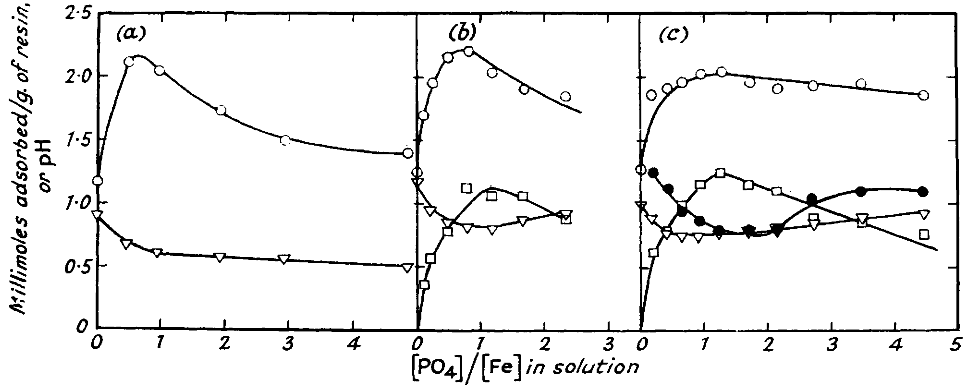
TABLE. 1. *Adsorption of iron, phosphate, and chloride by* I.R.A.-400-Cl.

Solution	Resin, millimole adsorbed/g. of resin		
$[PO_4]/[Fe]$	Fe	PO_4	Cl
(*a*) *Resin* 1·000 *g.*; $FeCl_3$ (pH 1·02) 50 *ml.*; 4·85M-H_3PO_4.			
0·00	0·01	Nil	2·17
0·50	—	,,	2·25
0·97	0·02	,,	2·11
1·95	0·02	,,	2·05
2·93	0·02	,,	2·05
4·85	0·02	,,	2·12
9·75	0·04	0·17	1·85

Solution	Resin, millimole adsorbed/g. of resin		
$[PO_4]/[Fe]$	Fe	PO_4	Cl
(*b*) *Resin* 3·00 *g.*; 25 *ml. of solutions* 0·1M *in* Fe *and* 2·86M *in* Cl, *but containing varying amounts* (0·1—0·585M) *of* PO_4^{3-}.			
1·00	0·14	0·07	2·24
1·97	0·16	0·14	2·22
2·94	0·18	0·19	2·16
5·85	0·16	0·23	2·06

Although addition of phosphoric acid to ferric chloride solution caused a fall in the pH of the solutions in equilibrium with the cation-exchanger, this was accompanied by an increased adsorption of iron, which rose to a maximum for a ratio of phosphoric acid to iron in the original solution of nearly 1 : 1 (Fig. 1*a*). There was simultaneous adsorption of phosphate, which likewise passed through a maximum (Figs. 1*b* and *c*).

FIG. 1. *Adsorption of iron and phosphate from* $FeCl_3$–H_3PO_4 *solutions by Zeo-Karb* 225-H (0·500 g.).



