Bull. Chem. Soc. Jpn., 59, 169—174 (1986)

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

Yasushi Inoue,* Hiromichi Yamazaki, and Akira Osawa
Department of Nuclear Engineering, Faculty of Engineering, Tohoku University,
Aramaki, Sendai 980

(Received July 15, 1985)

The sodium isotopic exchange rate between the hydrous tin(IV) oxide ion exchanger in the Na^+ form and aqueous solutions was determined radiochemically. When the dried exchanger was used, the rate of the first step was controlled by the rate of the equilibration of water in the exchanger with the solutions, while the second step was found to be controlled by the diffusion of sodium ions in the particles (particle diffusion). When the exchanger had been sufficiently immersed in solutions in advance, the particle diffusion controlled the rate from the beginning. From the dependency of the rate of particle diffusion on the apparent particle size and the specific surface area of the exchanger, and on the sodium-ion concentrations in the solutions, the process controlling the rate is considered to be the diffusion in the primary particles, which are formed at the initial stage of precipitation and which aggregate to form the hydrous tin(IV) oxide gel. The diffusion constants and their activation energy (35 ± 2 KJ mol^{-1}) were also evaluated.

The ion-exchange equilibrium, the effect of thermal treatment, and other important properties were previously studied on a hydrous tin(IV) oxide ion exchanger prepared by the method recommended by the present authors.[1] Although the investigation of ion-exchange kinetics is very important for understanding the ion-exchange mechanism of the material, there has been only a little information to date. The measurement of the isotopic exchange rate of cations between the corresponding salt forms of ion exchangers and aqueous solutions is especially interesting because it provides fundamental data which are useful for elucidating ion-exchange kinetics.

This paper will deal with the results of radiochemical experiments undertaken to measure the isotopic exchange rate of sodium ions between the hydrous tin(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 tin(IV) oxide prepared by the method recommended previously was classified into three particle sizes by using Japan Industrial Standard sieves; it was then converted to the H^+ form by treating it with a 0.1 mol dm^{-3} HCl solution.[1] The exchanger was air-dried and stored in a desiccator containing a saturated NH_4Cl solution. Table 1 shows the particle size and some properties of each sample. The average particle radius was estimated by approximating the particle shape to a sphere by means of this equation: $4/3\pi r^3\rho N=W$, where ρ is the density of the sample, and N, the number of particles per W g, as counted under an optical microscope.

The exchanger in the H^+ form was converted to the Na^+ form by treating it with solutions, prepared by the desired combinations of NaCl and NaOH (pH 11), with the same compositions as those used for the rate measurement. The exchanger in the Na^+ form was then labeled with ^{22}Na by equilibrating it with a ^{22}Na solution having the same chemical compositions as the above solutions for about 2 d at room temperature. After having been washed with the solutions (free from ^{22}Na) used for converting to the Na^+ form, the exchanger was used for the rate measurement (wet system), or it was dried again to a constant weight over a saturated NH_4Cl solution and then also used for the experiments (dried system).

Apparatus and the Measurement of the Isotopic Exchange Rate. All the experiments were performed in a nitrogen atmosphere. The rate was measured in solutions with the same compositions as those used for converting the exchanger to the Na^+ form, by using the same apparatus as before.[2] Otherwise, an ion-exchange reaction occurs between H^+ and Na^+ ions, since the ion-exchange capacity for Na^+ strongly depends on the pH and on the concentration of the solution.[1] A 0.2-g to 0.5-g portion of the sample was placed in the cage and immesed in 200 cm^3 of a solution of a desired composition while the cage was being rotated. The frequency of revolution was measured

Table 1. Particle Size and Some Properties of the Samples

Particle size	Radius	Density	Ion-exchange Capacity[2]	Composition[3]	Specific Surface Area
mesh[1]	μm	g cm^{-3}	mmol g^{-1}	mol H_2O(mol Sn)$^{-1}$	m^2 g^{-1}
−70+100	86	3.52±0.08	1.160±0.008	2.14±0.02	174±8
−100+145	64	3.45±0.08	1.168±0.008		167±8
−145+200	45	3.48±0.08	1.165±0.008		178±8

1): Japan Industrial Standard mesh. 2): Exchange capacity for Na^+ at pH 11.0 (Ionic strength=0.10). 3): The water content was calculated from the weight loss at 850 °C.

