689. *Ion-exchange Properties of Cellulose Phosphate.*

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The ion-exchange properties of cellulose phosphate prepared by the urea–phosphoric acid method have been investigated. This material has been shown to possess a high affinity for certain cations, principally Th^{4+}, Ti^{4+}, U^{4+}, Ce^{4+}, Fe^{3+}, ZrO^{2+}, and UO_2^{2+}, which are adsorbed from 4N-acid. The influence of the preparative conditions and structure of the ester on its ion-exchange properties is described and discussed.

A PHOSPHORIC ester of cellulose was prepared in connection with the flameproofing of textile fabrics by Coppick and Hall.[1] Its value as a cation-exchange material was later pointed out by workers at the Southern Regional Research Laboratory, U.S.A.,[2,3] and it has been used for the precipitation of proteins.[4] We have examined [5] the use in inorganic chromatography of paper prepared from such material by W. & R. Balston Ltd. The cation-exchange behaviour of cellulose phosphate was significantly different from that of sulphonic acid resins; in particular, ferric ions were strongly adsorbed, and were not eluted from columns of this material by 0·5N-hydrochloric acid.

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[1] Coppick and Hall, "Flameproofing Textile Fabrics," Reinhold Publ. Corp., New York, 1947, pp. 179 *et seq.*

[2] Jurgens, Reid, and Guthrie, *Textile Res. J.*, 1948, **18**, 42.

[3] Hoffpauir and Guthrie, *ibid.*, 1950, **20**, 617.

[4] *Idem, J. Biol. Chem.*, 1949, **178**, 207.

[5] For a preliminary communication see Kember and Wells, *Nature*, 1955, **175**, 572.

W. & R. Balston Ltd. have shown[6] that Coppick and Hall's method of preparation, which consisted of impregnating cellulose with a solution of urea and phosphoric acid followed by heating at 130—170° and yielded a material containing up to 5% of phosphorus, can be extended to give more highly substituted cellulose, fibrous in character, insoluble in acid and alkali, and having an ion-exchange capacity up to 10 mequiv./g. This compares favourably in capacity with convential ion-exchange resins, yet has the high reaction rate associated with the hydrophilic cellulose matrix.[7]

Cellulose phosphate has also been prepared by treating cellulose with phosphorus oxychloride and sodium hydroxide[8] or pyridine.[9] The latter reaction is accompanied by degradation of the cellulose and some chlorination of hydroxyl groups.[10] The work now described was carried out with material prepared by the reaction of urea and phosphoric acid, the principal product from which is believed to be monoammonium monocellulose hydrogen phosphate.[10,11,12] Its physical nature permits packing in columns through which aqueous solutions can be passed, so it can therefore be used similarly to conventional ion-exchangers.

EXPERIMENTAL

Preparation of Cellulose Phosphate.—Strips (*ca.* 9 g.) of wood-pulp cellulose (99% α-cellulose) were steeped in a solution of urea (50% w/w) and orthophosphoric acid (18% w/w), and the excess of liquor uniformly expressed until the required uptake had been obtained. Our experiments were restricted to a liquor : cellulose ratio of 3·0 (w/w), corresponding to a mean degree of substitution of 0·9. Higher values can be reached but the reproducibility of such samples was somewhat less satisfactory. The strips were heated (" cured ") in an oven (30 cm. cube), electrically heated to 130°, through which air preheated to the same temperature was vigorously forced (22 air changes per min.). After the required period the treated cellulose was plunged into water, macerated mechanically into fibres (where necessary), filtered off, washed with water, and spin-dried in a basket centrifuge. The moisture content was determined by heating the product for 4 hr. at 110° and the phosphorus content was measured spectrophotometrically by the vanadomolybdate method after wet oxidation.

