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Studies of the Hydrous Tin(IV) Oxide Ion-exchanger. III. Affinity for Cations and Some Applications

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The distribution coefficients of hydrous tin(IV) oxide for various cations were measured. The affinity series for alkali-metal ions and alkaline-earth-metal ions were $Li^+ \gg Na^+ > K^+ > Rb^+ \geqq Cs^+$ and $Mg^{2+} > Ca^{2+} > Sr^{2+} \approx Ba^{2+}$ respectively; the values decreased in the order of the increasing crystal radii of the cations. For transition-metal ions, which showed a markedly high affinity, the distribution coefficients had a strong correlation with the hydrolysis constants of the cations and the stability constants of their acetato complexes. Based on these findings, 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. By using NH_4Cl and $HClO_4$ solutions as eluants, nearly quantitative separations of Cs-Na-Li and Cs-Na-Sr were effected with a relatively small column. The applicability of the exchanger to the group separation of actinoids from long-lived fission products was also suggested.

Through a comprehensive study aimed at preparing a hydrous tin(IV) oxide ion-exchanger, the best conditions for synthesizing the exchanger were established; they have been reported previously. The method has the merits of simplicity and good reproducibility. The exchanger in the H^+ form prepared by this method has a composition of $SnO_2 \cdot 2.18H_2O$ and an ion-exchange capacity of 1.18 mmol Na^+ g^{-1} (at pH 11.3). The adsorption of cations on this material was confirmed to occur by means of an ion-exchange reaction, as shown by the fact that the equivalent amount of the hydrogen ion was released by the uptake of a definite amount of alkali-metal or alkaline-earth-metal ions. The material is an amphoteric ion-exchanger possessing at least two kinds of weakly dissociable ion-exchange sites. Other important properties of the exchanger, such as stability against various chemicals, stability during storage, dependence of the water content on the ionic composition, and physical properties, were also investigated, as has been described in the foregoing reports.[1)]

The affinity of the exchanger for various cations is important in understanding the characteristic of the exchanger. There have, however, been only a few reports on the selectivity of the hydrous tin(IV) oxide. Fuller and Donaldson reported this selectivity series: Cu(II)>Zn(II)>Co(II)≧Fe(II)>Ni(II)>Mn(II) and attempted the column separation of these transition-metal ions.[2)] However, such data for deducing the ion-exchange mechanism are conspicuously lacking at the present time.

The purpose of the present investigation is to understand the cation-exchange reaction of the exchanger through the examination of the distribution coefficients of various cations as a function of the pH, and to show the applicability of the exchanger to the selective separation of actinoids in high-level radioactive waste and to the chromatographic separation of alkali-metal and alkaline-earth-metal ions.

Experimental

Reagents and Apparatus. The hydrogen-ion and sodium-ion forms of the hydrous tin(IV) oxide were prepared by the procedure recommended previously.[1)] The exchanger in the Na^+ form was then converted to the NH_4^+ form by means of the column method; a solution of 0.3% NH_3 aq and 0.1 mol dm^{-3} NH_4Cl(pH 10.4) was passed through a column containing the Na^+-form exchanger until no sodium ion was detected in the effluent. The composition of the exchangers thus prepared is shown in Table 1. All the reagents used were of the highest-purity grade obtained from Wako Pure Chemical Industries, Ltd., or E. Merck AG. A well-type NaI (Tl) scintillation counter (Fuji Denki Model NHS-2) was used for the measurement of the γ-radioactivity. All the other apparatuses were the same as described previously.[1)]

Distribution Coefficients. The distribution coefficient, K_d, was determined in the following way unless otherwise noted.

A 0.50-g portion of the exchanger in the desired ionic form was placed in contact, in a thermostatted water bath at 25 °C, with 20 cm^3 of a suitable solution containing 1×10^{-4} mol dm^{-3} of the cation in question until the concentration of the cation in the supernatant solution became constant (about 3 to 14 d). The pH and the concentration of the cation in the solution were then measured. The K_d value was calculated by

Table 1. Composition of the exchangers

Ionic form	M^+ content	Water content[1)]	Composition		
	mmol/g M^+form	wt%	molar ratio		
			SnO_2	M_2O	H_2O
H^+	—	20.51	1	—	2.16
Na^+	1.22	16.81	1	0.116	1.77
NH_4^+	0.86	20.24	1	0.081	1.66

1): Calculated from weight loss when 0.50 g of exchanger was calcinated at 850 °C.

means of the following equation:

$$K_d = \frac{C_i - C_f}{C_f} \cdot \frac{V}{m} \ (\mathrm{cm^3\,g^{-1}}),$$

where C_i and C_f are, respectively, the initial and the final concentration in the solution; V, the volume of the solution in cm^3, and m, the weight of the exchanger in g.

