221. *Aluminium Phosphates. Part II.*[*] *Ion-exchange and* pH-*Titration Studies of Aluminium Phosphate Complexes in Solution.*

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The sorption of aluminium, phosphate, and chloride from solution by both cation- and anion-exchangers has been studied in batch experiments. The extent of sorption of phosphate (together with aluminium) by the cation-exchanger was found to be dependent both on the pH and on the mole ratio of phosphate to aluminium in the solutions. Sorption of aluminium (together with phosphate) by the anion-exchanger was negligible when chloride was present. These results, together with those of further batch experiments with the aluminium form of the cation-exchanger and those of pH titration experiments, have been interpreted in terms of the formation of complex phosphatoaluminium cations and anions, which are probably less stable than the corresponding ferric phosphate complexes. Some at least of the cationic complexes are binuclear, or polynuclear, and on this basis an explanation is offered of the difficulties encountered by Bjerrum and Dahm [1] in their calculations. No evidence of mixed chlorophosphatoaluminium complexes was found.

FROM their conductivity and pH measurements on solutions containing aluminium chloride and sodium dihydrogen phosphate Bjerrum and Dahm [1] found evidence for the formation of various phosphatoaluminium complexes which they assumed to be of the types $[Al(H_2PO_4)]^{2+}$, $[Al(HPO_4)]^{+}$, $[Al(H_2PO_4)_2]^{+}$, $[Al(HPO_4)_2]^{-}$, $[Al(HPO_4)_3]^{3-}$, etc. Nevertheless, their attempts to determine the complexity constants led to values which were not compatible with assumptions made. However, Jensen's measurements [2] of the solubility of aluminium tertiary phosphate in acid solutions containing phosphate and chloride indicated that pure phosphato-complexes only were formed in such solutions and that chlorophosphato-complexes were absent.

In their ion-exchange studies of aluminium phosphate solutions in phosphoric acid, Jameson and Salmon [3] found evidence for anionic complexes such as $[Al(HPO_4)_3]^{3-}$, which they believed to be the predominant one, and $[Al(HPO_4)_2]^{-}$—both of the type postulated by Bjerrum and Dahm.

From their ion-exchange and pH-titration studies Holroyd and Salmon [4] deduced that complex formation with phosphate was marked with several tervalent metals, including iron and aluminium, but, on the basis of conductivity measurements, Dede [5] concluded that the aluminium phosphate complexes were less stable than those of ferric phosphate.

A full knowledge of the nature of the aluminium phosphate complexes was evidently lacking and studies similar to those made of the ferric phosphate system [6] were accordingly undertaken.

EXPERIMENTAL

Procedure.—The experimental procedures were those previously described for ion-exchange [3, 6, 7] and pH-titration experiments.[4, 6] Where the aluminium or zinc forms of the cation-exchanger were used, these were prepared by the passage through a column of the exchanger of an excess of a solution of a salt of the metal. The metal was washed thoroughly and allowed to dry in the air. Samples (0·500 g.) were shaken with 50 ml. portions of acid solutions of known pH, and the proportion of metal that had passed into solution at equilibrium

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[*] Part I, *J.*, 1954, 4013.

[1] Bjerrum and Dahm, *Z. phys. Chem.*, Bodenstein Festband, 1931, 627.

[2] Jensen, *Z. anorg. Chem.*, 1934, **221**, 1.

[3] Jameson and Salmon, *J.*, 1954, 4013.

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

[5] Dede, *Z. anorg. Chem.*, 1922, **125**, 28.

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

[7] Genge and Salmon, *J.*, 1957, 256.

was determined. The total amount of metal present initially in the resin phase was determined by elution of the metal from separate samples of the same batch of resin by an excess of acid and estimation of metal in the eluate. This value was checked against the hydrogen ion capacity [6] of the same samples.

Materials.—The aluminium chloride solutions were prepared from aluminium metal of high (spectrographic) purity and hydrochloric acid of analytical grade. All other materials were of analytical grade. The resins used were Zeo-Karb 225 and Amberlite I.R.A. 400, the phosphate form of which was prepared by a method already given.[8]

Analytical Methods.—Aluminium was determined gravimetrically by means of 8-hydroxyquinoline ("oxine"). Interference by phosphate was avoided as follows: the acid solution containing aluminium and phosphate was made just alkaline to phenolphthalein by the dropwise addition of M-sodium hydroxide; the solution was heated to 40° and a 10% excess of alcoholic "oxine" reagent was added, followed by 25 ml. of 2M-ammonium acetate; precipitation was completed by heating the suspension to 100° for a short while.

