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Studies of a Hydrous Tin(IV) Oxide Ion Exchanger. VI. Rate of the Isotopic Exchange of Cobalt Ions between the Exchanger in the Cobalt Form and Aqueous Solutions

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The isotopic exchange rate of cobalt ions between a hydrous tin(IV) oxide ion exchanger and aqueous solutions was radiochemically measured in order to obtain fundamental data which could be useful for elucidating the ion-exchange kinetics of the material for the transition metal elements. This rate can be understood by considering that the cobalt in an exchanger exists as three species: (A_1) dissociated ions which can diffuse in the exchanger particles; (A_2) weakly bound ions to the exchange sites, which are in local equilibrium with A_1; and (B) covalently fixed ions to the exchange sites, which are exchanged very slowly with A_1. At a small ratio of the amount of B to the total amount of cobalt sorbed on the exchanger, the rate is controlled by the diffusion of A_1, with effective diffusion coefficient, $\overline{D}_{\mathrm{eff}}$, a value which depends on the concentration ratio of A_2 to A_1. When B predominates over A, the concentration ratio of B to A_1 greatly affects $\overline{D}_{\mathrm{eff}}$. The values of $\overline{D}_{\mathrm{eff}}$ and their activation energy (20 kJ mol^{-1}) were also estimated.

An investigation of ion-exchange kinetics is very important for understanding the ion-exchange mechanism of hydrous metal oxides. Measurements of the isotopic exchange rates of cations between exchangers and aqueous solutions provide fundamental data which are useful for elucidating ion-exchange kinetics. As one part of such a study in our series, radiochemical experiments were previously undertaken in order to measure the isotopic-exchange rate of sodium ions between hydrous tin(IV) oxide in the sodium form and the aqueous solutions of sodium salts. The rate-controlling step of the reaction was concluded to be the diffusion of ions in the primary particles, which were formed during the initial stage of precipitation and aggregated to form an oxide gel.[1] On the other hand, a study of the ion-exchange equilibrium revealed that transition metal ions, dissimilar to sodium ions, were sorbed on the exchanger by a bond which is partially covalent in character, rather than by a pure ionic bond.[2] Hence, the transition metal ions are expected to differ from sodium ions regarding their kinetic behavior. Conversely, a kinetic study will intensify the conclusion derived from the equilibrium studies made on the ion-exchange reactions of transition metal ions.

This paper deals with the isotopic exchange rates of cobalt ions between hydrous tin(IV) oxide in the cobalt form with various particle sizes and the aqueous solutions of cobalt salts with varying concentrations.

Experimental

Preparation of the Exchanger in the Cobalt Form Spiked with ^{60}Co. The hydrous tin(IV) oxide prepared by a previously recommended method was classified into three particle sizes by using Japan Industrial Standard sieves; it was then converted to the hydrogen form by treating it with a 0.1 mol dm^{-3} HCl solution.[3] After being washed with water, the exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl solution (relative humidity, 79%). Table 1 shows the particle size and some properties of each sample. The average particle radius was estimated by approximating the particle shape as a sphere, from the particle-size distribution measured in a 84.5 wt% glycerol solution by using a Seishin Enterprise Micron-Photo-Sizer (Model SKC-2000S). The specific surface area of the sample, after being heated at 110 °C to constant weight, was determined by the BET method (N_2 adsorption at −196 °C) using a Yanagimoto Surface Area Measuring Apparatus (Model GSA-10).

The exchanger in the hydrogen form was converted to the cobalt form(while being simultaneously labeled with ^{60}Co) in the following way (unless otherwise noted). The exchanger in the hydrogen form (0.30 g) was equilibrated for 10 d with 10 cm^3 of $Co(NO_3)_2$ solution containing ^{60}Co as a tracer with the same chemical composition and temperature as those used for the rate measurement. The acidity of the solution was adjusted by HNO_3 and by a mixture of 2-

Table 1. Particle Size and Some Properties of Samples

Particle size	Average radius	Density	Ion-exchange capacity[2)]	Composition[3)]	Specific surface area
mesh[1)]	μm	g cm^{-3}	mmol g^{-1}	mol H_2O (mol SnO_2)$^{-1}$	m^2 g^{-1}
−70+100	98±4	3.48±0.05	—	—	174±8
−100+145	70±3	3.44±0.05	0.67±0.02	2.20±0.03	180±5
−145+200	47±3	3.52±0.08	—	—	178±8

1) Japan Industrial Standard mesh. 2) Exchange capacity for Co^{2+} at pH 5 in 0.1 mol dm^{-3} $Co(NO_3)_2$ solution. 3) The water content was determined from the weight loss at 850 °C.

morpholinoethanesulfonic acid (MES) and NaOH, respectively, when the rate was measured at a pH lower or higher than 4. The MES-NaOH buffer solution had been confirmed to exert no effect on either the number of the cobalt ions taken up by the exchanger or the rate of the isotopic exchange. After having been separated from the solution by using a sintered glass filter under suction, the exchanger was used for the rate measurement.

The number of cobalt ions taken up by the exchanger was determined as follows. When the initial cobalt-ion concentration in the solution was lower than 0.045 mol dm^{-3}, the number of the ions taken up by the exchanger was calculated from the difference between the initial and final radioactivities present in the solution. When the initial cobalt ion concentration was higher than 0.045 mol dm^{-3}, the exchanger was dissolved in a 2.6 mol dm^{-3} hydrobromic acid solution containing 10% bromine, followed by a spectrophotometric determination of the cobalt ions in the solution, by using ammonium thiocyanate as a coloring reagent. The increase in the number of cobalt ions taken up by the exchanger with pH in the solution became sharp when the pH exceeded 5, indicating the commencement of hydrolysis of the cobalt ions in the solution. The rate was then measured at pH lower than 5.