The metal ions were added as their chlorides, except Fe^{3+}, Cr^{3+}, Th^{4+}, and UO_2^{2+}, for which the corresponding nitrates were used. The pH was adjusted by using a desired combination of 0.3 mol dm^{-3} $NaClO_4$, and 0.3 mol dm^{-3} $HClO_4$ or 0.3 mol dm^{-3} NaOH (ionic strength, 0.09). The analyses of Cs, Sr, Ba, Mn, Fe, Co, Cu, Zn, Sc, Y, La, Ce, Eu, Np, and Am were carried out radiometrically using ^{137}Cs, ^{85}Sr, ^{133}Ba, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{64}Cu, ^{65}Zn, ^{46}Sc, ^{88}Y, ^{140}La, ^{144}Ce, ^{152}Eu, ^{239}Np, and ^{241}Am respectively as tracers. Their radioactive purity was confirmed by means of gamma-ray spectrometry. The ^{239}Np tracer was prepared by milking from ^{243}Am by the method of Sill.[3] The oxidation state of neptunium at the tracer concentration was adjusted by the method of Inoue and Tochiyama.[4] The Th^{4+} and UO_2^{2+} were analyzed spectrophotometrically using arsenazo III[5] and 2-(5-bromo-2-pyridylazo)-5-(diethylamimo)phenol[6] respectively as coloring reagents, while the concentration of the other cations were determined by means of atomic-absorption spectrophotometry.

Column Operation. To 2 g of the exchanger in the NH_4^+ form was added a suitable amount of the solution used for converting the exchanger to the NH_4^+ form, and the slurry was poured into a glass column, 0.6 cm in inside diameter. The column thus prepared had a height of 4.5 cm. A solution containing 10 mequiv dm^{-3} of the desired cation was passed through the column at a flow rate of 0.1 cm^3 min^{-1}.

Results and Discussion

Distribution Coefficients. Figure 1 shows the K_d values for Co^{2+} as a function of the loading at a nearly constant pH value (2.03—2.07). The K_d values were nearly constant lower than 4×10^{-5} mequiv g^{-1}, wherefrom they decreased with an increase in the loading of the exchanger.

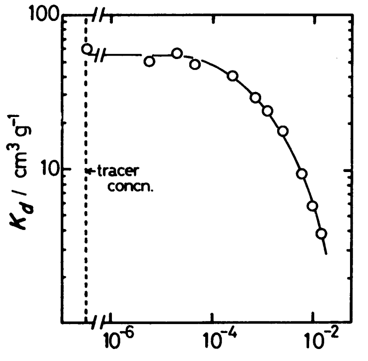

Fig. 1. Dependency of the distribution coefficient of Co^{2+} on loading.
Conditions; Ionic strength: 0.09 ($HClO_4$-$NaClO_4$), Temperature: 25 °C, pH: 2.03—2.07.

The cation-exchange reaction between A^+ and M^{n+} is expressed as:

$$n\bar{A}^+ + M^{n+} = \bar{M}^{n+} + nA^+, \tag{1}$$

for which the equilibrium constant, K, can be written as:

$$K = \frac{\bar{a}_M a_A^n}{\bar{a}_A^n a_M} = \frac{\bar{\gamma}_M[\bar{M}]\gamma_A^n[A]^n}{\gamma_M[M]\bar{\gamma}_A^n[\bar{A}]^n}. \tag{2}$$

In Eq. 2, a bar refers to the exchanger phase; a denotes the activity; [ ], the concentration, and γ, the activity coefficient. For the sake of simplicity, the charge in the cations is omitted in this expression. The distribution coefficient of M^{n+} is expressed as:

$$K_d = [\bar{M}]/[M] \ (\mathrm{cm^3\,g^{-1}}). \tag{3}$$

When the amount of M^{n+} uptaken is extremely small as compared with that of A^+ in the exchanger, $\bar{a}_A$ and $\bar{\gamma}_M$ are regarded as constant. Moreover, γ_M/γ_A^n is also constant if the ionic strength of the solution is kept constant. Under such conditions, the following equation holds:

$$\log K_d = \text{const.} - n \log [A], \tag{4}$$

which implies that a plot of log K_d *vs.* log [A] should be linear with a slope of $-n$.