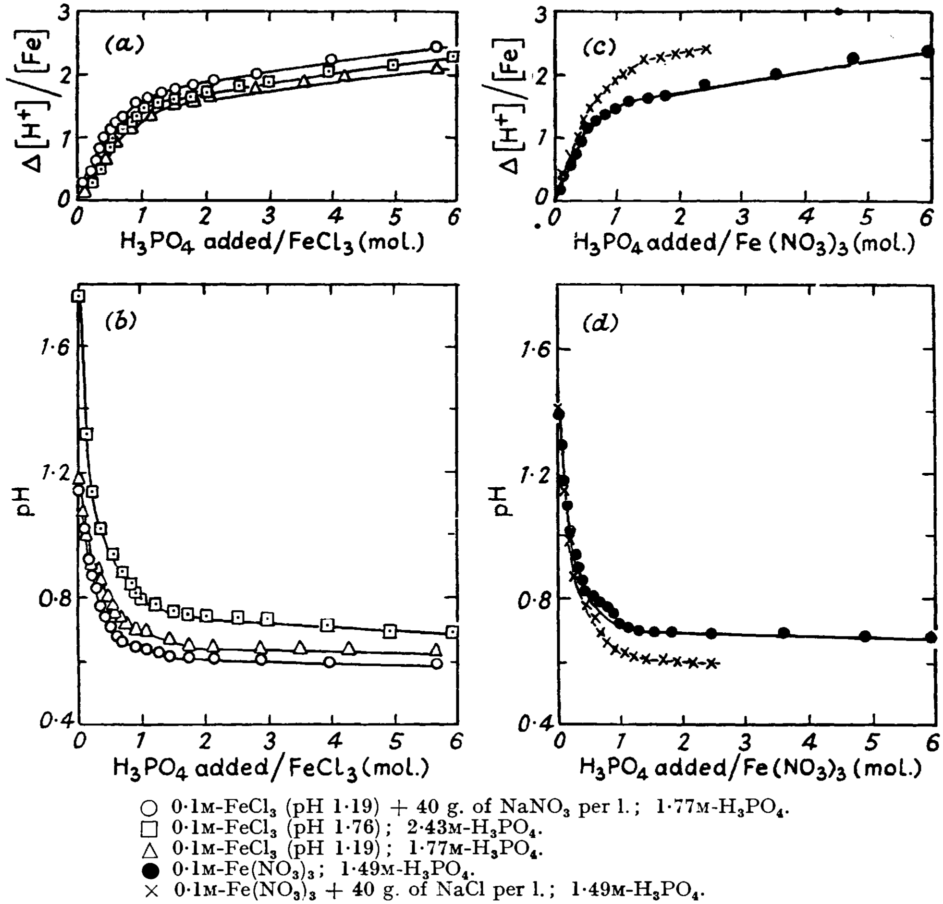
(*a*) 0·1M-$FeCl_3$ (pH 1·02) + 4·85M-H_3PO_4; 50 ml.
(*b*) 0·1M-$FeCl_3$ (pH 1·76) + 0·25M-H_3PO_4; 25 ml.
(*c*) 0·1M-$FeCl_3$ (pH 1·24) + 0·3M-H_3PO_4; 50 ml.

○ Total Fe adsorbed. ● Fe adsorbed as Fe^{3+}. □ Total PO_4 adsorbed. ▽ pH of solution (filtrate)

pH-*Titration of Ferric Chloride Solutions with Phosphoric Acid.*—pH-Titrations with a glass electrode–saturated calomel electrode system showed that addition of phosphoric acid caused a rapid fall in pH up to a mol. ratio of 1 : 1, but thereafter the pH remained practically constant even in the presence of a considerable excess of phosphoric acid (Fig. 2*b*). Addition of an inert electrolyte, such as sodium nitrate, had no effect on the course of the titration. When sodium dihydrogen phosphate was substituted for phosphoric acid the pH passed through a minimum at a mol. ratio of 1 : 1, the decrease in pH even at the minimum being, however, markedly less than with phosphoric acid.

Mixed Ferric Phosphate–Hydrochloric Acid Solutions.—The effect of addition of chloride to ferric phosphate solutions has been investigated. A difficulty was the very low solubility of ferric phosphate in dilute phosphoric acid. For anion-exchange studies it was preferable to keep the total phosphate concentration as low as possible and the solution used was 0·1M in iron and 1·5M in phosphoric acid. Although this would be in a state of metastable equilibrium at 25° (Jameson and Salmon, unpublished work) there was no precipitate of ferric phosphate after many months at room temperature. Since no adsorption of phosphate by the cation-exchanger was found with this solution (Table 2), it may be presumed that no precipitation occurred in the presence of resins either.

FIG. 2. pH *Titration of ferric chloride and nitrate with phosphoric acid.*



○ 0·1M-$FeCl_3$ (pH 1·19) + 40 g. of $NaNO_3$ per l.; 1·77M-H_3PO_4.
□ 0·1M-$FeCl_3$ (pH 1·76); 2·43M-H_3PO_4.
△ 0·1M-$FeCl_3$ (pH 1·19); 1·77M-H_3PO_4.
● 0·1M-$Fe(NO_3)_3$; 1·49M-H_3PO_4.
× 0·1M-$Fe(NO_3)_3$ + 40 g. of NaCl per l.; 1·49M-H_3PO_4.