Stability of Cellulose Phosphate in Acids and Alkalis.—The extent of hydrolysis of cellulose phosphate in 2N-sulphuric acid, 10% aqueous ammonium carbonate, 10% aqueous sodium carbonate, and N-sodium hydroxide was measured at room temperature (*ca.* 20°). The material used was " cured " for 2·5 hr. and then "conditioned" as below for 3 days; it contained 9·7% of phosphorus. The ester (5 g.) was shaken with the reagent (200 ml.), and 10 ml. portions were withdrawn at intervals. These were evaporated, organic matter was oxidised, and the solutions were analysed for phosphorus. The results (Fig. 1) show that alkaline hydrolysis is rapidly suppressed by the phosphate ions produced. Acid hydrolysis can be largely prevented by adding a greater excess of phosphate; thus the phosphorus content of the ester was lowered to 9·3% after 6 hours' shaking with 2N-sulphuric or -nitric acid, but remained at 9·7% in 2N-sulphuric acid containing 20% (w/v) of sodium dihydrogen phosphate after the same time. Phosphorus analyses refer to the monoammonium form of the ester which, unlike the H-form, can be dried at 110° without appreciable decomposition.

Adsorption of Metal Ions by Cellulose Phosphate.—The product obtained after 1 hour's curing (1 g.) was converted into the H-form with N-sulphuric acid in a column (2 cm. int. diam.) and a 0·1M-solution of the appropriate metal ion (500 ml.) in sulphuric acid solution (except for lanthanum and bismuth for which solubility considerations necessitated use of hydrochloric and nitric acid respectively) passed through at 2 ml. per min. at room temperature (*ca.* 20°). The column was washed with acid at the same concentration and the cellulose phosphate analysed for the metal after wet oxidation.

Adsorption of Thorium by Cellulose Phosphate.—To prevent the complications due to

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[6] Balston, unpublished information.
[7] Guthrie, *Ind. Eng. Chem.*, 1952, **44**, 2187.
[8] Peterson and Sober, *J. Amer. Chem. Soc.*, 1956, **78**, 751.
[9] Reid and Mazzeno, *Ind. Eng. Chem.*, 1949, **41**, 2828.
[10] Reid, Mazzeno, and Buras, *ibid.*, p. 2831.
[11] Nuessle, Ford, Hall, and Lippert, *Textile Res. J.*, 1956, **26**, 32.
[12] Davis, Findlay, and Rogers, *J. Text. Inst.*, 1949, **40**, T 839.

hydrolysis of the ester, the adsorption of thorium was investigated with a solution containing 7 g. of ThO_2 per l. and 2·5 g. of P_2O_5 per l. in 4N-sulphuric acid. This solution (300 ml.) was passed at 3 ml. per min. through columns (2 cm. int. diam.) containing the appropriate sample of cellulose phosphate (2 g. based on the dry monoammonium form) after conversion into the H-form with 2N-sulphuric acid. After adsorption it was convenient to wash the column with 2N-sulphuric acid, water, and 2N-ammonia and to elute the thorium as the carbonato-complex with 100 ml. of 10% ammonium carbonate solution followed by 100 ml. of water. Thorium was readily precipitated as hydrated oxide by boiling the eluate, and after acidification was determined by precipitation as oxalate.

Acidification of boiled eluates never yielded clear solutions and it was always necessary to filter off a small quantity of a gelatinous precipitate, which readily coagulated on boiling. The dried solid had the following analysis: H, 2·7; O, 22·6; P, 8·3; Th, 32·5%. "*Thorium cellulose phosphate,*" $C_{12}H_{18}O_{16}P_2Th$, requires H, 2·5; O, 20·2; P, 8·7; Th, 32·6%. The oxygen content was calculated as that available after formation of thorium pyrophosphate, the probable residue in the determination (Unterzaucher's method). It was impossible to obtain a reliable microanalysis for carbon and the individual results for hydrogen varied widely. This is attributed to the difficulty of completely burning carbonaceous matter occluded in the pyrophosphate glass—the combustion residues were always black (see below).

Titration of Cellulose Phosphate.—The ester (*ca.* 300 mg.) was converted into the H-form and washed free from excess of mineral acid before being transferred with water (50 ml.) to a titration cell containing calomel and glass electrodes and a mechanical stirrer, and through which nitrogen could be passed. The vigorously stirred suspension was titrated against 0·1N-sodium hydroxide; steady pH readings were obtained within a few minutes, even above pH 9 where the rate of reaction was slowest. After completion of the titration both the pulp and the liquid were analysed for phosphorus; these results show that approximately 6% of the total phosphorus was hydrolysed into the liquid phase during the process.

