October, 1985] © 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 2955—2959 (1985) 2955

Studies of the Hydrous Niobium(V) Oxide Ion Exchanger. II. Affinity for Various Cations

Yasushi Inoue,* Hiromichi Yamazaki, Kazushi Okada, and Kazuhiko Morita
Department of Nuclear Engineering, Faculty of Engineering, Tohoku University, Aramaki, Sendai 980

(Received February 13, 1985)

In order to elucidate the fundamental properties of hydrous niobium(V) oxide as a cation exchanger, the stoichiometry of cation exchange and the selectivity for various cations were studied. As the reversibility and the equivalent exchange between the cations were confirmed, this material showed an ideal cation-exchange reaction. The affinity series for alkali metal ions and alkaline earth metal ions were $Cs^+ \gg K^+ \gg Li^+$ and $Ba^{2+} \gg Sr^{2+} \geqq Ca^{2+} > Mg^{2+}$ respectively; the values decreased in the order of the increase in the hydrated ionic radii of the cations. For transition metal ions, the distribution coefficients had a strong correlation with the first hydrolysis constants of the cations and/or the first stability constants of their acetato complexes. Based on this finding, the transition metal ions are considered to be adsorbed on the exchanger by a bond partially covalent in character, rather than by a pure ionic bond. The pH-dependency of the distribution coefficients of the cations was discussed in terms of the effects of the dissociation of the exchange sites on the overall ion-exchange equilibrium.

Through a comprehensive study of preparing the hydrous niobium(V) oxide ion exchanger, a recommended procedure for synthesizing the exchanger was established, as has been reported previously.[1] The method has the merits of simplicity and good reproducibility. The exchanger thus prepared is a semitransparent, amorphous solid which is hard enough to be used for column operation; it can be converted to the pure H^+ form by conditioning it with a 0.1 mol dm^{-3} HCl solution. The material has the cation-exchange capacity of 2.3 mmol Na^+ g^{-1} (at pH 10) and possesses at least two kinds of weakly dissociable ion-exchange sites. Its stability against various chemicals and during storage was also investigated, as has been described in the foregoing report.[1]

Abe and Ito reported that the exchanger exhibited only a cation-exchange property,[2] but Sukharov *et al.* reported anion exchange with $Cr_2O_7^{2-}$.[3] However, a systematic study has not been made of exchange reactions on hydrous niobium(V) oxide. In the present investigation, the distribution coefficients of various cations were determined as a function of the pH in order to study the ion-exchange mechanism.

Experimental

Reagents and Apparatus. The niobium(V) chloride, of the highest purity grade, was obtained from the Mitsuwa Kagaku Yakuhin Kaisha, Ltd. All the other reagents used were of the highest purity grade and were obtained from Wako Pure Chemical Industries, Ltd., or E. Merck AG. A well-type NaI(Tl) scintillation counter (Fuji Denki Model NHS-2) was employed for the measurement of the γ-radioactivity. All the other apparatuses were the same as those described previously.[1]

Preparation of the Exchanger. Synthetic method No. 4 was chosen from the various methods of preparation described in the preceeding paper: Twenty-five grams of niobium(V) chloride were dissolved in 50 cm^3 of a concentrated hydrochloric acid, followed by dilution to 1 dm^3 with distilled water. The solution was hydrolyzed thermally by boiling it for 2 h in a 3-dm^3, round-bottomed flask equipped with a reflux condenser. The precipitate thus formed was washed with distilled water until no chloride ion was detected in the filtrate. Then the precipitate was air-dried at room temperature. The dried product was then immersed in distilled water to break it down into fine particles. The granules were dried again at room temperature. Particles larger than desired, if any, were ground in a porcelain mortar and sieved to obtain the required particle sizes. The exchanger of a desired particle size(−100 +200 mesh) was converted to the H^+ form by treating it with a 0.1 mol dm^{-3} HCl solution by the procedure described previously.[1] Finally, the exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl solution (relative humidity, 79% at 25 °C). The exchanger had a composition of $Nb_2O_5 \cdot 5.3H_2O$ and an ion-exchange capacity of *ca.* 1.5 mmol Na^+ g^{-1} at pH 8, where an inflection point was observed in the titration curve of the material.