Phosphate was determined by weight as ammonium phosphomolybdate, and chloride gravimetrically as silver chloride.

RESULTS

Ion-exchange Experiments.—The moles of aluminium and phosphate sorbed per equivalent of Zeo-Karb 225 (N_{Al} and $N_{\text{phosphate}}$ respectively) from mixtures of aluminium chloride solutions with phosphoric acid or sodium dihydrogen phosphate solutions—or mixtures of all three—are shown in Table 1. No phosphate was sorbed from the solutions of lowest pH, which were obtained with the mixtures of aluminium chloride and phosphoric acid solutions (Table 1*a*), but at the higher pH values obtained with the mixed solutions of aluminium chloride and sodium dihydrogen phosphate (Table 1*b*) a significant sorption of phosphate was observed. This sorption of phosphate reached a maximum when the mole ratio of PO_4 : Al in the solution was about 1·5 : 1 (at a mole ratio of PO_4 : Al = 6 : 1 it had fallen to 0·013 mole of PO_4 per equiv. of resin and the sorption of Al to 0·171 mole/equiv.). The sorption of phosphate was accompanied by an increased sorption of aluminium, which also passed through a maximum at the same mole ratio (PO_4 : Al = 1·5 : 1, approx.). The effects of changes in pH of the solutions on the sorptions of both phosphate and aluminium are shown in Table 1*c*. No chloride was sorbed by the cation-exchanger and even when aluminium chloride and phosphoric acid solutions of 2M-concentration were mixed in equal proportions (pH of solution = 0·12) only a trace of chloride was sorbed by the cation-exchanger when in equilibrium with the mixture.

No aluminium was sorbed by the chloride form of the anion-exchanger from mixtures of 0·1M-aluminium chloride with either phosphoric acid or sodium dihydrogen phosphate solutions (Table 2*a*, *b*) and the sorption of phosphate was slight. With the more concentrated solution (Table 2*c*) a slight, but significant, sorption of aluminium occurred and this was accompanied by an increase in phosphate sorption.

For solutions of any pH in the range 0·05—1·25, aluminium was removed from the aluminium form of Zeo-Karb 225 most readily by phosphoric acid, while hydrochloric, sulphuric, and perchloric acid were progressively less effective (Fig. 1*a*). With the zinc form of the resin, however, the metal was removed most readily by hydrochloric acid and, in this case, phosphoric acid was hardly more effective than perchloric acid.

pH-*Titration Experiments.*—The results of the pH-titration experiments with 0·1M-aluminium chloride and nitrate solutions are shown in Fig. 2*b*, together with the previous results for aluminium sulphate,[4] for purposes of comparison, and those of a similar solution to which ammonium sulphate had been added. The increases in hydrogen-ion concentration ($\Delta[H^+]$) over that of the initial solution are recorded in Fig. 2*a* as a plot of $\Delta[H^+]/[Al]$ against the mole ratio in solution of PO_4 : Al (cf. refs. 4 and 6).

Additions of sodium chloride or nitrate (to give a concentration, in the solution to be titrated, of up to 0·5M of the salt added) had little effect on the course of the pH-titration beyond causing a very slight increase in release of hydrogen ions (not shown in Fig. 2, but pH fell about 0·05 unit over the whole titration), but addition of sodium sulphate (0·5M) to the aluminium nitrate solution or of ammonium sulphate (Fig. 2) led to a markedly smaller release of hydrogen ions throughout the titration.

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[8] Salmon, *J.*, 1952, 2316.

