949. *Condensed Ions in Aqueous Solution. Part I. Ion-exchange Behaviour of Vanadate Ions.*

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The ionic species formed during condensation of vanadate ions in solution as the pH is lowered are subject to ionic-sieve effects in exchange reactions with anion-exchangers of the DeAcidite F.F. type. By means of this effect and by the use of resins of various weight-swellings, evidence has been obtained for the existence of di-, tri-, tetra-, hexa-, and deca-vanadate ions at different stages in the condensation.

EARLY studies of the vanadates were concerned primarily with the nature of the solid compounds which separated from solution,[1] but both Roscoe [2] and Rammelsberg [3] indicated that these materials were of increasing complexity as the acidity of the solutions was increased.

The first systematic studies of the nature of the species present in solution were those

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[1] Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1935, Vol. IX, p. 757.

[2] Roscoe, *Phil. Trans.*, 1868, **158**, 1; 1869, **159**, 679; 1870, **160**, 317.

[3] Rammelsberg, *Pogg. Annalen*, 1856, **98**, 249; *Wied. Annalen*. 1883, **20**, 928.

by Düllberg[4] who showed by cryoscopic measurements that ions containing three and six vanadium atoms were among those formed. This and subsequent work indicated possible stages in the condensation to be ortho-, pyro- (di-), meta- (probably tri-), tetra-, penta-, hexa-, octa-, and deca-vanadate.

Evidence for the existence of ortho- and pyro-vanadate ions in alkaline solutions has been provided by diffusion (Jander and Jahr[5]), dialysis (Brintzinger and Wallach[6]), potentiometric titration (Britton and Robinson;[7] Britton and Welford[8]), and by the work of Souchay and his collaborators.[9]

There appears to be general agreement that the next stage of condensation after pyrovanadate, corresponds to a metavanadate ion and that this occurs at about the neutral point. Düllberg,[4] Brintzinger and Wallach,[6] and Souchay and his co-workers[9] all concluded that this ion contains three vanadium atoms.

Evidence for a tetravanadate ion has been found by Jander and Jahr,[5] Brintzinger and Wallach,[6] and Trujillo and Tejera,[10] of whom the last named based their conclusions on solubility measurements. The formation of a pentavanadate ion, however, has been reported only by Jander and Jahr[5] and by Britton and Welford.[8] Since the last workers merely gave an empirical formula and since this ion was found in solutions of low pH it is probably a decavanadate.

The presence, in acid solutions, of hexavanadate ions has been reported by Düllberg,[4] Souchay,[9] Martinez and Trujillo,[11] and Ducret,[12] but was doubted by Britton and Welford[8] and by Jander and Jahr[5] who, however, found evidence of an unstable octavanadate.

Ducret[12] was of the opinion that an ion larger than the hexavanadate ion was formed in more strongly acid solutions and the empirical formula assigned by Britton and Welford to the most highly condensed ion which they detected could correspond to a decavanadate. The existence of such an ion was confirmed by Rossotti and Rossotti.[13]

The diversity of the reports together with the lack of knowledge of the pH ranges over which the various stages of condensation occurred indicated a need for further study. The ion-exchange techniques which proved useful for similar cases[14] have again been used.

EXPERIMENTAL

Preparation of Solutions.—Vanadic acid solutions (*ca.* 0·05 g.-atom of vanadium per l.; pH 2—2·1) were prepared by passage of solutions of analytical-grade ammonium vanadate (2 l., *ca.* 0·06 g.-atom of vanadium per l.) through a column of ZeoKarb 225 (H^+ form; 20 cm. long, 4 cm. in diameter). Part of the vanadium was sorbed on the resin as a dark band below the ammonium band and above the hydrogen band. This dark band consisted of quinquevalent (yellow) and quadrivalent (blue) species, of which the former were easily removed by washing, but the latter were displaced only on treatment with acid. No quadrivalent vanadium was present in the vanadic acid. The amount of reduced material present on the column decreased with use but was finite, even after many cycles (cf. Salmon and Tietze[15]). Vanadic acid solutions thus prepared were stable for several days after which precipitation might occur. The column was regenerated with 2N-acid and washed free from regenerant before re-use.

Vanadate solutions of higher pH were obtained, either by mixing vanadic acid and ammonium vanadate solutions or, more conveniently, by the addition of ammonia solution (*d* 0·880) to

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[4] Düllberg, *Z. phys. Chem.*, 1903, **45**, 129.