Measurement of the Isotopic Exchange Rate. The rate was measured in solutions with the same composition and temperature as those used for converting the exchanger to the cobalt form, by using the same apparatus as before.[4] Otherwise, an ion-exchange reaction would occur between hydrogen and cobalt ions, since the ion-exchange capacity for cobalt ions depends strongly on both the pH and the cobalt-ion concentration of the solution, and to some degree the temperature. A portion(<0.3 g) of the sample was placed in a cage and immersed in 200 cm^3 of a solution with the desired composition while the cage was being rotated. The frequency of revolution was measured with a Yokogawa, Model 2607, Photo Tachometer. The solution had been adjusted in advance to a constant (temperature within ±0.1 °C). Aliquots of the solution(0.2 cm^3) were removed at appropriate time intervals in order to measure the radioactivity with a well-type NaI(Tl)scintillation counter (Aloka Model ARC-361). The time of contact of the exchanger with the solution was taken as being the time elapsed between the immersion of the cage and the withdrawal of an aliquot of the solution. The fractional attainment of equilibrium, $F=C_t/C_\infty$, was calculated from these results; here, C_t is the total radioactivity of the solution at time t and C_∞ at $t=\infty$. C_∞ was calculated by $C_\infty=C_iM/(M+m)$, where C_i is the initial total radioactivity of the exchanger; m and M are the total amounts of cobalt ions in the exchanger and in the solution, respectively. Although the rate was measured by a batch method, an infinite solution-volume approximation was closely obeyed under the present experimental conditions; the ratio of the total amount of cobalt ions in the exchanger to that in solution was less than 0.05.

Results and Discussion

In order to study the efficiency of agitation, the effect of the stirring rate on the half-exchange time was examined at 30 °C for a pH 2.4 solution of 0.1 mol dm^{-3} Co^{2+}, by using exchanger particles with an average radius of 98 μm.

The time required for a half-exchange was independent of the stirring rate (from 950 to 1500 min^{-1}). It was also confirmed that no particle was broken during agitation at revolution rates of up to 1500 min^{-1}. On the basis of these results, a revolution rate of 1300 min^{-1} was adopted throughout the experiments.

Figure 1 shows a representative rate curve. As can be seen from the figure, about 80 percent of the cobalt in the exchanger was rapidly exchanged with Co^{2+} in the solution; the remainder was never exchanged during an experimental period of 2 d. This fact suggests the existence of at least two kinds of cobalt species sorbed on the exchanger: rapidly and hardly exchangeable species. For the rapidly exchangeable species, plots of F vs. $\sqrt{t}$ follow a straight line passing through the point of origin in the region $F<0.3$, indicating that the exchange rate is controlled by the diffusion of the ions within the particles (particle diffusion).[5] This is compatible with the results from an "interruption test": when the exchanger was removed from the solution for 1 h and then reimmersed, the rate immediately after reimmersion was greater than that prior to interruption.[6]

Figure 2 shows the influence of the amount of cobalt in the exchanger on the isotopic exchange rate. In any case, plots of F vs. $\sqrt{t}$ gave straight lines passing through the point of origin during the early stage of the exchange reaction. The slopes of the straigt lines, however, decreased with increasing amount of cobalt in the exchangers. This observation cannot be explained by the diffusion of a rapidly

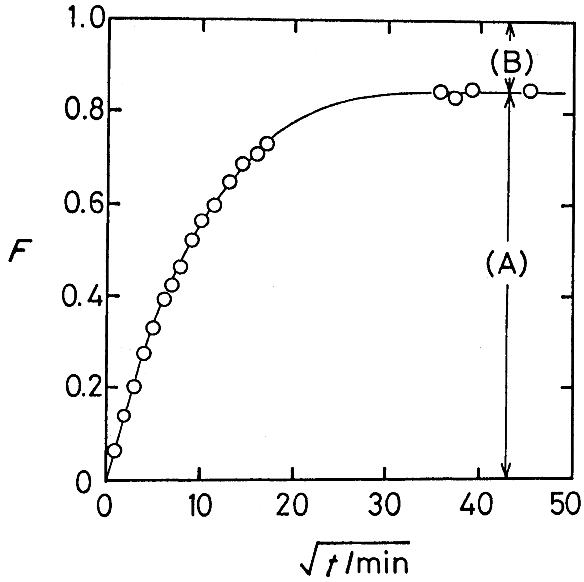

Fig. 1. Isotopic exchange rate of cobalt ions between hydrous tin(IV) oxide in the cobalt form and aqueous solutions. Particle radius, 98±4 μm; temperature, 30 °C; 0.1 mol dm^{-3} Co(NO$_3$)$_2$; pH, 2.4. (A): Fraction of rapidly exchangeable cobalt species. (B): Fraction of hardly exchangeable cobalt species.

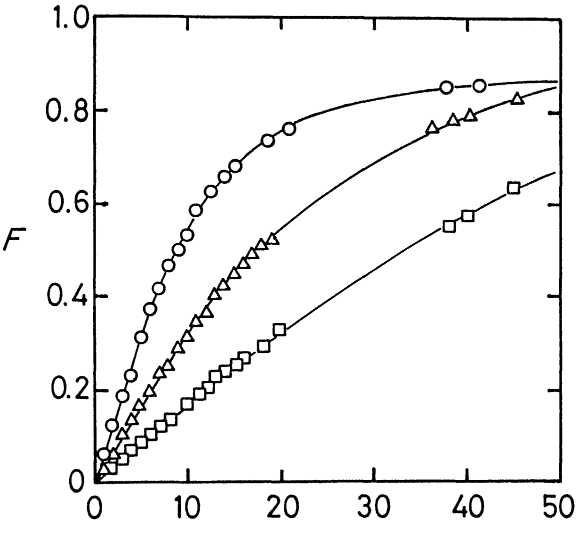

Fig. 2. Effect of the amount of cobalt sorbed in the exchanger on the isotopic exchange rate. Particle radius, 98±4 μm; temperature, 30 °C; 0.1 mol dm^{-3} $Co(NO_3)_2$. Amount of cobalt in the exchanger/mmol g^{-1}, ○: 0.14 (pH=2.4); △: 0.34 (pH=3.3); □: 0.67 (pH=4.9).

exchangeable species with a constant diffusion coefficient, but by assuming the coexistence of a nondiffusible species, which equilibrates with the diffusible species. The exchanger then contains three kinds of cobalt species, as follows:

A_1: Dissociated cobalt ions which can diffuse in the exchanger particles(the dissociated cobalt).