DISCUSSION

The fact that no complex ions are sorbed by the cation exchanger from the aluminium chloride–phosphoric acid solutions (Table 1*a*) provides a striking contrast with the results obtained with the ferric chloride–phosphoric acid solutions,[6, 9] from which sorption of phosphate, in the form of $FeHPO_4^+$ ions, occurred at pH values (0·74—0·79) appreciably lower than those recorded in Table 1*a*. Further, the resin appears to be saturated with aluminium ions [*i.e.*, $N_{Al} = 0{\cdot}33$; the higher values found experimentally (Table 1*a*) will be discussed below] and hence it may be deduced that the extent of complex formation with phosphate is not sufficient to displace the reaction:

$$\overline{\mathrm{Al}^{3+}} + 3\mathrm{H}^+ \rightleftharpoons \mathrm{Al}^{3+} + \overline{3\mathrm{H}^+} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

to the left (where barred symbols refer to ions in the resin phase) by a significant extent by lowering the concentration of free aluminium ions in solutions. Thus in this range of pH values the aluminium phosphate complexes are evidently less stable than the ferric ones.

At the higher pH values obtained with the aluminium chloride–sodium dihydrogen phosphate solutions the sorptions of phosphate and aluminium which occur resemble those previously observed for iron and phosphate [6, 9] and both pass through a maximum as the proportion of phosphate in solution is increased. As in the ferric chloride–phosphoric acid system at the higher pH values [9] the amounts sorbed are not consistent with the assumption of the sorption of monomeric complex ions. Now for the sorption of a complex ion together with free metal ions it has been shown that the following equation will apply: [9, 10]

$$pN_{Al} - qN_{\mathrm{phosphate}} = 1 \quad . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where p is dependent on the charge on the free metal ions only, while q depends on p and on both the charge and composition of the complex ion. While p is 3 ideally in the case of aluminium, the values obtained experimentally—from $p = (1/N_{Al})$ when $N_{\mathrm{phosphate}} = 0$—are always less than this (Table 1*a* and first values in Tables 1*b* and *c*). Evidently the "free" ions are sorbed as a mixture of Al^{3+}aq. and hydroxylated species [*e.g.*, $Al(OH)^{2+}$] in such proportions as to give a mean value of p which is just below 3. Since p appears to be close to a mean value of 2·90 over a wide range of pH, this value has been used in determining the values of q obtained from the experimental results by means of equation 2 (Table 1*b*, *c*).

As an example of the calculation of the values of q for the various possible complexes quoted in Table 1, which are again based on $p = 2{\cdot}9$, that for the complex $[Al_2(PO_4)]^{3+}$ may be considered; where moles complex/equiv. exchanger $= N_{\mathrm{phosphate}}$, and moles free Al/equiv. exchanger $= N_{Al} - 2N_{\mathrm{phosphate}}$ (*i.e.*, total Al less Al present in the complex which contains two Al atoms per PO_4 group). Hence equivs. complex/equiv. exchanger $= 3N_{\mathrm{phosphate}}$, equivs. free Al/equiv. exchanger $= 2{\cdot}9(N_{Al} - 2N_{\mathrm{phosphate}})$, and total equivs. present $= 1 = 2{\cdot}9N_{Al} - 2{\cdot}8N_{\mathrm{phosphate}}$, so that $q = 2{\cdot}8$.

It is evident that only at high mole ratios of phosphate to aluminium in solution (Table 1*b*) do the values of q found correspond to the sorption of monomeric complexes such as $AlHPO_4^+$, $AlH_2PO_4^{2+}$, or $Al(H_2PO_4)_2^+$. Otherwise, over the ranges of mole ratios (Table 1*b*) and of pH values (Table 1*c*) studied the sorption of binuclear (or possibly polynuclear) complexes, similar to those found in the case of the ferric phosphate complexes,[9] is indicated. The values of $pN_{Al} - qN_{\mathrm{phosphate}}$ shown in the last lines of Tables 1*b* and 1*c* have been derived by using the calculated values of q for the respective complexes indicated. It can be seen that the agreement with the required value of unity is good. From the general similarity between the types of binuclear complexes sorbed by the exchanger in

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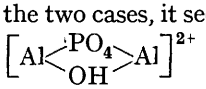
[9] Holroyd and Salmon, *J.*, 1957, 959.

[10] Salmon, *Rev. Pure Appl. Chem.*, 1956, **6**, 24.

the two cases, it seems reasonable to suppose that $[Al_2(PO_4)OH)]^{2+}$ has the bridged structure  $\left[Al\langle{}^{PO_4}_{OH}\rangle Al\right]^{2+}$ analogous to that of the corresponding ferric phosphate complex.[9, 11]

Bjerrum and Dahm [1] did not take into account, in their calculations, the possibility of the presence in solution of such binuclear phosphato-complexes. The difficulties which they encountered might well be due to this fact, for the present studies indicate that these bridged complexes may even be the predominant species in solution.

