Studies of the Hydrous Titanium Oxide Ion Exchanger. III. Distribution Coefficients and Some Applications*

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In order to understand the cation-exchange behavior of hydrous titanium oxide, the distribution coefficients of various cations were measured as a function of the pH and the ionic strength. The order of selectivity for alkali metal ions is $Cs^+ > Rb^+ > K^+ > Na^+$, for alkaline earth metal ions, $Ba^{2+} > Sr^{2+} > Ca^{2+}$, and for bivalent transition metal ions, $Zn^{2+} > Cu^{2+} > Co^{2+}$. From the dependency of the distribution coefficients on the pH, it is concluded that the apparent dissociation constants of the exchanger reported previously are not constant, but gradually decrease with the pH of the medium. By using ammonium chloride and ammonium nitrate solutions as eluents, nearly quantitative separations of ^{137}Cs—^{133}Ba and ^{137}Cs—^{89}Sr were achieved with a relatively small column.

The method of synthesizing hydrous titanium oxide as an ion exchanger proposed by the present authors has the merits of good reproducibility and the large ion-exchange capacity of the product. The adsorption of cations on this material was confirmed, through the measurement of the amount of hydrogen ion released by the uptake of a definite amount of sodium or strontium ions, to occur by cation-exchange reaction. Other important properties of the exchanger, such as its composition, stability against various chemicals, and its ion-exchange properties including ion-exchange capacity and acidity, have also been investigated, as has been described in the foregoing reports.[1,2] The studies of the application of hydrous titanium oxide have been concentrated on the recovery of uranium from seawater,[3] scarcely have been devoted to the chromatographic separations of cations except in a few cases—the separation of ^{134}Cs—^{90}Sr, ^{134}Cs—^{142}Pr,[4] and chromate and phosphate ions.[5]

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 chromatographic separation. As examples, the separations of ^{137}Cs—^{133}Ba and ^{137}Cs—^{89}Sr were performed by using ammonium nitrate and ammonium chloride solutions as eluents.

Experimental

Reagents and Apparatus. Hydrous titanium oxide was prepared by a method described previously.[2] The radioactive purity of the radioisotopes employed was confirmed in advance; all the reagents, of the highest grade of purity, were obtained from Wako Pure Chemical Industries, Ltd.

The equipment for the β- and γ-counting was the same as has been described previously.[1,2]

Distribution Coefficients. The distribution coefficients were determined in the following way, except as otherwise noted.

A half gramme of the exchanger of a desired ionic form was placed in contact, in a thermostat at 25 °C, with 50 cm³ of a suitable solution containing 2.0×10^{-4} M (1 M = 1 mol/dm³) of the cation in question until the concentration of the cation in the supernatant solution became constant (about 2 d). After filtration, the pH and the concentration of cations in the solution were measured. The amount of cation employed was less than 1% of the total ion-exchange capacity of the exchanger. The analysis of Na, K, Rb, Cs, Ca, Sr, Ba, Fe, Co, Cu, Zn, Ga, and Y was carried out radiometrically using ^{22}Na, ^{42}K, ^{86}Rb, ^{137}Cs, ^{45}Ca, ^{89}Sr, ^{133}Ba, ^{59}Fe, ^{60}Co, ^{64}Cu, ^{65}Zn, ^{72}Ga, and ^{90}Y respectively as tracers.

The distribution coefficients, K_d, were calculated by means of the following equation:

$$K_d = \frac{I-F}{F} \cdot \frac{V}{m} \quad (\text{cm}^3/\text{g}),$$

where I and F are the initial and the final radioactivity concentrations in the solution respectively; V, the volume of the solution in cm³, and m, the weight of the exchanger in g. The distribution coefficients thus obtained were not equilibrium values, as will be described later.

The total concentration of alkali metal ions was determined in the following way. To a 10-cm³ aliquot of the sample solution, an excess amount of a 6 M HCl solution was added. This was then heated to dryness and dissolved in water. Finally the alkali metal ion was indirectly determined by titrating the chloride ion with Fajans' method.