Distribution Coefficients. The distribution coefficients, K_d, were determined in the following way, unless otherwise noted.

A 0.30-g portion of the exchanger in the H^+ form was immersed in 18 cm^3 of the solution with a suitable pH value, adjusted by using a desired combination of 0.11 mol dm^{-3} NaCl and 0.11 mol dm^{-3} HCl or 0.11 mol dm^{-3} NaOH, for 2 d, at room temperature. A 2-cm^3 portion of the solution containing each metal ion was mixed with the above solution to make the concentration of the cation 1×10^{-4} mol dm^{-3} and the ionic strength 0.10 mol dm^{-3}. The mixture was then allowed to stand until the concentration of the cation in the supernatant solution became constant (about 2 to 9 d). The pH and the concentration of the cation in the supernatant solution were then measured. The K_d value, expressed in cm^3 g^{-1}, was calculated in the usual manner.

The metal ions were added as their chlorides, except Fe^{3+}, Th^{4+}, and UO_2^{2+}, for which the corresponding nitrates were used. The analyses of Cs, Sr, Ba, Mn, Fe, Co, Sc, Y, Ce, Eu, Np, and Am were carried out radiometrically using ^{137}Cs, ^{85}Sr, ^{133}Ba, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{45}Sc, ^{88}Y, ^{144}Ce, ^{152}Eu, ^{239}Np, and ^{241}Am respectively as tracers. Their radioactive purities were confirmed by means of γ-ray spectrometry. The ^{239}Np tracer was prepared by milking it from ^{243}Am by the method of Sill.[4] The oxidation state of neptunium at a tracer concentration was adjusted by the method of Inoue and Tochiyama.[5] The Th^{4+} and the UO_2^{2+} were analyzed

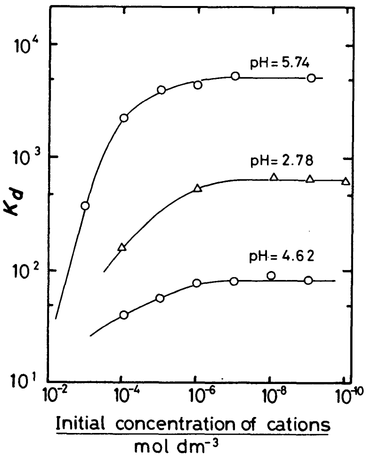

Fig. 1. Effect of the concentration of cations on their distribution coefficients.
○: Co^{2+}, △: Sc^{3+}.

spectrophotometrically using arsenazo III[6] and 2-(5-Bromo-2-pyridylazo)-5-(diethylamino)phenol[7] respectively as coloring reagents, while the concentrations of the other cations were determined by means of atomic-absorption spectrophotometry.

Ion-exchange Stoichiometry. The exchanger in the H^+ form was immersed in an alkaline solution of sodium ions, of a suitable concentration (ionic strength=0.016 mol dm^{-3}), for 2 d at room temperature, with intermittent shaking. This was followed by chemical analysis, and the ratio of the amount of sodium ions taken up in the exchanger to that of the hydrogen ions released from the exchanger was evaluated from the difference between the initial and final concentrations of the respective ions present in the solution. The Na^+ was converted to pure chloride and was indirectly determined by titrating the Cl^-. The OH^- and $CO_3{}^{2-}$ were determined by differential titration.