RESULTS AND DISCUSSION

Table 1 shows that certain ions (particularly Fe^{3+}, Ce^{4+}, UO_2^{2+}, U^{4+}, Th^{4+}, ZrO^{2+}, and Ti^{4+}) are strongly adsorbed from N-acid, in marked contrast to the behaviour on sulphonic acid resins. To elute these metals reagents are needed which form strong complexes with them. Thus thorium and uranyl are quantitatively eluted with 10% ammonium carbonate solution. Qualitatively, this reagent also removes uranous ion; acetone–hydrochloric acid can be used for iron, and ammonium fluoride solution for zirconium. Table 1 indicates that in some instances the maximum theoretical adsorption, calculated from the phosphorus content of the exchanger and the normal valency of the adsorbed ion, is exceeded, indicating that complex ions of lower valency are involved. At pH 3 the adsorption of

TABLE 1. *Adsorption (atoms of metal per atom of phosphorus) on cellulose phosphate*

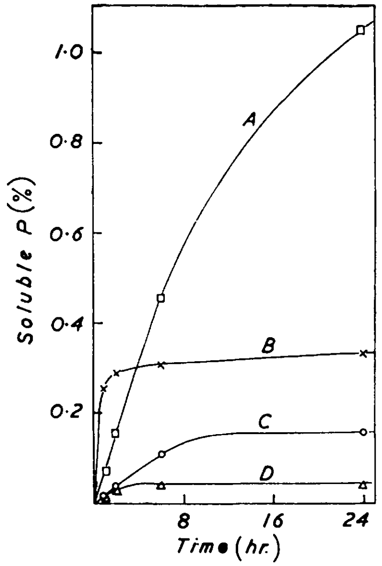
Ion	Adsorption			Maximum calc. value (normal valency)
	N-Acid	pH 2	pH 3	
Al^{3+}	0	1·00	—	0·67
Bi^{3+}	0·10	—	—	0·67
Ce^{4+}	0·52	*	—	0·50
Cu^{2+}	0	0·13	—	1·00
Fe^{2+}	0·31	0·38	—	1·00
Fe^{3+}	1·17	0·80	—	0·67
La^{3+}	0·06	0·25	—	0·67
Mg^{2+}	0	0·23	—	1·00
Mn^{2+}	0	—	0·43	1·00
Th^{4+}	0·46	0·73	0·91	0·50
Ti^{4+}	0·73	*	—	0·50
U^{4+}	0·24	—	—	0·50
UO_2^{2+}	0·43	0·66	0·82	1·00
Zn^{2+}	0·06	0·20	—	1·00
ZrO^{2+}	1·18	*	—	1·00

* A precipitate is formed at this pH.

thorium is accompanied by sulphate such that the Th : SO_4 ratio was 0·96, suggesting that $ThSO_4^{2+}$ or $Th(HSO_4)^{3+}$ is the species adsorbed.[13]

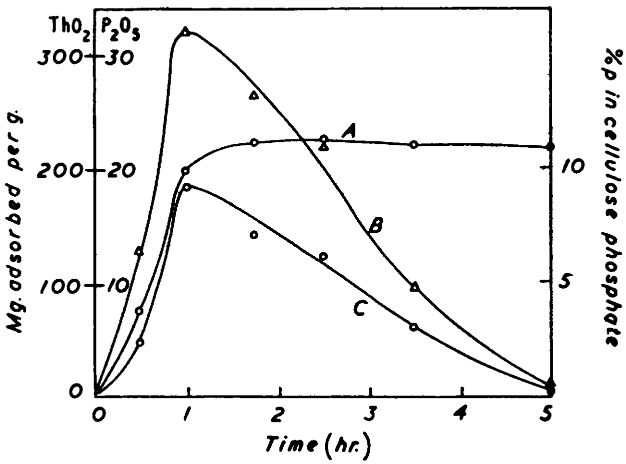
To study the variation in the ion-exchange properties of cellulose phosphate in acid solution with preparative conditions, the adsorption of thorium from 4N-sulphuric acid under standard conditions was measured. To minimise acid hydrolysis of the ester, phosphate ions were added to the thorium solution, but material eluted from these columns contained appreciable quantities of phosphate ($P_2O_5 : ThO_2 \sim 1 : 20$). This could not have arisen from the ion-exchange material itself since the thorium capacity did not diminish after several successive adsorption–elution cycles. The proportion of phosphate in the eluate increased as more was added to the original thorium solution (Table 2), suggesting that part of the thorium is adsorbed as a cationic species of thorium phosphate.

