Inorganic and Analytical Chemistry Using Ion-Exchange Resin. I.

Vanadium Ion Exchange in Cation-Exchange Resin Column.

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(Received May 30, 1949.)

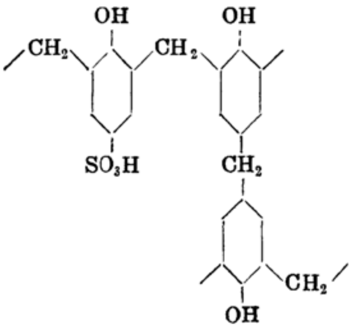
Introduction. How do amphoteric electrolytes react in the cation-exchange resin column? Though it has not yet been explained, it must be one of the most interesting problems in the chemistry using ion-exchange resin because of the possibility of its wide applications to the inorganic and analytical chemistry.[1]

In this report, the author has taken quinquivalent vanadium ion as the representative of amphoteric electrolytes, and has explained the behaviors of the ion in cation-exchange resin column.

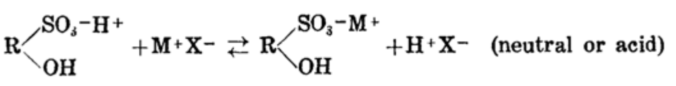
Property and Use of Cation-Exchange Resin.

(1) Type. The resin used in this research is phenol sulfonic acid type cation-exchange resin.

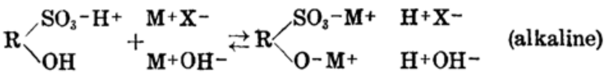
(2) Structure:



(3) The Formulas of Exchange Reactions:



$$\mathrm{R}\begin{array}{l}\diagup SO_3{}^-H^+\\ \diagdown OH\end{array} + M^+X^- \rightleftarrows \mathrm{R}\begin{array}{l}\diagup SO_3{}^-M^+\\ \diagdown OH\end{array} + H^+X^- \quad \text{(neutral or acid)}$$



$$\mathrm{R}\begin{array}{l}\diagup SO_3{}^-H^+\\ \diagdown OH\end{array} + \begin{array}{l}M^+X^-\\ M^+OH^-\end{array} \rightleftarrows \mathrm{R}\begin{array}{l}\diagup SO_3{}^-M^+\\ \diagdown O^-M^+\end{array} \begin{array}{l}H^+X^-\\ H^+OH^-\end{array} \quad \text{(alkaline)}$$

(4) The Exchange Capacity. The exchange capacity of the resin used in this research is 1.74 milliequivalents per gram.

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(1) It would be understood in the following papers.

(5) The Structure of the Resin Column.⁽²⁾ A burette (B) is cut about 20 cm. long, in the bottom of which well-washed glass-wool is packed (0.5 cm. in thickness). Upon the glass-wool the cation-exchange resin (20 meches) is poured together with distilled water. (The apparent volume of resin layer is 10 c.c. in water). (The existence of bubbles in it should be avoided.) By means of a thin rubber-tube (C), the bottom of the burette is connected with a thin glass-tube (D) as shown in Fig. 1. The other end of the glass-tube is placed 0.5 cm. higher than the top of the resin layer in order to keep the solution level above the resin. Under it a beaker (E) is placed to collect the effluent. Upon the burette (B) a separating funnel (A) is placed so that the sample solution and washings may drop on the resin column.

With such an apparatus, when the velocity of dropping is properly adjusted, the solution passes through the resin column at a constant rate.

(6) Method for Regeneration of the Resin. Add 1 N to 3 N hydrochloric acid to the resin in a beaker, then, after le ving them about 1 hour under occasional stirring, decant out the acid, wash with distilled water, and repeat these processes several times, thus the resin is almost perfectly washed. The resin thus obtained is put into the apparatus with distilled water, and washed perfectly by passing 500 c.c. of the acid and 500 c.c. of distilled water through it. In some cases, it is permitted to wash directly in the apparatus without treating it previously in the beaker.

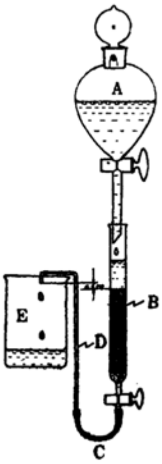

Fig. 1.