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 (Fuji Denki Model NHS-2). The time of 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 by means of this equation: $C_\infty=CM/(M+m)$, where C 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 measurement is for a limited solution-volume condition, the infinite solution-volume approximation is closely obeyed under the present experimental conditions (less than 0.5 g of the exchanger per 200 cm^3 of the solutions).

The specific surface area of the sample was determined by the BET method (N_2 adsorption at −196 °C) using a Perkin-Elmer Shell Model 212D Sorptometer.

Results and Discussion

The sodium isotopic exchange rate was measured with two types of sample: (a) as dried and (b) wet. The results for each type of experiment will be described separately for convenience.

(1) Dried System. 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 ($t_{1/2}$) became shorter as the revolution rate increased, and reached a constant value at 1200 min^{-1}. Furthermore, it was confirmed that no particles were broken down during the agitation. On the basis of these results, a revolution rate of 1300 min^{-1} was adopted throughout the experiment for the dried system.

Figure 1 shows a comparison of the isotopic exchange rates in 0.01 mol dm^{-3} solutions of different sodium salts, indicating that no difference was observed in the rates between anions in the solution. This observation also held when the concentration of Na^+ was varied up to 1 mol dm^{-3}.

Figure 2 shows the influence of the sodium-ion concentration on the rate. When the concentration was higher than 0.5 mol dm^{-3}, the rate was independent of the concentration. When the concentration was less than 0.5 mol dm^{-3}, however, the rate increased with the concentration. It can be considered, from the dependence of the rate on the sodium-ion cencentration, that the rate is determined by either the diffusion of sodium ions in the adherent film (film diffusion) or by a chemical reaction at the exchange site. Since the sodium ions in the exchanger phase are in equilibrium with those in the solution phase, in the isotopic exchange reaction no concentration gradient of sodium ions exists in the film. Hence, the rate of the isotopic exchange would seem to be independent of the concentration of the sodium ion, unless the self-diffusion rate of sodium ions in solutions depends on the sodium-ion concentration. As the self-diffusion coefficients in NaCl solutions are almost constant in the concentration range lower than 1 mol dm^{-3}, the film diffusion cannot be the rate-controlling step. Furthermore, the chemical reacion in the exchanger does not appear to control the rate, because all the sodium ions in the exchanger exist as dissociated ions and, therefore, will exchange instantaneously with the incoming ions at the exchange sites.

When the exchange rate is controlled by the diffusion of ions within the particles (particle

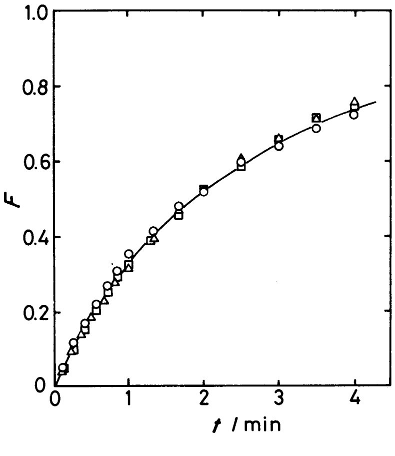

Fig. 1. Effect of diverse anions on the isotopic exchange rates (Dried system).
Sample, −70+100 mesh; Temperature, 5 °C; pH, 11.0, ○: 0.01 mol dm^{-3} Na(Cl,OH), △: 0.01 mol dm^{-3} $Na(NO_3,OH)$, □: 0.01 mol dm^{-3} $Na(ClO_4, OH)$.

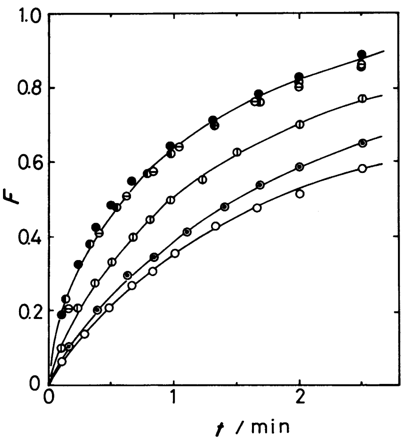

Fig. 2. Effect of Na^+ concentration on the isotopic exchange rates (Dried system).
Sample, −70+100 mesh; temperature, 5 °C; pH, 11.0; Na(Cl,OH) concd, ○: 0.01 mol dm^{-3}, ⊙: 0.05 mol dm^{-3}, ⦶: 0.1 mol dm^{-3}, ◐: 0.5 mol dm^{-3}, ●: 1 mol dm^{-3}, ⊖: 2 mol dm^{-3}.