Column Operation. Two grammes of the exchanger in H^+ form (100—200 mesh) were packed in a glass column, 7 mm in inside diameter, and completely converted into the NH_4^+ form by passing through a 3% NH_4OH solution. The flow rate of the effluent was kept nearly constant, 0.08—0.13 cm³/min, throughout a series of elutions. The radioisotopes used were carrier-free except for ^{133}Ba, the specific activity of which was about 2 mCi/mg.

Results and Discussion

Distribution Coefficents. Figures 1 and 2 show the dependency of the distribution coefficients of the alkali metal and alkaline earth metal ions on the pH. Table 1 presents the distribution coefficients of the other metal ions. The order of selectivity is $Cs^+ > Rb^+ > K^+ > Na^+$ for alkali metal ions and $Ba^{2+} > Sr^{2+} > Ca^{2+}$ for alkaline earth metal ions. These series follow the same pattern as those shown by strongly acidic cation-exchange resin. For bivalent transition metal ions, the series is $Zn^{2+} > Cu^{2+} > Co^{2+}$, assuming that the dependency of the distribution coefficients on the pH is about the same as that for alkaline earth metal ions.

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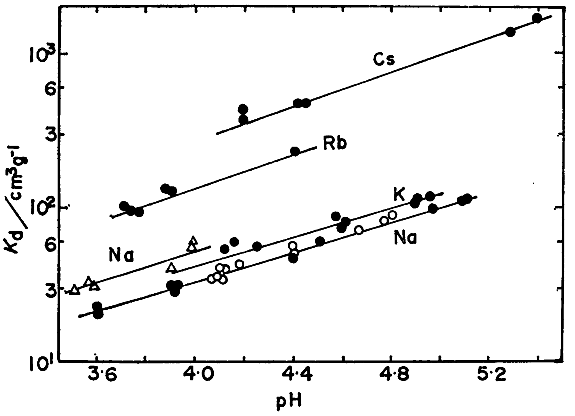

Fig. 1. Distribution coefficients for alkali metal ions ($RH+N^+ \rightarrow H^+ + RN$). Concentration of cations; Na^+, Rb^+, Cs^+: 2.0×10^{-4} M, K^+: 4.2×10^{-4} M. Exchanger; H^+ form. ○: 35—65 mesh, 500 mg, ●: 100—200 mesh, 500 mg, △: 100—200 mesh, 100 mg.

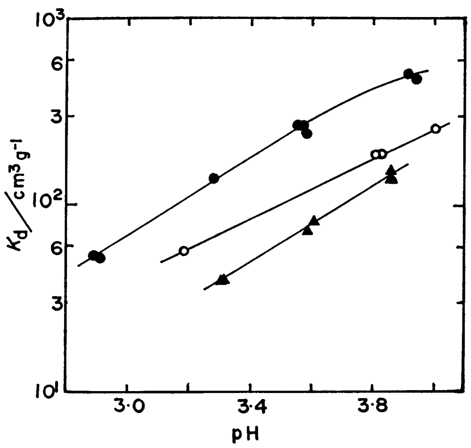

Fig. 2. Distribution coefficients for alkaline earth metal ions ($2RH+N^{2+} \rightarrow 2H^+ + R_2N$).
Concentration of cations; 2.0×10^{-4} M, ●: Ba^{2+}, ○: Sr^{2+}, ▲: Ca^{2+}.
Exchanger; H^+ form 100—200 mesh, 500 mg.

Table 1. Distribution coefficients of some cations

Ion	pH	K_d / $cm^3 g^{-1}$
Co^{2+}	3.62	$(8.7 \pm 0.2) \times 10$
	3.82	$(1.50 \pm 0.03) \times 10^2$
	3.92	$(2.05 \pm 0.04) \times 10^2$
Cu^{2+}	3.70	$(2.50 \pm 0.04) \times 10^2$
Zn^{2+}	2.19	6.7 ± 2.5
	3.96	$(4.7 \pm 0.1) \times 10^2$
Fe^{2+}	1.30	≈ 0
	2.43	4.8 ± 0.9
Fe^{3+}	1.08	4.2 ± 2.0
	1.40	$(2.5 \pm 0.2) \times 10$
Ga^{3+}	3.48	$(9.3 \pm 0.3) \times 10$
	3.79	$(4.0 \pm 0.3) \times 10$
Y^{3+}	3.41	$(3.7 \pm 0.3) \times 10$
	3.68	$(1.56 \pm 0.05) \times 10^2$
	3.83	$(3.8 \pm 0.3) \times 10^2$