The pH-dependency of the K_d values for Co^{2+}, Sr^{2+}, and Y^{3+} is shown in Fig. 2 for varying concentration of the cations in the solutions. The linear relation between log K_d and pH was observed as predicted from Eq. 4. The slopes of the straight lines, however, depended on the concentration and approached n only when the concentration became extremely dilute: For Co^{2+} and Sr^{2+}, $\leqq 10^{-7}$ mol dm^{-3}; for Y^{3+}, the tracer concentration. This strong dependency of the K_d values on the concentration of the cations may be ascribed to the limited amount of the cation-exchange sites in the

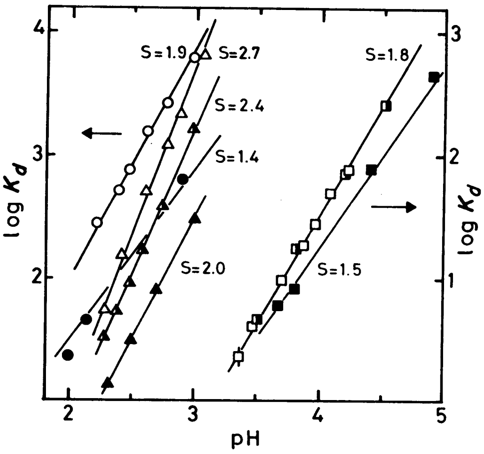

Fig. 2. Effect of the concentration of cations on their distribution coefficients.
Initial concentration of cation/mol dm^{-3}, Sr^{2+}; ■: 1×10^{-4}, ◧: 1×10^{-7}, □: 1×10^{-10}, Co^{2+}; ●: 1×10^{-4}, ○: 1×10^{-7}, Y^{3+}; ▲: 1×10^{-4}, ◭: 1×10^{-7}, △: 1×10^{-10}. S: Slope.

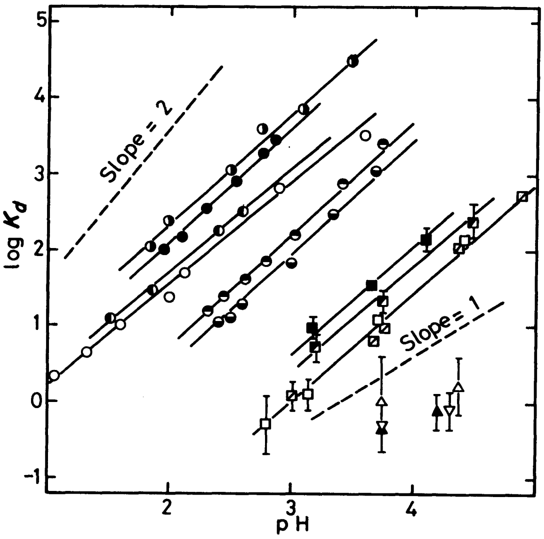

Fig. 3. Log K_d for some metal ions as a function of pH.
Conditions; Ionic strength: 0.09 ($HClO_4$–$NaClO_4$–$NaOH$), Temperature: 25 °C.
Slope; ◑: Cu^{2+} 1.4, ●: UO_2^{2+} 1.5, ◐: Zn^{2+} 1.4, ○: Co^{2+} 1.4, ⊖: Mn^{2+} 1.5, ◒: Ni^{2+} 1.5, ■: Mg^{2+} 1.5, ▨: Ca^{2+} 1.5, □: Sr^{2+} 1.5, ⊠: Ba^{2+} 1.5, △: Li^+ —, ▲: Na^+ —, ▽: Cs^+ —.