Results and Discussion

The Dependency of K_d Values on the Concentration of the Cations. Figure 1 shows the K_d values for Co^{2+} and Sc^{3+} as a function of their initial concentrations at constant pH values. The K_d values were nearly constant in the concentration region lower than 10^{-8} mol dm^{-3}, wherefrom they decreased with an increase in the concentration. The concentration-dependency of the K_d values may be ascribed to the limited amount of cation-exchange sites in the pH region adopted in the present experiment, since the uptake of Na^+ on the exchanger commences at about pH 4.[1] Because of this observation, a strict comparison of the selectivity for various cations should be made at a concentration lower than 10^{-8} mol dm^{-3}. However, it is very difficult to set up the above situation because of the limits of analytical sensitivities for some cations. Thus, an initial concentration of 1× 10^{-4} mol dm^{-3} was used mainly for the comparison of the K_d values of various cations.

Table 1. Verification of equivalence of exchange between Na^+ and H^+

Ionic strength	(I) Na^+ uptaken	(II) H^+ released	Stoichiometry
mol dm^{-3}	mequiv g^{-1}	mequiv g^{-1}	(I)/(II)
0.016 (OH^-/Cl^-=0.25)[a)]	1.77±0.06	1.76±0.03	1.01±0.04

a) : Molar ratio.
Conditions; Exchanger: 0.31 g, Solution: 300 cm^3, Duration of immersion: 2 d at room temperature.

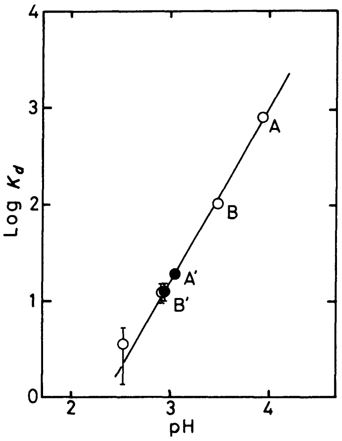

Fig. 2. Reversibility of the exchange reaction between Eu^{3+} and H^+.
Conditions; Ionic strength: 0.10 mol dm^{-3}(NaCl–HCl) at room temperature, Initial concentration of Eu^{3+}: 1×10^{-4} mol dm^{-3}.

Stoichiometry and Reversibility of the Exchange Reaction. Table 1 presents the results concerning the stoichiometry of the exchange reaction between H^+ on the exchanger and Na^+ in the solution. The equivalent ratio of the H^+ released to the Na^+ sorbed was unity, within the limits of experimental error (Table 1). Figure 2 shows the results concerning the reversibility of the ion-exchange reaction between Eu^{3+} and H^+. After the determination of the K_d values at several pH values (A, B in the figure), a small amount of a HCl solution (less than 0.5% in volume) was added to the supernatant solution to lower the pH. This new solution was then allowed to stand until a new equilibrium had been attained, and then the K_d values were measured again (A′, B′ in the fugure). The points A and B shifted to A′ and B′ respectively as a result of the change of the pH in the solutions. Since A′ and B′ fall on the same straight line as A and B, the exchange reaction between Eu^{3+} and H^+ is considered to be reversible. From the stoichiometry and the reversibility of the ion-exchange reaction, the hydrous niobium(V) oxide shows an ideal cation-exchange reaction.

Selectivity for Cations. Figure 3 shows the pH-dependency of the K_d values for the representative elements. The orders of selectivity for alkali metal ions: $Cs^+ \gg K^+ \gg Li^+$, and for alkaline earth metal

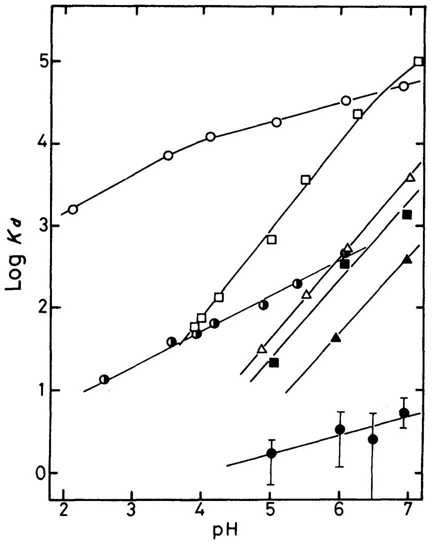

Fig. 3. Log K_d for some metal ions as a function of pH. Conditions; Ionic strength: 0.10 mol dm^{-3} (HCl-NaCl-NaOH) at room temperature, Initial concentration of cation: 1×10^{-4} mol dm^{-3}. Cation; ●: Li^+, ◑: K^+, ○: Cs^+, ▲: Mg^{2+}, ■: Ca^{2+}, △: Sr^{2+}, □: Ba^{2+}.