FIG. 1. *Hydrolysis of cellulose phosphate by acid and alkali.*



A, 2N-H_2SO_4. *B*, N-NaOH. *C*, 10% *Aq*. Na_2CO_3. *D*, 10% *Aq*. $(NH_4)_2CO_3$.

FIG. 2. *Influence of curing time.*



A, P *content*. *B*, ThO_2 *adsorbed*. *C*, P_2O_5 *adsorbed*.

TABLE 2.

	Product eluted		
Solution applied to column	ThO_2 (mg. per g. of cellulose phosphate)	P_2O_5 (mg. per g. of cellulose phosphate)	$100(P_2O_5/ThO_2)$
0·01M-$Th(SO_4)_2$ in 2N-H_2SO_4	373	10·5	2·8
0·01M-$Th(SO_4)_2$ in 2N-H_2SO_4, 0·013M with respect to PO_4 ...	390	20·0	5·1
0·01M-$Th(SO_4)_2$ in 2N-H_2SO_4, 0·20M with respect to PO_4 ...	426	40·0	9·4

Thorium ions are known to form complexes with phosphate in sulphuric acid solution in which the existence of species such as $Th(H_2PO_4)_2^{2+}$ and $ThH_2PO_4^{3+}$ have been postulated,[14] and from which well-defined substances corresponding to $Th(HPO_4)SO_4$ and $[Th(H_2PO_4)_3]_2SO_4$ crystallised.[15] Further evidence for the adsorption of an ion of lower valency is provided by the increased thorium capacity as the proportion of phosphate

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[13] Schulz and Herak, *Croatian Chem. Acta*, 1957, **29**, 49.
[14] Zebroski, Alter, and Heumann, *J. Amer. Chem. Soc.*, 1951, **73**, 5646.
[15] d'Ans and Dawihl, *Z. anorg. Chem.*, 1929, **178**, 252.

in the solution is increased. That cellulose phosphate possesses no anion-exchange properties whereby phosphate ions could be adsorbed was demonstrated by eluting a column through which neutral and acid solutions of sodium phosphate had been passed. No phosphate was detected in the eluate.

The thorium present as the acid-insoluble fraction of the eluates amounted to 1·3% of the total quantity adsorbed. This substance is insoluble in 10% mineral acids but dissolves in 10% aqueous ammonium carbonate. It seems probable that this is the thorium salt of cellulose phosphate, which has been degraded to a low degree of polymerisation and become soluble in ammonium carbonate.

Preliminary experiments indicated that the ion-exchange properties of cellulose phosphate, particularly in acid solution, are very dependent on the preparative conditions. The experimental variables were therefore studied. The composition of the phosphorylating reagent used was that recommended by Hoffpauir and Guthrie,[3] and contained urea (4 mol.) and phosphoric acid (1 mol.). Attempts to lower the molar ratio to 2 : 1 or 1 : 1 resulted in considerable charring during curing. This process was effectively carried out at 130° in a forced-draught oven (at 140° reaction was faster but less reproducible).