The adsorption of ions from this solution and from mixtures of it with 0·3M-hydrochloric acid by both exchangers has been studied. With the cation-exchanger (Table 2) iron was adsorbed to some extent, but less than from ferric chloride solutions of the same pH where

TABLE 2. *Adsorption of iron, phosphate, and chloride by Zeo-Karb* 225-H (0·500 *g.*) *from* 50 *ml. of a mixture of ferric phosphate solution* ([*Fe*] 0·1M, [PO_4] 1·5M) *and* 0·3M-*hydrochloric acid.*

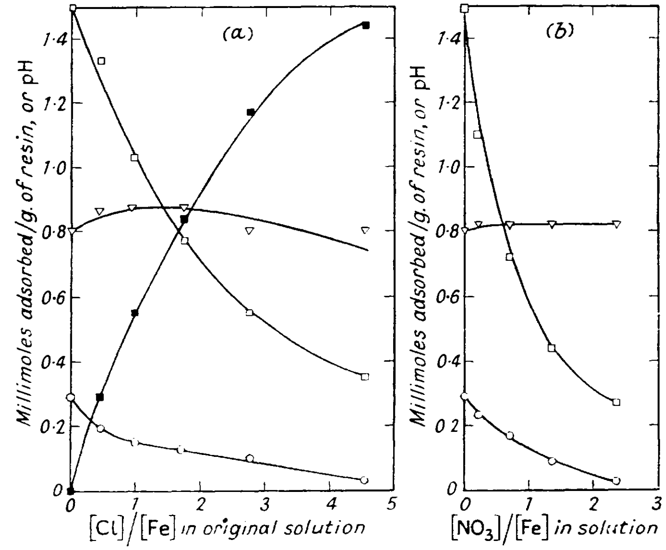
Solution		Resin, millimole adsorbed/g. of resin		Solution		Resin, millimole adsorbed/g. of resin	
[Cl]/[Fe]	pH *	Fe	PO_4	[Cl]/[Fe]	pH *	Fe	PO_4
0·00	0·75	0·55	Nil	1·71	0·78	0·67	Nil
0·41	0·79	0·58	,,	2·79	0·76	0·64	0·04
0·96	0·78	0·67	,,	4·53	0·74	0·70	0·06

* Of solution in equilibrium with the resin.

1·1—1·2 millimoles of iron are adsorbed per g. of resin. Phosphate was adsorbed only at high ratios of chloride to iron in the solutions, and chloride apparently not at all.

With the anion-exchanger both iron and phosphate were adsorbed from the ferric phosphate solution alone (in agreement with previous work, Part I), but as chloride was added to the solution this was readily adsorbed by the resin at the expense of both the iron and the phosphate (Fig. 3*a*).

FIG. 3. *Adsorption from* $Fe(H_2PO_4)_3$–HCl *and* $Fe(H_2PO_4)_3$–HNO_3 *solutions by* I.R.A. 400–PO_4 (1·000 g.).



(*a*) $Fe(H_2PO_4)_3$ solution, [Fe] 0·1M, [PO_4] 1·5M; HCl, 0·30M; 50 ml.
(*b*) $Fe(H_2PO_4)_3$ solution as in (*a*); HNO_3, 0·32M; 50 ml.

○ Total Fe adsorbed.
■ Total Cl adsorbed.
□ Total PO_4 adsorbed.
▽ pH of solution (filtrate).

DISCUSSION

The experiments with the ferric chloride–phosphoric acid solutions indicate that in them the complex present in major proportion must be a cationic complex, such as $[FeHPO_4]^+$ or $[FeH_2PO_4]^{++}$, since both the ion-exchange and the pH-titration data seem to confirm previous reports of a complex containing one phosphate group per iron atom. It seems unlikely that the chloroferriphosphate anionic complexes are formed unless they are weakly ionised—which is not in accord with conductivity data reported by Dede (*Z. anorg. Chem.*, 1922, **125**, 28) and Ricca and Meduri (*Gazzetta*, 1934, **64**, 235). The marked increase in conductivity found by these workers and attributed by them to the formation of a strong acid, $H_3[Fe(PO_4)Cl_3]$, appears to be due to the liberation of hydrochloric acid according to eqns. (1) or (2):

$$FeCl_3 + H_3PO_4 \rightleftharpoons [FeH_2PO_4]^{++} + H^+ + 3Cl^- \quad . \ . \ . \ . \ . \quad (1)$$

(cf. Jensen, *Z. anorg. Chem.*, 1934, **221**, 1)

$$FeCl_3 + H_3PO_4 \rightleftharpoons [FeHPO_4]^+ + 2H^+ + 3Cl^- \quad . \ . \ . \ . \ . \ . \quad (2)$$

(cf. Lanford and Kiehl, *J. Amer. Chem. Soc.*, 1942, **64**, 291).