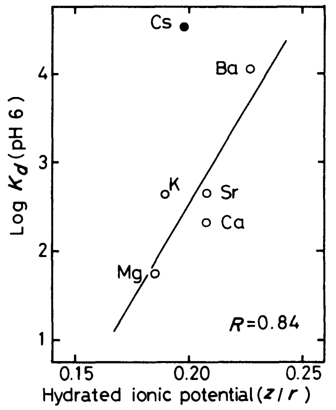

Fig. 4. Relation between log K_d and hydrated ionic potential of cation.
Hydrated ionic potential=z/r; z: Charge of cation, r: Hydrated ionic radius.[8] R: Correlation coefficient (except Cs^+).

ions: $Ba^{2+} \gg Sr^{2+} \geqq Ca^{2+} > Mg^{2+}$, are similar to that of strongly acidic ion-exchange resin, in which the selectivity coefficients for ions with the same ionic charge increase with a decrease in the hydrated ionic radii of the cations. This may be due to the increase in the strength of the electrostatic interaction between the hydrated cations and the fixed anionic groups. Such interaction must be closely related to the ionic potential of hydrated cations (hydrated ionic potential). In fact, the log K_d value at pH 6 for these cations closely correlates to their hydrated ionic potentials (the correlation coefficient was 0.84), as is shown in Fig. 4. Here, the hydrated ionic radii were those reported by Wiklander.[8] The selectivity for Cs^+, however, was markedly high, in spite of the smaller hydrated ionic potential.

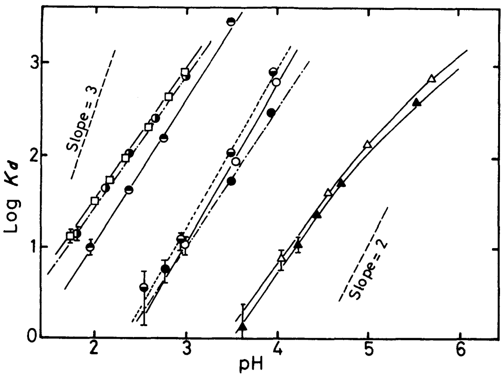

Fig. 5. Log K_d for some metal ions as a function of pH. Conditions; Ionic strength: 0.10 mol dm^{-3} (HCl-NaCl-NaOH) at room temperature, Initial concentration of cation: 1×10^{-4} mol dm^{-3}. Cation; □: UO_2^{2+}, ◑: Fe^{3+}, ◓: Sc^{3+}, ●: Y^{3+}, ⊖: Eu^{3+}, ○: Ce^{3+}, △: Co^{2+}, ▲: Mn^{2+}.

Figure 5 shows that the pH-dependency of the K_d values for bi- and tervalent transition metal ions was: $UO_2^{2+} \geqq Fe^{3+} > Sc^{3+} \gg Eu^{3+} \geqq Ce^{3+} \geqq Y^{3+} \gg Co^{2+} \geqq Mn^{2+}$. By comparing the figure with Fig. 3, the affinity for bivalent transition metal ions (except UO_2^{2+}) may be seen to be similar to that for alkaline earth metal ions. Furthermore, the affinity of the exchanger for tervalent cations is, on the whole, much greater than that for bivalent cations. Hence, the electrostatic force may be an important factor in deciding the selectivity of the hydrous niobium(V) oxide. This affinity series, however, is the exact reverse of what would be expected from the selectivity for alkali- and alkaline earth metal ions. Figure 6 shows the results for some actinoid ions. The Am(III) ion appears to have an affinity similar to those of other transition metal ions with the same charge. The actinyl species, such as NpO_2^+, NpO_2^{2+} and UO_2^{2+}, had, however, higher K_d values than those to be expected from their charges; the affinity for those species was greater than, or similar to, that for tervalent transition metal ions. This finding cannot be explained only in terms of the electrostatic interaction between the hydrated ions and the anionic sites in the exchanger.

