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Studies of the Hydrous Titanium Oxide Ion Exchanger. IV. Rate of the Isotopic Exchange of Sodium Ions between the Exchanger in the Na^+ Form and Aqueous Solution

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The isotopic exchange rate of Na^+ between hydrous titanium(IV) oxides, precipitated at pH 6 and 13, in the Na^+ form and aqueous solution of sodium salt was determined radiochemically. The rate in the exchanger precipitated at pH 6 is controlled by the diffusion of Na^+ in the exchanger particles (particle diffusion). The diffusion coefficient and its activation energy are 1.9×10^{-11} $m^2\,s^{-1}$ (pH 12, 5.0 °C) and 29 $kJ\,mol^{-1}$ (pH 12), respectively . The rate in the exchanger precipitated at pH 13 is also controlled by the particle diffusion. The rate is much slower than that in the other; this can be explained by assuming the existence of two kinds of independently diffusing ions (fast and slow species) in the exchanger. The diffusion coefficients are of the order of 10^{-12} and 10^{-13} $m^2\,s^{-1}$ for the fast and the slow species, respectively . Their activation energies are 48—60 $kJ\,mol^{-1}$ at pH 12. The marked difference in kinetics between two exchanges was interpreted in terms of the difference in the acid-base property and in the microstructure of the matrix.

Hydrous metal oxides are a group of promising materials for use in the processing of radioactive liquid waste. For use of these materials, an investigation of ion-exchange kinetics is very important. In order to provide data useful for elucidating ion-exchange kinetics, we have undertaken radiochemical experiments to measure the isotopic exchange rate of Na^+ between hydrous metal oxides and surrounding solutions.[1—3] The rate of the reaction cannot be understood in terms of a unified view, since the rate-determining step differs from material to material. Further investigations should be carried out for many kinds of exchanges in order to understand the ion-exchange kinetics of hydrous metal oxides.

The ion-exchange properties of hydrous titanium(IV) oxide are strongly affected by the synthetic conditions,[4] especially by the pH of the solution at precipitation. It is interesting to know whether the same is also true in kinetic behavior. This induced us to use two types of hydrous titanium(IV) oxides, precipitated at pH 13 and 6, for studying the isotopic exchange rate of Na^+. These pH values were selected as representative of basic and acidic media for precipitation; pH 13 is the pH where the exchanger with the largest specific ion-exchange capacity can be prepared, and the exchanger precipitated from acidic solution shows kinetic properties similar to other hydrous metal oxides. The results for two exchangers were compared with each other and are discussed in terms of the differences in the acid-base properties and in the microstructure of the materials.

Experimental

Properties of the Exchanger. The average particle radius was estimated by approximating the particle shape as a sphere. The particle-size distribution was measured in 82.6 wt% glycerol solution by using a Seishin Enterprise Micron-Photo-Sizer, Model SKC-2000C. The specific surface area of the exchanger, after being heated at 130 °C, was determined by the BET method (N_2 adsorption at −196 °C) by using a Yanagimoto Surface Area Measuring Apparatus, Model GSA-10. The pore-size distribution and the pore volume were calculated by Inkley's method from the adsorption isotherm of N_2 at −196 °C.[5] The density of the exchanger was measured in the usual manner by using a 10 cm^3 pycnometer. The water content was determined from the weight losses of the exchanger heated to 900 °C. Thermogravimetry was carried out by a Seiko Instruments Inc. thermal analysis system, Model SSC5020, connected to a TG/DTA module, Model TG/DTA300. The measurement was performed in a nitrogen atmosphere at a heating rate of 10 $°C\,min^{-1}$.

The ion-exchange capacity for Na^+ was measured as follows. The exchanger (0.06 g) in the H^+ form was immersed in 10 cm^3 of various solutions, prepared by the desired combinations of 0.10 $mol\,dm^{-3}$ NaCl and 0.10 $mol\,dm^{-3}$ NaOH solutions, for 7 d at room temperature with intermittent shaking. This was followed by pH measurement and by determination of the sodium ions. The sodium ions were converted to an equivalent amount of sodium chloride and indirectly determined by titrating the chloride ions (Fajans' method). The amount of the ions taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of the ions in the solutions.