The selectivity series for alkali metal ions is the same as that found by Heitner-Wirguin *et al.*,[6] but the order for Co^{2+} and Cu^{2+} is reversed. The possible reasons for this conflicting result are as follows: (1) The concentration of the cations adopted by them is 0.01 M, which is considerably higher than that used in the present experiment; (2) Their ion exchanger contains about 4% of oxalate as an impurity; (3) The properties of the exchangers themselves differ from each other as a result of the difference in the synthetic methods. If the oxalate groups contained in their ion exchanger are considered to act as exchanging sites, the improvement in the selectivity for an ion will increase its prominence with the stability of the oxalato-complex. Since the stability constant of oxalato-complex of Cu^{2+} is not larger than that of Co^{2+},[7] the second possibility seems unlikely. As the inversion of the selectivity cannot be considered to occur in such a low concentration as this, the third possibility appears most promising.

Figure 1 also shows that the distribution coefficients of the sodium ion did not depend on the particle size of the ion exchanger. This observation suggests that the exchanging sites are distributed uniformly within the body of the exchanger, which corresponds to the fact that the ion-exchange capacity is independent of the particle size of the ion exchanger, as has been pointed out previously.[1] The distribution coefficients of the sodium ion were affected by the ratio between the volume of the liquid phase and the weight of the exchanger. This means that the curves in Fig. 1 do not show true equilibrium values, although two phases have been in contact with each other until the adsorbed amount of the sodium ion becomes constant.

Figure 3 indicates that a linear relationship held between the logarithms of the distribution coefficients of the cesium ion on the ion exchanger in the Na^+ form and the concentration of the sodium ion at a constant pH. The slope of the line increased with the pH until it reached unity at pH 7. When the solution became more basic than this, essentially the same relation was obtained at any pH. Figure 4 shows the relation at

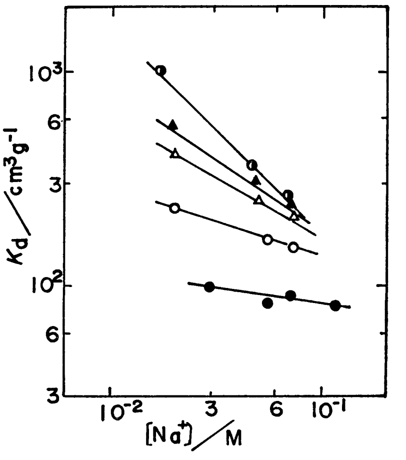

Fig. 3. Dependency of distribution coefficients of Cs^+ on the concentration of Na^+ ($RNa+Cs^+ \rightarrow RCs+Na^+$). Exchanger; Na^+ form, 100—200 mesh, 500 mg. pH; ●: 3, ○: 4, △: 5, ▲: 6, ◑: 7.

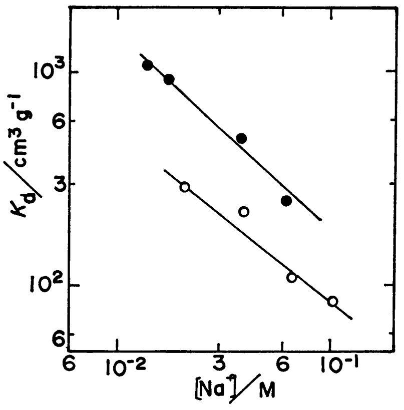

Fig. 4. Dependency of distribution coefficients of Cs^+ on the concentration of Na^+ at pH 8. Exchanger; Na^+ form, 100—200 mesh, 500 mg.
○: Forward reaction ($RNa+Cs^+ \rightarrow RCs+Na^+$),
●: reverse reaction ($RCs+Na^+ \rightarrow RNa+Cs^+$).

pH 8 as an example. The distribution coefficients obtained from the forward- and the reverse reactions did not agree with each other. Therefore, the reaction never reached equilibrium, as in the H^+-Na^+ exchange reaction mentioned above. This introduces the problem that it is difficult to discuss the relation in terms of the theory of chemical equilibrium. However, if the curves determined from the forward- and the reverse reactions run parallel with each other, it is natural to assume that the curve in true equilibrium may be somewhere between, and parallel with, them. Therefore, one can discuss the dependency of the apparent distribution coefficients on various factors from the viewpoint of the chemical equilibrium theory with due regard to the limitation imposed by the assumption.

