57. *Ion-exchange Studies of Phosphates. Part I. Ion-exchange Sorption and* pH-*Titration Methods for Detection of Complex Formation*

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The sorption of metal and phosphate from solutions of the metal phosphates in phosphoric acid by the phosphate form of an anion-exchange material has provided evidence of complex formation between phosphate ions and the tervalent ions of aluminium, chromium (aged solutions), iron, and indium, and also bismuth (solutions of bismuth phosphate in hydrochloric acid). With the bivalent metals a slight sorption of metal by the anion-exchange material was found for manganese, but none for barium, calcium, cadmium, cobalt, copper, mercury, magnesium, nickel, lead, strontium or zinc.

The results of pH titrations of solutions of the metal sulphates with phosphoric acid have also indicated complex formation with tervalent aluminium, chromium (aged solutions), iron, and indium, but not (to any significant extent) with bivalent cadmium, cobalt, copper, magnesium, manganese, nickel, or zinc.

The sorption of phosphate with the metal from solutions of the metal phosphate in phosphoric acid by the hydrogen form of a cation-exchange material has been observed for tervalent aluminium (slight) and chromium (aged solutions) and bivalent manganese (slight), but not for tervalent iron and indium, or for bivalent barium, cadmium, calcium, cobalt, copper, mercury, magnesium, nickel, lead, strontium, or zinc.

It has been shown [1-3] that complex formation in solution between phosphate and the tervalent ions of iron, aluminium, and chromium could be demonstrated by the sorption of the metal ions together with phosphate ions on an anion-exchange resin or of phosphate ions together with metal ions on a cation-exchange resin. In addition, Everest and Salmon [4] have used anion exchange studies to show the formation of complexes between quadrivalent germanium and phosphate. In the present work the species sorbed by cation- and anion-exchange materials respectively from phosphoric acid solutions of some bi- and ter-valent metal phosphates have been examined. The results, which show complex formation to be much more important with tervalent than with bivalent metals, have been checked by the pH-titration method which had already proved useful in the study of aluminium and iron phosphate complex compounds.[2, 5, 6]

Experimental

Ion-exchange Experiments.—Solutions were prepared by saturating portions (*ca.* 150 ml.) of 1M-phosphoric acid with various metal phosphates. Each solution was then diluted with 1/20th of its own volume of 1M-phosphoric acid so that the possibility that metal phosphate might crystallize on the resin would be avoided. With antimony, bismuth, and stannous phosphates so little of the phosphate dissolved in the phosphoric acid solution used that the metal ions could not be detected readily by standad qualitative tests. Ion-exchange experiments were not carried out with these phosphates, except that of bismuth which was dissolved in 0·5N-hydrochloric acid.

To each of two 50 ml. portions of each of the final solutions were added 0·500 g. of Zeo Karb 225-H and 1·000 g. of I.R.A.-400-PO_4 respectively. The solutions were kept in contact with the resin in a stoppered flask for at least a week, with frequent shaking. The resin was filtered off into a small column and washed with water, rapidly at first to remove the bulk of the adhering solution, and then until the washings were free from metal or phosphate. The species sorbed on the resin were eluted with nitric or, in a few cases, hydrochloric acid (300 ml.; 3N). The

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[1] Salmon, *J.*, 1952, 2316.
[2] *Idem, J.*, 1953, 2644.
[3] Jameson and Salmon, *J.*, 1954, 28, 4013; 1955, 360.
[4] Everest and Salmon, *J.*, 1955, 1444.
[5] Bjerrum and Dahm, *Z. phys. Chem.*, *Bodenstein Festband*, **1931**, **627**.
[6] Salmon and Wall, unpublished work.

eluate was evaporated to small bulk and portions tested for metal ions and phosphate by standard procedures.

pH-*Titration Experiments.*—Phosphoric acid (approx. 1·5M) was added to a metal sulphate solution (25 ml.; 0·1M in metal ion) in small portions from a burette. The pH of the solution was measured initially and after each addition of phosphoric acid with a glass electrode–saturated calomel electrode system and commercial pH meter. The pH values which are given in Fig. 1 have been converted into hydrogen-ion concentrations and the increase in hydrogen-ion concentration ($\Delta[H^+]$) over that of the original solution derived, and in Fig. 2 the values of $\Delta[H^+]/[M]$ have been plotted against the corresponding values of $[H_3PO_4]/[M]$, where $[M]$ = total metal-ion concentration. Allowance was made in the calculation for the progressive dilution of the solution on addition of the phosphoric acid. The metal sulphates were chosen for these experiments because a wide range of pure sulphate was available and also because a comparison with the pH-titrations already carried out with the chlorides of iron [2] and aluminium [6] could thus be made.

FIG. 1. pH-*Titrations of metal sulphate solutions* (0·1M *in metal*) *with phosphoric acid* (1·5M).

