434. *The Separation of Quadrivalent and Quinquevalent Vanadium from Phosphoric Acid by Ion-exchange Resins; Some Observations on the Reduction of Quinquevalent Vanadium by Ion-exchange Resins.*

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By use of cation-exchange resins, vanadium, in both the quadrivalent and the quinquevalent state, has been separated from phosphoric acid solutions. The adsorption of quinquevalent vanadium was accompanied by a partial or even complete reduction to the quadrivalent state.

IN another investigation we needed to determine phosphoric acid in the presence of vanadium. Difficulties were encountered in applying the usual methods because of interference. The volumetric method using bismuth oxyperchlorate (Salmon and Terrey, *J.*, 1950, 2813) was not applicable to samples containing appreciable quantities of vanadium because the colour of the solutions obscured the yellow colour of the indicator at the end point. Kakihana (*Bull. Chem. Soc. Japan*, 1949, **22**, 242) has described the separation of quinquevalent vanadium from solutions by cation-exchange resins, but not in the presence of phosphate. No investigations concerning the ion-exchange separation of quadrivalent vanadium from phosphate solutions appear to have been reported.

In the present work solutions obtained by dissolving vanadium pentoxide in hydrogen peroxide were mixed with known volumes of phosphoric acid or potassium dihydrogen phosphate solutions of known concentration. The mixed solutions were passed through columns of cation-exchange material, either directly or after previous reduction to the quadrivalent state. Removal of vanadium from the solutions was sufficiently effective in both cases to permit determination of phosphate in the effluent by titration with bismuth oxyperchlorate (see Tables 1 and 2).

TABLE 1. *Removal of quadrivalent vanadium from phosphate solution by Zeo-Karb* 215(H) *and determination of phosphate in the effluent.*

Solution:				Effluent:
P_2O_5, mg.	V_2O_5, mg.	Vol., ml.	Method of reduction	P_2O_5, found, mg.
91	45	35	SO_2	90
100	23	15	,,	100, 101, 102, 105
,,	28	15	,,	98, 101
,,	45	20	,,	105, 105
,,	56	20	,,	100, 101
120	23	15	,,	117, 118
120	23	15	Hg	117, 118, 118

Although the experiments on the separation of quadrivalent vanadium were carried out exclusively with Zeo-Karb 215(H), yet in the work with quinquevalent vanadium not only were several resins used, but the separation from phosphoric acid was compared with that from other acids (Table 2).

It proved possible also to separate the vanadium at least partly from the solutions of vanadium pentoxide in hydrogen peroxide alone by means of the hydrogen forms of Zeo-Karb 215 and 225 and of Amberlite I.R.120. This supports the views of certain workers (*e.g.*, Meyer and Pawletta, *Z. anorg. Chem.*, 1927, **161**, 361) that in such solutions there exists, after the decomposition of the per-compounds initially present, an equilibrium between vanadyl [V(v)] cations, such as VO_2^+, and vanadate anions. The fact that the vanadium is as readily removed from phosphoric acid solutions as it is from sulphuric acid or hydrochloric acid solutions would appear to be in accord with the views of Jander and Jahr (*Kolloid Beih.*, 1934, **41**, 1, 297) that at low pH values vanadyl [V(v)] phosphates rather than phosphovanadic acids are present.

The separation of vanadium from potassium phosphate solutions was also effectively achieved provided that not too much phosphate—and hence potassium—was present. The potassium ions introduced seemed to be adsorbed more readily than the vanadium or vanadyl ions. This view is supported by the fact that with resins in the ammonium or sodium forms the adsorption of vanadium from phosphoric acid solutions was greatly reduced. This suggests that the ion being adsorbed is not one carrying a high charge and may consequently be VO_2^+ (Carpenter, *J. Amer. Chem. Soc.*, 1934, **56**, 1847).

TABLE 2. *The separation of quinquevalent vanadium by cation-exchange resins.*

Solution:				Resin:		Effluent:	Eluate:
V_2O_5, mg.	Acid or salt added	P_2O_5, mg.	pH	Type	V, %, adsorbed	P_2O_5, mg.	V (IV), %
50	None	Nil	2·2	Z.K. 215 (H) (*ca.* 15 g.)	30	—	All *
50	H_3PO_4	100	1·9	,,	100	100, 100	100
42	,,	50	1·9	,,	100	50	All *
42	KH_2PO_4	74	3·2	,,	50	—	100
50	,,	37	2·8	,,	100	—	100
38	H_2SO_4	Nil	1·9	,,	95	—	All *
51	HCl	Nil	2·0	,,	100	—	All *
50	H_3PO_4	100	1·9	Z.K. 215 (NH_4) (*ca.* 15 g.)	62	—	All *
50	None	Nil	2·2	Z.K. 225 (H) (*ca.* 15 g.)	40	—	70
50	H_3PO_4	100	1·9	,,	100	102	Some *
42	KH_2PO_4	74	3·2	,,	60	—	55
51	,,	37	2·8	,,	87	—	Some *
42	H_3PO_4	100	1·9	Z.K. 216 (H) (*ca.* 5 g.)	79	—	100
50	,,	100	1·9	,,	71	—	100
51	None	Nil	2·2	I.R. 120 (H) (*ca.* 5 g.)	60	—	All *
42	H_3PO_4	100	1·9	,,	75	—	All *
50	,,	100	1·9	,,	—	104	All *
50	KH_2PO_4	37	2·8	,,	60	—	100
51	H_2SO_4	Nil	1·9	,,	60	—	All *
50	H_3PO_4	100	1·9	I.R. 120 (Na) (*ca.* 5 g.)	20	—	Some *
42	H_3PO_4	100	1·9	I.R.C. 50 (H) (*ca.* 5 g.)	1	—	Nil *
50	,,	100	1·9	,,	1	—	Nil *

* Estimated qualitatively from the colour of the effluent.