(7) Method for Saturating the Sulfonic Group with H^+. The sulfonic group of the resin treated as suggested in (6) is completely saturated with H^+, and of course phenolic-OH group also remains in the form of OH.

(8) Method for Saturating Only the Sulfonic Group with Na^+ or NH_4^+. Wash the resin in a beaker as mentioned in (6), pour 1 N sodium chloride solution (*p*H, if necessary, is moderated about 7 with sodium hydroxide), or 1 N ammonium chloride solution (*p*H, also about 7 with ammonium hydroxide) into the beaker, and stir the resin thoroughly. After decantation, wash the resin twice with distilled water, add again 1 N sodium chloride solution (*p*H, about 7) or ammonium chloride solution (*p*H, about 7), and leave it for hours under occasional stirring.

Then, transfer the resin to the apparatus, pass 300–500 c.c. of 1 N sodium chloride or 1 N ammonium chloride solution (*p*H, about 7) through it, and then wash it with 500 c.c. of distilled water.

(9) Method for Saturating Both Sulfonic Group and Phenolic-OH Group with Na^+ or NH_4^+. By using alkaline solution of 1 N sodium chloride (*p*H, 10 ~ 12, with sodium hydroxide) or alkaline solution of 1 N ammonium chloride (*p*H, 10 ~ 12 with ammonium hydroxide), not only in the sulfonic group but also in the phenolic-OH group H^+ is exchanged with Na^+ or NH_4^+.

Therefore, if above-mentioned alkaline solution of 1 N sodium chloride or 1 N ammonium chloride is passed through the resin column till the *p*H of effluent becomes equal to that of the poured solution, not only sulfonic group but also phenolic-OH group of the resin is saturated with Na^+ or NH_4^+.

(10) Notations of the Resin Column. For convenience' sake, the resin columns are described by the following notations:

Cation-Exchange Resin (Phenol-sulfonic acid type): C
Cation-Exchange Resin, when all groups remain H^+: C^{HH}
Cation-Exchange Resin, when only sulfonic group is saturated with NH_4^+ : C^{NH_4H}

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(2) Similar apparatus had been used by K. Helrich and W. Rieman III. (*Anal. Chem.*, **19** (1947), 651).

Cation-Exchange Resin, when only sulfonic group is saturated with Na^+ : C^{NaH}
Cation-Exchange Resin, when all groups are saturated with NH_4^+ : $C^{NH_4^+ NH_4^+}$
Cation-Exchange Resin, when all groups are saturated with Na^+ : C^{NaNa}

Preparation of Vanadium Standard Solutions.

The standard solution of vanadium (600γ V/c.c.) was prepared with ammonium metavanadate (E. Merck). It was standardized with normal solution of potassium permanganate after reducing it with sulfur dioxide (the excess of sulfur dioxide was expelled with carbon dioxide). Thus, 600γ of V/c.c. was decided. Then solutions containing 60γ/c.c., 6.0γ/c.c. and 0.6γ/c.c. were prepared. Similarly, the solutions of 261γ/c.c., 26.1γ/c.c., 13.1γ/c.c., 6.5γ/c.c. and 3.3γ/c.c. were also prepared.

Experiment I. Quinquivalent Vanadium Ion Exchange in C^{HH}.

Vanadium solutions of various concentrations and *p*H (*p*H was adjusted with ammonium hydroxide and hydrochloric acid) were passed through C^{HH} in this experiment. In each case, after passing the sample solution, 100 c.c. of distilled water was passed for washing (flow rate was 1.5 c.c./min.(3) and nearly the same in all the following experiments), effluent was gathered in a beaker, alkalized with ammonium hydroxide, concentrated to proper volume by heating on a water-bath, and neutralized with 0.2 N sulfuric acid using methyl orange as indicator after transferring the solution into a separating funnel. Then, vanadium in it was colorimetrically determined by the oxine-chloroform method(4) using the Pulfrich Stufen Photometer (Zeiss). The results are shown in Table 1.

Table 1.