TABLE 1. *Sorption of aluminium and phosphate by Zeo Karb* 225 (H-*form*, 0·500 *g.*) *from mixed solutions* (50 *ml.*) *of aluminium chloride and phosphoric acid or sodium dihydrogen phosphate.*

(*a*) $AlCl_3$ (0·1M), H_3PO_4 (0·33M); Al only sorbed.

Solution:									
Mole ratio PO_4 : Al	0·00	0·21	0·40	0·72	1·03	1·40	1·84	3·02	4·90
pH at equilibrium	1·24	1·20	1·14	1·10	1·06	1·05	1·02	1·03	1·03
Resin:									
N_{Al}	0·35	0·35	0·35	0·34	0·35	0·35	0·34	0·34	0·34
p	2·86	2·86	2·86	2·94	2·86	2·86	2·94	2·94	2·94

(*b*) $AlCl_3$ (0·1M), NaH_2PO_4 (0·33M).

Solution:								
Mole ratio PO_4 : Al	0·00	0·60	0·96	1·04	1·40	1·75	2·08	2·73
pH at equilibrium	1·36	1·41	1·47	1·45	1·52	1·60	1·71	1·82
Resin:								
N_{Al}	0·343	0·342	0·367	0·390	0·404	0·412	0·371	0·364
$N_{phosphate}$	—	0·008	0·022	0·026	0·043	0·053	0·036	0·040
p	2·92	—	—	—	—	—	—	—
q	—	—	2·9	5·0	4·0	3·6	2·1	1·4
Poss. complex *	—	—	a	c	b	b	d	e/f
q for complex	—	—	2·8	4·8	3·8	3·8	1·9	0·9/0·95
$pN_{Al}-qN_{phosphate}$	—	—	1·00	1·01	1·01	0·99	1·01	1·02

(*c*) $AlCl_3$ (0·1M), H_3PO_4 (0·33M), NaH_2PO_4 (0·33M).

Solution:								
Mole ratio PO_4 : Al	1·04	——►	throughout					
pH at equilibrium	1·06	1·12	1·13	1·18	1·19	1·29	1·34	1·45
Resin:								
N_{Al}	0·340	0·345	0·360	0·370	0·370	0·370	0·380	0·390
$N_{phosphate}$	—	0·005	0·012	0·015	0·019	0·019	0·020	0·026
p	2·94	—	—	—	—	—	—	—
q	—	—	3·7	4·8	3·8	3·8	5·1	5·0
Poss. complex *	—	—	b	c	b	b	c	c
q for complex	—	—	3·8	4·8	3·8	3·8	4·8	4·8
$pN_{Al}-qN_{phosphate}$	—	—	1·00	1·00	1·00	1·00	1·01	1·01

* a = $[Al_2(PO_4)]^{3+}$; b = $[Al_2(PO_4)(OH)]^{2+}$; c = $[Al_2(PO_4)(OH)_2]^+$; d = $[AlHPO_4]^+$; e = $[AlH_2PO_4]^{2+}$; f = $[Al(H_2PO_4)]_2^+$; and N_{Al} and $N_{phosphate}$ are the moles of aluminium and phosphate respectively sorbed per equivalent of resin.

The results of the anion-exchange studies of the aluminium chloride–phosphate system (Table 2) are very similar to those obtained in studies of the ferric chloride–phosphate system.[6] In both systems no sorbable anionic complexes appear to be formed, even at high molar ratios of phosphate to metal (Table 2, *a*, *b*, and ref. 6). A twenty-fold increase in the concentrations of solutions (Table 2*c*) produced a slight degree of sorption only. There is evidently little tendency for chloro-complexes to be formed, as was indicated by Jensen.[2]

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[11] Holroyd, Jameson, Odell, and Salmon, *J.*, 1957, 3239.