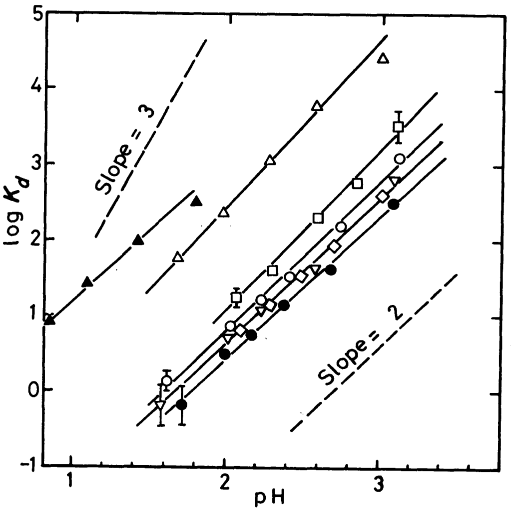

Fig. 4. Log K_d for some metal ions as a function of pH.
Conditions; Ionic strength: 0.09 ($HClO_4$–$NaClO_4$), Temperature: 25 °C.
Slope; ▲: Fe^{3+} 2.0, △: Sc^{3+} 2.3, □: Cr^{3+} 2.2, ○: Eu^{3+} 2.1, ◇: Y^{3+} 2.1, ▽: Ce^{3+} 2.1, ●: La^{3+} 2.0.

pH region adopted in the present experiment, since the isoelectric point of the exchanger is around pH 4, as has been reported previously.[1] Because of this observation, it is preferable to use a concentration lower than 10^{-7} mol dm^{-3} in making a strict comparison of the selectivity of the exchanger between various cations. The lack of the sensitivity of the analytical methods for some cations, however, makes this very difficult. As the next best way, the distribution coefficients for various cations were compared at the lowest possible concentration and the constant initial concentration of the cations in solution, 1×10^{-4} mol dm^{-3}.

Figure 3 shows the pH-dependency of the K_d values for uni- and bivalent cations. Based on the selectivity, these cations can be grouped into three classes: transition metal>alkaline earth metal>alkali metal, in the same manner as ion-exchange resin. However, the order of selectivity for the alkaline-earth-metal ions, $Mg^{2+}>Ca^{2+}>Sr^{2+}\approx Ba^{2+}$, is the exact reverse of what would be expected from the ion-hydration theory, which claims that the strength of the electrostatic interaction between a hydrated cation and a fixed anionic group determines the ion-exchange selectivity of the strongly acidic resin; in fact, the selectivity coefficients for ions with the same charge increase with a decrease in the hydrated ionic radius. The selectivity series for transition-metal ions was $Cu^{2+}\geqq UO_2^{2+}>Zn^{2+}\geqq Co^{2+}>Mn^{2+}\geqq Ni^{2+}$. Figure 4 shows the results for tervalent transition-metal ions. When these results are compared with those for bivalent transition-metal ions, the affinity of these ions is not so great as would be expected from their charge. These affinity series, together with those for alkaline-earth-metal ions, show that the selectivity is higher for metal ions of a smaller crystalline radius than for those of a larger one; this cannot be explained by the ion-hydration theory. The slopes of the straight lines were smaller than the expected n, which is predicted from Eq. 4, as is shown in Figs. 3 and 4.

Since the amount of alkali-metal ions uptaken was very small in an acidic medium, a comparison of the affinity for these ions cannot be made by the use of the hydrogen-ion form. Thus, the ion-exchange reactions between Na^+ and the other alkali-metal ions were examined in an alkaline medium, as is shown in Fig. 5. This figure indicates that linear relationships with a slope of -1 held between the log K_d for alkali metal ions and the logarithm of the concentration of Na^+ in the solution; this agrees well with Eq. 4. This agreement appears unreasonable, however, because the decrease in the concentration of Na^+ from 0.1 mol dm^{-3} to 0.01 mol dm^{-3} will increase the activity coefficient of the cations and decrease the concentration of Na^+ in the exchanger. The change in log γ_M/γ_{Na}, however, is estimated to be smaller than 0.02 from the Debye-Hückel equation. The decrease in Na^+ in the exchanger was analyzed and found to be smaller than 0.04 mmol g^{-1}. Consequently, the present experimental conditions satisfy the assumptions made for deducing Eq. 4. Figure 5 also indicates that the order of the selectivity is: $Li^+\gg K^+>Rb^+\geqq Cs^+$. The distribution coefficients for Li^+, Na^+, and Cs^+ on the exchanger in NH_4^+ form were measured by the column method described in the experimental section; the results are presented in Table 2, along with the experimental conditions. The order of the selectivity, $Li^+\gg Na^+>Cs^+$, like that observed in Fig. 5, is the reverse of what would be expected from the ion-hydration theory.