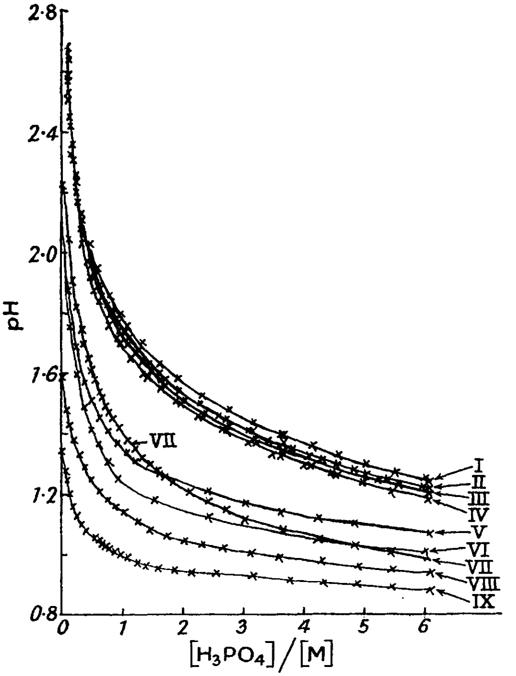
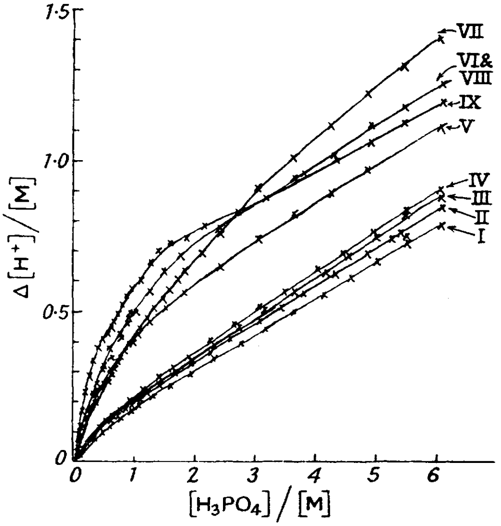


FIG. 2. *Increase in hydrogen-ion concentration during* pH *titration.*



I = K^+ (5·86), Ni^{2+} (5·18), $[Cr(H_2O)_6]^{3+}$ (3·14).
II = Mg^{2+} (5·41), Zn^{2+} (5·40), Co^{2+} (3·90).
III = Mn^{2+} (4·98).
IV = Cd^{2+} (5·27), Cu^{2+} (4·18).
V = Cr^{3+} (2·23) [aged 9 weeks at 25°].
VI = Cr^{3+} (2·03) [aged 24 weeks at 40°].
VII = Al^{3+} (3·13).
VIII = In^{3+} (1·59).
IX = Fe^{3+} (1·34).

The figures in parentheses refer to the pH values of the sulphate solutions used (no phosphate added).

In the case of the chromic sulphate solutions the results obtained depended on whether the pH-titration was carried out rapidly (completed in 1 hr.) or slowly (solutions aged before pH measurements). In order to study the effect of ageing, various known amounts of phosphoric acid were added to 100 or 150 ml. portions of chrome alum solution (0·1M in Cr) and the mixtures kept in sealed containers at 25° or 40°. After various intervals of time samples were withdrawn and cooled to *ca.* 20° before pH measurements were made.

Results.—*Anion-exchange experiments.* Sorption of the metal with the phosphate on the anion exchange material was observed for tervalent aluminium, bismuth (from 0·5N-hydrochloric acid solution), chromium (aged solutions), indium, and iron, and for bivalent manganese (slight trace only). No sorption of metal was found for bivalent barium, cadmium, calcium, cobalt, copper, lead, magnesium, mercury, nickel, strontium, and zinc.

Cation-exchange experiments. Sorption of phosphate on the cation-exchange material was observed for aluminium, chromium (aged solutions), and bivalent manganese (very slight trace), but not for tervalent bismuth (no bismuth sorbed either from 0·5N-hydrochloric acid), indium, or iron, or for bivalent barium, cadmium, calcium, cobalt, copper, lead, magnesium, mercury, nickel, strontium or zinc.

pH-*Titrations.* The results are shown in Figs. 1 and 2. The curves are very nearly identical with those for potassium sulphate in the cases of bivalent cadmium, cobalt, copper, magnesium, manganese, nickel, and zinc, and tervalent chromium sulphates $\{[Cr(H_2O)_6]^{3+}$, not aged$\}$. It may be deduced that in these cases the increase in hydrogen-ion concentration of the solutions is due solely to the hydrogen ions of the phosphoric acid added and that there is no complex formation. Support for this conclusion is provided by the fact that this group includes the ion $[Cr(H_2O)_6]^{3+}$ (solutions not aged) for which no interaction with phosphate occurs during the time taken to carry out a pH-titration (at room temperature).

