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Studies of the Hydrous Niobium(V) Oxide Ion Exchanger. IV. The Rate of the Isotopic Exchange of Sodium Ions between the Exchanger in the Na^+ Form and Aqueous Solutions

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The rate of the isotopic exchange of sodium ions between the hydrous niobium(V) oxide ion exchanger in the Na^+ form and aqueous solutions was determined radiochemically. Since the fractional attainment of equilibrium was independent of the sodium-ion concentration in the solutions ($\geqq 0.1$ mol dm^{-3}), and inversely proportional to the square of the particle radius, the isotopic exchange rate on the hydrous niobium(V) oxide is controlled by the diffusion of the sodium ions in exchanger particles. The self-diffusion coefficients of sodium ions ($D=3.1\times10^{-7}$ cm^2 s^{-1} at 25 °C) and their activation energy ($E_a=27\pm4$ kJ mol^{-1}) were also determined.

An investigation of ion-exchange kinetics is very important for understanding the ion-exchange mechanism of hydrous metal oxides. A measurement of the rate of the isotopic exchange of cations between ion exchangers and aqueous solutions provides fundamental data which are useful for elucidating ion-exchange kinetics. As a part of the study in our series, radiochemical experiments were previously undertaken to measure the rate of the isotopic exchange of sodium ions between hydrous tin(IV) oxide in the Na^+ 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 at the initial stage of precipitation and aggregated to form the oxide gel.[1] It is especially interesting to know whether we can generalize this view regarding the isotopic-exchange rate for a variety of hydrous metal oxides.

This paper deals with the rate of the isotopic exchange of sodium ions between hydrous niobium(V) oxide in the Na^+ form and aqueous solutions and with the comparison between this and the hydrous tin(IV) oxide cases.

Experimental

Preparation of the Exchanger in the Na^+ Form Spiked with ^{22}Na. The hydrous niobium(V) oxide was prepared by a previously recommended method. The sample was classified into four particle sizes by using Japan Industrial Standerd sieves; it was then converted to the H^+ form by treating it with a 0.1 mol dm^{-3} HCl solution. After being washed with water, the exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl solution (relative humidity, 79%).[2] Table 1 shows the particle size and some properties of each sample. The average particle radius was estimated by approximating the particle shape by a sphere, from the particle-size distribution measured in a 83 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 H^+ form was converted to the Na^+ form by treating it on a column with a Na^+ solution, followed by labeling with ^{22}Na by equilibrating with the ^{22}Na solution for 2 d at room temperature. After having been washed with a solution free from ^{22}Na, the exchanger was used for the rate measurements. The Na^+ solutions having the same chemical composition were used throughout these three procedures; the solutions prepared by the desired combinations of NaCl and NaOH were used when the rate was measured at pH 11.0, and buffer solutions, 0.1 mol dm^{-3} NaH_2PO_4 (72.2 vol%)-0.05 mol dm^{-3} $Na_2B_4O_7$ (27.8 vol%) solution and 0.1 mol dm^{-3} NaH_2PO_4 (46.5 vol%)-0.05 mol dm^{-3} $Na_2B_4O_7$ (53.5 vol%), respectively, were used when the rate was measured at pH 6.0 and 8.0.

Measurement of the Isotopic Exchange Rate. All the rate measurements were performed in a nitrogen atmosphere by using the same apparatus as descrived earlier.[3] The rate was measured in solutions with the same compositions as those

Table 1. Particle Size and Some Properties of Samples

Particle size	Average radius	Density	Ion-exchange capacity[b]	Composition[c]	Specific surface area
mesh[a]	μm	g cm^{-1}	mmol g^{-1}	molH_2O (molNb_2O_5)$^{-1}$	m^2 g^{-1}
−48+60	145±4	2.38±0.05	2.34±0.02	—	321±5
−70+80	107±3	—	—	—	314±5
−100+120	74±2	—	—	6.45±0.06	—
−145+200	52±2	2.39±0.05	2.36±0.02	—	317±5

a) Japan Industrial Standard mesh. b) Exchange capacity for Na^+ at pH 11.0 (ionic strength=0.1). c) The water content was determined from the weight loss at 850 °C.

used for converting the exchanger to the Na^+ form; otherwise, the ion-exchange reaction would occur between H^+ and Na^+ ions, since the ion-exchange capacity for Na^+ strongly depends on the pH and on the concentration of the solution. A 0.05-gram to 0.17-gram portion of the sample was placed in a cage and immersed in 200 cm^3 of a solution of the desired composition while the cage was being rotated. The frequency of the 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 taken out at appropriate time intervals in order to measure the radioactivity with a well-type NaI(Tl)-scintillation counter(Aroka Model ARC-361). The time of the contact of the exchanger with the solution was taken as the time elapsing between the immersion of the cage and the withdrawal of an aliquot of the solution. The fractional attainment of equilibrium, $F(t)=C_t/C_\infty$, 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 using $C_\infty=C_iM/(M+m)$, where C_i is the initial total radioactivity of the exchanger, and m and M, the total amounts of Na^+ in the exchanger and in the solution, respectively. Although the rate was measured by a batch method, the infinite solution-volume approximation is closely obeyed under the present experimental conditions: less than 0.17 g of the exchanger per 200 cm^3 of the solution.