Thus, the ion-exchange reaction may be brought

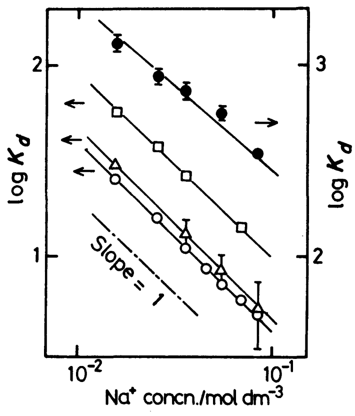

Fig. 5. Log K_d for alkali metal ions as a function of Na^+ concentration.
Conditions; Exchanger: 0.50 g (Na^+ form), Solution: 20 cm^3, pH: 10.5—10.9, Temperature: 25 °C.
Metal ion; ●: Li^+, □: K^+, △: Rb^+, ○: Cs^+.

TABLE 2. DISTRIBUTION COEFFICIENT OF NH_4^+-FORM EXCHANGER FOR ALKALI- METAL IONS(COLUMN METHOD)

	Loading mequiv	Eluant	Elution rate cm^3/min	K_d cm^3/g
Li^+	0.020	5×10^{-2} mol dm^{-3} NH_4Cl	0.07 ~ 0.12	40±0.5
Na^+	0.020			9.8±0.3
Cs^+	0.020			4.2±0.2

Column: 0.6 cmϕ×4.5 cm(NH_4^+ form, 100—200 mesh, 2 g).

about by an electrostatic interaction between an unhydrated cation and the negatively charged site in the exchanger, similar to a weakly acidic resin, such as the carboxylic-acid and phosphonic-acid types. Such interaction would be closely related to the ionic potential of the cations. Figure 6 shows the correlation between log K_d at pH 3 and the ionic potential. Here, the ionic radii used were those obtained by using crystals in which the ion has the coordination number of 6,[7] while the log K_d values which could not be obtained by the experiment were those estimated from the extrapolation of the linear log K_d *vs.* pH plot. The correlation coefficient (R) is 0.76. At pH 2 and 4, the R values were 0.65 and 0.83 respectively. Therefore, as a whole, the affinity of the exchanger for various cations is associated with the electrostatic interaction between an unhydrated cation and the anionic site in the exchanger. However, the selectivity series for transition-metal ions deviates markedly from this relation; these ions have high K_d values, even in such an acidic medium as when a negligible amount of the representative element is adsorbed. This finding compels us to consider that factors other than the electrostatic force may play an important part in deciding the selectivity of the exchanger. In order to know such factors, the K_d values for metal ions at pH 3 were compared with their first hydrolysis constants[8] (Fig. 7) and the first stability constants of their acetato

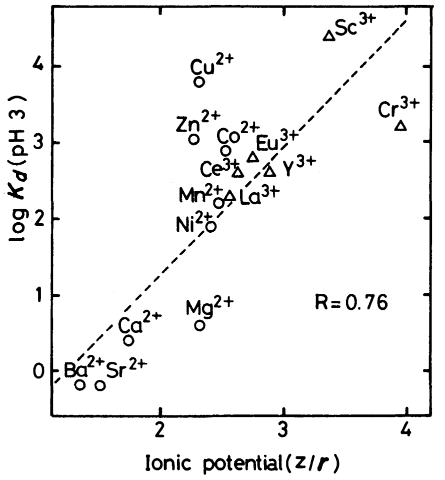

Fig. 6. Relation between logK_d and ionic potential of cation.
Ionic potential≡z/r; z: Charge of cation, r: Ionic radius (coordination number (6)).[7]
R: Correlation coefficient.