[5] Jander and Jahr, *Z. anorg. Chem.*, 1933, **211**, 49; 1933, **212**, 1; 1934, **220**, 201.

[6] Brintzinger and Wallach, *ibid.*, 1934, **224**, 103.

[7] Britton and Robinson, *J.*, 1933, 512.

[8] Britton and Welford, *J.*, 1940, 764.

[9] Carpeni and Souchay, *J. Chim. Phys.*, 1945, **42**, 149; *Bull. Soc. chim. France*, 1946, **13**, 160; Souchay, *ibid.*, 1951, **18**, 932; Souchay and Chauveau, *Compt. rend.*, 1957, **244**, 1923.

[10] Trujillo and Tejera, *Anal. Fis. Quim.*, 1954, **50**, *B*, 399.

[11] Martinez and Trujillo, *ibid.*, 1949, **45**, *B*, 719; 1950, **46**, *B*, 639; 1951, **47**, *B*, 699.

[12] Ducret, *Ann. Chim. (France)*, 1951, **6**, 705.

[13] Rossotti and Rossotti, *Acta Chem. Scand.*, 1956, **10**, 457.

[14] (*a*) Everest and Salmon, *J.*, 1954, 2438; (*b*) *J.*, 1955, 1444; Everest and Popiel, *J.*, 1956, 3183; *J.*, 1957, 2433; *J. Inorg. Nucl. Chem.*, 1958, **6**, 153.

[15] Salmon and Tietze, *J.*, 1952, 2324.

vanadic acid. In either case the mixed solutions were left before use for periods varying from several hours (pH <5 or >8) to several days (pH 5—8), to permit equilibrium to be reached.

Anion-exchange Resins.—The anion-exchangers used were the strongly basic DeAcidite F.F. resins, air-dried in the chloride form, in varying degrees of cross-linking, and similar laboratory prepared resins made according to the method of Pepper, Paisley, and Young.[16] The chloride form of a resin, as received, was treated with 2N-hydrochloric acid, washed with water, and allowed to dry in air. All the resins used had capacities of the order of 3·8 milliequivs./g. of air-dried resin and experience showed that the effective pore sizes of these resins in a given solution were in direct relation to their weight-swelling values, regardless of any differences in method of preparation. These values, which provide a measure of the swelling which occurs when a dry resin is placed in water, were measured by the method of Pepper *et al.*[16]

Batch Experiments.—Two procedures were used. In the first 0·5 g. of resin was left in contact with 75 ml. of vanadic acid–ammonium vanadate solution, of known pH and vanadium content, for known times at room temperature, with occasional swirling. The resin and the aqueous phase were separated by filtration through a small glass column (*ca.* 1 cm. in diameter and 8 cm. in length), with a sintered disc (porosity grade 2, sealed in), and aliquot parts of the filtrate analysed for vanadium and used for pH measurement. The chloride on the resin was then removed and was determined by a method given previously,[14a] as was the capacity of the resin.

In the second procedure 0·5 g. of resin (or less, where specified) was left in contact with 100 ml. of solution under the above conditions. The two phases were separated by decantation and aliquot parts of the aqueous phase used for the determination of vanadium, chloride, and pH.

The *R* value, as defined by Everest and Salmon,[14a] which expresses the ratio of the mean number of vanadium atoms per unit of ionic charge in the vanadate ions sorbed on the resin, was then derived as follows:

In the first case;

$$R = \frac{\text{G.-atoms of V in soln. initially} - \text{g.-atoms of V in soln. finally}}{\text{Capacity of resin sample} - \text{g.-atoms of Cl on resin finally}}$$

where the resin capacity is given in g.-equivs.

In the second case

$$R = \frac{\text{G.-atoms of V in soln. initially} - \text{g.-atoms of V in soln. finally}}{\text{G.-atoms of Cl in soln. finally}}$$

which expression does not involve the value of resin capacity.

Column Experiments.—A volume of solution containing more vanadium than was required to saturate the exchanger with vanadium (by a factor of several-fold) was passed through a column (1 × 8 cm.) containing 1 g. of resin during 2 days. The effluent was then free from chloride, and vanadate ions only were sorbed on the resin. The resin was washed thoroughly, the vanadate ions were then displaced by use of 2N-sulphuric acid, and vanadium was determined in the effluent. For the experiments *R* was given by the ratio (g.-atoms of V sorbed on resin)/(capacity of resin sample in g.-equivs.).