Table 1. Particle Size and Some Properties of Samples

Sample	Average radius	Density	Composition	Specific surface area	Specific pore volume
	µm	$g\,cm^{-3}$	$mol\ H_2O\ (mol\ TiO_2)^{-1}$	$m^2\,g^{-1}$	$cm^3\,g^{-1}$
Ti6	156±7 127±3 86±4	2.17±0.02	1.73±0.02	270±4	0.22±0.01
Ti13	110±3 48±5	2.41±0.03	1.39±0.02	118±4	0.084±0.001

Preparation of the Exchanger in Na^+ Form Spiked with ^{22}Na. Hydrous titanium(IV) oxide was precipitated by two ways: (1) By adding 1 $mol\,dm^{-3}$ NaOH solution into 1 $mol\,dm^{-3}$ $TiCl_4$ solution to make pH 6 (Ti6) and (2) by mixing these solutions in the reverse order to make pH 13 (Ti13). After being washed and dried at 70 °C, the precipitate was ground and classified into three particle sizes by using Japan Industrial Standard sieves; it was then converted to H^+ form by being treated with a 0.05 $mol\,dm^{-3}$ 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 % at 25 °C). Table 1 shows the particle size and some properties of each sample. The exchanger in H^+ form was then converted to Na^+ form by treating it with solutions having the same chemical composition as those used for the rate measurement. The exchanger was then labeled with ^{22}Na by equilibrating it with a ^{22}Na solution having the same chemical composition as the above mentioned solution for longer than 2 d at room temperature. After being separated from the solution by filtration under suction, the exchanger was used for a rate measurement. The Na^+ solutions used for these procedures were prepared by desired combinations of NaCl and NaOH, or NaCl and NaOH-2-cyclohexylaminoethanesulfonic acid (CHES) or 2-morpholinoethanesulfonic acid (MES) buffer solutions. The presence of the buffer reagents was experimentally confirmed to affect neither the Na^+ exchange capacity nor the reaction rate.

Measurement of the Isotopic Exchange Rate. All of the rate measurements were performed in a nitrogen atmosphere by using the apparatus described earlier.[6] The rate was measured in a solution with the same composition as that used for converting the exchanger to the Na^+ form; otherwise, the ion-exchange reaction would occur between H^+ and Na^+, since the ion-exchange capacity for Na^+ strongly depends on the pH and the concentration of the solution. A 0.1 g 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. By rotating the cage we can contact the exchanger particles with a rapid stream of the solution with a flow rate determined by the revolution rate, and mix the solution to keep it homogeneous. The frequency of revolution was measured with a Yokogawa Phototachometer, Model 2607. 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 elapsed time between immersing the cage and withdrawing an aliquot of the solution. The fractional attainment of equilibrium $F=Q_t/Q_\infty$, was calculated from these results; here, Q_t is the total radioactivity of the solution at time t and Q_∞ at $t=\infty$. Q_∞ was calculated using $Q_\infty=Q_iM/(M+m)$. Here Q_i is the initial total radioactivity of the exchanger; m and M are 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 was closely obeyed under the present experimental conditions; the ratio of the total amount of Na^+ in the exchanger to that in the solution was less than 0.02, unless as otherwise noted.

Results and Discussion

Figure 1 shows the uptake curves for Na^+ on each exchanger. The minimum pH at which Na^+ are sorbed was significantly lower for Ti13 than for Ti6, and Ti13 has much larger capacity than Ti6 at any pH of the solution. Table 1 indicates that the specific surface area and the specific pore volume of Ti13 are considerably smaller than those of Ti6. The comparison however should not be considered quantitative because of the