In order to understand the important factors affecting the selectivity for the transition metal ions, the K_d values for the metal ions at pH 3 were compared with their ionic potentials, their first hydrolysis constants,[9] and the first stability constants of their acetato complexes.[11] The results are shown in Table 2. Here, the ionic radii used were those obtained by using crystals in which the ion had the coordination number of 6[10] and the log K_d values which could not be obtained by the experiment were those estimated from the extrapolation of the log K_d *vs.* pH plot in Fig. 5. This table indicates that the K_d values correlate more strongly with the stability constants (R=0.96) and the hydrolysis constants (R=0.91) than with the ionic potential

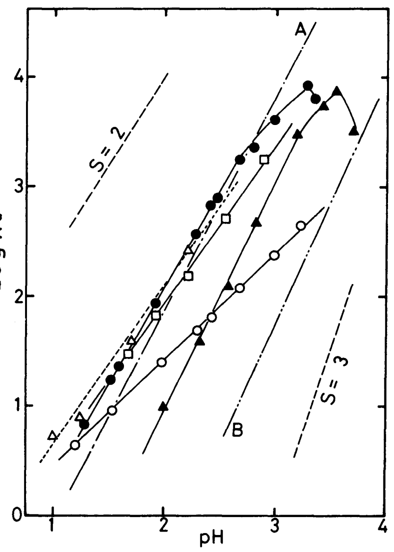

Fig. 6. Log K_d for some actinoid ions as a function of pH. Conditions; Ionic strength: 0.10 mol dm^{-3} ($HClO_4$-$NaClO_4$), Temperature: 40±3 °C. Concentration of cations; △: Th(IV) 1.8×10^{-5} mol dm^{-3}, □: U(VI) 1.3×10^{-5} mol dm^{-3}, ○: Np(V) tracer $S=0.97$, ●: Np(VI) tracer in 4×10^{-4} mol dm^{-4} $KMnO_4$ $S=1.8$, ▲: Am(III) tracer S=2.1, A: Sc^{3+} tracer, B: Y^{3+} tracer. S: Slope.

TABLE 2. INTERACTION BETWEEN EXCHANGING CATIONS AND EXCHANGE SITES

Metal ion	log K_d(at pH 3)	A[1]	B[2]	C[3]
UO_2^{2+}	3.66	—	2.61	−5.8
Fe^{3+}	3.62	4.35	3.36	−2.19
Sc^{3+}	3.40	3.39	—	−4.3
Eu^{3+}	2.10	2.76	2.13	−7.8
Ce^{3+}	1.90	2.61	1.91	−8.3
Y^{3+}	1.73	2.88	1.68	−7.7
Co^{2+}	0.14	2.53	1.10	−9.65
Mn^{2+}	0.02	2.46	0.8	−10.59

$R=0.83$
$R=0.96$
$R=0.91$

1) $A=z/r$: Ionic potential; z=Change of cation, r=Ionic radius(coordination number (6)).[10] 2) B=log K_{11} (CH_3COO^-): First stability constant(equilibrium quotient at 25 °C and ionic strength 0.1).[11] 3) C=log K_{11} (OH^-): First hydrolysis constant.[9]
R=Correlation coefficient.

($R=0.83$). Therefore, we can conclude that, in the ion-exchange reactions for transition metal ions, the formation of a covalent bond between the anionic sites in the exchanger and metal ions is a factor in determining the selectivity of the exchanger, along with the remote coulombic interaction.

