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Studies of the Hydrous Zirconium(IV) Oxide Ion Exchanger. II. The Rate of 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 Na^+ between hydrous Zr^{IV} oxide in the Na^+ form and aqueous solutions of sodium salts was determined radiochemically. The rate is controlled by particle diffusion, film diffusion, or both, according to the conditions. The exchange rate is controlled by particle diffusion, when the exchanger particles are large (radius, 171 μm), the solutions are more concentrated than 0.1 $mol\,dm^{-3}$ Na^+ and the flow rate through the exchanger particles is high, whereas under the opposite conditions film diffusion is the rate-controlling step. The activation energies of Na^+ diffusion are 30±3 and 18.9±0.5 $kJ\,mol^{-1}$ for particle and film diffusion, respectively.

An investigation of ion-exchange kinetics is very important for understanding the ion-exchange mechanism of hydrous metal oxides. A measurement of the isotopic exchange rate of cations between ion exchangers and solutions provides fundamental data which are useful for elucidating ion-exchange kinetics. The authors undertook radiochemical experiments to measure the Na^+ isotopic exchange rates for hydrous Nb^V and Sn^{IV} oxides. The rate controlling step of the reaction was different between two oxides; for the hydrous Nb^V oxide the exchange rate was controlled by the diffusion of Na^+ in the exchanger particles,[1] while for the hydrous Sn^{IV} oxide it was controlled by the diffusion of Na^+ in the primary particles, which were formed during the initial stage of precipitation and aggregated to form an oxide gel.[2] Further investigations, therefore, should be carried out for a variety of other hydrous metal oxides in order to understand the ion-exchange kinetics of these kinds of materials.

This paper deals with the results of radiochemical experiments undertaken to measure the isotopic exchange rate of Na^+ between hydrous Zr^{IV} oxide in the Na^+ form and aqueous solutions of sodium salts.

Experimental

Preparation of the Exchanger in the Na^+ Form Spiked with ^{22}Na. The hydrous Zr^{IV} oxide prepared by a previously recommended method[3] was classified into four particle sizes by using Japan Industrial Standard sieves; it was then converted to the H^+ form by treating it 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. These properties were determined by the methods described in a preceding paper.[1] The exchanger in the H^+ form was then converted to the 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 solutions, except for the experiments carried out in 0.01 $mol\,dm^{-3}$ Na^+ solutions, where 3-(cyclohexylamino)-1-propane sulfonic acid was added as a buffer reagent. The presence of the buffer reagent was confirmed by a preliminary experiment to affect neither the Na^+ exchange capacity nor the rate of the reaction.

Measurement of the Isotopic Exchange Rate. All of the rate measurements were performed in a nitrogen atmosphere by using the same apparatus as described earlier.[4] 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^+ ions, since the ion-exchange capacity for Na^+ strongly depends on the pH and on the concentration of the solution. A 0.1 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. By rotating the cage we can contact the exchanger particles with a rapid stream of the solution

Table 1. Particle Size and Some Properties of the Samples

Average radius	Density	Composition	Specific surface area	Specific pore volume
μm	$g\,cm^{-3}$	$mol\,H_2O(mol\,ZrO_2)^{-1}$	$m^2\,g^{-1}$	$cm^3\,g^{-1}$
171±5	2.51±0.03	—	—	0.12±0.01
125±4	—	3.66±0.04	288±2	—
88±1	—	—	—	—
56±3	2.48±0.04	—	—	0.10±0.01

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, Model 2607, phototachometer. 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 $Q_\infty=Q_iM/(M+m)$, where Q_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 was closely obeyed under the present experimental conditions; the ratio of the total amount of Na$^+$ in the exchanger to that in solution was less than 0.02, unless as otherwise noted.

Results and Discussion

The fractional pore volume of the hydrous Zr$^{\mathrm{IV}}$ oxide was found to be 0.28±0.02 on the basis of the density and the pore volume of the material (Table 1). Figure 1 shows the pore-size distribution; no significant difference was observed between samples with different particle radii. As the diameters of a large majority of the pores are around twice as large as those of hydrated Na$^+$ ions (reported to be 1.2 to 1.4 nm$^{5)}$), the ions (unhydrated or hydrated) can move fast along the pores in the hydrous Zr$^{\mathrm{IV}}$ oxide. Since the pores, functioning as the main paths of the ions, occupy a large fraction of the total volume, the particles of hydrous Zr$^{\mathrm{IV}}$ oxide can be regarded as being homogeneous from the standpoint of kinetics.