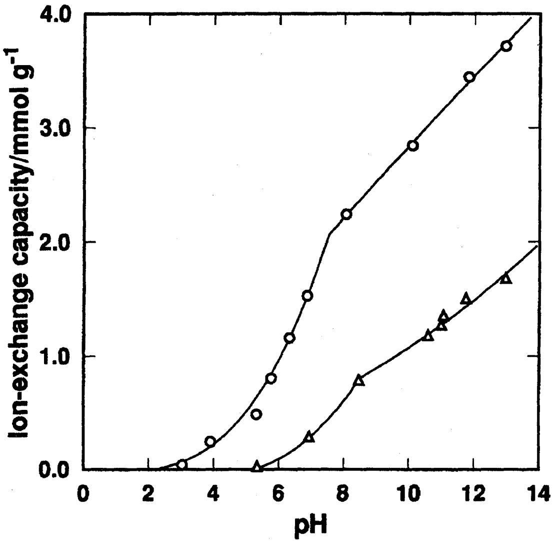

Fig. 1. Uptake curves for Na^+. m (exchanger amount)/V (solution volume)=0.06 g/10 cm^3. The initial concentration of cation: 0.10 mol dm^{-3}. Exchanger, △: Ti6; ○: Ti13.

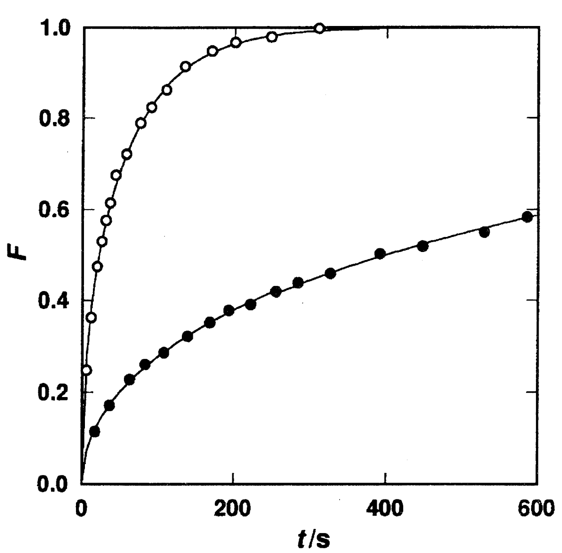

Fig. 2. Isotopic exchange rates of Na^+ between hydrous titanium(IV) oxide in Na^+ form and aqueous solution. 0.1 mol dm^{-3} Na^+-solution; pH, 12.0. ○:Ti6 (r=127 μm; Temperature, 5.0 °C); ●:Ti13 (r=110 μm; Temperature, 30.0 °C).

following reason. In order to measure accurately these values, water in the exchanger should be completely removed. Being heated at 130 °C, which is the highest temperature possible without structural change, Ti6 and Ti13, respectively, were dehydrated to 10 and 20 % of the original water content. Hence, the specific surface area and the specific pore volume must be underestimated; the degree is higher in Ti13 than in Ti6. In spite of this uncertainty, we can conclude that the differences in these values between two exchangers are enormous. The majority of the pores in Ti6 was determined to have diameters of around 2.8 nm, which is larger than the diameter of hydrated Na^+ ions (reported to be 1.2 to 1.4 nm[7)]). The value in Ti13, however, could not be measured due to the interference of water, but may be much narrower than in Ti6 because of smaller specific surface area and specific pore volume. Hydrated Na^+ ions, therefore, can move freely in pores in Ti6 but will very likely be subject to geometrical obstruction in Ti13.

From these observations, we can consider that two materials differ appreciably with each other, both in the acid-base property and in the microstructure of the matrices.

The revolution rate of the cage between 1100 and 1300 min^{-1} did not affect the isotopic exchange rate, indicating adequate agitation. On the basis of this fact, the revolution rate of 1300 min^{-1} was adopted throughout the experiments.

When isotopic exchange rate is controlled by the diffusion of ions in homogeneous spherical exchangers (particle diffusion) immersed in a well-stirred solution of approximately infinite volume, the fractional attainment of equilibrium, *F(t)*, can be obtained by solving the following equation:[8)]

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

where

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

D is the diffusion coefficient of the ions in the exchanger, and r the radius of the particles. When F is smaller than 0.85, Bt values can be calculated to a fairly good approximation from the measured values of F by using an equation derived by Reichenberg:[9)]

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

In this case, a plot of Bt against t gives a straight line passing through the point of origin.

Isotopic exchange rates were measured on two exchangers at pH 12.0, where the exchangers take up a large amount of Na^+. The results are shown in Fig. 2, which clearly indicates that the rate is very much faster on Ti6 than on Ti13. Thus, these exchangers differ markedly with each other in their kinetic properties as well as equilibrium ones. Hereafter, the results for each exchanger will be described separately for convenience.