Selectivity for Cations in Tracer Concentrations. The cation-exchange reaction is expressed as a combination of the following two reactions:

$$HR \rightleftharpoons H^+ + R^-, \tag{1}$$

$$nR^- + M^{n+} \rightleftharpoons R_nM, \tag{2}$$

where R^- denotes the dissociated form of the exchanger, and M^{n+} the exchanging cations. The equilibrium constants for these reactions can be written as:

$$K_a = \frac{a_H\bar{a}_R}{\bar{a}_{HR}} = \frac{a_H\bar{m}_R\bar{\gamma}_R}{\bar{m}_{HR}\bar{\gamma}_{HR}}, \tag{3}$$

$$K = \frac{\bar{a}_{R_nM}}{\bar{a}_R{}^n a_M} = \frac{\bar{m}_{R_nM}\bar{\gamma}_{R_nM}}{\bar{m}_R{}^n\bar{\gamma}_R{}^n m_M\gamma_M}, \tag{4}$$

where a represents the activity; m, the concentration and γ, the activity coefficient. A bar refers to the exchanger phase. (For the sake of simplicity, the charge of the species is omitted in these expressions.)

From the material balance,

$$\bar{m}_R + \bar{m}_{HR} + n\,\bar{m}_{R_nM} = E \tag{5}$$

E is the total ion-exchange capacity. If the concentration of the exchanging cation, M^{n+}, is negligibly small,

$$\bar{m}_R + \bar{m}_{HR} = E \tag{5'}$$

holds.

From Eqs. 3 through 5′, distribution coefficients of M^{n+} can be written as:

$$K_d = \frac{KK_a{}^n\bar{\gamma}_{HR}{}^n\gamma_M}{\bar{\gamma}_{R_nM}}\cdot\frac{E^n}{\left[1+\dfrac{K_a\bar{\gamma}_{HR}}{a_H\bar{\gamma}_R}\right]^n}\cdot\frac{1}{a_H{}^n}. \tag{6}$$

If the pH of the solution is very low, Eq. 6 can be simplified to:

$$\log K_d = \text{constant} + n\text{pH}, \tag{7}$$

while in highly alkaline solutions:

$$\log K_d = \text{constant}. \tag{8}$$

As has been reported previously,[1] the exchanger commences the uptake of Na^+ at around pH 4, and it increases in its ion-exchange capacity for Na^+ with pH. Consequently, at the tracer concentration, the plot of log K_d *vs.* pH will show a straight line with a slope of n in the pH range lower than around 4. The deviation of the results in Figs. 5 and 6 from Eq. 7 may be ascribed to the strong dependency of the K_d values on the concentration of cations (Fig. 1), but it cannot be explained only from this reason, because the slope of the straight line was not appreciably affected by the concentration, as is evident from the results on Sr^{2+} (Fig. 7). Figure 7 also shows that the K_d value for Sr^{2+} is independent of the pH values in the pH region higher than 8; this agrees with Eq. 8. As is shown in Figs 6 and 8, for uni- and bi-charged cations, the straight lines have approximately the same slopes (Co^{2+}: 1.7, NpO_2^+: 0.97, NpO_2^{2+}: 1.8), as would be predicted from Eq. 7, while the tervalent cations show slopes (Y^{3+}: 2.3, Sc^{3+}: 1.8, Am^{3+}:

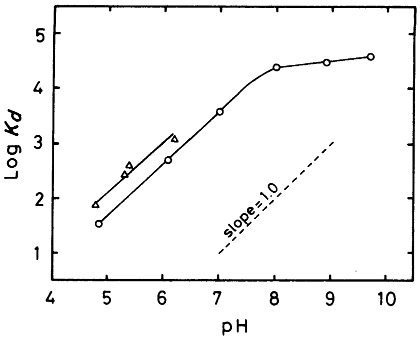

Fig. 7. Effect of the concentration of Sr^{2+} on the pH-dependency of the K_d values.
Ionic strength: 0.10 mol dm^{-3} (NaCl-NaOH) at room temperature, Initial concentration of Sr^{2+}/mol dm^{-3}; ○: 1×10^{-4}, △: 1×10^{-8}.