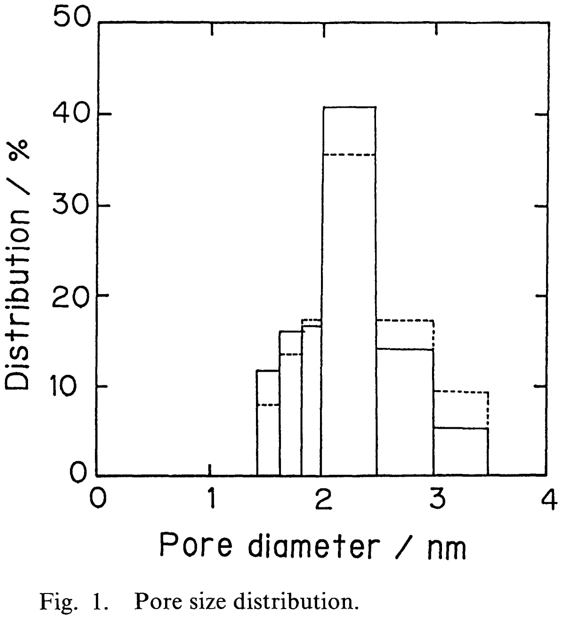

Fig. 1. Pore size distribution.
Particle radius, ----: 171 μm, ——: 125 μm.

When the isotopic exchange rate is controlled by the diffusion of ions in homogeneous spherical exchangers immersed in a well-stirred solution of approximately infinite volume (particle diffusion), the fractional attainment of equilibrium (F) can be obtained by solving the equation,$^{6)}$

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

where

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

$\bar{D}$ is the diffusion coefficient of the ions in the exchanger, and r the radius of the particles. When F is less than about 0.3, Eq. 1 can be approximated by a simpler form,$^{7)}$

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

which holds to a fairly good approximation. A plot of F against the square root of the contact time, therefore, must give a straight line passing through the point of origin in the region of F less than 0.3.

When F is smaller than 0.85, the Bt values can be calculated to a fairly good approximation from the measured values of F by using an equation derived by Reichenberg,$^{8)}$

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

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

When the rate is controlled by the diffusion of the ions in the liquid film on the surface of the particles (film diffusion), F is given by

$$F=1-\exp\left(-\frac{3DCt}{r\delta\bar{C}}\right) \tag{5}$$

under infinite solution-volume conditions. D is the Na$^+$ diffusion coefficient in the solution, C and $\bar{C}$ the concentration of Na$^+$ in the solution and that in the exchanger, respectively, and δ the film thickness.$^{6)}$

Span et al. and Tsai analyzed the ion-exchange rates in the case where the diffusion of ions was about equally fast in the exchanger particles and in the film.$^{9,10)}$ They suggested that any decrease in the product of $(\bar{C}/C)\times(\bar{D}/D)\times(\delta/r)$ favored particle diffusion over film diffusion control; the contribution of these processes to the overall rate can be judged according to the manner of deviation from linearity between F and $\sqrt{t}$ or between $-\log(1-F)$ and t.

Figure 2 shows the effect of the frequency of revolution of the cage on the rate of the isotopic exchange between the samples with an average radius 171 μm and 0.1 mol dm^{-3} Na$^+$ solutions at pH 12. The rate increased with the revolution frequency up to 1310 min^{-1}, wherefrom the linearity between F and $\sqrt{t}$ held during the initial stage of the reaction. This fact indi-