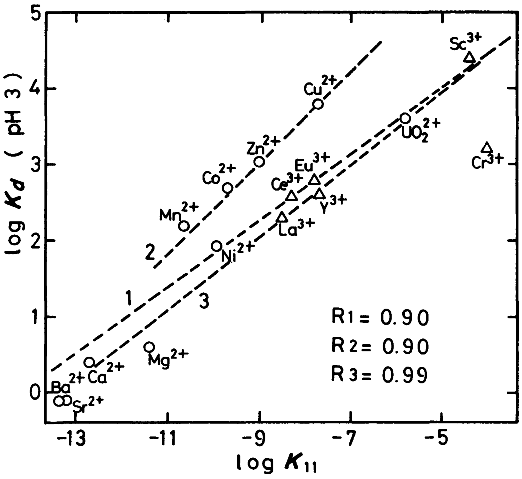

Fig. 7. Relation between logK_d and first hydrolysis constant of cation.
K_{11}: First hydrolysis constant.[8] R: Correlation coefficient.

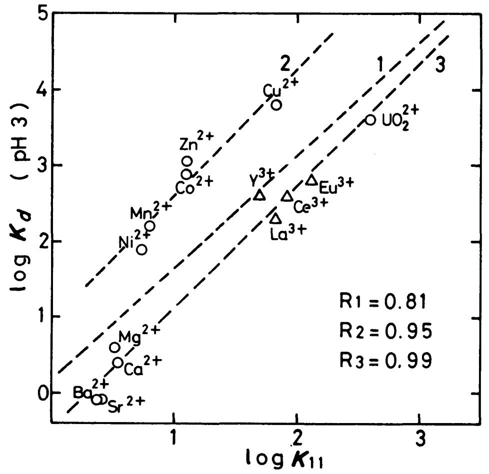

Fig. 8. Relation between log K_d and stability constant of $ML^{(n-1)+}$(L^-: CH_3COO^-).
K_{11}: Stability constant; equilibrium quotient at 25 °C and ionic strength 1.0.[9] R: Correlation coefficient.

complexes[9] (Fig. 8). As can be seen from Fig. 7, the K_d values have a strong correlation with the hydrolysis constant (R_1=0.90). Also, the softness of metal ions as Lewis acid affects the correlation: metal ions with characteristics between hard and soft acids, Cu^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, and Mn^{2+}, show larger K_d values than on hard acids, such as uranyl(VI), lanthanoid, and alkaline-earth-metal ions. When metal ions are divided into two such groups, the K_d values can be more closely related to the hydrolysis constants and the first stability constants of acetato complexes (R_2, R_3). Consequently, we can conclude that the formation of a covalent bond between the anionic sites in the exchanger and metal ions plays a part in determining the selectivity of the exchanger, along with the remote coulombic interaction.

The Separation of Actinoids from Fission Products. As the K_d values for UO_2^{2+} are considerably higher than those for other transition-metal ions, it is considered possible to use the exchanger for separating actinoids from fission products in radioactive liquid waste. For this purpose, it is necessary to examine the selectivity for actinoids in a concentrated nitrate medium. Figure 9 shows the pH-dependency of the K_d values for Th^{4+}, UO_2^{2+}, NpO_2^{+}, NpO_2^{2+}, and Am^{3+} in a 1 mol dm^{-3} nitrate medium at 50 °C. Tracer concentrations of neptunium and americium were used, whereas the concentrations of Th^{4+} and UO_2^{2+} were 9.5×10^{-5} mol dm^{-3} and 1.1×10^{-5} mol dm^{-3} respectively, because of the limited sensitivity of the analytical method used for the present experiment. If we consider the dependency of the K_d values on the concentration (Figs. 1 and 2), the K_d values for these last two elements will be higher than those in Fig. 9 when their concentrations are at a tracer level. Thus, the difference in affinity between Th^{4+} and other actinoid ions is much greater than that shown in Fig. 9. For the same reason, the U(VI) ion shows an affinity higher than that indicated in the figure. The Np(V) ion showed a K_d value higher than 10^4 cm^3 g^{-1} at pH 3 where the uptake of alkali-metal ions was negligibly small. The Np(VI) ion also showed a high affinity, similar to that of the U(VI) ion, but it did not differ so markedly from the Np(V) ion as would be expected from the difference in charge. The high affinities for uranyl and neptunyl species cannot be explained only in terms of the electrostatic interaction between the ions and the anionic sites in the exchanger; it must also be ascribed to the formation of a bond with a partially covalent character, as has been mentiond before. On the other hand, Am^{3+} and Eu^{3+} exhibited almost the same affinity as the Np(VI) ion. Similar to Sr^{2+}, Co^{2+}, or Y^{3+} in a tracer concentration, the slopes of the straight lines of the log K_d *vs.* pH plot were found to be +1 and +2 for the Np(V) and Np(VI) ions respectively. For the Np(VI) ion, the plot deviated from linearity above pH 2.6. This deviation is probably due to a hydrolysis of the ions. The slope of this plot for Am^{3+} and Eu^{3+} was not 3, but about 2, despite the tracer concentration. Korotkin reported, in his study of the hydrolysis of Am(III) at concentrations lower than 10^{-6} mol dm^{-3}, that Am(III) exists as $Am(NO_3)^{2+}$ in a 0.1 mol dm^{-3} nitrate solution.[10] Based on this view, it may be considered that the nitro complexation is responsible for the behavior of Am^{3+} and Eu^{3+} similar to that of a double-charged cation such as NpO_2^{2+}.