Analysis.—Vanadium was determined, after reduction to the quadrivalent state with sulphur dioxide or preferably sodium sulphite, by titration with potassium permanganate solution. Elimination of interference by chloride in the solutions could be achieved by evaporation of the V^{IV} solutions to small bulk (not to dryness) in the presence of 3N-sulphuric acid, followed by dilution before titration.

Chloride was determined by weight as silver chloride. pH measurements were made with a Cambridge pH meter with a glass–saturated calomel electrode system.

pH *Titrations.*—The procedure used was similar to that of Ducret;[12] vanadic acid was titrated with ammonia solution, and the pH was measured immediately after mixing and again after the solution had reached equilibrium.

Spectrophotometric Measurements.—These were made with 1 cm. quartz cells and a Unicam S.P. 500 spectrophotometer with solutions of 0·025 g.-atom of vanadium per litre.

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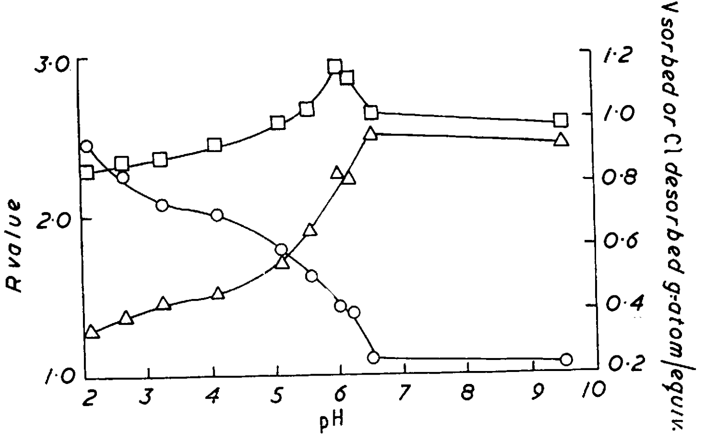
[16] Pepper, Paisley, and Young, *J.*, 1953, 4097.

RESULTS AND DISCUSSION

In experiments with vanadic acid solutions (pH 2, *ca.* 0·05 g.-atom/l.), carried out within the time limits of their stability and with resin of a normal degree of cross linking (weight-swelling 0·70), no consistent changes in the value of R with time could be detected, where R is the ratio of the mean number of vanadium atoms to ionic charge (x/z) in the vanadate ions $(H_wV_xO_y)^{z-}$ sorbed by the resin.[14a]

Studies made with the same resin, but with solutions of varying pH (Fig. 1), and with times of contact of up to 100 hr. showed that, whilst the value of R increased with decrease in pH, the corresponding values of vanadium sorption and chloride release—from which R is derived—increased with rise in pH, but reached a maximum value at pH *ca.* 6·5, above which the chloride release remained constant while the vanadium uptake decreased.

FIG. 1. *Experiments with vanadate solutions* (75 *ml.*) *of various* pH *values and a resin of weight-swelling value of* 0·70.



G.-atoms of V sorbed per equiv. of resin (□), g.-equiv. of Cl desorbed per equiv. of resin (△), R value (○).

Such behaviour can be explained by the assumption that larger ions (*i.e.*, with higher R values) are formed in increasing amounts as the pH is lowered, but are excluded, at least partially, by the resin structure.

If such an ionic-sieve mechanism is effective, the maximum in the vanadium sorption curve should correspond to the sorption of the largest ions which can penetrate the resin structure without hindrance. Larger ions, formed in maximum concentration at lower pH, are not sorbed owing to their size and low concentration, whilst smaller ions are not sorbed owing to their relatively lower affinity for the resin and their low concentration. The mean value of $R = 1{\cdot}33$ at this peak in vanadium sorption would then indicate the sorption of a tetravanadate ion ($x = 4$, $z = 3$).

Support for the view that exclusion was occurring with the resin of weight-swelling value 0·70 was provided by the results of similar experiments with resins of other weight-swelling values.