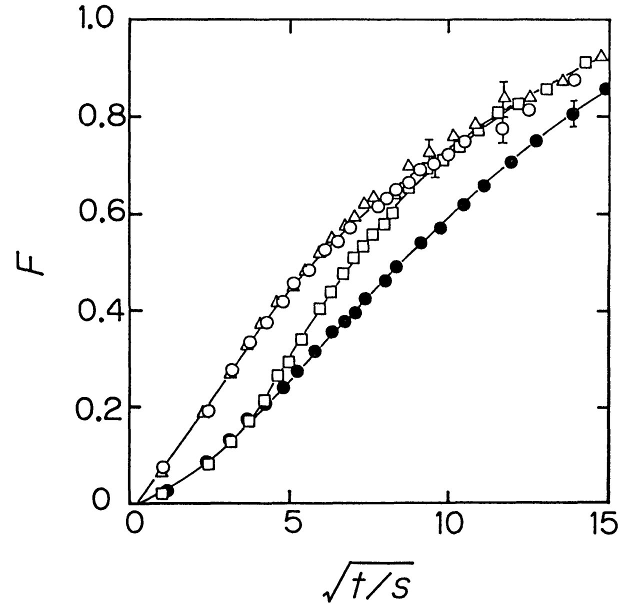

Fig. 2. Effect of agitation on the isotopic exchange rates (F vs. $\sqrt{t}$ plots).
Particle radius, 171 μm; Temperature, 1.0 °C; 0.1 mol dm^{-3} Na$^+$ solution; pH, 12.0.
Revolution frequency of the cage/min^{-1}, ○: 1430; △: 1310; □: 1160; ●: 860.

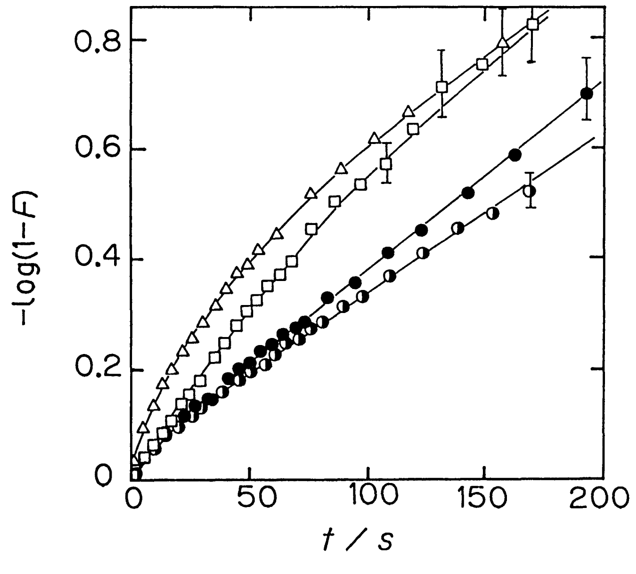

Fig. 3. Effect of agitation on the isotopic exchange rates (−log (1−F) vs. t plots).
Particle radius, 171 μm; Temperature, 1.0 °C; 0.1 mol dm^{-3} Na$^+$ solution; pH, 12.0.
Revolution frequency of the cage/min^{-1} △: 1310; □: 1160, ●: 860; ◑: 660.

cates that the exchange rate is controlled by Na$^+$ diffusion in the exchanger particles (Eq. 3). When the revolution rate was slower than 1160 min^{-1}, the plot of F against $\sqrt{t}$ became sigmoid. Hence, the rate cannot be controlled solely by particle diffusion. When the same data were plotted with t as the abscissa against

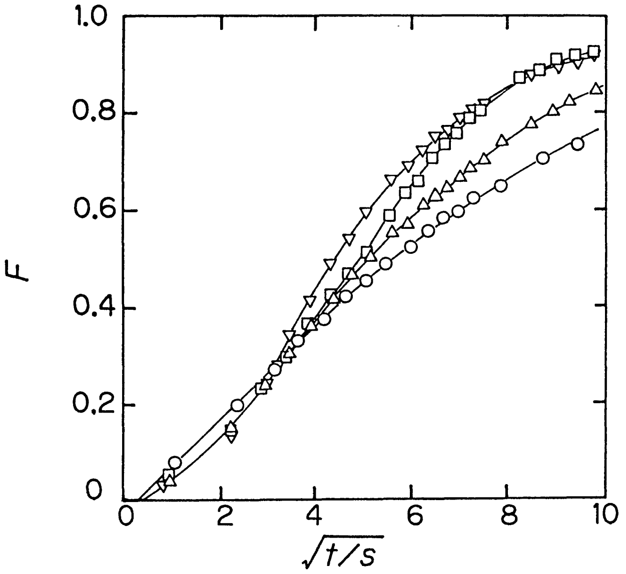

Fig. 4. Effect of particle size on the isotopic exchange rates.
Temperature, 1.0 °C; 0.1 mol dm^{-3} Na$^+$ solution; pH, 12.0; Revolution frequency of the cage, 1310 min^{-1}.
Particle raduis/μm, ○: 171; △: 125; □: 88; ▽: 56.