The ion-exchange reaction between the monovalent cation, M^+, and the n-valent cation, N^{n+}, and the equilibrium constant can be expressed by the following equations:

$$nMR + N^{n+} = NR_n + nM^+, \tag{1}$$

$$K = \frac{a_{NR_n}(a_M)^n}{(a_{MR})^n a_N} = \frac{f_N[NR_n](a_M)^n}{\gamma_N[N^{n+}](a_{MR})^n}, \tag{2}$$

where a denotes the activity, R^-, the matrix anion of the exchanger, [ ], the concentration, f_N, the activity coefficient of the N^{n+} ion in the exchanger, and γ_N, the activity coefficient of the N^{n+} ion in the solution.

The distribution coefficient, K_d, of the N^{n+} ion is expressed by this equation:

$$K_d = \frac{[NR_n]}{[N^{n+}]} \quad (cm^3/g). \tag{3}$$

By combining Eqs. 2 and 3, we obtain

$$K = K_d \frac{f_N(a_M)^n}{\gamma_N(a_{MR})^n}. \tag{4}$$

When the amount of N^{n+} is negligible as compared with that of M^+, a_{MR} and f_N are regarded as constant. Moreover, γ_N is also constant if the ionic strength of the solution is kept constant. Under such conditions, the following equation holds, by taking the logarithm of Eq. 4:

$$\log K_d = \text{const} - n \log a_M. \tag{5}$$

That is, if the logarithm of the distribution coefficients of N^{n+} is plotted against pH, a straight line possessing the slope of n should be obtained.

The results in Figs. 1 and 2 cannot be explained by this argument because the slopes are about a half of the valency of the exchanging cation, N^{n+}. Since the experimental condition satisfies the assumption for deducing Eq. 5, this contradiction compels us to consider that K must depend on the pH.

If the solution is acidic enough to permit the participation of only ion-exchange sites with the lowest apparent pK_a value[2] in the ion-exchange reaction, and if the cations to be exchanged are present as hydrated ions, it can be regarded that the reaction of Eq. 1 on the H^+-form exchanger is a combination of the following two reactions:

$$HR = H^+ + R^-, \qquad K_H = \frac{a_H a_R}{a_{HR}}, \tag{6}$$

$$nR^- + N^{n+} = NR_n, \qquad K_N = \frac{a_{NR_n}}{(a_R)^n a_N}. \tag{7}$$

Accordingly,

$$K = K_H{}^n \cdot K_N. \tag{8}$$

Equation 6 represents the acid dissociation of the exchanger, and Eq. 7, the reaction of the anionic form of the exchanger with the exchanging cation, N^{n+}. As a similar conflict between Eq. 5 and the experimental results was observed for every kind of ion examined, it was considered that the contradiction was attributable to the gradual decrease in the acid dissociation constant, K_H, of the ion exchanger with the pH. Accordingly, it is considered that the pK_i described in the previous paper[2] is not constant, but a certain average value.

If this discussion holds true, the relation of Eq. 5 should hold in the ion-exchange reaction between alkali metal ions in an alkaline medium, where the acid dissociation can be ignored. In the ion-exchange reaction between Na^+ and Cs^+ in a basic medium, the results obeyed Eq. 5 as was expected (Fig. 4).

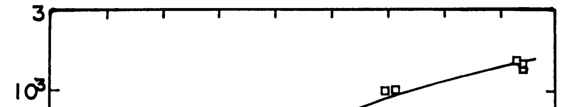

Fig. 5. Dependency of distribution coefficients of Cs^+ on pH ($RNa+Cs^+ \rightarrow RCs+Na^+$).
Exchanger; Na^+ form, 100—200 mesh, 500 mg. I/mol dm^{-3}; □: 0.012—0.029, ○: 0.050—0.062, △: 0.063—0.080, ●: 0.11—0.12.