A_2: Cobalt bound weakly(possibly ionically) to the exchange sites(the bound cobalt). This species is always in equilibrium with the dissociated cobalt.

B : Cobalt fixed strongly(possibly covalently) to the exchange sites (the fixed cobalt). This species exchanges very slowly with the dissociated cobalt, much slower than the diffusion of the dissociated cobalt.

The isotopic exchange reaction of cobalt ions is expressed by $\overline{Co^*}+Co=\overline{Co}+Co^*$, where a bar indicates the exchanger phase, an asterisk shows the cobalt spiked with ^{60}Co, which is initially in the exchanger phase. The rate of the reaction can be conveniently analyzed by dividing it into three cases.

The first is that there exists A_1 and B in the exchanger. In this case, A_1 may be the only species involved in the reaction, as is suggested from Fig. 1. In spherical exchanger particles, the change of $[\overline{A_1(r,t)^*}]$ and F with time are given by

$$\partial[\overline{A_1(r,t)^*}]/\partial t=\mathrm{div}\,(\overline{D}\ \mathrm{grad}\,[\overline{A_1(r,t)^*}]), \tag{1}$$

and

$$F=\frac{\int_V\int_0^t[\overline{A_1(r,t)^*}]\,\mathrm{d}t\mathrm{d}V}{\int_V\int_0^\infty[\overline{A_1(r,t)^*}]\,\mathrm{d}t\mathrm{d}V+\int_V\int_0^\infty[\overline{B(r,t)^*}]\,\mathrm{d}t\mathrm{d}V}, \tag{2}$$

where $[\overline{A_1(r,t)^*}]$ and $[\overline{B(r,t)^*}]$, respectively, refer to the local concentrations of A_1 and B of the spiked cobalt at a distance r from the center of the particles at time t, $\overline{D}$, the diffusion coefficient of the dissociated cobalt(A_1) in the exchanger, and, V, the volume of the exchanger phase. Since the reaction is performed approximately under the infinite solution volume condition, we can set

$$\int_V\int_0^\infty[\overline{A_1(r,t)^*}]\,\mathrm{d}t\mathrm{d}V=4\pi r_0^3[\overline{A_1^*}]_0/3, \tag{3}$$

and

$$\int_V\int_0^\infty[\overline{B(r,t)^*}]\,\mathrm{d}t\mathrm{d}V=4\pi r_0^3[\overline{B^*}]_0/3, \tag{4}$$

where $[\overline{\cdot\cdot}]_0$ refers to the average concentration of the enclosed species in the exchanger phase at time 0, and r_0 is the radius of the exchanger. The average concentration of the spiked A_1 at time t is expressed by

$$[\overline{A_1(t)^*}]=3\int_V[\overline{A_1(r,t)^*}]\,\mathrm{d}V/4\pi r_0^3.$$

This corresponds to the specific radioactivity of A_1 in the exchanger phase and can be experimentally determined by measuring the radioactivity of the solutions at time t. When Eq. 1 is solved under the conditions of no radioactivity in the solution at time 0, and of infinite solution volume, we obtain[7)]

$$\int_V\int_0^t[\overline{A_1(r,t)^*}]\,\mathrm{d}t\mathrm{d}V=\frac{4\pi r_0^3[\overline{A_1^*}]_0}{3}\left[1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-En^2t)\right], \tag{5}$$

where

$$E=\overline{D}\,\pi^2/r_0^2. \tag{6}$$

Substituting Eqs. 3, 4 and 5 to Eq. 2, we obtain

$$F=\frac{1}{R_1+1}\left[1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-En^2t)\right], \tag{7}$$

where

$$R_1=[\overline{B^*}]_0/[\overline{A_1^*}]_0. \tag{8}$$

Since the isotopic effect of cobalt ions can be ignored, the following relation holds:

$$R_1=[\overline{B^*}]_0/[\overline{A_1^*}]_0=[\overline{B}]/[\overline{A_1}], \tag{9}$$

where $[\overline{\cdot\cdot}]$ refers to the equilibrium concentration of the enclosed species in the exchanger phase. The concentration quotient, R_1, depends on such experimental conditions as the pH, temperature and cobalt-ion concentration in the solution ($[Co^{2+}]$).

The second case is that there exist only the A_1 and A_2 species in the exchanger. Since the exchange reaction between these species is much faster than the diffusion of A_1 in the exchanger, the local concentration of A_2 is always in equilibrium with that of A_1. Furthermore, the specific radioactivity of A_1 is always equal to that of A_2 at any place in the exchanger particles:

$$R_2=[\overline{A_2(r,t)^*}]/[\overline{A_1(r,t)^*}]=[\overline{A_2}]/[\overline{A_1}]. \tag{10}$$

Similar to R_1, the concentration quotient, R_2, depends on the experimental conditions, but is constant throughout a given experimental run. As J. Grank deduced, the rate equation of the isotopic exchange reaction under these conditions is[7]

$$\partial[\overline{A_1(r,t)^*}]/\partial t = \mathrm{div}\,(\overline{D}_{\mathrm{eff}}\,\mathrm{grad}\,[\overline{A_1(r,t)^*}]), \tag{11}$$

where

$$\overline{D}_{\mathrm{eff}} = \overline{D}/(R_2+1). \tag{12}$$

Here, $\overline{D}_{\mathrm{eff}}$ is the effective diffusion coefficient of the ions. The fractional attainment of equilibrium, F, can be obtained by solving Eq. 11 using the same initial and boundary conditions as those used in Eq. 7,

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-E'n^2t), \tag{13}$$

where

$$E' = \overline{D}_{\mathrm{eff}}\,\pi^2/r_0^2. \tag{14}$$

Equation 13 implies that the rate of isotopic exchange accompanying the equilibrium between the dissociated cobalt (A_1) and the bound cobalt(A_2) is controlled by the diffusion of the dissociated cobalt in the exchanger particles with the effective diffusion coefficient: that is, the diffusion coefficient of the dissociated cobalt modified by the concentration ratio between A_1 and A_2.