The rapid increase in hydrogen-ion concentration in the course of the titration of the sulphates of aluminium, chromium (solutions aged at 25° or 40°), indium, and iron, on the other hand, indicates the occurrence of reactions of a type previously reported,[2] namely,

$$Fe^{3+} + H_3PO_4 \rightleftharpoons FeHPO_4^{+} + 2H^{+}$$

and hence of complex formation.

The increase in hydrogen-ion concentration is less in the titration of iron and aluminium sulphates than it is in the titration of the corresponding chlorides.[2, 6] This may arise because the chloro-complexes of these metals are more labile than the sulphato-complexes and the chloro-groups are more easily displaced by phosphate than are the sulphate groups.

In the case of chromium, ageing of the sulphate solution alone (no phosphate added) caused an increase in hydrogen-ion concentration (pH fall from 3·14 to 2·06—2·48 depending on time and temperature of ageing), but the increase was always greater with phosphate present and also dependent on the phosphoric acid concentration (Fig. 2), thus showing the formation of phosphato-complexes to be occurring. Nevertheless, the reactions are slow and, whilst equilibrium was reached after three weeks at 40°, it was probably still not reached after 9 weeks at 25° as the pH values recorded then were markedly lower than those obtained after five weeks.

DISCUSSION

The correlation between the results of the anion-exchange and pH-titration studies is satisfactory. According to both methods complex formation occurs with the tervalent metals, but not with the bivalent ones to any significant extent. The only exception, according to the anion-(and also cation-)exchange experiments, is bivalent manganese. The sorption of manganese on the anion-exchange material was only slight, but was consistently observed when the experiment was repeated with both commercial and pure manganese phosphate (the latter prepared by Salmon and Terrey's [7] method). The differences between the pH-titration curves for the bivalent metals (Fig. 1) are barely greater than the experimental error, but may indicate a very slight degree of complex formation for cadmium and copper, and possibly manganese. Nevertheless, it is not considered wise to assign stabilities (even qualitatively) to the bivalent metal complexes or yet to compare them with those predicted by Irving and Williams.[8]

The cation-exchange experiments with the phosphate solutions provide evidence of complex formation for aluminium, chromium, and possibly manganese(II) only, but not for iron or indium for both of which complex formation is indicated by the other two methods. The results obtained are in accord with those of Jameson and Salmon for aluminium, chromium, and iron.[3] Only in the case of chromium is an appreciable amount of phosphate sorbed by the cation exchanger from pure phosphate solution, yet it has been found [2, 6] that the cationic complexes of aluminium and iron are sorbed by the exchanger when present, as in solutions containing the anion of a strong acid (*e.g.*, in $AlCl_3$–NaH_2PO_4 or $FeCl_3$–H_3PO_4 solutions). Thus with the tervalent metals indium, iron, and (to a lesser extent) aluminium the equilibria :

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

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[7] Salmon and Terrey, *J.*, 1950, 2813.

[8] Irving and Williams, *J.*, 1953, 3192.

must lie well to the right in the pure phosphate solutions. Although the concentration of HPO_4^{2-} ions must be low in the solutions of phosphoric acid used, the presence of anionic complexes in them shows that the phosphate group must act as a chelate group in the complexes. Otherwise if equilibria of the type:

$$M^{3+} \rightleftharpoons [M(H_2PO_4)]^{2+} \rightleftharpoons [M(H_2PO_4)_2]^{+} \rightleftharpoons [M(H_2PO_4)_3]^{0}$$
$$\rightleftharpoons [M(H_2PO_4)_4]^{-} \rightleftharpoons [M(H_2PO_4)_5]^{2-} \text{ etc.}$$

were involved, four or more phosphato-groups would have to be co-ordinated to the central atom. Complexes with so many ligand groups, which would be expected to show a greater tendency to dissociate into those containing fewer attached groups (including cationic ones) except at high phosphate-ion concentrations, have not been observed in the quantitative ion-exchange studies carried out so far.[2, 3, 6] Thus, although chelation must involve some steric strain in forming the four-membered ring, the increased stability arising from it must more than compensate for this.

The sorption of bismuth by the anion-exchange material from the solution of bismuth phosphate in hydrochloric acid is in accord with Jensen's evidence [9] for the existence of an anionic chloro-phosphato-bismuth complex.

It is possible that complexes of marked stability only would be detected by the methods used—thus, we have not observed the interaction between calcium and phosphate ions reported by other workers.[10] Nevertheless, the results indicate clearly a difference in behaviour between the bivalent and tervalent metals which is certainly greater than might have been expected. This difference may be exploited in ion-exchange chromatography with phosphoric acid as eluant and a preliminary account has already been given of its application in the separation of tervalent from bivalent metals.[11]

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[9] Jensen, *Z. anorg. Chem.*, 1934, **219**, 238.
[10] Davies and Hoyle, *J.*, 1953, 4134; Gosselin and Coghlan, *Arch. Biochem. Biophys.*, 1953, **45**, 301.
[11] Genge, Holroyd, Salmon, and Wall, *Chem. and Ind.*, 1955, 357.