−log (1−F) as the ordinate (Fig. 3), a linear relation was obtained in the region of larger F at a revolution rate slower than 1160 min^{-1}. The linear part broadened, and its slope decreased with decreasing revolution rate of the cage. This observation suggests that an increased contribution of film diffusion to the overall exchange rate is due to an increase in δ. The rate of Na$^+$ diffusion in the film, however, does not entirely control the exchange rate, even at such a slow revolution rate as 660 min^{-1}, since the shoulder is observed during the early stage of the exchange reaction.

Figure 4 shows the effect of particle size on the rate in a 0.1 mol dm^{-3} Na$^+$ solution at a revolution frequency of 1310 min^{-1}. The overall rate increased with decreasing particle size. The relation between F and $\sqrt{t}$, initially linear at 171 μm, deviated from linearity and became sigmoid when smaller particles were used. This shows the increasing contribution of film diffusion to the overall rate with decreasing particle size, since higher δ/r favors film diffusion control. In order to realize pure particle diffusion control, particles as large as those with a radius of 171 μm should be used, even when the revolution rate of the cage is very high.

Figure 5 shows the influence of the Na$^+$ concentration on the exchange rate at a high revolution frequency of 1310 min^{-1}. The rate was independent of the concentration of the solutions. This fact also suggests particle diffusion control, since Eq. 1 does not involve term C.

The effect of temperature on the isotopic exchange rate was then studied under the conditions which were required to realize pure particle diffusion control. The results are shown in Fig. 6, which indicate that the rate increases with temperature. The $\bar{D}$ values were then

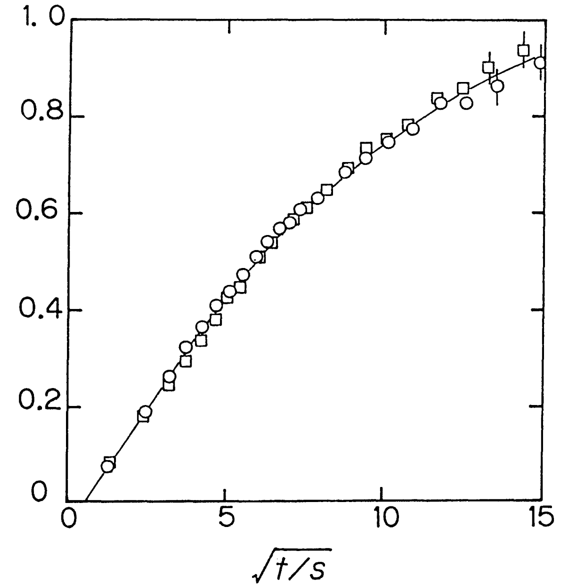

Fig. 5. Effect of Na$^+$ concentration on the isotopic exchange rates-1.
Temperature, 1.0 °C; pH, 12.0; Revolution frequency of the cage, 1310 min^{-1}; Particle radius, 171 μm.
Na$^+$ concentration in solutions/mol dm^{-3}, ○: 0.10; □: 1.0.

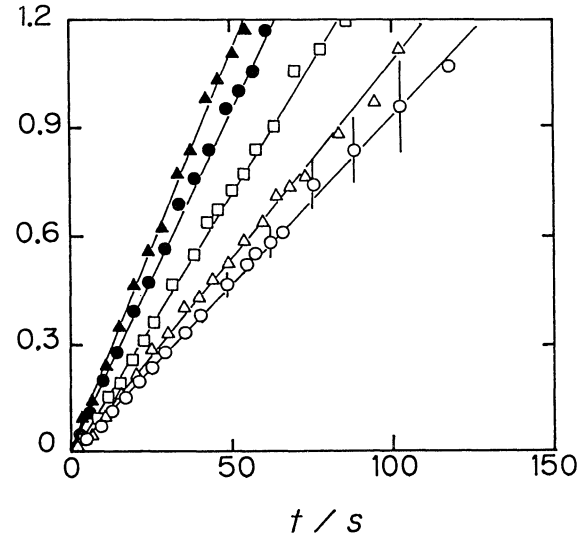

Fig. 6. Effect of temperature on the isotopic exchange rate (Particle diffusion).
0.1 mol dm^{-3} Na$^+$ solution; pH, 12.0; Revolution frequency of the cage, 1310 min^{-1}; Particle radius, 171 μm.
Temperature/ °C, ○: 1.0; △: 5.0; □: 10.5; ●: 15.1; ▲: 20.1.