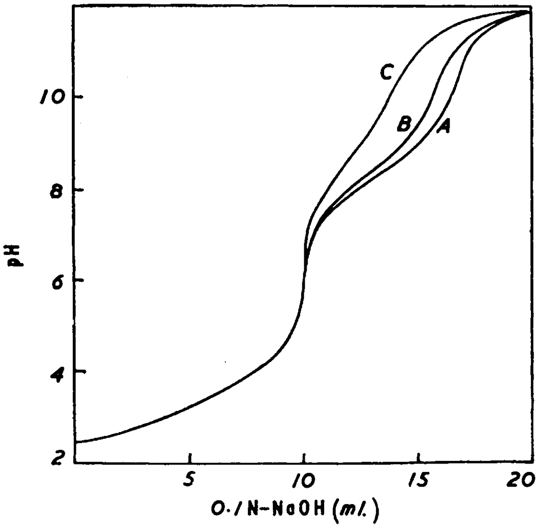

FIG. 3. *Titration curves of cellulose phosphate.*

Curing for (*A*) 1·0, (*B*) 2·5, (*C*) 5·0 *hr.*

The effects of varying the curing time are shown in Table 3 and Fig. 2. The quantity of phosphate present in the eluates from these adsorption tests closely paralleled the thorium capacity, thus providing further evidence for cationic thorium phosphate. Short curing gives material which readily disperses in water to a white slimy pulp which retains a considerable amount of water after spin-drying (moisture contents of these materials were moderately reproducible). After longer curing the product was hard, brittle, and cream-coloured, and was broken into fibres only after vigorous mechanical treatment to give material with a low moisture content after spin-drying. The physical character of " overcured " cellulose phosphate would be an advantage in ion-exchange practice since such samples have less resistance to the flow: the flow rate of water was 30 times greater through columns prepared from material cured for 3·5 hr. than from that cured for 1·0 hr.

By analogy with the variations in the water-regain values of ion-exchange resins these results suggest that curing causes cross-linking. Indeed slow drying is known to cause wet cellulose to become horny, which is ascribed to cross-linking of the fibrils by development of crystalline regions.[16]

[16] Spurlin, " Cellulose and Cellulose Derivatives," Interscience Publ. Inc., New York, 1954, p. 696.

Contrary to the findings of Reid *et al.*[10] who stated that the urea–phosphoric acid method afforded only the primary ester, we have found by alkali-titration that even after 1 hour's curing, and before all the phosphorylating reagent had reacted, 32% of the phosphoric acid groups were diesterified. The proportion of cross-linking through phosphoric acid groups increases with curing time, as shown in Fig. 3 and Table 3. Although the most overcured sample showed negligible capacity for thorium in acid solution, its capacity for sodium ions in alkaline solution was unchanged and good agreement was obtained between the phosphorus content of the sample titrated (21·2 mg.) and that calculated from the first end-point (21·4 mg.). Similar proof that every phosphorus atom in cellulose phosphate carries an acidic group was found when the sample heated for 1 hr. was titrated (Found: P, 28·5 mg. Calc.: P, 28·9 mg.). If cellulose phosphate is converted into the H-form and washed free from excess of mineral acid, and an aqueous suspension is kept at room temperature for several days, some hydrolysis of ester linkages occurs. The hydrolysis of primary groups is suppressed by the phosphoric acid produced and the secondary groups are thus preferentially attacked. The removal of cross-linking is demonstrated by the results of titrations carried out on samples which had been stored as aqueous suspension of the H-form (" conditioned ") for 3 and 7 days (Table 3). These provide minimum values for cross-linking since some hydrolysis of these linkages probably occurs during titration. Further proof that this conditioning destroys cross-linking is given by the higher moisture contents.

TABLE 3.