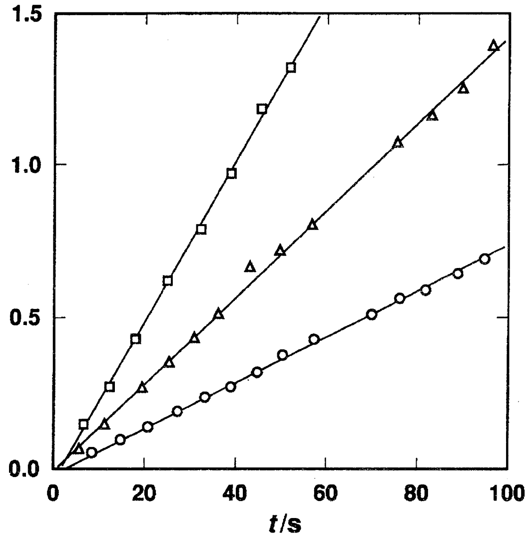

Fig. 3. Effect of particle size on the isotopic exchange rates (Ti6). Temperature, 5.0 °C; 0.1 mol dm^{-3} Na^+-solution; pH, 12.0. Particle radius/μm, ○: 156; △: 127; □: 86.

Isotopic Exchange Rate on Ti6. Figure 3 shows the effect of particle size on the rate in a 0.1 mol dm^{-3} Na^+ solution of pH 12.0, indicating that the *Bt–t* plot gives a good linearity for any particle size. The slopes of the lines, i.e., B values, are inversely proportional to the square of particle radii, as expected from Eq. 2. The isotopic exchange rate is, therefore, controlled by the particle diffusion.

Table 2. Effect of Temperature and pH on Diffusion Coefficients (Ti6)

pH	Temperature °C	D $m^2\,s^{-1}$	E_a $kJ\,mol^{-1}$	D_0 $m^2\,s^{-1}$
12.0	5.0	$(1.9\pm0.1)\times10^{-11}$	29±4	6.8×10^{-6}
	10.0	$(2.3\pm0.2)\times10^{-11}$		
	15.0	$(3.0\pm0.2)\times10^{-11}$		
	20.0	$(3.6\pm0.3)\times10^{-11}$		
9.0	5.0	$(3.4\pm0.3)\times10^{-11}$		

Particle radius, 156 μm. 0.1 mol dm^{-3} Na$^+$-solution.

The effect of temperature on the rate was studied in solutions of pH 12.0. The diffusion coefficients evaluated from these results are presented in Table 2. When log D was plotted against $1/T$, a good linearity was obtained. From the Arrhenius equation, $D = D_o\exp(-E_a/RT)$, activation energy E_a and constant D_o were determined. The activation energy (29±4 kJ mol^{-1}) is similar to those reported for diffusion of Na$^+$ in other hydrous metal oxides (27±4 and 30±3 kJ mol^{-1} in the hydrous niobium(V) oxide and hydrous zirconium(IV) oxide, respectively) and sulfonated polystyrene type resin (35 kJ mol^{-1}).[2,3,10] This suggests that the activation process of the diffusion and in turn the nature of the interaction of Na$^+$ with the exchange sites does not greatly differ from other exchangers.

The effect of pH on the rate is shown in Fig. 4, which indicates that the rate is faster at pH 9.0 than at pH 12.0. Cations diffusing through the exchanger would interact with the dissociated ion-exchange sites, and the increase of these sites with pH makes the rate slow, due to increasing frequency of the electrostatic interaction between ions and these sites.

Isotopic Exchange Rate on Ti13. Figure 5 shows the effect of particle size on the rate in a 0.1 mol dm^{-3} Na$^+$ solution of pH 12.0. The rate-determining step is considered to be the diffusion of ions in the exchanger particles, because the rate decreases with increasing particle size as expected from Eqs. 1 and 2. The relation between Bt and t, however, deviates from linearity at higher values of Bt. The Bt–t profile at pH 6.0 was similar, but the rate is faster; half exchange time was 135 and 400 s at pH 6.0 and pH 12.0, respectively (r=110 μm, 30.0 °C). This kinetic behavior characteristic of Ti13 cannot be explained by the diffusion of only one kind of ions with a constant diffusion coefficient. Thus we should introduce multiple diffusion coefficients for analyzing the data by the particle diffusion control. When we assumed that there exist two kinds of independently moving Na$^+$ species in the exchanger, the fractional attainment of equilibrium could be represented as follows;