From Figs. 1 and 2, the isotopic exchange reaction of cobalt ions between the hydrous tin(IV) oxide in the cobalt form and the aqueous solutions of cobalt salts is considered to be a mixed type of the two cases discussed above. The fractional attainment of equilibrium of the isotopic exchange reaction is then

$$F = \frac{R_2+1}{R_1+R_2+1}\left[1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-E'n^2t)\right], \tag{15}$$

by combining Eq. 7 with Eq. 13.

The values of $(R_2+1)/(R_1+R_2+1)$ and E' can be determined by fitting the experimental F vs. t plots to Eq. 15, by using the nonlinear least-squares method. The fraction of B to the total cobalt in the exchanger was then evaluated from $1-(R_2+1)/(R_1+R_2+1)$ and $\overline{D}_{\mathrm{eff}}$ from Eq. 14 by using the particle radius shown in Table 1. Hereafter, the cobalt species exchanged within 2 d is collectively called the exchangeable species; its equilibrium concentration is $[\overline{A}]=[\overline{A_1}]+[\overline{A_2}]$.

Figure 3 shows the effect of particle size on the rate in a 0.1 mol dm^{-3} cobalt solution. For any particle size, the experimental data agreed well with Eq. 15 by applying the values of $(R_2+1)/(R_1+R_2+1)$ and E' required to give the best fit. As is shown in Fig. 4, E', thus obtained, was inversely proportional to the square of the particle radius, as expected from Eq. 14. This indicates that the particle diffusion of the dissociated cobalt controls the isotopic exchange rate of the exchangeable species. In this case, the effective diffusion coefficient of the exchangeable species, $\overline{D}_{\mathrm{eff}}$, should be used instead of the diffusion coefficient of the dissociated cobalt, $\overline{D}$.

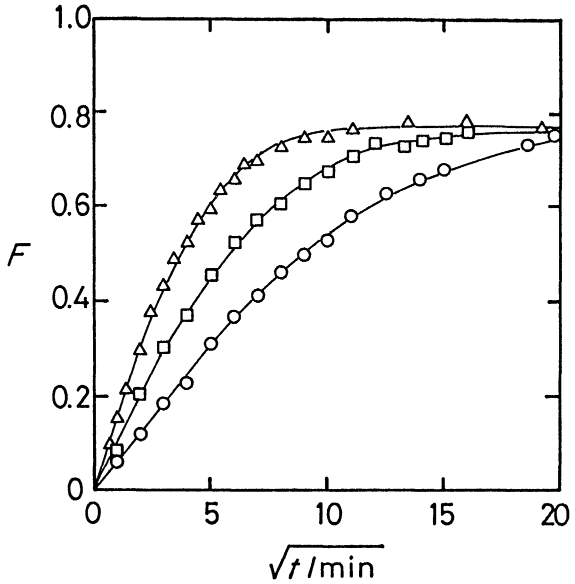

Fig. 3. Effect of particle size on the isotopic exchange rate. Temperature, 30 °C; 0.1 mol dm^{-3} Co(NO$_3$)$_2$; pH, 2.4. Particle radius/μm; ○: 98±4; □: 70±3; △: 47±3. ——: Curves calculated by Eq. 15.

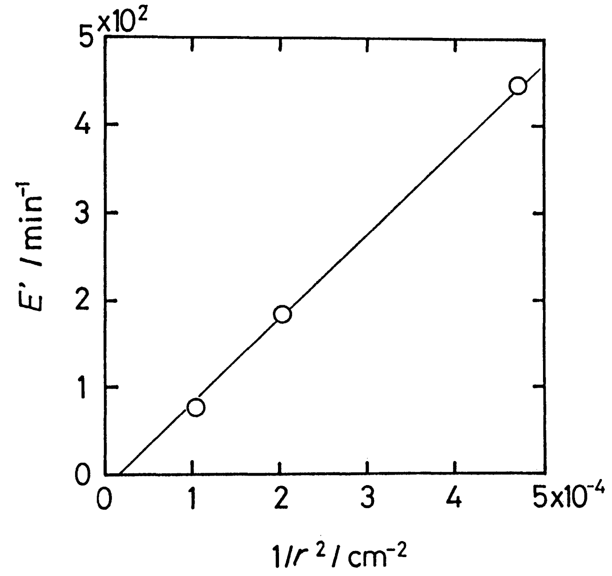

Fig. 4. Relation between particle radius and E'. Temperature, 30 °C; 0.1 mol dm^{-3} Co(NO$_3$)$_2$; pH, 2.4.