Curing time (hr.)	1·0	2·5	5·0
As prepared:			
P content (%)	9·88	11·2	10·9
g. of water per g. of dry ester	3·5	0·95	0·55
% of phosphoric acid groups disubstituted	32	41	57
ThO_2 capacity (mg. of ThO_2 per g. of ester)	319	223	10
P_2O_5 capacity (mg. of P_2O_5 per g. of ester) *	18·4	12·2	0·6
P_2O_5/ThO_2 (%)	5·8	5·5	6·0
Stored as suspension of H *form for* 3 *days*:			
P content (%)	8·24	9·63	9·42
g. of water per g. of dry ester	7·0	2·6	1·2
% of phosphoric acid groups diesterified	15	20	34
ThO_2 capacity (mg. of ThO_2 per g. of ester)	274	299	101
P_2O_5 capacity (mg. of P_2O_5 per g. of ester) *	3·5	2·0	0·4
P_2O_5/ThO_2 (%)	1·3	0·7	0·4
Stored as suspension of H *form for* 7 *days*:			
P content (%)	7·92	9·28	9·24
g. of water per g. of dry ester	8·9	2·7	1·4
% of phosphoric acid groups diesterified	9	—	25
ThO_2 capacity (mg. of ThO_2 per g. of ester)	240	268	221
P_2O_5 capacity (mg. of P_2O_5 per g. of ester) *	2·4	0·6	0·0
P_2O_5/ThO_2 (%)	1·0	0·2	0·0

* Phosphorus adsorbed with thorium as cationic complex.

Table 3 shows that by reducing the amount of cross-linking the thorium capacity of overcured samples can be restored, although if " conditioning " is excessively prolonged this effect will be outweighed by the reduction in capacity caused by hydrolysis. Although a sample cured for 2·5 hr. and stored for 3 days has a similar thorium capacity to one cured for 1 hr. without any subsequent treatment, and the latter contains a higher proportion of diesterified phosphoric acid groups, yet the physical properties of the former sample (lower moisture content and a nine-fold greater flow rate of liquids through columns of the material) indicate that some other form of cross-linking resists conditioning. This residual cross-linking is probably that caused by heating of wet cellulose (cf. above) although it may also be connected with the fact that the N : P ratio of overcured material exceeds the theoretical ratio of 1·0 required for the monoammonium salt of cellulose phosphate and found for the sample cured for 0·5 hr. (observed value 1·08; N by Kjeldahl method). Thus this ratio reached 1·21 for overcured samples and after acid-washing was still 0·27. A high N : P ratio has been observed previously to be a feature of more severe curing conditions and to be accompanied by some loss of ion-exchange properties (as measured by the persistence of flameproofing qualities, after soaking of the NH_4-form in calcium chloride solution; flameproofing has been shown to be associated with the NH_4- or H-form of cellulose phosphate but not with the calcium or other metal-cation form).[17] Side reactions leading to the formation of the diamide $Cell\cdot O\cdot P(O)(NH_2)_2$ and cellulose carbamate $Cell\cdot O\cdot CO\cdot NH_2$ have been postulated,[1,11] although the former is now excluded by the finding that every phosphorus atom carries exchangeable hydrogen.

Table 3 also shows that the adsorption of thorium as cationic phosphate is considerably reduced on conditioned cellulose phosphate and reaches zero on a sample cured for 5 hr. and conditioned for 7 days. However no simple relation exists between the proportion of diesterified phosphoric acid and either the thorium capacity or the amount of adsorbed phosphate. The exact structure of any sample of ester depends, not only on its phosphorus content and the proportion of diesterified phosphoric acid, but also on the extent of the other mode of cross-linking, which it is not possible to measure. If it is required to reduce the adsorption of phosphate or if practical considerations make reduced resistance to flow of liquid desirable, the use of cellulose phosphate which has been somewhat overcured and subsequently conditioned is an advantage.

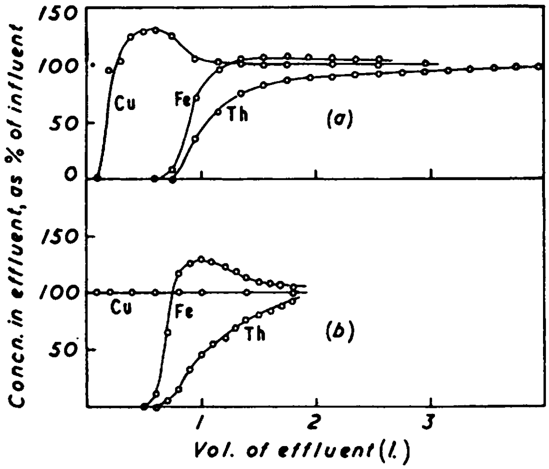

FIG. 4. *Break-through curves for adsorption of copper, iron, and thorium from* (*a*) 0·1N- *and* (*b*) N-H_2SO_4.