Results and Discussion

In order to ascertain the efficiency of agitation, the effect of the stirring rate on the half-exchange time was examined for pH-11 solutions of different NaCl concentrations. The time required for half-exchange became shorter as the revolution rate increased, and reached a constant value at 1050 min^{-1}. Furthermore, it was confirmed that no particles were broken down during the agitation of the revolution rate up to 1500 min^{-1}. On the basis of these results, a revolution rate of 1300 min^{-1} was adopted throughout the experiment.

The comparison of the isotopic exchange rates in up to 1 mol dm^{-3} solutions of different sodium salts indicated that no difference was observed in the rates between anions in the solutions (Cl^-, ClO_4^-, and SO_4^{2-}).

Figure 1 shows the results of the method called "interruption test" in 0.1 mol dm^{-3} sodium concentration; the exchangers were removed from the solution for 1 h and then reimmersed. The rate immediately after reimmersion was greater than that prior to the interruption, suggesting that the rate is controlled by particle diffusion.

When the isotopic exchange rate is controlled by the diffusion of the ions in spherical exchangers immersed in a well-stirred solution of approximately an infinite volume, the fractional attainment of equilibrium, $F(t)$, can be obtained by solving the following equation:[4)]

$$F(t) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-Bn^2t), \tag{1}$$

$$B=\pi^2D/r^2, \tag{2}$$

D is the self-diffusion coefficient of the ions in the exchanger and r refers to the radius of the particles. When $F(t)$ is less than about 0.4, Eq. 1 can be approximated by a simpler form:[5)]

$$F(t) = \frac{6}{r}\left(\frac{Dt}{\pi}\right)^{1/2}, \tag{3}$$

which holds to a fairly good approximation. Therefore, a plot of $F(t)$ against the square root of the contact

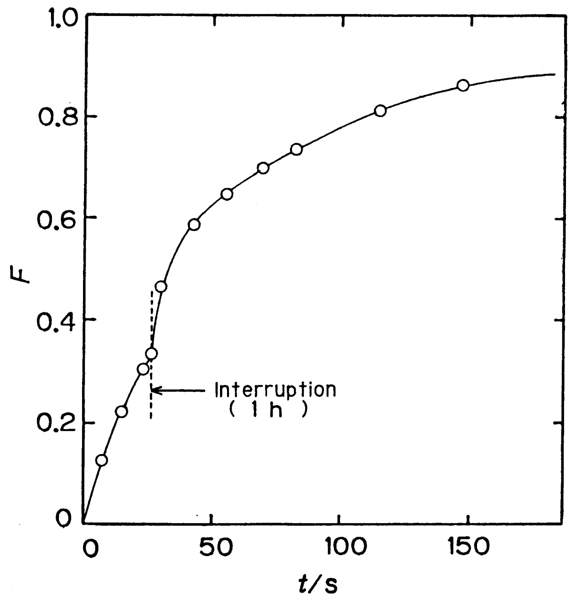

Fig. 1. Interruption test. Sample, −70+80 mesh; temperature, 5.0°C; 0.10 mol dm^{-3} Na(Cl,OH); pH, 11.0.

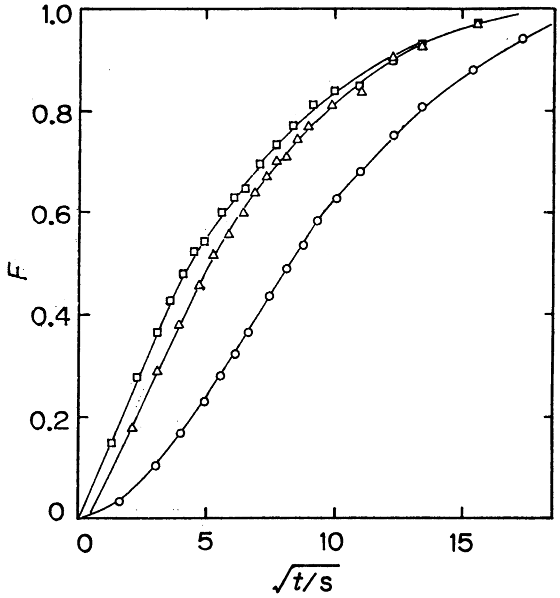

Fig. 2. Effect of Na^+ concentration on the isotopic exchange rates. Sample, −70+80 mesh; temperature, 5.2°C; pH, 11.0; Na(Cl,OH) concn/mol dm^{-3}, ○: 0.01, △: 0.10, □: 1.0.

time must give a straight line passing through the point of origin in the region in which $F(t)$ is less than 0.4.