$$F = \alpha F_1 + (1-\alpha)F_2 \tag{4}$$

where α is the fraction of the rapidly exchangeable

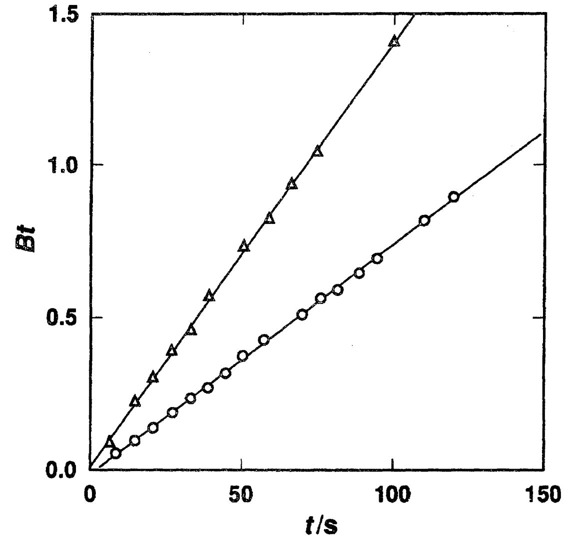

Fig. 4. Effect of pH on the isotopic exchange rate (Ti6). Temperature, 5.0 °C; 0.1 mol dm^{-3} Na$^+$-solution; Particle radius, 156 μm. pH, △: 9.0; ○: 12.0.

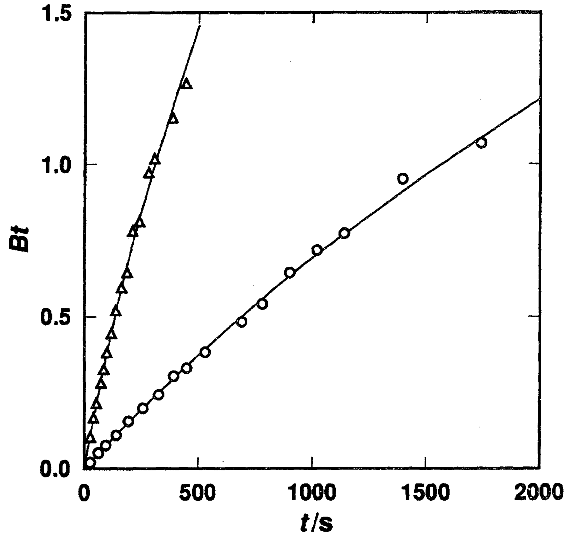

Fig. 5. Effect of particle size on the isotopic exchange rate (Ti13). Temperature, 30.0 °C; 0.1 mol dm^{-3} Na$^+$-solution; pH, 12.0. Particle radius/μm, ○: 110; △: 48. Solid line is the best fit to the experimental data of Eq. 4.

species (fast species), F_1 is the attainment of equilibrium of the fast species, $(1-\alpha)$ is the fraction of the slowly exchangeable species (slow species), and F_2 is the attainment of equilibrium of the slow species. The values of $B_1(B_1=\pi^2 D_1/r^2$; D_1 is the diffusion coefficient of the fast species), $B_2(B_2=\pi^2 D_2/r^2$; D_2 is the diffusion coefficient of the slow species) and α can be determined by fitting the experimental F vs. t plots to Eq. 4 by using the nonlinear least-squares method. When $\alpha=0.4$, the best fitted line was obtained as shown in Fig. 5.