The ratio of the amount of the fixed cobalt to the total amount of cobalt sorbed on the exchanger(B-fraction) was evaluated as a function of pH, as is shown in Fig. 5. The B-fraction 0.47±0.04 at pH 1.5 decreased with increasing pH, reaching nearly zero at pH 4.2. In order to determine the rate of the exchange reaction between the dissociated cobalt(A_1)

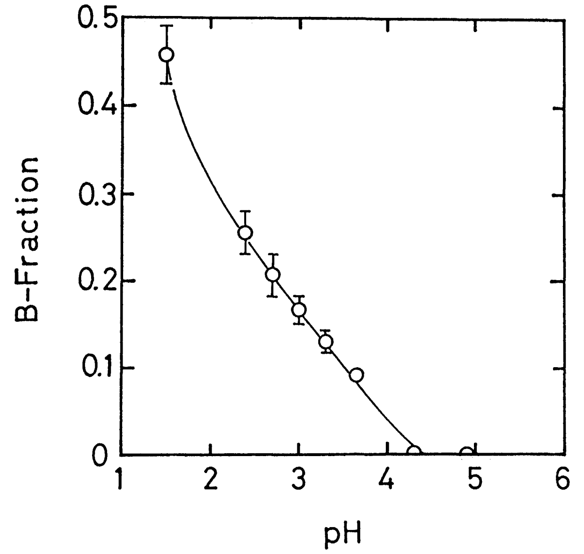

Fig. 5. The pH dependence of B-fraction (the ratio of the fixed cobalt to the total cobalt sorbed on the exchanger). Temperature, 30 °C; 0.1 mol dm^{-3} Co(NO$_3$)$_2$.

Table 2. Influence of the Type of ^{60}Co Labeling on B-Fraction and $\overline{D}_{\mathrm{eff}}$

Duration of labeling with ^{60}Co	B-fraction1)	$\overline{D}_{\mathrm{eff}}$ 2)
d		cm^2 s^{-1}
3	0.06±0.01	(1.1±0.1)×10^{-9}
15	0.12±0.02	(1.2±0.1)×10^{-9}
S3)	0.25±0.03	(1.2±0.1)×10^{-9}

Temperature, 30 °C; 0.10 mol dm^{-3} Co(NO$_3$)$_2$; pH, 2.4. 1) The ratio of the hardly exchangeable ^{60}Co to the total ^{60}Co in the exchanger. 2) The effective diffusion coefficient of cobalt ions in the exchanger. 3) The exchanger was converted to the cobalt form, simultaneously labeled with ^{60}Co.

and the fixed cobalt(B) in the exchanger phase, a comparison of the B-fractions of ^{60}Co was made for samples prepared by two types of ^{60}Co labeling: one was labeled for some time after the conversion to the cobalt form, and the other was labeled simultaneously with the conversion. $\overline{D}_{\mathrm{eff}}$ for these samples were also evaluated. The conversion and the labeling were performed at 30 °C by using a 0.10 mol dm^{-3} cobalt solution with pH 2.4. The results are shown in Table 2, which show that the exchange rate of the exchangeable species was independent of the type of labeling. The exchange between A$_1$ and B was very slow compared with the diffusion of A$_1$, since the B-fraction of the ^{60}Co in the exchanger labeled for 3 d after the conversion was only about 20 percent of that in the exchanger labeled simultaneously with conversion.

In the high pH region, the reaction between A$_1$ and B in the exchanger is considered to have little effect on the initial rate because of very small value of the B-fraction in this region(Fig. 5). In this case, the B-fraction and the $\overline{D}_{\mathrm{eff}}$ of cobalt ions, respectively, can be determined from the plateau and the initial slope of F vs. $\sqrt{t}$ plots, which were fitted to Eq. 15.

In the low pH region, where the B-fraction is large, the exchange between A$_1$ and B possibly affects the isotopic exchange rate, since any decrease of the specific radioactivity of B-fraction during the experimental period of 2 d(about 8 percent of that of total cobalt in the exchanger) cannot be ignored. This causes some ambiguity in the evaluation of the B-fraction. In spite of this fact, the B-fraction obtained by curve-fitting can be taken as an adequate value, since the procedure, itself, leads to an error(±9%) comparable to the ambiguity mentioned above. When the B-fraction is high, in the course of the diffusion of the dissociated cobalt ions, the exchange of these ions with the fixed cobalt cannot be neglected. If this reaction is very fast compared with the diffusion of the dissociated cobalt, R_1 should be added to the denominator of $\overline{D}_{\mathrm{eff}}$ defined in Eq. 12 in order to incorporate the contribution of the exchange reaction between the A$_1$ and the B species. Since the rate of this reaction is very slow, however, the concentration quotient, $\overline{R}_1$, cannot be directly applicable to expression of $\overline{D}_{\mathrm{eff}}$. Instead, the factor α, which is a certain function of R_1(nearly proportional to R_1), should be introduced. Then, in the region of low pH where the B-fraction is high, the effective diffusion coefficient of the dissociated cobalt is expressed by

$$\overline{D}_{\mathrm{eff}}=\overline{D}/(R_2+\alpha+1), \qquad (16)$$

instead of Eq. 12 for the region of low B-fraction (high pH region).

Figure 6 shows the influence of [Co^{2+}] on $\overline{D}_{\mathrm{eff}}$ at the

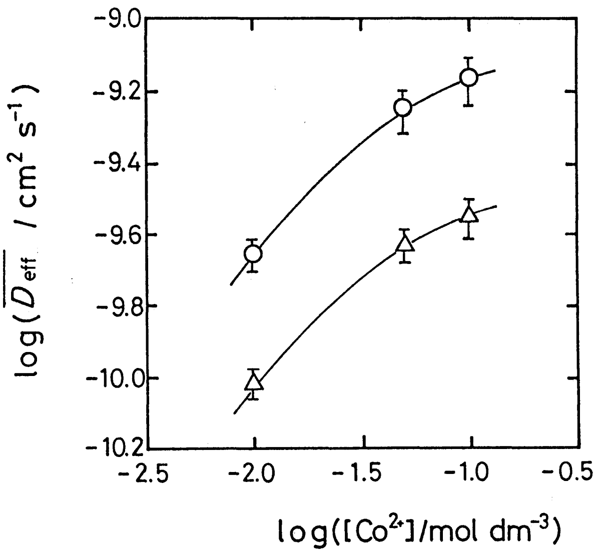

Fig. 6. Effect of cobalt-ion concentration in solution on $\overline{D}_{\mathrm{eff}}$. Particle radius, 98±4 μm; temperature, 30 °C; [NO$_3^-$], 0.2 mol dm^{-3}. Exchange capacity for cobalt ions/mmol g^{-1}, ○: 0.25; △: 0.35.