Experiment number			1	2	3	4	5	6
Sample solution	*p*H		1.0	5.0	7<	7<	7<	12.0
	Amount of V	γ/c.c.	0.6	1.2	1.2	6.0	6.0	0.6
		Total amount (γ)	60.0	60.0	60.0	60.0	60.0	60.0
	Total volume (c.c.)		100.0	50.0	50.0	10.0	10.0	100.0
Amount of washings (c.c.)			100	100	100	100	100	100
V, found in effluent (γ)			0	0	0	0	0	0

As obviously shown in Table 1, quinquivalent vanadium is completely captured by C^{HH} independently of *p*H of the solutions. Therefore, C^{HH} cannot be used for the separation of vanadium from other cations.

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(3) Accordingly, space velocity is 9.

(4) At a *p*H corresponding to the intermediate color of methyl orange, quinquivalent vanadium reacts with 8-hydroxyquinoline to give a compound soluble in chloroform with a Bordeaux red to black color. This sensitive and persistent color of the vanadium-8-hydroxyquinoline salt in chloroform layer can be used for the most sensitive and accurate colorimetric determination of this element.

Experiment II. Qninquivalent Vanadium Ion Exchange in C^{NaNa}.

Using C^{NaNa}, nearly the same process(5) as in. Expt. 1 was carried out. The results are shown in Table 2.

Table 2.

Experiment number			7	8	9	10	11	12
Sample solution	pH		12.4	12.1	5.4	5.4	5.0	1.3
	Amount of V	γ/c.c.	6.0	6.0	1.0	6.0	6.0	1.0
		Total amount (γ)	60.0	60.0	60.0	60.0	60.0	60.0
	Total volume (c.c.)		10.0	10.0	60.9	10.0	10.0	60.0
Amount of washings (c c.)			50.0	50.0	50.0	50.0	50.0	50.0
V, found in effluent (γ)			59.6	59.4	60.1	60.0	60.2	17.5
Error		γ	−0.4	−0.6	+0.1	0.0	+0.2	−42.5
		%	−0.6	−1.0	+0.2	0.0	+0.3	−70.8

In Expts. 7, 8, 9, 10 and 11, where pH 5.0 or more is used, vanadium passes through C^{NaNa} within experimental error, while in Expt. 12, namely in case of pH 3, only a little part of vanadium is detected in the effluent.

Experiment III. Quinquivalent Vanadium Ion Exchange in C^{NaH}.

Using C^{NaH}, much the same process(6) as in Expt. 1 was carried out. The results are shown in Table 3.

Table 3.

Experiment number			13	14	15	16	17	18	19	20	21
Sample solution	pH		10.0	8.0	5.4	5.0	3.0	3.0	2.2	2.2	1.8
	Amount of V	γ/c.c.	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4
		Total amount (γ)	36.0	48.0	24.0	24.0	24.0	24.0	24.0	24.0	24.0
	Total volume (c.c.)		15.0	20.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Amount of washings (c.c.)			50.0	50.0	70.0	70.0	70.0	70.0	70.0	70.0	70.0
V, found in effluent (γ)			36.4	-8.5	24.0	24.0	21.3	20.4	16.9	16.5	7.0
Error		γ	-0.4	-0.5	0.0	0.0	- 2.7	- 3.6	- 7.1	- 7.5	-17.0
		%	-1.1	-1.0	0.0	0.0	-11.3	-15.0	-29.6	-31.3	-70.9
$\frac{\text{V found in effluent}}{\text{V in sample solution}} \times 100$			101.1	101.0	100.0	100.0	88.7	85.0	70.4	68.7	29.1

In Expts. 13, 14, 15 and 16, namely where pH 5.0 or more is used, vanadium passes through C^{NaH} within the experimental error. And, in

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(5) Ammonium hydroxide was not added before concentrating the effluent.

(6) The pH of sample solutions were adjusted with ammonium hydroxide and nitric acid. Ammonium hydroxide was not added before concentrating the effluent.

Expts. 17–21, namely *p*H 3 (Expts. 17 and 18), *p*H 2.2 (Expts. 19 and 20) and *p*H 1.8 (Expt. 21), the lower the *p*H of the sample solutions, the larger the amount of vanadium captured by C^{NaH} becomes.