Figure 2 shows the influence of the sodium ion concentration on the rate. When the concentration was higher than or equal to 0.1 mol dm^{-3}, although there was very small induction period of the exchange reaction in 0.1 mol dm^{-3} solution, the rate of the exchange reaction was independent of the concentration of the solutions; the straight lines between $F(t)$ and $t^{1/2}$ had the same slope within the experimental errors. In the case of a 0.01 mol dm^{-3} solution, a linear relation did not hold between $F(t)$ and $t^{1/2}$. This cannot be understood by the film diffusion control, since a plot of $-\log(1-F(t))$ against t was sigmoid. This observation can be understood by considering that the equilibrium of sodium ion concentrations between the surface of the exchanger and in the solution was temporarily disturbed by the rinsing of the particles after the labeling, and that the surface concentration of sodium ions approaches equilibrium at a rate proportional to the concentration in the solutions when the exchanger was again immersed in the solution for the rate measurement. The result in a 0.01 mol dm^{-3} solution is ascribed to an overlapping of the rate of the reestablishment of the equilibrium surface-concentration of sodium ions and the isotopic exchange rate.

As has been previously described, this material is considered to have at least two kinds of dissociable ion-exchange sites owing to the presence of an inflection point at pH 7.3 in the cation-uptake curve.[2,6,7] This means that the sites contributing to the exchange reaction have different acidities in each side of the inflection point; only sites having high acidity effect the exchange reaction in a solution of pH lower than 7.3, and, at a higher pH, less acidic sites also participate in the exchange reaction. The exchange rate, however, was independent of pH, as is shown in Fig. 3. Consequently, the change of the electronic density on the exchange sites, which results in the difference in the acidity among the sites, has no influence on the exchange rate.

Figure 4 shows the effect of the particle size on the rate for a 0.1 mol dm^{-3} sodium ion concentration. Here, Bt values were calculated from the measured values of $F(t)$ by using the equation derived by D. Reichenberg:

$$Bt = 2\pi - \frac{\pi^2}{3} F(t) - 2\pi\left(1 - \frac{\pi}{3} F(t)\right)^{1/2}. \tag{4}$$

This equation gives a fairly good approximation in the region where $F(t)$ is less than 0.85.[8] The reason why the Bt–t plots were used instead of Eq. 3 is because the fast rate of the exchange reaction causes a decrease in the number of experimental points falling within the limit of the validity of the equation ($F(t) < 0.4$), due to a technical difficulty. When the rate is controlled by the particle diffusion, the plot of Bt against t must give a straight line passing through the point of origin, and the slope of this straight line, i.e., B, is inversely proportional to the square of the particle radius. This figure shows that the plot agrees well with this expectation, irrespective of the particle sizes. In a solution of 1.0 mol dm^{-3} sodium ion concentration, the same dependency was also obtained. Table 2 shows the relation between the particle radii(r) and B, as well as the D calculated from these values. Since D is independent

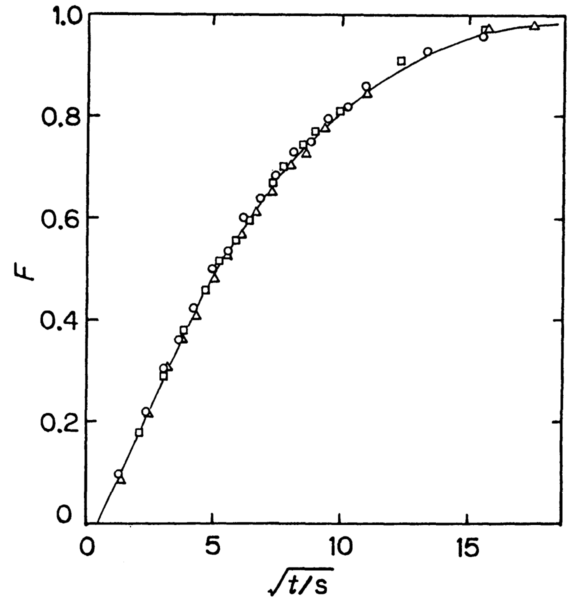

Fig. 3. Effect of pH on the isotopic exchange rates. Sample, −70+80 mesh; temperature, 5.2 °C; 0.1 mol dm^{-3} Na$^+$; pH, ○: 6.6, △: 8.0, □: 11.0.