constant exchange capacity for the ions (0.25 or 0.35 mmol g^{-1}). $\overline{D}_{\mathrm{eff}}$ increased with [Co^{2+}], which is unusual in the particle-diffusion controlled exchange rate. The reason for this observation is considered to be as follows. By combining the concentration quocient $R_2(=[\overline{\mathrm{A}}_2]/[\overline{\mathrm{A}}_1])$ and the proportionality of α to $R_1(=[\overline{\mathrm{B}}]/[\overline{\mathrm{A}}_1])$ with Eq. 16, we can set $\overline{D}_{\mathrm{eff}}=\overline{D}[\overline{\mathrm{A}}_1]/f([\overline{\mathrm{Co}}])$, where $f([\overline{\mathrm{Co}}])$ is a function of ion-exchange capacity for cobalt ions. When the exchange capacity is constant, $\overline{D}_{\mathrm{eff}}$ depends only on $[\overline{\mathrm{A}}_1]$ at a given temperature. As was shown in Fig. 6, the ratio of $\overline{D}_{\mathrm{eff}}$ between different exchange capacities is almost independent of the concentration of cobalt in the aqueous phase. [Co^{2+}] is then considered to govern $[\overline{\mathrm{A}}_1]$. The large exchange capacity of hydrous tin(IV) oxide for cobalt ions at pH <4, where sodium ions, ionic in nature, are not taken up at all,[8] suggests that most of the cobalt ions in the exchanger are either bound or fixed to the exchange sites. The interaction between the ions and the sites makes the activity of anionic sites very small. Therefore, $[\overline{\mathrm{A}}_1]$ may be determined by the Donnan equilibrium of cobalt-electrolyte sorption between the exchanger and the aqueous solution.

Figure 7 shows the influence of the equilibrium concentration of the exchangeable cobalt species ($[\overline{\mathrm{A}}]$) on the effective diffusion coefficients. $[\overline{\mathrm{A}}]$ was calculated by fitting experimental F vs. t plot to Eq. 15. As can be seen from the figure, irrespective of [Co^{2+}], $\overline{D}_{\mathrm{eff}}$ increased sharply with decreasing $[\overline{\mathrm{A}}]$ in the high $[\overline{\mathrm{A}}]$ region, and then gradually in the region of $[\overline{\mathrm{A}}]$ <0.1 or 0.2 mmol g^{-1}.

The dependence of $[\overline{\mathrm{A}}]$ and $[\overline{\mathrm{B}}]$ on the pH is shown in Fig. 8. This figure shows that $[\overline{\mathrm{B}}]$ depends little on the pH, while $[\overline{\mathrm{A}}]$ increases appreciably with the pH. Since the equilibrium concentration of the dissociated cobalt in the exchanger ($[\overline{\mathrm{A}}_1]$) is constant for a given concentration of cobalt ions in solution, the increase in $[\overline{\mathrm{A}}]$ brings about an increase in $R_2(=[\overline{\mathrm{A}}_2]/[\overline{\mathrm{A}}_1])$ on account of the replacement of hydrogen at exchange sites with A$_1$ to form A$_2$. This reaction proceeds more readily with increasing pH. Since $\overline{D}_{\mathrm{eff}}$ can be expressed by Eq. 12 in the region of high $[\overline{\mathrm{A}}]$, the increase of R_2 may be directly reflected in $\overline{D}_{\mathrm{eff}}$. On the other hand, $\overline{D}_{\mathrm{eff}}$ is expressed by Eq. 16 in the region of high B-fraction. As $[\overline{\mathrm{A}}_1]$, $[\overline{\mathrm{B}}]$ and then R_1 were

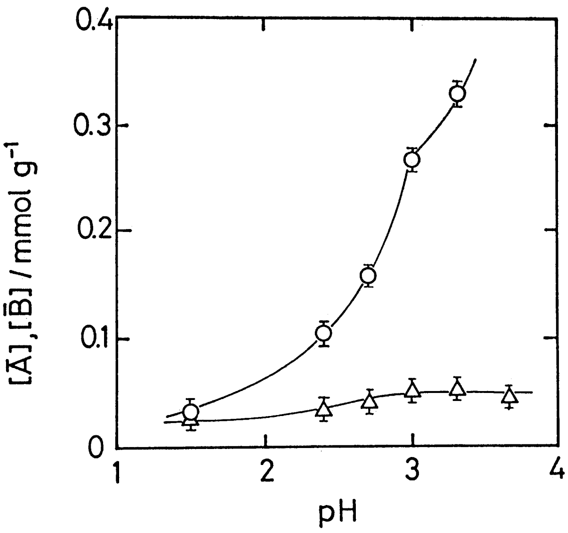

Fig. 8. The pH-dependence of equilibrium concentration of the A and the B species in the exchanger. Particle radius, 98±4 μm; temperature, 30 °C; [NO$_3^-$], 0.1 mol dm^{-3}. ○: $[\overline{\mathrm{A}}]$; △: $[\overline{\mathrm{B}}]$.