Table 2. Effect of Temperature on the Na$^+$ Particle Diffusion Coefficients

Temperature	$\bar{D}$	E_a	$\bar{D}_\mathrm{o}$
°C	cm^2 s^{-1}	kJ mol^{-1}	cm^2 s^{-1}
1.0±0.1	(2.74±0.15)×10^{-7}	30±3	0.178
5.0	(3.24±0.08)×10^{-7}		
10.5	(4.36±0.12)×10^{-7}		
15.1	(5.40±0.10)×10^{-7}		
20.1	(6.35±0.12)×10^{-7}		

Particle radius, 171±4 μm. Revolution frequency of the cage, 1310 min^{-1}. 0.1 mol dm^{-3} Na(Cl, OH), pH 12.0±0.1.

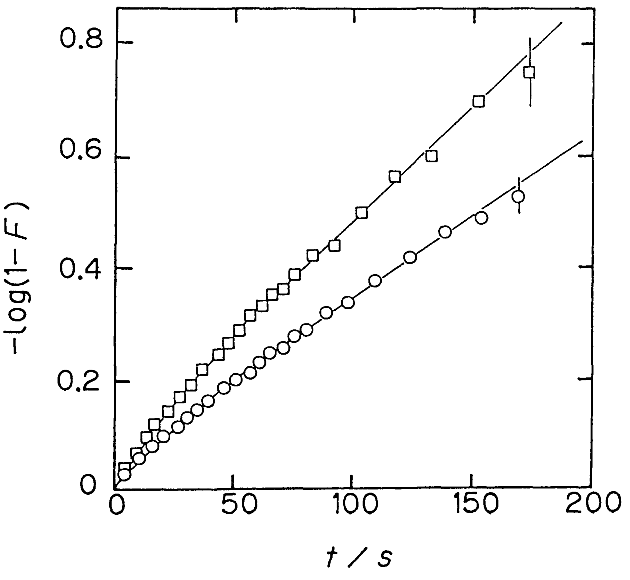

Fig. 7. Effect of Na$^+$ concentration on the isotopic exchange rates-2.
Temperature, 1.0 °C; pH, 12.0; Revolution frequency of the cage, 660 min^{-1}; Particle radius, 171 μm.
Na$^+$ concentration in solutions/mol dm^{-3}, ○: 0.10; □: 1.0.

evaluated by means of Eq. 2 from the slopes of these lines and the average radius of the particles (Table 2). When $\ln \bar{D}$ was plotted against $1/T$, good linearity was obtained. From the Arrhenius equation, $\bar{D}=\bar{D}_\mathrm{o}\exp(-E_\mathrm{a}/RT)$, the activation energy, E_a, and the constant, $\bar{D}_\mathrm{o}$, were determined. The activation energy (30±3 kJ mol^{-1}) is similar to that reported for Na$^+$ diffusion in other hydrous metal oxides (35±2 and 27±4 kJ mol^{-1}, respectively, in the hydrous Sn$^{\mathrm{IV}}$ oxide and in the hydrous Nb$^{\mathrm{V}}$ oxide) and in a sulfonated polystyrene type resin (35 kJ mol^{-1}).[1,2,11] The larger $\bar{D}$ in hydrous Zr$^{\mathrm{IV}}$ oxide, as compared with that in other kinds of exchangers, therefore, is due to a larger $\bar{D}_\mathrm{o}$. According to Eyring, this means either a large distance between the equilibrium positions in the process of diffusion or activation accompanied by an increase in entropy, or both.[12]

Figure 7 shows the influence of the Na$^+$ concentration on the exchange rate at a slow revolution rate of the cage (660 min^{-1}). Dissimilarly to the case of a higher revolution rate, the exchange rate increased with Na$^+$ concentration in solution. In the region where $-\log(1-F)$ is linear with t and the film diffusion controls the rate, the rate increases with the ratio $C/\bar{C}$, as can be