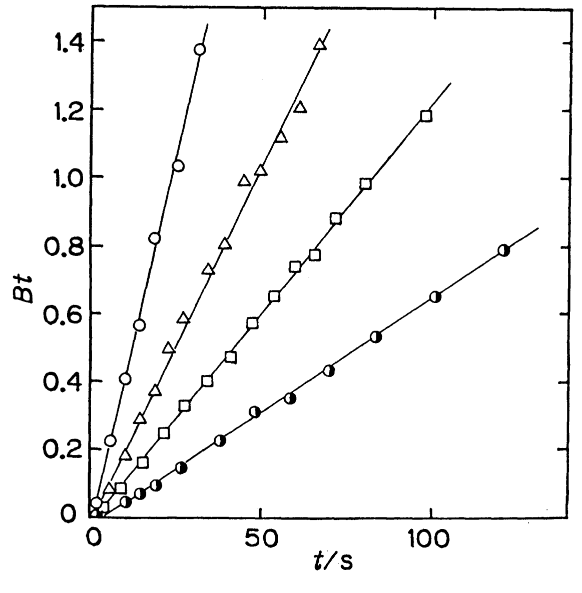

Fig. 4. Effect of particle size on the isotopic exchange rates. Temperature, 5.2 °C; 0.10 mol dm^{-3} Na(Cl,OH); pH, 11.0; particle size/mesh, ◑: −48+60, □: −70+80, △: −100+120, ○: −145+200.

Table 2. Effect of Particle Size on the Isotopic Exchange Rates

Na^+ concentration in the solution	Ion-exchange capacity[a)]	Particle size	B	D
$mol\,dm^{-3}$	$mmol\,g^{-1}$	$r/\mu m$	s^{-1}	$cm^2\,s^{-1}$
0.10	2.34±0.02	145±4	$(0.67\pm0.02)\times10^{-2}$	$(1.4\pm0.1)\times10^{-7}$
		107±3	$(1.24\pm0.02)\times10^{-2}$	$(1.4\pm0.1)\times10^{-7}$
		74±2	$(2.13\pm0.09)\times10^{-2}$	$(1.2\pm0.1)\times10^{-7}$
		52±2	$(4.45\pm0.13)\times10^{-2}$	$(1.2\pm0.1)\times10^{-7}$
1.0	2.90±0.04	145±4	$(0.59\pm0.02)\times10^{-2}$	$(1.3\pm0.1)\times10^{-7}$
		107±3	$(1.36\pm0.07)\times10^{-2}$	$(1.6\pm0.2)\times10^{-7}$
		74±2	$(2.77\pm0.08)\times10^{-2}$	$(1.5\pm0.1)\times10^{-7}$
		52±2	$(5.64\pm0.29)\times10^{-2}$	$(1.5\pm0.2)\times10^{-7}$

Temperature: 5.2±0.1 °C. a) Exchange capacity for Na^+ at pH 11.0.

Table 3. Effect of Temperature on Na^+ Self-Diffusion Coefficients

Na^+ concentration in the solution	Temperature	D	E_a	D_0
	°C	$cm^2\,s^{-1}$	$kJ\,mol^{-1}$	$cm^2\,s^{-1}$
$0.10\,mol\,dm^{-3}$	0.2	$(1.2\pm0.1)\times10^{-7}$	27±4	6.5×10^{-3}
	5.2	$(1.4\pm0.1)\times10^{-7}$		
	10.2	$(1.7\pm0.1)\times10^{-7}$		
	19.8	$(2.3\pm0.2)\times10^{-7}$		
	29.6	$(3.8\pm0.4)\times10^{-7}$		

Particle size: −48+60 mesh.