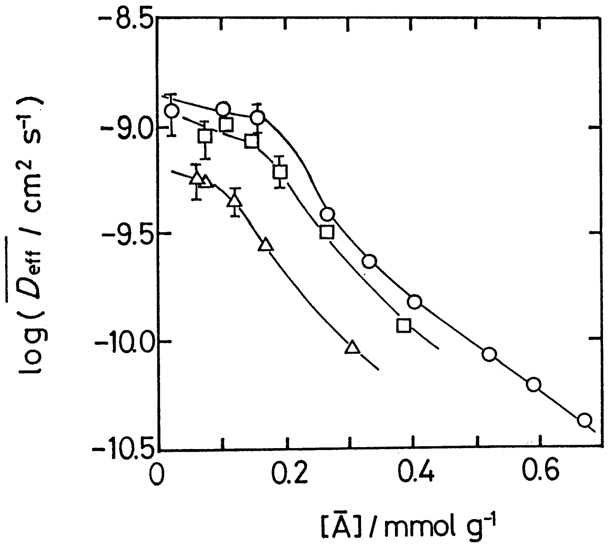

Fig. 7. Effect of equilibrium concentration of the exchangeable cobalt ($[\overline{\mathrm{A}}]$) on $\overline{D}_{\mathrm{eff}}$. Particle radius, 98±4 μm; temperature, 30 °C; [NO$_3^-$], 0.2 mol dm^{-3}. Cobalt-ion concentration in solution/mol dm^{-3}, ○: 0.1; □: 0.05; △: 0.01.

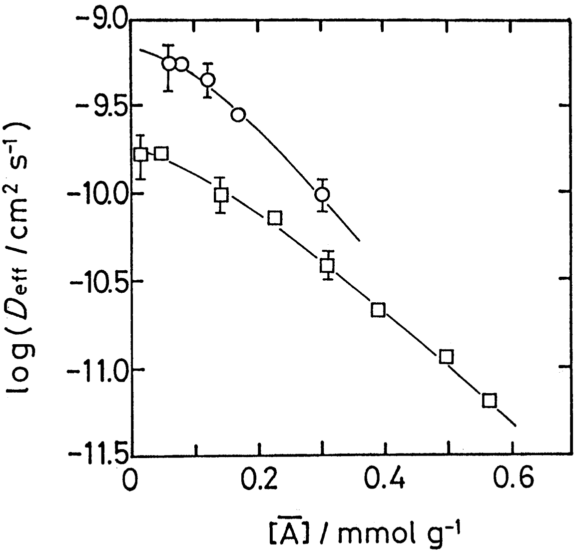

Fig. 9. Effect of concentration of nitrate ions in solution on $\overline{D}_{\mathrm{eff}}$ at various $[\overline{\mathrm{A}}]$. Particle radius, 98±4 μm; temperature, 30 °C; [Co^{2+}], 0.01 mol dm^{-3}. $[\overline{\mathrm{A}}]$: Equilibrium concentration of the A species in the exchanger. Concentration of nitrate ions/mol dm^{-3}, ○: 0.2; □: 0.02.

constant for solutions of a given cobalt concentration, the factor α can be considered almost constant. The decrease in R_2 with lowering pH makes R_2 comparable to R_1, which is independent of the pH. $\overline{D}_{\mathrm{eff}}$ in low $[\overline{\mathrm{A}}]$ region then become insensitive to any further decrease in the $[\overline{\mathrm{A}}]$ value.

Figure 9 shows the effect of the concentration of nitrate ions on the relation between log $\overline{D}_{\mathrm{eff}}$ and $[\overline{\mathrm{A}}]$. $\overline{D}_{\mathrm{eff}}$ is large in the case of higher concentration of the anions and the difference in $\overline{D}_{\mathrm{eff}}$ decreased with increasing $[\overline{\mathrm{A}}]$, which increases with pH in the surrounding solution. The exchanger is amphoteric and uptakes anions from solutions with pH lower than 4; the uptake capacity for anions increases with decreasing pH, as was reported in our previous paper.[8] In a cation exchange occurring in the exchanger without acid dissociation (pH<4), cations are considered to diffuse with accompaning anions in the exchanger with a low electrostatic field, compared with an acid-dissociated exchanger, such as a strongly acidic resin. The diffusion of cations is, therefore, faster in the former than in the latter exchanger. This is the reason why $\overline{D}_{\mathrm{eff}}$ strongly depends on the uptake capacity of anions, pH and the concentration of anions in the solutions.

Figure 10 shows the influence of temperature on $\overline{D}_{\mathrm{eff}}$ at various $[\overline{\mathrm{A}}]$. $\overline{D}_{\mathrm{eff}}$ depended on the temperature at $[\overline{\mathrm{A}}]$ higher than 0.1 mmol g^{-1}, while it did not at lower $[\overline{\mathrm{A}}]$ values. By combining $R_2=[\overline{\mathrm{A}}_2]/[\overline{\mathrm{A}}_1]$ with Eq. 12 for $\overline{D}_{\mathrm{eff}}$ in high $[\overline{\mathrm{A}}]$, $\overline{D}_{\mathrm{eff}}$ can be expressed as $\overline{D}_{\mathrm{eff}}=\overline{D}([\overline{\mathrm{A}}_1]/[\overline{\mathrm{A}}])$. $[\overline{\mathrm{A}}_1]$ is constant in solutions of a given cobalt-ion concentration, (described above). Therefore, the activation energy of the diffusion coefficient of cobalt ions can be determined from the temperature dependence of the $\overline{D}_{\mathrm{eff}}$ values at constant $[\overline{\mathrm{A}}]$ value. Plots of ln $\overline{D}_{\mathrm{eff}}$ vs. $1/T$ at constant $[\overline{\mathrm{A}}]$ of 0.2 or 0.3 mmol g^{-1} give a linear relation, as shown in Fig. 11. From the Arrhenius equation, $\overline{D}=\overline{D}_0\exp(-E_a/RT)$, the activation energies, E_a, were determined: $E_a=19\pm3$ kJ mol^{-1} at $[\overline{\mathrm{A}}]=0.2$ mmol g^{-1} and $E_a=20\pm2$ kJ mol^{-1} at $[\overline{\mathrm{A}}]=0.3$ mmol g^{-1}. Since they agree with each other within the experimental error, the mechanism of the diffusion of cobalt ions in the exchanger is considered to be unchanged by the composition of the exchanger. The temperature dependence of $[\overline{\mathrm{A}}]$ and $[\overline{\mathrm{B}}]$ was examined at pH 2.5, as is shown in Fig. 12. $[\overline{\mathrm{B}}]$ increased with the temperature, while $[\overline{\mathrm{A}}]$ was little affected by the temperature. Since $[\overline{\mathrm{A}}_1]$ is not affected by the temperature in an exchanger immersed in solu-