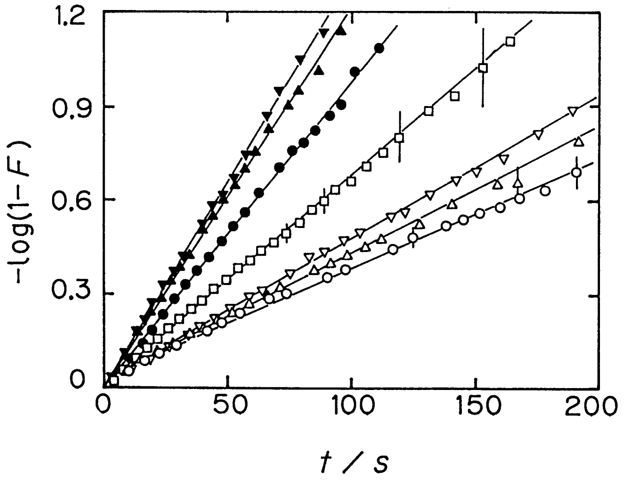

Fig. 8. Effect of temperature on the isotopic exchange rates (film diffusion).
0.01 mol dm^{-3} Na$^+$ solution; pH, 11.0; Revolution frequency of the cage, 104±4 min^{-1}.
Particle radius, 171 μm; Temperature/ °C, ○: 3.1; △: 5.2; ▽: 11.1; □26.3.
Particle radius, 125 μm; Temperature/ °C, ●: 15.2; ▲: 22.9, ▼: 24.6.

expected from Eq. 5. The Na$^+$ exchange capacity of hydrous Zr$^{\mathrm{IV}}$ oxide at pH 12 increased from 0.67 mmol g^{-1} in a 0.1 mol dm^{-3} Na$^+$ solution to 0.99 mmol g^{-1} in a 1 mol dm^{-3} Na$^+$ solution. The concentration dependence of the exchange rate suggests that film diffusion mainly controls the rate at a low flow rate of the solution through the exchanger particles.

In order to realize pure film-diffusion control, the experimental conditions should be such as those to minimize the value of $C/\overline{C}$ and the flow rate of the solution through the exchanger particles. The $C/\overline{C}$ ratio determined experimentally at pH 10 to 12 decreased with decreasing Na$^+$ concentration, reaching a minimum at 2×10^{-3} mol dm^{-3}, wherefrom it increased due to an abrupt decrease in $\overline{C}$. At this concentration, however, the infinite solution volume approximation is not obeyed in the present experimental conditions. The authors, therefore, adopted a 0.01 mol dm^{-3} Na$^+$ solution with pH 11.0 as a concentration to obtain a $C/\overline{C}$ as small as possible under the infinite solution volume condition. The revolution rate of the cage was set to 104±4 min^{-1}, and supplementary agitation was made by using a magnetic stirrer to keep the surrounding solution homogeneous.

The isotopic exchange rate at varying temperatures was measured as is shown in Fig. 8. The plots of $-\log(1-F)$ vs. t, except for smaller particles at 9.9 °C, were straight lines passing through the point of origin, indicating pure film diffusion control. Furthermore, the exchange rate increased with temperature and with decreasing particle size. The activation energy of Na$^+$ diffusion in the film (E_a') can be determined from the Arrhenius plot, since all parameters, except D, in the exponential term in Eq. 5 can be assumed to be constant over the limited temperature range studied; $E_a'=18.9\pm0.6$ and 18.8 ± 0.5 kJ mol^{-1}, respectively, for the exchangers with $r=171$ and 125 μm. They agreed well with the activation energy reported for the Na$^+$ diffusion coefficient in a NaCl solution (18.4 kJ mol^{-1}).[13] These results indicate that the rate of Na$^+$ diffusion in the film governs the rate of Na$^+$ isotopic exchange between hydrous Zr$^{\mathrm{IV}}$ oxide and 0.01 mol dm^{-3} Na$^+$ solutions. The film thickness (δ) was estimated from the slopes of the lines in Fig. 8 by using D values which were calculated from Robinson's data.[13] In this evaluation, the exchange capacity expressed volumetrically (mmol Na$^+$ cm^{-3}) was used. The film thickness was 2.3×10^{-3} cm at $r=171$ μm and 1.6×10^{-3} cm at $r=125$ μm, which were compatible with the values estimated from a hydrodynamic measurement (10^{-3} to 10^{-2} cm).[6] The increase in δ with particle radius is consistent with both the theoretical and empirical relations between the film thickness and the dimensionless hydrodynamic numbers.[6]

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