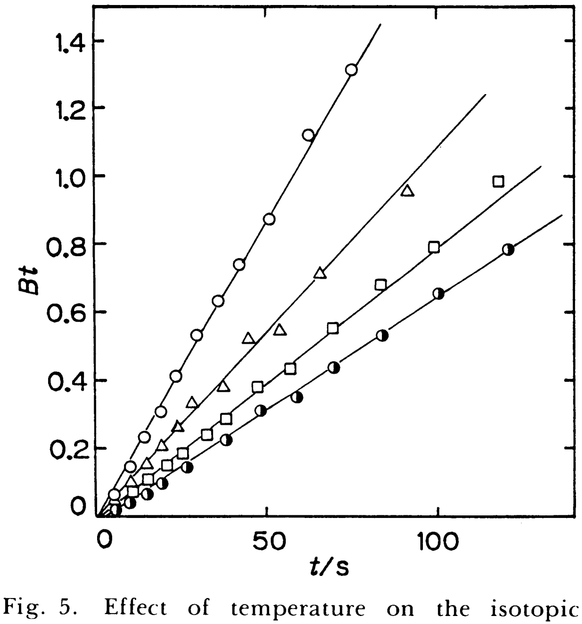

Fig. 5. Effect of temperature on the isotopic exchange rates. Sample, −48+60 mesh; 0.10 $mol\,dm^{-3}$ Na(Cl,OH); pH, 11.0; temperature/°C, ◑: 5.2, □: 10.2, △: 19.8, ○: 29.6.

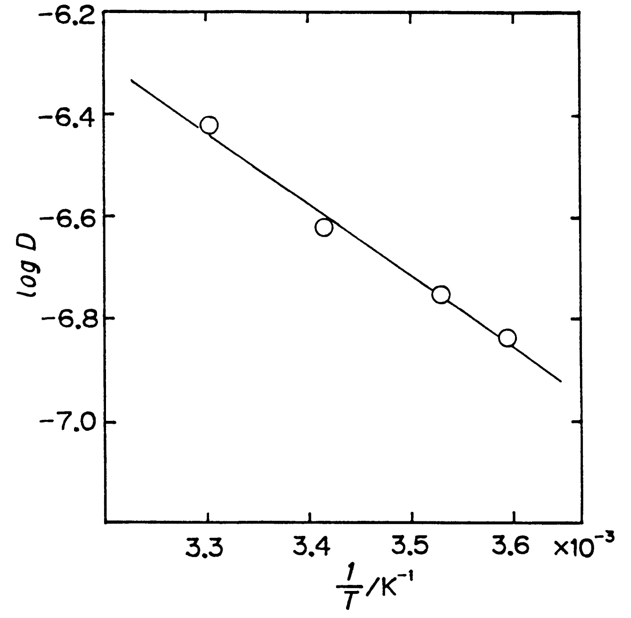

Fig. 6. Arrhenius plots of Na^+ self-diffusion coefficients. Sample, −48+60 mesh; $0.10\,mol\,dm^{-3}$ Na(Cl,OH); pH, 11.0.

of the particle size, B is inversely proportional to $1/r^2$. Furthermore, since the self-diffusion coefficients of sodium ions are independent of the concentration in solutions, the mechanism of the diffusion of sodium ions in the exchanger is considered to be unchanged by the composition of the material.

When these results are combined with the preceding discussion, the isotopic exchange rate on the hydrous niobium(V) oxide in a Na^+ solution higher than 0.1 $mol\,dm^{-3}$ is controlled by the diffusion of the sodium ions in the exchanger particles.

The effect of temperature on the isotopic exchange rates was studied in a 0.1 $mol\,dm^{-3}$ sodium ion solution, as is shown in Fig. 5. This figure indicates that the rates of the exchange increased with temperature. The self-diffusion coefficients of sodium ions were then evaluated from the slopes of these lines by using Eq. 2. These values are summarized in Table 3. When log D was plotted against $1/T$, a good linearity was obtained (Fig. 6). From the Arrhenius equation, $D=D_O \exp(-E_a/RT)$, the activation energy, E_a, and the constant, D_O, were determined. The self-diffusion coeffient of sodium ions at 25 °C ($D=3.1\times10^{-7}$ cm^2 s^{-1}) and its activation energy ($E_a=27\pm4$ kJ mol^{-1}) in the hydrous niobium(V) oxide are similar to those reported for sodium ion diffusion in a sulfonated polystyrene type cation-exchange resin of 16% divinylbenzene ($D=2.7\times10^{-7}$ cm^2 s^{-1} at 25 °C, and $E_a=35$ kJ mol^{-1}).[9]

These findings shows that in the hydrous niobium(V) oxide the diffusion of the counter ions in the exchanger particles is the rate-determining step of the exchange reaction in a Na$^+$ solution higher than 0.1 mol dm^{-3}. This differs from the case of the hydrous tin(IV) oxide; the rate-controlling step is the diffusion of the counter ions in the primary particles, which are formed during the initial stage of precipitation and aggregate to form the hydrous tin(IV) oxide gel. We can, therefore, conclude that the rate of the ion-exchange reaction of hydrous metal oxides cannot be generally interpreted in terms of the same rate-controlling step. Hence, in the analysis of the ion-exchange rates of these materials, the rate-controlling step should be clarified for each.

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