If the iron present as such a complex is subtracted from the total iron adsorbed, it is found that the amount of ferric ions, Fe^{+++}, adsorbed does fall with the pH of the solution as would be expected (Fig. 1*c*). The assumption of adsorption of the complex, $[FeH_2PO_4]^{++}$, together with ferric ions leads to a high value for the capacity of the resin (4·6—5·0 milliequiv./g.) while the assumption that $[FeHPO_4]^+$ is adsorbed leads to a more reasonable value (3·6—4·2 milliequiv./g.; capacity found 3·75 milliequiv./g.). Further, the results of the pH titrations when interpreted in terms of hydrogen ions liberated per iron atom (Fig. 2*a*) indicate that two, or nearly two, hydrogen ions are liberated per iron atom at a mol. ratio of phosphoric acid to ferric chloride of 1 : 1. The liberation of hydrogen ions in the titration of ferric chloride with sodium dihydrogen phosphate (0·7 mol. per iron atom at a mol. ratio of 1 : 1) is in accord with the equation

$$FeCl_3 + NaH_2PO_4 \rightleftharpoons [FeHPO_4]^+ + H^+ + Na^+ + 3Cl^-$$

It thus appears that the complex $[FeHPO_4]^+$ is present and is adsorbed by the resin together with simple ferric ions. At higher $H_3PO_4 : FeCl_3$ ratios the cationic complex is apparently replaced by an un-ionised or anionic complex, possibly $[Fe(HPO_4)_2]^-$, which is not adsorbed by the anion-exchanger in the presence of chloride. In fact, no complex ions are adsorbed by this exchanger from these solutions unless a high concentration of phosphate (Table 1*a*) or of chloride (Table 1*b*) is present.

Although the low adsorption of iron by the cation-exchanger is in accord with complex formation, evidence for cationic complexes comes only from the solutions containing the highest mol. ratio of hydrochloric acid to ferric phosphate (Table 2). The corresponding experiments with the anion-exchanger (Fig. 3*a*) show, however, that anionic complexes are formed in all the solutions. In Table 3 the data are interpreted in terms of the capacity of the resin on the supposition that various complexes are adsorbed.

TABLE 3. *Adsorption of a complex ion, free phosphate, and chloride by* I.R.A. 400–PO_4 (1·000 *g.; capacity* 2·1—2·4 *milliequiv./g.*) *from ferric phosphate–hydrochloric acid solutions.*

[Cl]/[Fe] in solution	0·00	0·41	0·96	1·71	2·79	4·53
[Cl]/[PO_4] in solution	0·00	0·03	0·06	0·11	0·19	0·30
Free phosphate adsorbed as HPO_4'', % *	35	40	45	50	60	70
Complex postulated	Total milliequivs. adsorbed/g. of resin					
$[Fe(PO_4)_3]^{6-}$	2·62	2·50	2·33	2·20	2·17	2·06
$[Fe(HPO_4)_3]^{3-}$	1·74	1·95	1·81	1·80	1·85	1·98
$[Fe(PO_4)_2Cl_2]^{5-}$	—	2·20	2·06	2·01	2·03	2·03
$[Fe(PO_4)Cl_n]^{n-}$	—	1·91	1·79	1·81	1·87	2·00

* Remainder as H_2PO_4'; based on adsorption of phosphate and chloride by samples of known capacity from phosphoric–hydrochloric acid solutions having the same ratios of [Cl]/[PO_4].

It is apparent that, while adsorption of $[Fe(PO_4)_3]^{6-}$ or $[Fe(PO_4)_2Cl_2]^{5-}$ would account for the known capacity of the resin, the adsorption of ions such as $[Fe(PO_4)Cl_n]^{n-}$ (*e.g.*, $[Fe(PO_4)Cl_3]^{3-}$) would not. It is difficult, however, to reconcile the adsorption of $[Fe(PO_4)_2Cl_2]^{5-}$ ions, which should be present in increasing amount as the chloride ion concentration is raised, with the rapid decrease in adsorption of the complex (Fig. 3*a*). Thus it appears that the complex ion adsorbed in major amount is a triphosphatoferric ion. The high values calculated for the capacity of the resin on the basis of the adsorption of $[Fe(PO_4)_3]^{6-}$ when little or no chloride is present indicate that some $[Fe(HPO_4)_3]^{3-}$ ions are also adsorbed.