diffusion), the sodium-ion concentration of a solution does not affect the rate, provided that the structure of the exchanger is unchanged and the change in the ionic composition of the exchanger does not affect the self-diffusion coefficients of sodium ions in the particles. Figure 3 shows the composition of the exchanger as a function of the sodium-ion concentration of the solutions. This figure suggests a strong correlation between the $t_{1/2}$ and the exchange capacity of the samples; the $t_{1/2}$ markedly changed with the sodium-ion concentration in the range lower than 0.5 mol dm^{-3}, where the capacity changed with the concentration, while it was unchanged in the concentration range higher than 0.5 mol dm^{-3}, where the capacity was nearly constant. Therefore, it appears to the present authors that the isotopic exchange rate is controlled by the particle diffusion and that the diffusion coefficients are affected by the composition of the exchanger.

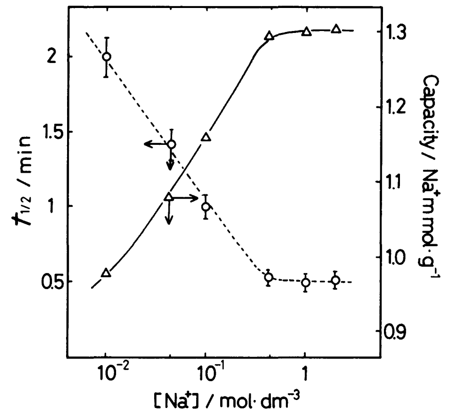

Fig. 3. Effect of Na$^+$ concentration on the half-exchange time and the exchange capacity (Dried system).
○: Half exchange time, △: Ion-exchange capacity for Na$^+$ at pH 11.0.

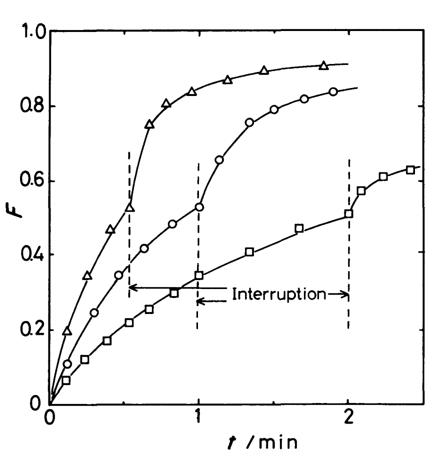

Fig. 4. Interruption test (Dried system).
Sample, $-70+100$ mesh; Temperature, 5 °C; pH, 11.0, □: 0.01 mol dm^{-3} Na(Cl,OH), ○: 0.1 mol dm^{-3} Na(Cl,OH), △: 1 mol dm^{-3} Na(Cl,OH).

Figure 4 shows the results of the method called "interruption test"; the exchangers were removed from the solution for 1 h and then reimmersed. In any concentration of sodium ions, the rate immediately after reimmersion was greater than that prior to the interruption. When these findings are combined with the above discussion, it can be concluded that, in solutions of any concentration, the rate is controlled by the particle diffusion.

When the isotopic exchange rates are controlled by the diffusion of ions in spherical exchangers immersed in a well-stirred solution of approximately an infinite volume, the fractional attainment of equilibrium can be obtained by solving this equation:[3]

$$F(t) = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{\pi^2 D n^2 t}{r^2}\right), \qquad (1)$$

where D is the self-diffusion coefficient of the ions in the exchanger and where r refers to the radius of the particles. When F is less than about 0.4, Eq. 1 is approximated by a simpler form:

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

which gives a fairly good approximation.[4] Therefore, a plot of F against the square root of the contact time must give a straight line passing through the point of origin in the region of F less than 0.4.