Thus in experiments with a more open resin (weight-swelling 1·04) the peak in vanadium sorption was replaced by a steady rise in sorption with fall in pH while the value of R rose to above three at about pH 2. With a more tightly cross-linked resin, on the other hand, a maximum in vanadium sorption occurred but at a higher pH (*ca.* 7), and this corresponded to an ion with an R value of unity.

With a resin of weight-swelling value 0·74 it was observed that the value of R remained close to 2 over the pH range 4·5—6, which again corresponded to a maximum in the sorption of vanadium.

In the sorption of ions comparable in size with the effective pore size of the resin, slow rates of exchange were encountered. The results obtained with resin of weight-swelling value 1·04 and vanadic acid are shown in Table 1 which shows a steady state after 100 hr., and the values of R corresponding to this state are those included in subsequent graphs and Tables.

TABLE 1. *The variation of exchange with time, with vanadic acid* (100 *ml.*, pH *ca.* 2) *and* 0·5 *g. of resin* (1·04 *weight-swelling*).

Time (hr.)	Cl desorbed (mg. equiv.)	V sorbed (mg.-atom)	R
5	0·754	1·926	2·56
10	0·781	2·022	2·59
25	0·892	2·384	2·67
50	0·995	2·795	2·90
60	1·020	2·978	2·97
80	1·013	2·949	2·91
90	1·038	3·048	2·94
100	1·017	2·986	2·94

For solutions of vanadic acid (*ca.* 0·05 g.-atom/l. at pH 2), the sorption of an ion of R 3·3 by resins of weight-swelling about 1·4 or greater is indicated (Fig. 2) with partial exclusion of this at lower values of weight swelling.

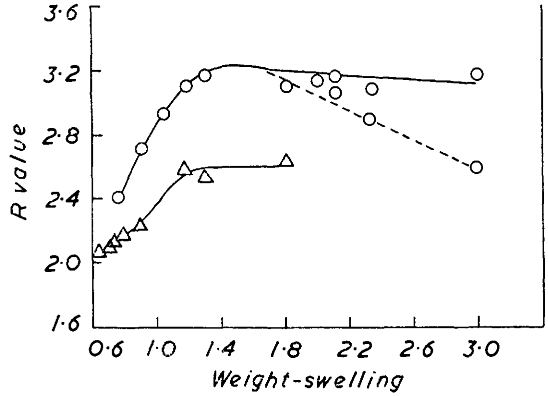


FIG. 2. *Variation of R with weight-swelling for solutions in the low* pH *range.*
Mean R values at pH 2 (○) and 4 (△).

A value of $R = 3·33$ is consistent with the sorption of a decavanadate ion ($x = 10$, $z = 3$). The fact that this ion has a large affinity for the resin, coupled with the presence in it of ten vanadium atoms, leads to a high removal of vanadium from solution (in some cases 75%), with the possible consequence of an increase in the charge on the decavanadate ion (if it is capable of losing more protons) and a tendency for a reversal of the condensation to yield smaller ions. A decrease in R value with increased weight-swelling, as observed (Fig. 2 broken curve), could arise from either of these causes. If the decrease in vanadium concentration is kept below 50% by the use of 0·25 g. quantities of resin this decrease in R is minimized (Fig. 2, full curve). No higher R values were detected with resin of weight-swelling values up to 17 and a maximum value of 3·33 was confirmed (Table 2).

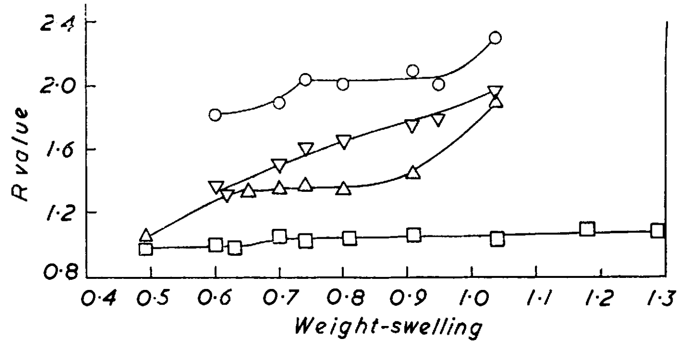
TABLE 2. *Values of R obtained with vanadic acid* (100 *ml.*) *and* 0·25 *g. samples of resins of high weight-swelling values.*

Weight-swelling	R values					Mean R value
7·4	3·21	3·44	3·34	3·23	3·49	3·34
17·5	3·13	3·23	3·23	3·26	3·14	3·20

