283. *Ion-exchange Studies of Phosphates. Part III.*[1] *Complex Formation between Tervalent Metals and Orthophosphoric Acid.*

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Equilibrium batch experiments with various tervalent-metal (Al, Fe, Ti, In, Sc, Yb, Er, Nd, and La) forms of a strong cation-exchange resin and orthophosphoric and perchloric acid solutions are used to assess the degree of complex formation. Where possible, comparison is made with conclusions based on the results of pH titrations of the metal chloride solutions with phosphoric acid.

With perchloric acid there is little sign of complex formation, but with phosphoric acid there is found a regular variation in the degree of complex formation with the ionic radius (non-hydrated) of the metal. There is an optimum ionic radius for complex formation of approximately 0·7 Å, corresponding closely to that of titanium(III) and a gradual decrease at higher or lower radii.

An explanation of this is offered in terms of the ease of formation of a four-membered chelate ring, and it is shown that the optimum radius of 0·7 Å is that required to give the least strain and the minimum distortion of bond angles.

PREVIOUSLY we showed[1] that the degree of complex formation between metals and orthophosphoric and other acids could be estimated from results of equilibrium batch experiments with the metal form of a strong cation-exchange resin and the acid. This suggested the possibility of comparing the tendencies to complex formation of a number of metals of the same valency with phosphoric acid and covering a wide range of ionic radii. Results obtained in this way with many metals and with both phosphoric and perchloric acids are given.

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[1] Part II, Genge and Salmon, *J.*, 1957, 256.

Another method which has been used to estimate the degree of complex formation is that of pH titrations with use of the complexing acid and a suitable solution of the metal.[2] Under conditions where the complexes formed are soluble, results so obtained are used to verify those obtained by the ion-exchange method.

EXPERIMENTAL

Resins.—The strong cation-exchanger, Zeo-Karb 225 (approximately 10% cross-linked), of bead size 20—40 mesh was used for all the batch experiments. The metal form of the resin was prepared in each case as previously described.[1] With each batch, the total metal capacity was determined on 0·500 g. samples by complete elution with 2N-hydrochloric acid and analysis of the eluate. The total hydrogen capacity of the same sample was then determined as previously described [3] and the resin was used only if these two capacities were very nearly equal, showing complete loading.

Procedure.—For the batch experiments, 0·500 g. samples of the metal form of the resin were left, with occasional gentle swirling, for 7 days at room temperature (20° ± 3°) (which proved sufficient for attainment of equilibria) with 50 ml. of the acid of known pH.[1] A 25 ml. portion was then analysed for the metal. Analysis for La, Nd, Yb, and Er in the presence of phosphate proved difficult and it was found more convenient in these cases to filter off the resin into a small column (10 cm. × 1 cm. diam. with a sealed-in grade 2 sintered-glass disc) and wash thoroughly. The metal on the resin was then eluted with 2N-hydrochloric acid and determined in the eluate. The amount originally removed from the resin by the acid was then obtained by difference. In all cases, the final results are given as the percentage of the metal originally present on the resin which had been removed by the acid. All work with titanium(III) had to be carried out in an inert atmosphere, and an apparatus and technique were developed. A wide-necked glass cylinder (250 ml.) was fitted with a rubber bung carrying a dropping funnel, two inlet tubes to the top of the cylinder, and an outlet tube from the bottom. One inlet tube was for nitrogen and the other, which contained 0·500 g. of the hydrogen form of the resin supported on a glass-wool plug, was connected through a glass junction to two burettes. At the start of each experiment, the whole apparatus was filled with water and then emptied by passing nitrogen. Acidified titanous chloride, which is reasonably stable towards atmospheric oxidation, was run in from one burette and diluted with water from the other before reaching the resin. When an excess had been used, water alone was passed through to wash the resin. The collecting cylinder was then cleaned by alternately filling with water and blowing out with nitrogen. The resin was then dropped into the cylinder by pushing away the glass wool with a nickel wire, and 50 ml. of acid were added, and left for 7 days as in the normal batch experiments. For analysis, it was satisfactory if 25 ml. of the solution was rapidly withdrawn with a pipette and transferred immediately to an excess of iron alum solution.

pH *Titrations.*—The method used was that described by Holroyd and Salmon [2] but, for this work, *ca.* 0·75M-phosphoric acid was added in small quantities from a 5 ml. burette to 50 ml. of the metal chloride solution *ca.* 0·05M in metal. The pH was measured originally and after each addition on a pH meter with a glass electrode–calomel electrode system. pH values were converted to hydrogen-ion concentrations after the method of Holroyd and Salmon [2] and the quotient $[H_3PO_4]/[M]$ was plotted both against pH and against $\Delta[H]/[M]$, allowance being made in all cases for the increase in volume of the solution due to the addition of the phosphoric acid.

The titrations were carried out with iron(III), titanium(III), aluminium, and indium and also with potassium as a non-complexing system.