Figure 5 shows the effect of the particle size on the rate. A linear relation with the same slope between F and $\sqrt{t}$ held, irrespective of the particle size, but the straight lines did not pass through the point of origin; the displacement of the intercept from the origin increased with the particle size. In order to clarify the rate of the initial portion of the exchange reaciton, the effect of the particle size on the rate was

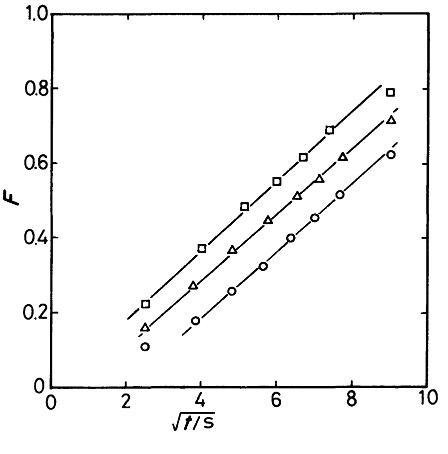

Fig. 5. Effect of particle size on the isotopic exchange rates (Dried system, I).
Temperature, 5 °C; 0.1 mol dm^{-3} Na(Cl,OH); pH, 11.0. Particle size/mesh; ○: $-70+100$, △: $-100+145$, □: $-145+200$.

measured under conditions of a slower rate (sodium-ion concentration, 0.01 mol dm^{-3}; revolution rate, 400 min^{-1}). The results are shown in Fig. 6. The F vs. $\sqrt{t}$ curves consist of two linear parts; the rate of exchange decreased with the particle size in the first step ($F<0.2$), but not in the second step. The latter step corresponds to the curves in Fig. 5. When the rate of this step is controlled by the particle diffusion, as has been claimed previously, the rate should depend on the particle size (Eq. 2). The experimental data, however, do not support this view. To solve the discrepancy, the specific surface area of each sample was determined; the results are shown in Table 1. This indicates that the surface areas of all the samples are the same, regardless of their apparent particle sizes. This can be understood by considering that the particles of the hydrous tin(IV) oxide are aggregates of the crystallites, subsequently called "primary particles," which have been produced at the beginning of precipitation, and that the surface area measured by the BET method is the internal surface attributable to the primary particles. If the diffusion of Na$^+$ within the primary particles is rate-controlling, the independence of the rate from the apparent particle size can be easily explained, since the size of the primary particles is irrelevant to the apparent particle sizes. When the shape of the primary particle is assumed to be spherical, the radius of the crystallite, r, can be calculated as $r=3/\rho S$, where ρ is the density (g cm^{-3}), and S, the specific surface area (cm^2 g^{-1}), of the exchanger. From the results in Table 1 the radius of the primary particle can be calculated to be $(4.9\pm0.3)\times10^{-7}$ cm.

Goodman and Gregg confirmed the existence of crystallites of hydrous tin(IV) oxide dried at 300 °C and determined their size ($1.5—8.0\times10^{-7}$ cm) with an electron microscope.[5] Heitner and Albu pointed out the possibility that hydrous thorium(IV) oxide is an aggregate of smaller units.[6] Hence, it is natural to consider that the particle of hydrous tin(IV) oxide consists of primary particles.

Provided the particle diffusion in the primary particles is rate-controlling, the ions should diffuse fast through the openings of the gel. In order for the ions to diffuse rapidly, these must be sufficient water in the openings. The water content of the dried sample is, however, less than that of the wet sample equilibrated with the test solutions, as is shown in Table 2. On the other hand, the rate of the penetration of the solution may reasonably be assumed to be faster into the smaller than into the larger particles. On the basis of these discussions, the rate of the first step is considered to be controlled by the rate of the equilibration of the water in the exchanger.

In conclusion, the rate of the exchange reaction on the dried system is initially controlled by the rate of the penetration of the solution into the particles, and subsequently by the diffusion rate of ions in the primary particles. In order to examine the latter step in detail, experiments were also carried out on the wet system.

(2) Wet System. In the wet system, the rate of

Table 2. Comparison of Water Contents of the Samples

Na$^+$-concentration of the solution	Water content[1]/wt%	
	Dried-sample[2]	Wet-sample[3]
0.01 mol dm^{-3}	18.3 ± 0.1	19.5 ± 0.1
0.1 mol dm^{-3}	18.0 ± 0.1	19.5 ± 0.1
1 mol dm^{-3}	17.8 ± 0.1	19.4 ± 0.1

1): Weight loss at 850 °C. 2): Dried over a saturated NH$_4$Cl solution. 3): Immediately after the separation from the Na$^+$ solution.