Experiment IV. Quinquivalent Vanadium Ion Exchange in C^{NH_4H}.

In Expts. I, II and III, the outline of the quinquivalent vanadium ion exchange in the column of cation-exchange resin is shown, so, in the next experiments the more detailed study has been carried out through C^{NH_4H}, which is very convenient for various practical and theoretical purposes.

Table 4.

Experiment number			22	23	24	25	26	27	28	29	30
Sample solution	*p*H		7.6	7.2	6.4	6.4	5.0	5.0	4.7	4.2	3.8
	Amount of V	γ/c.c.	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
		Total amount (γ)	26.1	52.2	13.1	13.1	13.1	26.1	26.1	26.1	26.1
	Total volume (c.c.)		10.0	20.0	5.0	5.0	5.0	10.0	10.0	10.0	10.0
Amount of washings(c.c.)			60.0	60.0	30.0	30.0	30.0	60.0	60.0	60.0	60.0
ε of effluent			0.466	0.905	0.264	0.258	0.260	0.412	0.460	0.405	0.169
V, found in effluent (γ)			26.0	51.9	13.2	13.0	13.1	26.2	25.6	22.1	8.0
ε_0 (Theoretical value)			0.469	0.911	0.261	0.261	0.261	0.469	0.461	0.469	0.160
Error	$\varepsilon-\varepsilon_0$		−0.003	−0.006	−0.003	−0.003	−0.001	−0.003	−0.009	−0.064	−0.300
	γ		−0.1	−0.3	−0.1	−0.1	0	−0.1	−0.5	−4.0	−18.1
	%		−0.4	−0.6	−0.8	−0.8	0	−0.4	−1.9	−15.3	−69.3
$\dfrac{\text{V found in effluent}}{\text{V in sample solution}}\times 100$			99.6	99.4	100.8	99.2	100.0	100.4	98.1	84.7	30.7

After passing vanadium solution (in this case *p*H was adjusted with ammonium hydroxide and sulfuric acid) through C^{NH_4H} and washing with 30–60 c.c. of distilled water, effluent was gathered in a separating funnel and neutralized with 0.2 N sulfuric acid using methyl orange as indicator. Then, vanadium in it was colorimetrically determined by the oxine-chloroform method. The results are shown in Table 4.

In Expts. 22, 23, 24, 25, 26 and 27, namely, where *p*H 5.0 or

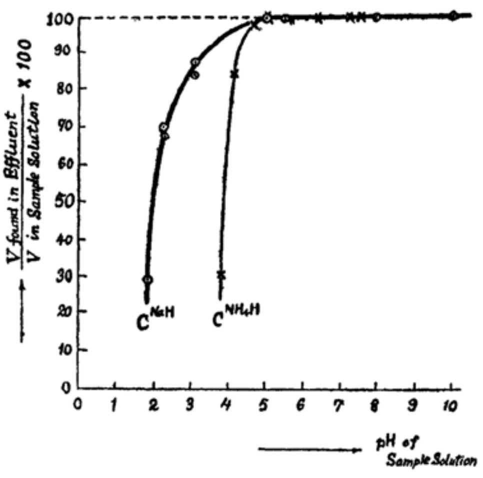

Fig. 2.

more is used, vanadium exactly passes through C^{NH_4H}. However, as *p*H decreases, the amount of vanadium captured by C^{NH_4H} increases just as in Expt. III.

In Fig. 2, the relation between the vanadium found in effluents and *p*H of sample solutions is illustrated in the case of C^{NaH} and C^{NH_4H}.

Conclusion.

Quinquivalent vanadium in aqueous solution is thoroughly captured by C^{HH} independently of *p*H of passing solutions. It passes, however, quantitatively through C^{NaNa}, C^{NaH} or C^{NH_4H}, if the *p*H of the passing solution is higher than 5.0; but it is partially captured by them, when the *p*H is lower than 5.0.⁽⁷⁾

The author wishes to thank Dr. Eiiti Minami, Professor of Analytical Chemistry, Tokyo University, and Mr. Masatake Honda, who have given him kind advice and suggestion in this problem.

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