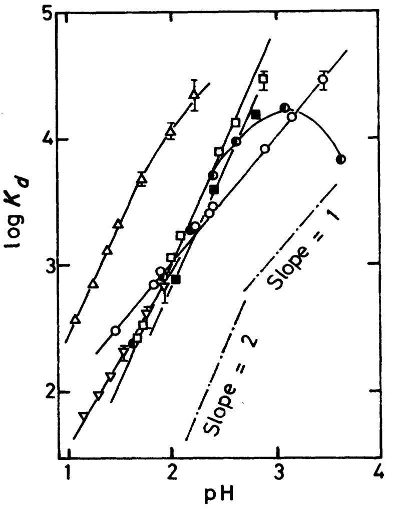

Fig. 9. Log K_d for some actinoid ions as a function of pH.
Conditions; Exchanger: 0.25 g, Solution: 20 cm^3, Ionic strength: 1.0 (HNO_3-NH_4NO_3), Temperature: 50 °C.
Concentration of cation; Δ: Th(IV) 9.5×10^{-5} mol dm^{-3}, ∇: U(VI) 1.1×10^{-5} mol dm^{-3}, ○: Np(V) tracer, ◐: Np(VI) tracer in 4×10^{-3} mol dm^{-3} $KMnO_4$, □: Am(III) tracer, ■: Eu(III) tracer.

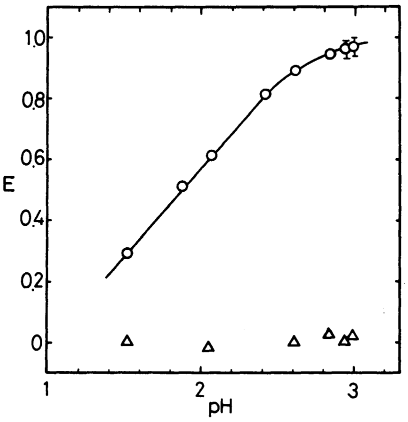

Fig. 10. Separation of UO_2^{2+}-Sr^{2+} by hydrous SnO_2 (Batch method).
Conditions; Exchanger: 0.25 g, Solution: 20 cm^3, Ionic strength: 1.0 (HNO_3-NH_4NO_3), Temperature: 50 °C.
Initial concentration; ○: UO_2^{2+} 1.1×10^{-3} mol dm^{-3} Δ: Sr^{3+} 1.0×10^{-3} mol dm^{-3}.

$$E\equiv\frac{C_{\mathrm{initial}}-C_{\mathrm{final}}}{C_{\mathrm{final}}}\ \text{or}\ \frac{a_{\mathrm{initial}}-a_{\mathrm{final}}}{a_{\mathrm{final}}};\quad C=\mu\mathrm{g\,U/cm^3},$$

a=cpm/cm^3.

As has been mentiond above, the exchanger exhibits a high selectivity for actinoids in a 1 mol dm^{-3} nitrate