The decrease in adsorption of the complex ion with increasing mol. ratio of hydrochloric acid to ferric phosphate is attributed to the displacement to the right of equilibria such as :

$$[Fe(PO_4)_3]^{6-} \rightleftharpoons [Fe(HPO_4)_3]^{3-} \rightleftharpoons [Fe(HPO_4)_2]^- \rightleftharpoons [Fe(HPO_4)]^+ \rightleftharpoons [Fe]^{+++}$$

by reactions of the type :

$$[Fe(HPO_4)_3]^{3-} + 2H^+ \rightleftharpoons [Fe(HPO_4)_2]^- + H_3PO_4$$

(The co-ordination number of iron is presumably made up to four or six by co-ordination with water molecules.)

Since equilibria of the type postulated above would be displaced to the left by addition of phosphoric acid, the results obtained with the ferric chloride–phosphoric acid solutions can be explained on the same basis. Hydrochloric acid thus appears to function as a source of hydrogen ions and the close similarity of the results obtained when nitric acid was used in place of hydrochloric acid (Figs. 2*c*, 2*d*, and 3*b*; Table 4) supports this view.

Only with higher chloride-ion concentrations (Table 1*b*) does the formation of chloroferriphosphate complexes appear to be important.

Table 4. *Adsorption of iron and phosphate by Zeo-Karb* 225-H (0·500 *g.*) *from* 50 *ml. of a mixture of* 0·1M-*ferric nitrate* (pH 1·4) *with* 0·3M-*phosphoric acid.*

Solution		Resin, millimoles adsorbed/g.		Solution		Resin, millimoles adsorbed/g.	
$[PO_4]/[Fe]$	pH *	Fe	PO_4	$[PO_4]/[Fe]$	pH *	Fe	PO_4
0·68	0·80	2·25	0·91	1·09	0·80	2·35	1·25
0·88	0·80	2·25	1·10	1·33	0·80	2·37	1·30

* Of solution in equilibrium with the resin.

The slight retention of phosphate from solutions containing iron, phosphate, and chloride by columns of Zeo-Karb 225 reported in Part I was presumably due to adsorption of $[FeHPO_4]^+$ ions. The fact that the retention was not greater can probably be ascribed to the difference in conditions. In the batch experiments, the solution was present in excess, the resin was apparently saturated, and time had been allowed for equilibrium to be established. In the column experiments, however, the resin was greatly in excess and was not saturated, while equilibrium conditions were not achieved.

Experimental

The experimental procedure was the same as in Part I except for the following points.

Preparation of Solutions.—Electrolytic iron was used. For the chloride and phosphate solutions, a known volume of the acid of known strength was used and the solutions so obtained were oxidised with hydrogen peroxide as before.

Apparatus.—Because smaller quantities of resin were employed, it was possible to use smaller columns (1 cm. internal diam., 10 cm. long, above sintered disc).

Procedure.—At least 3 weeks, with frequent shaking, were allowed for solutions and resin to come to equilibrium. The solution was then filtered through the dry column and the filtrate kept for analysis and pH measurement. The resin was then transferred to the column and washed rapidly with water (*ca.* 50 ml.) under suction. The column was filled with water and the resin washed with a further 800 ml. of water before elution with 500 ml. of 2—3N-nitric acid. Aliquots of the eluate were used for analyses. The difficulty in eluting iron from a cation-exchanger reported by Goudie and Rieman (*Analyt. Chem.*, 1952, **24**, 1067) was not encountered.

In all cases, the sum of the iron adsorbed by the resin and that remaining in solution tallied closely with that originally present. Thus the possibility of complexes being decomposed on washing of the resins may be ruled out (cf. Leden, *Svensk Kem. Tidskr.*, 1952, **64**, 145). In the experiments represented in Fig. 1*c*, the phosphate content of the solutions in equilibrium with the resin was also checked and the total of phosphate originally present was accounted for.

Analysis.—Iron was determined, after elimination of nitric acid, by titration with standard potassium dichromate solution or, when only small amounts were present, colorimetrically with thiocyanate after precipitation of phosphate present with zirconium oxychloride. Phosphate was determined gravimetrically as ammonium phosphomolybdate. Chloride was determined as silver chloride. Blank experiments showed the nitric acid used for elution to be free from iron, phosphate, and chloride.

Capacity of the Resins.—The capacity of the cation exchanger was determined by passing 250 ml. of 0·5N-sodium chloride through a column containing 0·500 g. of resin in the hydrogen form and determining the acid liberated in the effluent. For the anion-exchanger 500 ml. of 2—3N-nitric acid were passed through a column containing 1·000 g. of the chloride form of the resin, and the chloride content of the effluent was determined.

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