Although the original solutions before passage through the columns were yellow, yet when the columns were eluted with 2N-acid (HCl or H_2SO_4) before re-use, the eluate was blue, indicating that the vanadium had been reduced to the quadrivalent state. This reduction was quantitative with Zeo-Karb 215 and 216 and Amberlite I.R.120 and could be repeated a number of times with the same material (at least a dozen times with two columns of Zeo-Karb 215), but with Zeo-Karb 225 the reduction was only partial. In the cases where only part of the vanadium was adsorbed by the resin, that appearing in the effluent was all in the quinquevalent state and only that eluted from the column was reduced.

In the preparation of vanadium pentoxide sols by means of Amberlite I.R.100(H) and Dowex 50(H), Devlin, McNabb, and Hazel (*J. Franklin Inst.*, 1949, **248**, 251) found that the Amberlite resin caused partial reduction of vanadate to vanadyl [V(IV)] ions, but these authors appear to assume that reduction preceded adsorption, a view hardly compatible with our results.

That some resins at least possess mild reducing properties has been known for some time. For example, the reducing properties of Amberlite I.R.1 have been described by Boyd, Schubert, and Adamson (*J. Amer. Chem. Soc.*, 1947, **69**, 2818), who attributed this property to the presence of phenolic groups in the resin. Devlin, McNabb, and Hazel apparently ascribe the reduction by Amberlite I.R.100 to the same cause.

Of the resins used in our work, the reducing properties of Zeo-Karb 215 (phenolsulphonic acid) and Zeo-Karb 216 (carboxylic acid type, with some phenolic and sulphonic acid groups) could be similarly accounted for. The fact that reduction occurs only on adsorption and not just on contact could be explained by postulating that the phenolic groups only cause reduction of the vanadium when they are in the ionic form. At the pH of our solution the ionisation of the phenolic groups would be negligible, the exchange capacity being due to the more strongly acidic groups (*e.g.*, SO_3H), but as the pH rises during washing of the column with water the phenolic groups would tend to ionise and thus become effective as reducing agents.

The behaviour of Amberlite I.R.C.50 (carboxylic acid, weakly acidic, monofunctional) in neither adsorbing nor reducing can also be understood, but the explanation just given cannot account for the reducing properties of Zeo-Karb 225 or of Amberlite I.R.120 (both sulphonated cross-linked polystyrene, monofunctional) for they do not contain phenolic groups as far as is known. Whatever is responsible for their ability to reduce, it is apparently effective only on adsorption. It is noteworthy that Zeo-Karb 225 is a much weaker reducing agent than the resins known to contain phenolic groups.

Solutions containing quinquevalent vanadium compounds might prove useful for detecting reducing properties in ion-exchange resins, as the change in colour accompanying reduction makes it easy to observe and the reduction product is easily removed from the resin.

EXPERIMENTAL

Ion-exchange Columns.—These were of the conventional type. Two sizes were used, one holding about 5 g. of resin (dry weight) the other 15 g. After use the columns were regenerated by elution with 2N-acid (HCl or H_2SO_4) and then washed until free from acid.

Solutions.—The vanadium pentoxide solutions were made by dissolving weighed quantities of the pure oxide (examined spectroscopically) in hydrogen peroxide (20-vol.) in the cold. The solutions so obtained evolved oxygen for some time, finally giving a clear dark red solution containing quinquevalent vanadium and no peroxide (as shown by titration with standard ferrous sulphate). As solid material slowly separated from these solutions, they were filtered and analysed immediately before use.

Phosphate solutions were made either from weighed quantities of potassium dihydrogen phosphate or by diluting concentrated phosphoric acid and standardising the resulting solutions against bismuth oxyperchlorate.

Analysis.—Vanadium was determined by titration with standard potassium permanganate, after reduction to the quadrivalent state when necessary. When vanadium was determined in eluates from the columns, sulphuric acid (2N) was used as the elutriant.

The results for the total of vanadium found in the effluent and eluate were found slightly to exceed the quantity initially present. This may be due to small quantities of organic material from the resins, which would be oxidised by potassium permanganate.

Phosphate was determined by titration with bismuth oxyperchlorate (Salmon and Terrey, *loc. cit.*).

Reduction of Vanadium to the Quadrivalent State.—For both the column experiments and the analysis this was most conveniently achieved by the use of liquid sulphur dioxide, excess of which was removed by boiling. This method of reduction was preferred to that using mercury (McCay and Anderson, *J. Amer. Chem. Soc.*, 1922, **44**, 1018). A Jones reductor could not be used with solutions containing phosphoric acid because some insoluble zinc phosphate was formed.

In the column experiments with quadrivalent vanadium the sulphuric acid, formed in the reaction with sulphur dioxide, interfered in the final titration of the phosphate. It was best removed before passage of the solutions through the columns by addition of a very small excess of barium hydroxide; the slight amount of barium remaining in solution was then removed by the resin together with the vanadium and so did not interfere in the titration.

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