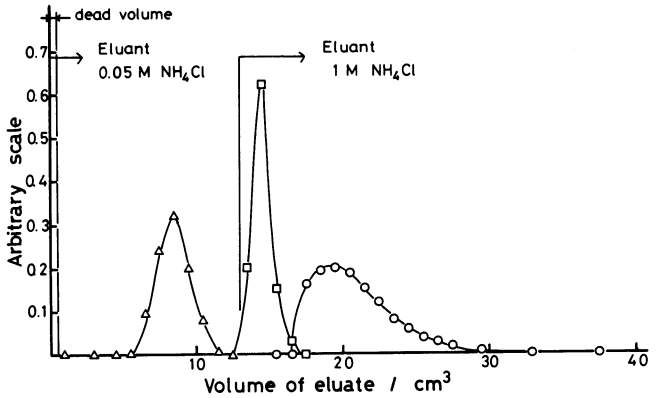

Fig. 11. Separation of Cs^+-Na^+-Li^+ by NH_4^+-form exchanger.
Column: 0.6 cmϕ×4.5 cm (100—200 mesh, 2.0 g), Elution rate: 5—6 $cm^3 h^{-1}$, Loading: 0.020 mequiv of each cation, Cation; △: Cs^+, □: Na^+, ○: Li^+.

medium, regardless of their oxidation states. Hence, actinoids may be selectively separated from such long-lived fission-products as ^{137}Cs and ^{90}Sr. The uptake of UO_2^{2+} and Sr^{2+}, both of 10^{-3} mol dm^{-3}, was measured in a 1 mol dm^{-3} nitrate medium at varying pH values, as is shown in Fig. 10. This figure shows that UO_2^{2+} could be separated nearly quantitatively from Sr^{2+} by a single-batch-operation at pH 2.8. As the exchanger exhibits a higher affinity for Sr^{2+} than for Cs^+, the quantitative separation of UO_2^{2+} will be much easier from Cs^+ than from Sr^{2+}. These facts suggest the applicability of the exchanger for separating actinoids from ^{137}Cs and ^{90}Sr, which are the major constituents of fission products in aged, high-level liquid wastes.

Separation of Li–Na–Cs and Na–Cs–Sr. In order to confirm the applicability of the exchanger to chromatographic separation, attempts were made to separate Li^+, Na^+, Cs^+, and Sr^{2+} by using the exchanger in a salt form which exhibits different affinities for these ions. The results are presented in Fig. 11. In this experiment, the exchanger in the NH_4^+ form was used. Cs^+ was quantitatively eluted with a 0.05 mol dm^{-3} NH_4Cl solution, while Na^+ and Li^+ were eluted with a 1 mol dm^{-3} NH_4Cl solution, in that order. The yield of the sodium ion was 99% at the eluate volume where Li^+ elution commenced. Lithium ions, however, showed a heavy tailing, which indicates that the neutral solution of ammonium salt was less effective. Figure 12 shows the separation of Na^+, Cs^+, and Sr^{2+}. After Cs^+ and Na^+ had been eluted with the NH_4Cl solution in a manner similar to that shown in Fig. 11, a 0.1 mol dm^{-3} $HClO_4$ solution was passed through, and then the Sr^{2+} was quantitatively eluted with 21 cm^3 of this eluant.

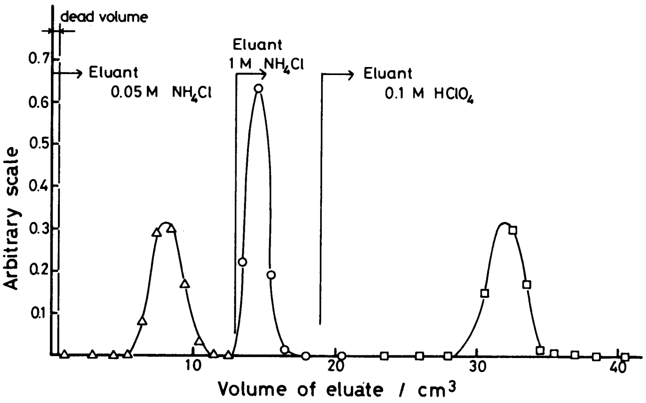

Fig. 12. Separation of Cs^+-Na^+-Sr^{2+} by NH_4^+-form exchanger.
Conditions are the same as those in Fig. 11.
Cation; △: Cs^+, ○: Na^+, □: Sr^{2+}.

References

1) Y. Inoue and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **55**, 3782 (1982); **57**, 1534 (1984).

2) J. D. Donaldson and M. J. Fuller, *J. Inorg. Nucl. Chem.*, **30**, 1083, 2841 (1968); **32**, 1703 (1970).

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

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

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

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

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

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

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

10) Yu. S. Korotkin, *Radiokhimiya*, **15**, 766 (1973).