The amounts of aluminium and of zinc removed from the cation-exchanger Zeo-Karb 225 by the various acids, which are shown in Fig. 1, indicate the tendency for the reaction

$$\overline{M^{m+}} + mH^+ \rightleftharpoons M^{m+} + \overline{mH^+} \qquad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

to proceed from left to right. Any complex formation in solution will lower the effective concentration of M^{m+} and hence will drive the reaction from left to right. Hence for each metal the lowest curve must represent the closest approach to the simple equilibrium of equation 3, with a minimum disturbance from complex formation in solution, whilst the higher curves must correspond to an increasing degree of complex formation. As already indicated,[7] measurements made at the same pH values correspond to the same concentrations of $H_2PO_4^-$, Cl^-, and ClO_4^- ions for phosphoric, hydrochloric, and perchloric acid—although the total phosphate concentration is high this is present mainly as undissociated phosphoric acid. Hence with aluminium there is evidently a decreasing tendency to complex formation in the order phosphate > chloride > perchlorate, but with zinc it decreases in the order chloride > phosphate > perchlorate. The marked extent of complex formation between aluminium and phosphate can be seen from a comparison of the data in Figs. 1*a* and*b*, which shows that while zinc is removed from the resin phase by solutions of a given pH more easily than is aluminium in the cases of hydrochloric and perchloric acid (*i.e.*, the ion of higher charge shows the greater affinity for the resin), the reverse is true in the case of phosphoric acid.

TABLE 2. *Sorption of chloride, phosphate, and aluminium by* I.R.A.-400 (Cl-*form,* 1·000 *g.*) *from mixed solutions* (*total* 50 *ml.*) *of aluminium chloride and phosphoric acid or sodium dihydrogen phosphate.*

(*a*) $AlCl_3$ (0·1M), H_3PO_4 (0·33M); Cl and PO_4 only sorbed.

Solution:								
Mole ratio PO_4 : Al	0	0·28	0·62	1·03	1·84	3·02	4·90	8·40
pH at equilibrium	1·66	1·45	1·34	1·25	1·16	1·15	1·16	1·16
Resin:								
N_{Cl}	1·00	1·00	0·97	0·95	0·97	0·94	0·91	0·86
$N_{phosphate}$	—	0·00	0·00	0·003	0·023	0·034	0·053	0·086

(*b*) $AlCl_3$ (0·1M), NaH_2PO_4 (0·33M); Cl and PO_4 only sorbed.

Solution:		
Mole ratio PO_4 : Al	0·82	2·17
Resin:		
N_{Cl}	0·98	0·94
$N_{phosphate}$	0·007	0·029

(*c*) $AlCl_3$ (2M), H_3PO_4 (2M).

Solution:		
Mole ratio PO_4 : Al	0	1·00
pH at equilibrium	0·25	0·12
Resin:		
N_{Cl}	0·99	0·91 *
$N_{phosphate}$	—	0·053 *
N_{Al}	—	0·024 *

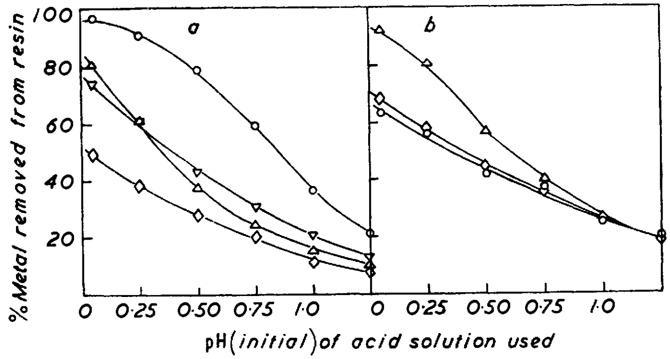
* I.R.A.-400 used in the phosphate form. N_{Al}, N_{Cl}, and $N_{phosphate}$ represent the moles of aluminium, chloride, and phosphate respectively sorbed per equivalent of resin.