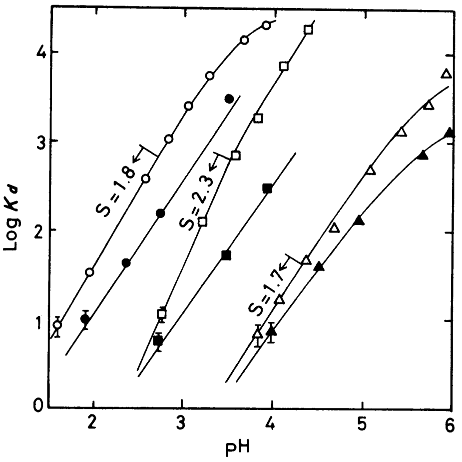

Fig. 8. Effect of the concentration of Co^{2+}, Y^{3+}, and Sc^{3+} on the K_d values.
Ionic strength: 0.10 mol dm^{-3} (HCl-NaCl-NaOH) at room temperature, Initial concentration of cations/mol dm^{-3}, Co^{2+}; ▲: 1×10^{-4}, △: 1×10^{-8}, Y^{3+}; ■: 1×10^{-4}, □: 1×10^{-10}, Sc^{3+}; ●: 1×10^{-4}, ○: 1×10^{-10}.

2.1) smaller than those to be expected from Eq. 7 in spite having the conditions which satisfy this equation. This contradiction may be solved by considering that the charge in the exchanger is not balanced only by these reactions, (1) and (2). The first explanation can be based on the Donnan exclusion principle, which claims that the electrolytes with counter ions (in this case, cations) of a higher charge will be more easily introduced in the exchanger than those of a lower charge, if the co-ions (anions) have the same charge. As the exchanger is mainly in the undissociated form in the pH range lower than 4, the chloride ions can easily diffuse into the exchanger by means of Donnan adsorption. Accordingly, the lowering of the slope of the straight lines will be more pronounced for tervalent than for uni- and bivalent cations. The second explanation is that the charge in the exchanger, instead of the H$^+$, will be balanced by the release of Na$^+$ which is trapped in an exchanger phase surrounded by a solution with a high Na$^+$-concentration, even in a solution with a low pH.

In any case, further investigation must be carried out before the cation-exchange mechanism can be unambiguously understood.

References

1) Y. Inoue, H. Yamazaki and Y. Kimura, *Bull. Chem. Soc. Jpn.*, submitted for publication.

2) M. Abe and T. Ito, *Nippon Kagaku Zasshi*, **86**, 1259 (1965).

3) V. V. Sakharov, N. E. Ivanova, S. S. Korovin, and M. A. Zakharov, *Russ. J. Inorg. Chem.*, **19**, 313 (1974).

4) C. W. Sill, *Anal Chem.*, **38**, 802 (1966).

5) Y. Inoue and O. Tochiyama, *J. Inorg Nucl. Chem.*, **39**, 1443 (1977).

6) H. Onishi, *Analyst*, **12**, 1153 (1963).

7) D. A. Johnson and T. M. Florence, *Anal. Chim. Acta*, **53**, 73 (1971); *Talanta*, **22**, 253 (1975).

8) L. Wiklander, *Ann. Royal Agr. Coll. Sweden*, **14**, 1 (1946).

9) C. F. Baes, Jr., and R. E. Mesmer, "The Hydrolysis of Cations," John Wiley and Sons, New York (1976).

10) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.*, **B 25**, 925 (1969); **A 32**, 751 (1976).

11) A. E. Martell and R. M. Smith, "Critical Stability Constants, Volume 3: Other Organic Ligands," Plenum Press, New York (1977), p. 3.