The relative affinities of Cu^{2+}, Fe^{3+}, and Th^{4+} were demonstrated by passing a solution containing 5 mequiv./l. of each of the ions in 0·1N-sulphuric acid through a column of cellulose phosphate prepared with short curing time. The breakthrough curves (Fig. 4) show the relative affinity order $Th^{4+} > Fe^{3+} > Cu^{2+}$; in N-sulphuric acid (Fig. 4) the affinity order was the same, but with increasing selectivity for Th^{4+}. Thus at the end of the experiment the quantities of metal adsorbed were in the equivalent proportion of Th/Fe = 2·8 from 0·1N- and Th/Fe = 3·8 from N-acid solution. In neither case was copper found.

The different affinity of cellulose phosphate for various cations enables several chromatographic separations to be carried out. Thus bismuth and lead are both adsorbed on the top of a column of cellulose phosphate in the H-form from 0·1N-nitric acid, and lead is quantitatively eluted free from bismuth with N-nitric acid. Complete recovery of bismuth is obtained by elution as the anionic complex formed with N-hydrochloric acid.

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[17] Little, ref. 1, pp. 199—203.

Separations in neutral solutions have also been achieved. Mixtures of copper with cadmium, cobalt, or nickel are adsorbed on the top of ion-exchange columns in the sodium form. Elution with N-magnesium chloride quantitatively removes the second component, leaving copper on the column, from which it can be completely recovered by using N-hydrochloric acid. These separations are extensions of those already briefly described for paper strips; [5] either under- or over-cured and stored cellulose phosphate may be used.

There are several references to ion-exchange materials carrying phosphonate [18-20] or phosphate groups [20,21] but the affinity of cellulose phosphate for certain cations in strongly acid solution is remarkable. Kennedy *et al.*[20,22] investigated the behaviour of polymers from allyl phosphate and phosphonate and report an order of affinities Th^{4+}, $U^{4+} > UO_2^{2+}$, $Fe^{3+} > La^{3+} > H^+ > Cu^{2+}$, Co^{2+}, $Ca^{2+} > Na^+$, which agrees with our results for cellulose phosphate. These experiments were carried out at acidities not exceeding 0·2N, although the limitation which prevented their extension to higher acidity appeared to be one of reaction rate rather than displacement of the equilibrium. It is significant that it is those cations with phosphates precipitated below pH 2 which are most strongly adsorbed, although the acidity at which adsorption occurs on cellulose phosphate is considerably higher than that which permits precipitation from solution. Kennedy has pointed out that the bonds between, *e.g.*, Th^{4+}, Fe^{3+}, UO_2^{2+} and phosphate or phosphonate groups are at least partially covalent. The marked dependence of ion-exchange properties in acid solution on the structure of the exchange material supports the belief that directional, covalent bonds are formed between resin sites and adsorbed ions. The greater flexibility of a cellulose matrix which is not cross-linked permits the correct stereochemical configuration for compound formation. Similarly, under the standard conditions of testing, no thorium is adsorbed on to the commercial resins Duolite C-60 and C-61, which possess respectively phosphonous and phosphonic acid groups attached to a hydrocarbon matrix. A somewhat analogous situation to the adsorption of cations in acid solution occurs at the other end of the pH scale in the strong adsorption of aurocyanide ions on weakly basic resins which would be expected to have no anion-exchange capacity in strongly alkaline media.[23] This has been attributed to ion-pair formation between the resin sites and the highly polarisable aurocyanide ions.[24] The greater polarisability of the phosphate group than of the sulphate group [25] probably results in bonds of greater covalent character on exchange material carrying the former function than on resins of sulphonic acid type. The order of polarisability phosphate > water > sulphate has been used to explain the inversion of the affinity order of the alkali metals on phosphonic acid exchange materials.[19]

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