With similar solutions, but at pH 4 (Fig. 2), the sorption of an ion having an R value close to 2 was observed with resins of weight-swelling below 0·75, but increasing amounts of a larger ion, presumably the decavanadate, were sorbed by more open resins. An ion with an *R* value of 2 was sorbed from solutions of pH 5 (Fig. 3) over a range of weight-swelling, indicating the presence of such an ion in solution in significant concentrations, together with small amounts of smaller ions, which were sorbed when the ion present in major proportion was excluded at low weight-swellings, and of larger ions which were sorbed with it by more open resins. At pH 6·5 (Fig. 3), however, a smaller ion having an *R* value of 1·33 was evidently in preponderance, probably together with ions of $R = 1$ and larger ions of $R = 2$. Results obtained with solutions of pH 6 (Fig. 3) also indicated the presence of an ion of $R = 1·33$, but in smaller amounts together with that of $R = 2$. The *R* values rise steadily from the lower weight-swelling value 0·6 to the higher value 1·05.

Evidently at pH 6·5 the tetravanadate ions ($x = 4$, $z = 3$) are present in solution as the predominant species, but as the pH is lowered, even to pH 6, they give way increasingly to the ion of $R = 2$. A value of $R = 2$ would correspond to a hexavanadate ($x = 6$, $z = 3$) or an octavanadate ($x = 8$, $z = 4$) ion, but a consideration of the weight-swelling values which will permit free entry of ions of *R* values 3·33, 2, and 1·33 respectively (Figs. 2 and 3; Table 3) shows that the ion of $R{=}2$ is much closer in size to the tetravanadate than to the decavanadate and is, therefore, presumably a hexavanadate.

FIG. 3. *The variation of R with weight-swelling for solutions in the middle* pH *range.*



Mean *R* values at pH 5 (○), 6 (▽), 6·5 (△), and 7 (□).

At pH 7 (Fig. 3), the formation of an ion of $R{=}1$ in appreciable concentration was apparent. That this was a trivanadate ion ($x = 3$, $z = 3$) was shown by the fact that it was capable of entering resins of only slightly lower weight-swellings than those which permitted the entry of tetravanadate ions (Table 3). This conclusion was supported by the fall of *R* below 1 for the most tightly cross-linked resins (Fig. 3), by the exchange reactions of these resins with solutions of higher pH (Table 4) in which *R* values of about 0·66 [corresponding to the divanadate ion ($x = 2, z = 3$)] or slightly higher, were obtained. An indication was thus obtained that ions existed in alkaline solution which were smaller than those of $R = 1$ and since these appeared to contain two vanadium atoms ($x = 2, z = 3$), the value of $R = 1$ would correspond to a trivanadate ion.

TABLE 3. *Approximate minimum weight-swelling values of resins which just permit the entry of various vanadate ions* $H_wV_xO_y^{z-}$.

R value	3·33	2·00	1·33	1·00
x (estimated)	10	6	4	3
Weight-swelling	1·40	0·75	0·65	0·60

TABLE 4. *R values obtained from experiments with vanadate solutions at* pH 10.

Weight-swelling	*R* values					Mean *R* value
0·70	0·77	0·77	0·77	0·78	0·77	0·77
0·63	0·80	0·83	0·85	0·84	0·84	0·83
0·60	0·77	0·78	0·78	0·77	0·81	0·78
0·49	0·68	0·69	0·70	0·69	0·68	0·69

To ascertain the effects of changes in the vanadium concentration, which occurred during the ion-exchange process, on the nature of the ions in solution, batch experiments with solutions of pH 7 and with varying weights of resin (Table 5), and also column experiments with 1 g. samples of resin and excess of solutions of vanadic acid of varying concentration (pH *ca.* 2, Table 6), have been carried out. The results of both series of experiments showed that the degree of condensation is not sharply dependent on concentration and hence that the results of the batch experiments given in Figs. 2 and 3 would indicate reliably the species present in solution at the various pH values.