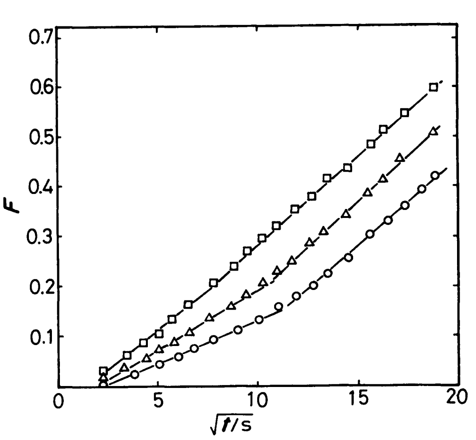

Fig. 6. Effect of particle size on the isotopic exchange rates (Dried system, II).
Temperature, 5 °C; Revolution rate, 400 min^{-1}; 0.01 mol dm^{-3} Na(Cl, OH); pH, 11.0. Particle size/mesh; ○: −70+100, △: 100+145, □: 145+200.

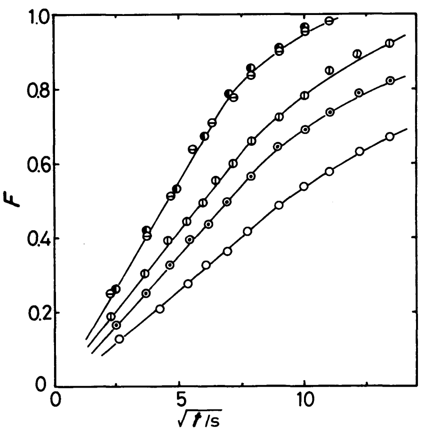

Fig. 7. Effect of Na$^+$ concentration on the isotopic exchange rates (Wet system).
Sample, −70+100 mesh; Temperature, 5 °C; pH, 11.0; Na(Cl, OH) concd, ○: 0.01 mol dm^{-3}, ⊙: 0.05 mol dm^{-3}, ⦶: 0.1 mol dm^{-3}, ⊖: 0.5 mol dm^{-3}, ◐: 1 mol dm^{-3}.

Table 3. Effect of Temperature on Na^+ Self-diffusion Coefficient

Na^+ concentration in the solution / mol dm^{-3}	Temperature / °C	D / $m^2\ s^{-1}$	E_a / KJ mol^{-1}	D_0 / $m^2\ s^{-1}$
0.01	5.0	1.2×10^{-20}	35±2	4.7×10^{-14}
	20.0	2.1×10^{-20}		
	30.0	4.0×10^{-20}		
	40.0	6.8×10^{-20}		
1	5.0	5.3×10^{-20}	34±2	2.2×10^{-14}
	12.5	9.3×10^{-20}		
	20.0	1.2×10^{-19}		
	25.0	1.5×10^{-19}		

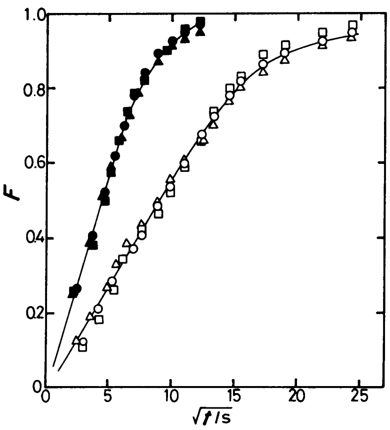

Fig. 8. Effect of particle size on the isotopic exchange rates (Wet system).
Temperature, 5 °C; pH, 11.0; Open marks: 0.01 mol dm^{-3} Na(Cl,OH), Filled marks: 1 mol dm^{-3} Na(Cl, OH). Particle size/mesh; ○●: −70+100, △▲: −100+145, □■: −145+200.