It is more difficult to assess the position in the " complexing series " of sulphuric acid since it will behave in part at least as a dibasic acid (cf. phosphoric acid which in this pH range is effectively monobasic), but in the pH range 0·50—1·25 sulphate appears to form stronger complexes with aluminium than does chloride. This conclusion is borne out by a consideration of the pH-titration results (Fig. 2) from which it is evident that in this pH range the presence of sulphate adversely affects the release of hydrogen ions by reactions such as:

$$2Al^{3+} + H_3PO_4 \rightleftharpoons Al_2PO_4^{3+} + 3H^+ \quad . \; . \; . \; . \; . \; . \quad (4)$$

This effect, which is markedly dependent on the amount of sulphate present, indicates that the sulphate ion forms complexes with aluminium which approach in stability those

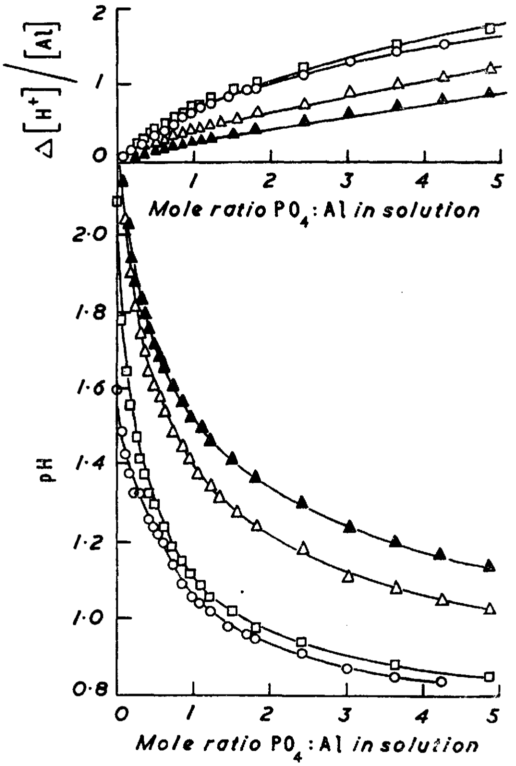
FIG. 1. *Removal of (a)* Al^{3+} *and (b)* Zn^{2+} *from Zeo-Karb 225 by various acids.*



○ H_3PO_4. △ HCl. ▽ H_2SO_4. ◇ $HClO_4$.

FIG. 2. *Titration of aluminium salt solutions (0·1M in Al) with phosphoric acid.*

○ $AlCl_3$.
△ $Al_2(SO_4)_3$.
▲ $Al_2(SO_4)_3 + (NH_4)_2SO_4$.
□ $Al(NO_3)_3$.



formed by the phosphate ion. Hence competitive complex formation by sulphate will limit the left-to-right reaction of equation 4 (for example), while sulphato-complexes present in the solution may exert a buffering effect:

$$AlSO_4^{+} + H^+ \rightleftharpoons AlHSO_4^{2+} \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

The formation of chloro-complexes of aluminium appears to be slight at pH values above 0·75 (Fig. 1*a*) and in fact the pH-titration curve for aluminium chloride with phosphoric acid follows a very similar course to that for aluminium nitrate (Fig. 2).

A comparison of the pH-titration curve of any given aluminium salt (*e.g.*, nitrate, Fig. 2) with that of the corresponding ferric salt [4, 6] shows that at any stage in the addition of the phosphoric acid the release of hydrogen ions is always less with the aluminium salt—except in the case of sulphate solutions at high mole ratios of phosphate to metal. Now the cation- and anion-exchange experiments (Tables 1 and 2) have provided evidence that the complexes formed in such solutions containing aluminium salts and phosphate are predominantly cationic. It may thus be inferred from the pH titration results that the cationic phosphatoaluminium complexes are formed less readily than the corresponding phosphatoferric ones, an inference in accord with conclusions based on the cation-exchange experiments.

When the metal form of a cation-exchanger is left in contact with a solution of phosphoric acid, a solution of the metal phosphate in phosphoric acid is formed by the ion-exchange process (equation 3). Now it has been shown that in aluminium or ferric phosphate solutions of this type the complexes formed are of the triphosphato (anionic) type.[3, 12] Hence the fact that the amount of aluminium (Fig. 1*a*) removed from the aluminium form of Zeo-Karb 225 by phosphoric acid under any given conditions is always less than the amount of iron(III) removed from the ferric form of the exchanger [7] suggests that anionic phosphatoaluminium complexes are less stable than the corresponding anionic phosphatoferric complexes.

The statement that complex formation between aluminium and phosphate is marked [4] has been substantiated by the present studies. At the same time support has been provided for Dede's conclusion that the aluminium phosphate complexes are less stable than the ferric phosphate complexes.[5]

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[12] Jameson and Salmon, *J.*, 1954, 28.