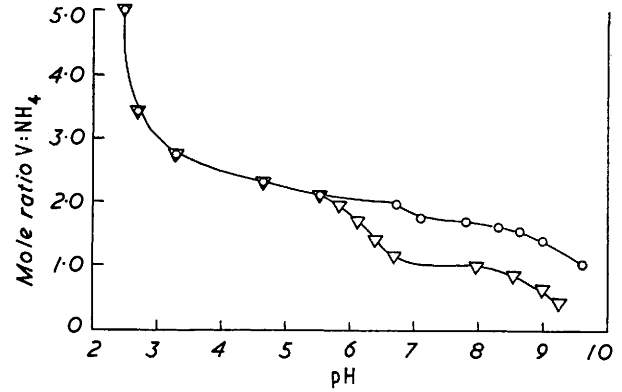
TABLE 5. *The variation of R value with change of vanadate concentration at* pH 7.

Solutions: V concn. (g.-atom/l.)	Resins Sample (g.)	Weight-swelling	Mean *R*	Solutions: V concn. (g.-atom/l.)	Resins Sample (g.)	Weight-swelling	Mean *R*
0·14	0·5	1·04	1·12	0·035	0·2	1·04	0·96
0·14	0·5	0·91	1·14	0·035	0·2	0·91	0·99
0·14	0·5	0·74	1·15	0·035	0·2	0·74	1·03
0·07	0·3	1·04	1·01				
0·07	0·3	0·91	1·02				
0·07	0·3	0·74	1·13				

TABLE 6. *Column experiments with vanadic acid solutions and a resin of weight-swelling value* 1·82.

V concn. (g.-atom/l.)	*R* values				Mean *R*
0·05	3·27	3·41	3·31	3·30	3·32
0·005	2·80	2·84	2·81	2·83	2·82

FIG. 4. *Titration of vanadic acid* (0·06 *g.-atom* V/*l.*) *with* N-*ammonia.*



pH values: initial (○), final (▽), identical initial and final (circle inside triangle).

The observed fall in *R* of vanadic acid solutions with dilution (Table 6) could be due to increased ionisation of the acid (to $x = 10$, $z = 4$, $R = 2{\cdot}5$) which would be consistent with the observations of Rossotti and Rossotti.[13] Thus, whilst it is not possible to maintain a constant ionic strength in the aqueous phase in these experiments our conclusions are not seriously affected by changes in concentration during the ion-exchange process, with the one exception already noted (Fig. 2), where this was overcome by modifying the procedure.

The present results thus indicate the following sequence of condensation: at pH 10 divanadate ($x = 2$, $z = 3$); at pH 7 trivanadate ($x = 3$, $z = 3$); at pH 6·5 tetravanadate ($x = 4$, $z = 3$); at pH 5 hexavanadate ($x = 6$, $z = 3$); at pH 2 decavanadate ($x = 10$, $z = 3$), and possibly at lower concentration ($x = 10$, $z = 4$). Of these ions the trivanadate, hexavanadate, and decavanadate appear to persist over a wide pH range, while the tetravanadate exists over a narrow range only.

The greater stability of the hexavanadate and trivanadate ions seems to be shown by the appearance of inflections in the curve (Fig. 4) at mole ratios of $V : NH_4$ ($= R$) of 2 : 1 and 1 : 1 (at pH values of about 5·5 and 7·5) in the titration of vanadic acid with ammonia solution.

TABLE 7. *Wavelengths corresponding to a transmission density of* 50% *for vanadate solutions* (0·025 *g.-atom/l.*) *in* 1 *cm. cells.*

pH	8·8	8·5	8·0	7·5	6·7	6·6	6·45	6·4	5·2	3·9
Wavelength (Å)	3860	3880	3870	3870	4680	4990	5090	5180	5210	5180

The rapid conversion of trivanadate into tetravanadate and thence into hexavanadate in region pH 7—5 does in fact coincide with a shift in the edge of an absorption band in the spectra of the vanadates in aqueous solution (0·025 g.-atom/l.). This can be seen from Table 7 where the values of 50% transmittency are shown. This shift results in the appearance of a yellow or orange colour.

It is evident that the tendency for inorganic complex cations to be inhibited in their exchange reactions with tightly cross-linked resins, observed by Gustavson and Holm,[17] is also shown by the reactions of complex anions with the corresponding exchangers (cf. ref. 18), and in the case of the bulky isopolyvanadate ions to permit separation by the ionic-sieve effect.

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[17] Gustavson and Holm, *Svensk Kem. Tidskr.*, 1952, **64**, 137.

[18] Herber, Tongue, and Irvine, *J. Amer. Chem. Soc.*, 1955, **77**, 5840.