Analysis.—Titanium(III) was determined by addition of excess of ferric alum solution and subsequent titration of the ferrous iron with standard potassium dichromate, sodium diphenylaminesulphonate being used as indicator. Iron(III) was also determined by titration with standard dichromate after reduction to ferrous iron.

Aluminium and scandium were estimated by addition of excess of standard ethylenediaminetetra-acetic acid, and back-titration of the excess with standard zinc sulphate in 50% ethanol solution at pH 4·5 with dithizone as indicator.[4] Indium, lanthanum, neodymium,

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[2] Holroyd and Salmon, *J.*, 1956, 269.

[3] Salmon, *J.*, 1953, 2644.

[4] Lukaszewski, Redfern, and Salmon, *Lab. Practice*, 1957, **6**, 390.

ytterbium, and erbium were determined by a similar back-titration method, but in aqueous solution at pH 10·0 with Eriochrome Black T as indicator.[5]

RESULTS AND DISCUSSION

The amount of each metal removed from the resin with phosphoric and perchloric acids at pH 0·25, 0·50, 0·75, and 1·00 are shown in Fig. 1 where the percentage of metal removed is plotted against the (non-hydrated) ionic radius.

Published tables of ionic radii are incomplete and, for this work, the values for Ti, Fe, Al, La, In, and Sc are taken from the list obtained theoretically by Pauling.[6] The remainder, for Nd, Yb, and Er, not given by Pauling, are taken from a list by Goldschmidt. An increment of 0·6, which is a reasonably constant difference between the Pauling and Goldschmidt series, has been added to the latter values to bring them into line with the others.

Curves obtained with perchloric acid being considered first, these show clearly that there is little or no tendency to form complex ions. There is a steady drop in the percentage of metal removed by the acid at any given pH with increase in ionic radius. This is to be expected since the smallest ion will be the most heavily hydrated and therefore the least firmly held on the resin. The curves obtained with phosphoric acid, on the other hand, show the occurrence of considerable complex formation, particularly with the metals of smaller ionic radius. Thus, with Al, Fe, Ti, In, and Sc, a high percentage of metal is removed and the curve shows a maximum at approximately 0·7 Å corresponding most closely to the ionic radius of titanium. The rare-earth metals, with larger ionic radii, show a lower removal but again the expected drop with increase in ionic radius is apparent.

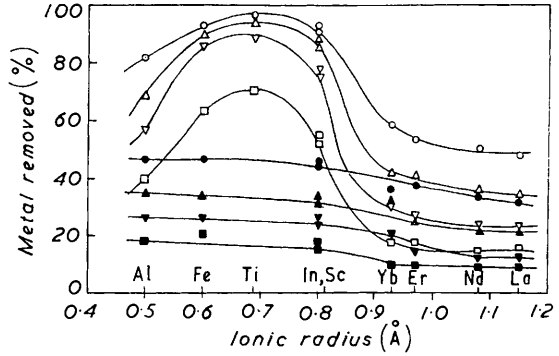

FIG. 1.

○ H_3PO_4, pH = 0·25
△ H_3PO_4, pH = 0·50
▽ H_3PO_4, pH = 0·75
□ H_3PO_4, pH = 1·00

● $HClO_4$, pH = 0·25
▲ $HClO_4$, pH = 0·50
▼ $HClO_4$, pH = 0·75
■ $HClO_4$, pH = 1·00

The curves in Fig. 2 show the results of the pH titrations with titanium, iron, aluminium, and indium together with those of potassium for comparison. These results are substantially in agreement with those obtained in the ion-exchange experiments and, in both sets of results, the degree of complex formation is in the order Ti > Fe > In > Al. Further, the ion-exchange experiments show that this order is the same over a wide range of pH values. Previous work[1,8c] has indicated that the formation of chloro-complexes is likely to be very slight under these conditions.

In the ion-exchange experiments, the complexes formed will tend to be anionic and mononuclear.[9] Further, there are never more than three phosphate groups associated

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[5] Genge and Salmon, *Lab. Practice*, 1957f **6**, 695.

[6] Pauling, *J. Amer. Chem. Soc.*, 1927, **49**, 765.

[7] Goldschmidt, *Trans. Faraday Soc.*, 1929, **25**, 253.

[8] (*a*) Holroyd and Salmon, *J.*, 1957, 959; (*b*) Holroyd, Jameson, Odell, and Salmon, *J.*, 1957, 3239; (*c*) Salmon and Wall, *J.*, 1958, 1128; (*d*) Brownlow, Salmon, and Wall, unpublished work.