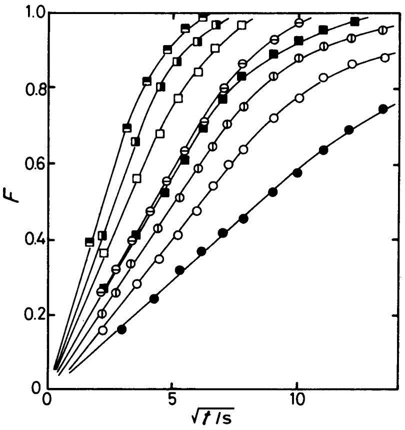

Fig. 9. Effect of temperature on the isotopic exchange rates (Wet system).
Sample, −70+100 mesh; 0.01 mol dm^{-3} Na(Cl,OH); pH, 11.0; ●: 5.0 °C, ○: 20.0 °C, ⦶: 30.0 °C, ⊖: 40.0 °C; 1 M Na(Cl,OH); pH, 11.0; ■: 5.0 °C, □: 12.5 °C, ◨: 20.0 °C, ⬒: 25.0 °C.

the exchange reaction became constant at a revolution rate greater than 1000 min^{-1}, irrespective of the sodium-ion concentration. Hence, a revolution rate of 1100 min^{-1} was adopted throughout the subsequent experiments.

Figure 7 indicates that the dependency of the rate on the sodium-ion concentration was similar to that for the dried system (Fig. 2) and that the straight lines between F and $\sqrt{t}$ in the F range smaller than about 0.5 passed through the point of origin. This relation means that the rate is controlled by the particle diffusion from the beginning of the reacion.

The effect of the particle size on the rate is shown in Fig. 8, which indicates that the rate is controlled by the diffusion of sodium ions within the primary particles, since it was independent of the particle size, in the same manner as in the second step in the dried system.

The fractional attainment of equilibrium against the square root of the time was studied in sodium-ion solutions of 0.01 and 1 mol dm^{-3} as a function of the temperature, as is shown in Fig. 9. The figure indicates that the rate of the exchange reaction increased with the temperature. The self-diffusion coefficients of sodium ions, D, were then evaluated by means of Eq. 2 from the slopes of the straight lines and the average radius of the primary particles. These values are summarized in Table 3. When log D was plotted against $1/T$, a good linearity was obtained. From the Arrhenius equation, $D = D_0 \exp(-E_a/RT)$, the activation energy, E_a, and the constant, D_0, were determined. As the activation energies obtained in solutions of 0.01 and 1 mol dm^{-3} agreed well with each other, the mechanism of the diffusion of sodium ions in the exchanger is considered to be unchanged by the compositions of the exchangers. The self-diffusion coefficients of sodium ions at 5 °C have been reported by Barrer and Rees, and by Dyer and Gill, to be $2.1\times10^{-18}\ m^2\ s^{-1}$ in analcite and $2.0\times10^{-17}\ m^2\ s^{-1}$ in crystalline zirconium(IV) phosphate respectively.[7,8] These values are larger than the present results. The $t_{1/2}$ is, however, considerably shorter for hydrous tin(IV) oxide (a few minutes) than for analcite and crystalline zirconium(IV) phosphate (a few hours), because in the case of the hydrous tin(IV) oxide, the particle size practically controlling the exchange rate is smaller than the apparent particle size. Such a fast exchange rate for the hydrous tin(IV) oxide is of great practical value.

References

1) Y. Inoue and H. Yamazaki, *Bull. Chem. Soc. Jpn.*, **55**, 3782 (1982); **57**, 1534, 3437 (1984); **58**, 1292 (1985).

2) T. R. E. Kressman and J. A. Kitchener, *Faraday Discuss. Chem. Soc.*, **7**, 90 (1949).

3) F. Helfferich, "Ion Exchange," McGraw-Hill, New York (1963), Chap. 6.

4) G. E. Boyd, A. W. Adamson, and L. S. Myers, *J. Am. Chem. Soc.*, **69**, 2836 (1947).

5) J. F. Goodman and S. J. Gregg, *J. Chem. Soc.*, **1960**, 1162.

6) G. W. Heitner and A. Y. Albu, *J. Appl. Chem.*, **15**, 445 (1962).

7) R. M. Barrer and L. V. C. Rees, *J. Chem. Soc.*, **1959**, 709.

8) A. Dyer and J. S. Gill, *J. Inorg. Nucl. Chem.*, **39**, 665 (1976).