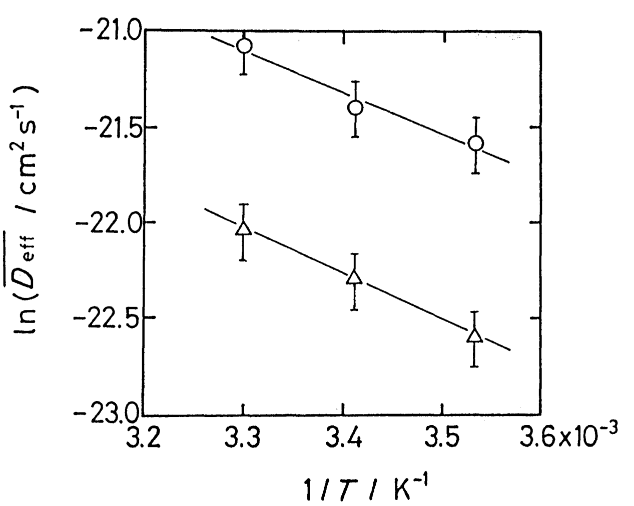

Fig. 11. Arrhenius plots of $\overline{D}_{\mathrm{eff}}$. Particle radius, 98±4 μm; 0.1 mol dm^{-3} Co(NO$_3$)$_2$. Equilibrium concentration of the exchangeable species in the exchanger ($[\overline{\mathrm{A}}]$)/mmol g^{-1}, ○: 0.2; △: 0.3.

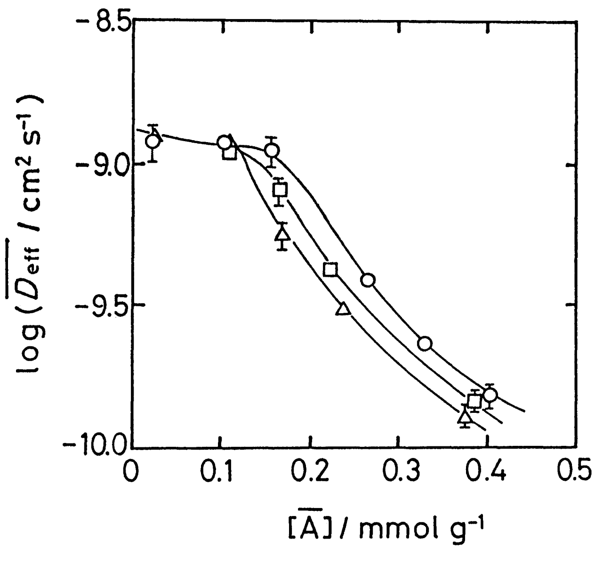

Fig. 10. Temperature-dependence of $\overline{D}_{\mathrm{eff}}$ at various concentrations of the exchangeable species ($[\overline{\mathrm{A}}]$). Particle radius, 98±4 μm; 0.1 mol dm^{-3} Co(NO$_3$)$_2$. Temperature/°C, △: 10; □: 20; ○: 30.

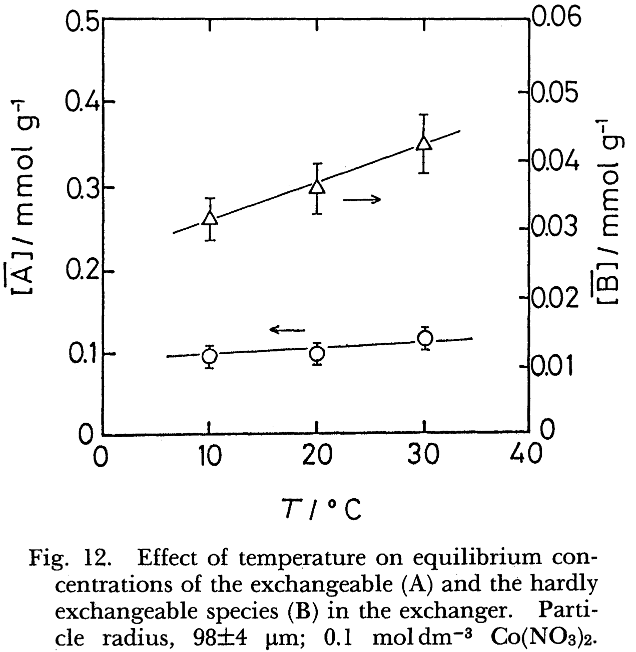

Fig. 12. Effect of temperature on equilibrium concentrations of the exchangeable (A) and the hardly exchangeable species (B) in the exchanger. Particle radius, 98±4 μm; 0.1 mol dm^{-3} Co(NO$_3$)$_2$. ○: $[\overline{\mathrm{A}}]$; △: $[\overline{\mathrm{B}}]$.

tions of a given cobalt-ion concentration, the concentration ratio of A_2 to A_1, R_2, is independent of the temperature, while that of B to A_1, R_1, is increased with the temperature. In the region of low $[\overline{A}]$, where $\overline{D}_{\text{eff}}$ is expressed by the equation $\overline{D}_{\text{eff}}=\overline{D}/(R_2+\alpha+1)$, therefore, the increase in α and in $\overline{D}$ with the temperature compensates each other, so that $\overline{D}_{\text{eff}}$ is almost independent of the temperature.

As has been described above, the isotopic exchange rate of cobalt ions between a hydrous tin(IV) oxide ion-exchanger and aqueous solutions can be understood by a model which assumes the presence of three kinds of cobalt species in the exchanger. This conclusion also supports the view advocated by the present authors from equilibrium studies that the transition metal ions are sorbed on the exchanger by a bond that is partially covalent in character, rather than by a pure ionic bond.

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