[9] Jameson and Salmon, (*a*) *J.*, 1954, 28; (*b*) *J.*, 1954, 4013; (*c*) *J.*, 1955, 360; (*d*) Salmon and Wall, unpublished work.

with one metal atom of co-ordination number six,[9] which suggests that the complexes are of a chelate type with the phosphate acting as a bidentate ligand. Over the pH range used in the titration experiments (1·0—3·0) the complex ions will tend to be cationic and binuclear or multinuclear, but uninuclear complexes are also formed, for example, with iron.[1,2,8] The largest increases in $\Delta[H]/[M]$ are associated with chelate formation:

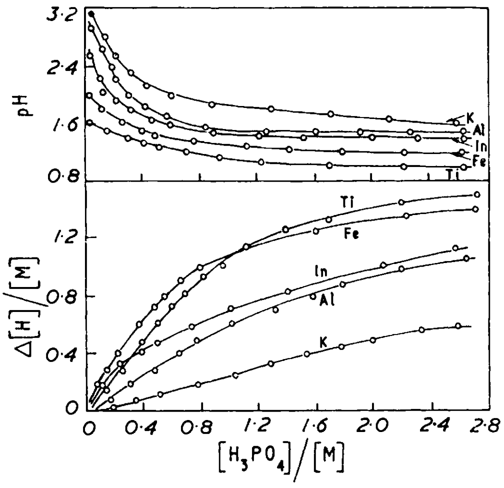
$$M^{3+} + H_3PO_4 \rightleftharpoons MHPO_4^{+} + 2H^{+} \; (H^{+}:M = 2:1)$$

rather than the formation of multinuclear ions by bridging:

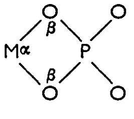
$$2M^{3+} + H_3PO_4 \rightleftharpoons M_2PO_4^{3+} + 3H^{+} \; (H^{+}:M = 3:2)$$

Thus the very large increases in [H] obtained with iron and titanium probably reflect the greater tendency on the part of these metals to form chelate complexes.

FIG. 2.



The chelate complexes (inset) are formed essentially as four-membered rings and the tendency to form such complexes will be related to their stability. This, in turn, will be related to the size of the metal ion. If the size of the metal ion is such that the ring can be formed under strain-free conditions there will be every incentive for chelate rings to be formed and the resulting complex ion will show the maximum enhancement of stability owing to the " chelate effect." But if the metal ion is too large or too small, bridge structures will tend to be more stable. In the extreme case, very large cross-linked structures may be formed, leading to precipitation.



From the results, it appears that the ideal size is approximately 0·70 Å and that this is the explanation of the maximum complexing obtained with titanium and the lower values with other metals having ionic radii on either side of this. The metals considered in this work are all probably forming complexes by use of the outer *d* orbitals, that is, by sp^3d^2 hybridisation, and, although the general arguments used would still be true, it is not considered safe to extend the argument to the case of metals using inner *d* orbitals, particularly where ligands other than phosphate and aquo-groups may be involved.

It may be observed that whilst trischelate complexes are formed by aluminium, iron,[9a,b] and indium,[9d] monochelate structures are formed by iron [3,8] and, by inference from the present studies, titanium, but not apparently to any significant extent by alumimium or indium.[8c,d] The greater stability of the trischelate structures thus makes possible their formation over a wide range of ionic radii.

It is possible, with simple theoretical considerations, to calculate the optimum ionic radius for a strain-free ring. Using Pauling's values [10] for the ionic radii of O^{2-} and P^{5+} (1·40 and 0·34 Å) respectively, and assuming that the four oxygen atoms are grouped about the phosphorus atom tetrahedrally (O–P–O bond angle = 109°), we find the O–O distance to be 2·83 Å, showing that the oxygen atoms are roughly touching each other. It is not possible to reduce the phosphorus bond angle and equally it is not possible to keep both oxygen and metal bond angles (α and β) at 90°. If the strain is distributed between the two oxygen bond angles and the metal bond angles so that α is 84° and β is 83·5°, the M–O distance is 2·12 Å and the metal radius must be 0·72 Å.

Several factors suggested the use of ionic rather than covalent radii. Thus the interaction is between M^{3+} and effectively HPO_4^{2-} and will involve bonds of a highly polar character. Hence the oxygen atoms in P–O–M will carry effectively one unit of negative charge which may be increased further by the polar character of the P–O bond (about 40% for a single bond according to Pauling [11]). Further, the bonding of the two oxygen atoms to two other atoms (M and P) will reduce effectively the double-bonding between the phosphorus and the oxygen atom so that the bonds will be restored to 1·74 Å as compared with the commonly encountered 1·55 Å.[12] In addition the general similarities observed between the crystal structures of several heavy-metal phosphates and certain silicates [13] suggests that in these phosphates the structure is approximately one of large contiguous O^{2-} ions with smaller interstitial P^{5+} ions.

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[10] Pauling, " The Nature of the Chemical Bond," 2nd Edn., Cornell Univ. Press, 1940, p. 346.

[11] Pauling, *op. cit.*, p. 70.

[12] Van Wazer, *J. Amer. Chem. Soc.*, 1956, **78**, 5709.

[13] Wells, " Structural Inorganic Chemistry," 2nd Edn., Oxford Univ. Press, 1950, p. 488.