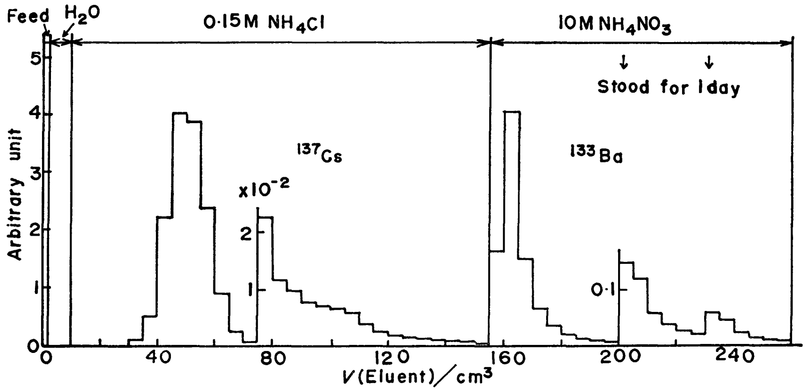

Fig. 6. Separation of ^{137}Cs and ^{133}Ba.
Column: 0.7 cm $\phi \times 3.8$ cm (NH_4^+ form, 100—200 mesh, 2 g).
Flow rate: 0.10—0.13 cm^3/min.

The relationship between the distribution coefficient of the cesium ion on the exchanger in the Na^+ form and the pH is compatible with the argument presented above, as is shown in Fig. 5.

Gallium behaved differently; that is, the distribution coefficient decreased with the pH. This unusual behavior is attributable to the hydrolysis of the ion, because the gallium ion hydrolyzes at a pH value above 2.

Separations of ^{137}Cs—^{89}Sr and ^{137}Cs—^{133}Ba. In order to confirm that the hydrous titanium oxide ion exchanger could be used for the chromatographic separation, an attempt was made to separate the long-lived fission products, Cs, Sr, and Ba ions.

The results for the ^{137}Cs—^{133}Ba separation are represented in Fig. 6. Cs^+ and Ba^{2+} were eluted with 0.15 M ammonium chloride and 10 M ammonium nitrate solutions respectively. The sharp elution peaks were followed by slight tailings. ^{137}Cs could be quantitatively recovered by the use of 150 cm^3 of the eluent, but the recovery of ^{133}Ba was only 94% even after passing through 160 cm^3 of the eluent.

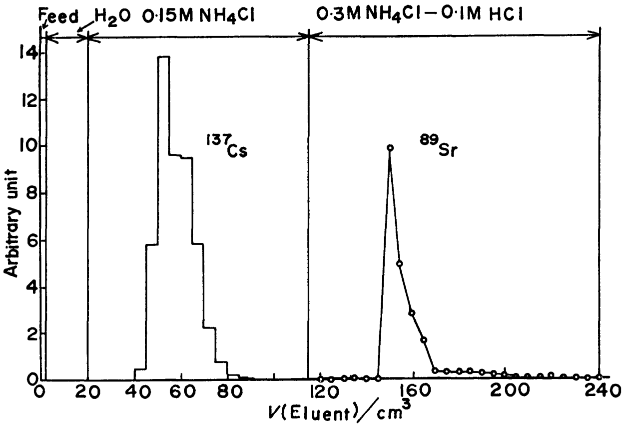

Fig. 7. Separation of ^{137}Cs and ^{89}Sr.
Column: 0.7 cm $\phi \times 3.8$ cm (NH_4^+ form, 100—200 mesh, 2 g). Flow rate: 0.08 cm^3/min.

Figure 7 shows the separation of ^{137}Cs—^{89}Sr. After the ^{137}Cs had been eluted by a 0.15 M ammonium chloride solution in a manner similar to that shown in Fig. 6, a 0.3 M ammonium chloride–0.1 M hydrogen chloride solution was passed through. In this case, also, some tailings appeared after the sharp elution peaks. ^{89}Sr, however, could be recovered nearly quantitatively by letting 125 cm^3 of this eluent flow through.

Therefore, we can conclude that the complete separation of ^{137}Cs from ^{89}Sr is possible.

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