Care must be taken in the analysis because the sensitivity is not high enough to obtain accurate α values since three fitting parameters, B_1, B_2 and α, can compensate each other. Experimental data, therefore, could be reproduced with almost the same degree of certainty when α is varied widely, from 0.3 to 0.5. To obtain α unequivocally, it is necessary to perform an experiment with a principle different from the present one. As is shown in Fig. 6, B_1 and B_2 are inversely proportional to the square of the particle radii at constant α. This indicates that the diffusion coefficient of each species, fast and slow, can be estimated by means of Eq. 2. Hence, we can conclude that the isotopic exchange rate of Na^+ in Ti13 is also controlled by the particle diffusion. The assumption made for analyzing the kinetic data, that is, the existence of two kinds of independently moving Na^+ species may also be compatible with the following finding. Thermogravimetric curves of Na^+ form exchangers, shown in Fig. 7, drop monotonously in Ti6, whereas in two steps in Ti13. This suggests the presence of two easily distinguishable kinds of sites, that is, the presence of Na^+ ions in two different environmental conditions in Ti13, in contrast to Ti6.

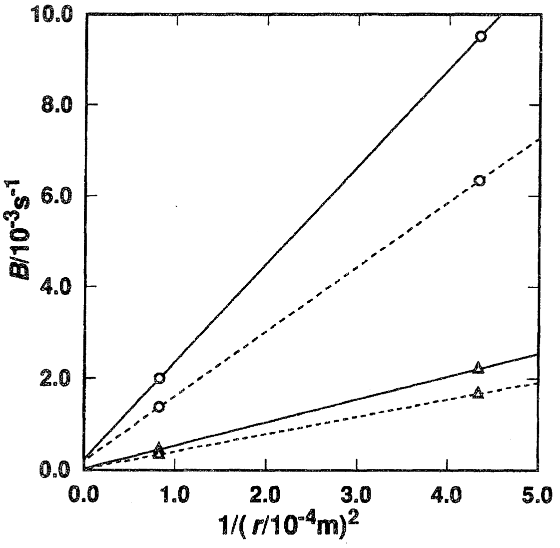

Fig. 6. Relation between particle radius (r) and B (Ti13). Temperature, 30.0 °C; 0.1 mol dm^{-3} Na^+-solution; pH, 12.0. ○: fast species; △: slow species. ——: $\alpha=0.3$; ·····: $\alpha=0.5$.

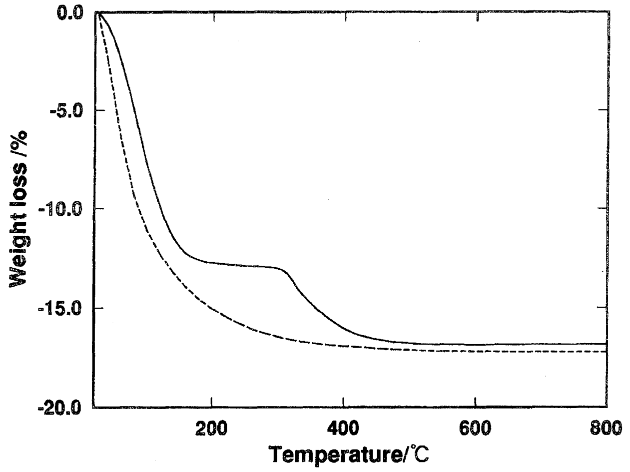

Fig. 7. TGA curves of the exchanger in Na^+ form. Conversion to Na^+ form using 0.1 mol dm^{-3} Na^+-solution of pH 12.0. Exchanger, ·····: Ti6, ——: Ti13.

Table 3. Diffusion Coefficients and Their Activation Energies (Ti13)

α	0.3	0.4	0.5	$E_a^{b)}$/kJ mol^{-1}
$D_1^{a)}/10^{-12}m^2 s^{-1}$	2.3±0.1	1.9±0.1	1.6±0.1	48±4
$D_2^{a)}/10^{-13}m^2 s^{-1}$	5.3±0.2	4.6±0.2	4.0±0.2	60±5

a) Values in 30.0 °C. b) Calculated by assuming $\alpha=0.4$.

The effect of temperature on each diffusion coefficient was determined by assuming $\alpha=0.4$. The plot of $\log D$ against $1/T$ gave a good linearity, and the activation energies were calculated from the Arrhenius equation (Table 3). The activation energies for both species were significantly greater than those for strongly acidic ion-exchange resin, other hydrous metal oxides and Ti6. These differences may be due to the differences in the interaction energy of Na^+ and sites and in the microstructure of the matrices; in Ti13, Na^+ ions do not move so freely as in other hydrous metal oxides because of the narrower diffusion path.

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