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Studies of the Hydrous Titanium Oxide Ion Exchanger. VII. Effects of pH at Precipitation on the Isotopic Exchange Rate of Na^+ and Cs^+ Ions between the Exchanger in the Relevant Ionic Form and Aqueous Solutions

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The isotopic exchange rate of Na^+ and Cs^+ between hydrous titanium(IV) oxide in the relevant ionic form and aqueous solutions was measured radiochemically. Four kinds of exchangers were precipitated at various pH's: pH 4, 6, 8, and 10. The rate of each alkali metal ion was controlled by the diffusion of the ions in the exchanger particles at any pH of the surrounding solutions. At high pH of the solution, the diffusion of Cs^+ in the exchangers precipitated at pH 4 and 6 was faster than that of Na^+, but the difference of diffusion coefficients between two ions was negligible in the exchangers precipitated above pH 8. The diffusion coefficient in a particular exchanger decreased with increasing amount of ions taken up on the exchanger, owing to the increase of frequency of the electrostatic interaction between ions and dissociated ion-exchange sites. The difference of diffusion coefficients among exchangers was interpreted in terms of the difference in the microstructure of the exchanger matrix.

Hydrous titanium(IV) oxide is one of the promising materials for use in the processing of radioactive liquid waste. This material, however, is liable to vary in ion-exchange capacity and surface properties with synthetic conditions.[1,2] In addition to these properties, we previously reported that kinetic behavior also changed with pH at precipitation; the isotopic exchange rate of Na^+ between the exchanger in the Na^+ form precipitated at pH 6 and aqueous solution was much faster than that on the exchanger precipitated at pH 13.[3] This aroused our interest regarding to how kinetic and equilibrium properties of hydrous titanium(IV) oxide vary with pH at precipitation. Furthermore, comparing the rate between two alkali metal ions, which are both considered to be sorbed electrostatically on hydrous titanium(IV) oxide, we can obtain the effect of ionic size on the rate of transfer of ions.

This paper discusses the results of experiments undertaken to measure the isotopic exchange rate of Na^+ and Cs^+ between hydrous titanium(IV) oxide exchangers, precipitated at several pH's, in the relevant ionic form and aqueous solutions with varying pH.

Experimental

Preparation of the Exchanger in the Salt Form Spiked with Radioisotopes. Hydrous titanium(IV) oxide was precipitated by adding 1 mol dm^{-3} NaOH solution into 1 mol dm^{-3} $TiCl_4$ solution with vigorous stirring to make pH 4, 6, 8, and 10. After 2 d, the precipitate was separated from the mother liquor by filtration under suction, and was then uniformly dispersed into distilled water. The precipitate was filtered again after being completely sedimented, and dried at 70 °C. The resulting product was ground and classified into several particle sizes 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 it was 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). These exchangers are referred to as P4, P6, and so on corresponding to the pH at which the exchanger was precipitated.

The exchanger in the H^+ form was then converted to a salt (Na^+ or Cs^+) form by treating it with solutions having the same chemical composition as those used for the rate measurement. The exchanger was then labeled with a radioisotope (^{22}Na or ^{137}Cs) by equilibrating it with a radioisotope solution having the same chemical composition as the above mentioned solution for longer than 2 d at room temperature. After it was separated from the solution by filtration under suction, the exchanger was used for a rate measurement. The solutions of metal ions used for these procedures were prepared by desired combinations of NaCl (CsCl) and NaOH (CsOH) solutions in which Goods' buffer reagents were added to adjust the pH. The Goods' buffers used were 2-(*N*-morpholino)ethanesulfonic acid (pH 6), 2-(cyclohexylamino)-ethanesulfonic acid (pH 9), and 3-cyclohexylaminopropanesulfonic acid (pH 11). The presence of the buffer reagents between 0.005 and 0.05 mol dm^{-3} was experimentally confirmed not to affect the reaction rate.

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 a 84.8 wt% glycerol solution using a Seishin Enterprise micro-photo-sizer, Model SKC-2000C. The specific surface area of the exchanger in the H^+ form, after heating it at 120 °C, was measured by the BET method (N_2 adsorption at -196 °C). The pore size distribution and the pore volume were calculated by Inkley's method from the adsorption isotherm of N_2 at -196 °C.[4] The density of the exchanger was measured in the usual manner using a 10-cm^3 pycnometer. The water content was calculated from the weight loss of exchanger heated to 900 °C. Table 1 shows the particle size and some properties of the exchanger.

The uptake curves of the exchanger for Na^+ and Cs^+ as well as Cl^- were measured by a batch method; the exchanger (0.06 g) in the H^+ form was immersed in 10 cm^3 of various solutions, prepared by the desired combination of 0.10 mol dm^{-3} NaCl (CsCl) and either 0.10 mol dm^{-3} NaOH (CsOH) solutions or 0.10 mol dm^{-3} HCl solution. This was followed by pH measurement and by measurement of alkali metal and chloride ions. The alkali metal ions were converted to an equivalent amount of corresponding chloride and indirectly measured by titrating the chloride ions. The amount of ions taken up by the exchanger was evaluated from the difference between the initial and the final concentrations of respective ions in the solution.

The ion-exchange isotherm between Na^+ and Cs^+ was measured as follows. The exchanger (0.05 g) in the Na^+ form was immersed in 5 cm^3 of various solutions prepared by the desired combination of 0.10 mol dm^{-3} Na^+- and 0.10 mol dm^{-3} Cs^+ solutions. The fraction of the ions in the exchanger and the solution was evaluated from the difference between the initial and the final concentrations of respective ions in the solution. The concentrations of alkali metal ions were measured by atomic absorption spectrometry.

Measurement of the Isotopic Exchange Rate. Rate measurements were done in a nitrogen atmosphere using the apparatus described earlier.[5] The rate was measured in a solution with the same chemical composition as that used for converting the exchanger to the salt form; otherwise, an ion-exchange reaction would occur between H^+ and the metal ions, since the amount of ions taken up 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. The frequency of rotation was kept constant at 1300 min^{-1}, which is experimentally confirmed to be sufficient agitation. The solution had been adjusted in advance to a constant temperature of 10.0 °C within ±0.1 °C. Samples of solution (0.2 cm^3) were taken out at appropriate times 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 a sample of the solution. The fractional attainment of equilibrium, $F=Q_t/Q_\infty$, was calculated from these results; here, Q_t is total radioactivity of 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^+ or Cs^+ 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 these experimental conditions; the ratio of the total amount of alkali metal ions in the exchanger to that in the solution was less than 0.02, unless otherwise noted.

Results and Discussion

Table 1 shows that these hydrous titanium(IV) oxides have a large porosity, which is the product of the specific pore volume and the density, and large internal surface area, and contain plenty of water molecules in the pore. Thus, a perfect network of paths of the diffusing ions may develop in the particles and the particles of hydrous titanium(IV) oxide can be regarded as being homogeneous from the standpoint of ion-exchange kinetics.

Figures 1 and 2 show the uptake curves on each exchanger. These samples are amphoteric ion-exchangers with larger ion-exchange capacities for cations than for anions. P10 exchanger sorbs more cations than P4, and does not take up anions as much as P4. The isoelectric point decreases from pH 4.8 in P4 to pH 4.0 in P10. Cation exchange ability, therefore, increases with increasing pH at precipitation. The amount of Cs^+ sorbed on the exchanger is larger than that of Na^+ below pH 7, but the order is reversed above this pH. In the higher pH region the difference of uptake between Na^+ and Cs^+ increases with pH. This result suggests dependence of the relative affinity of the exchanger for the ions on pH

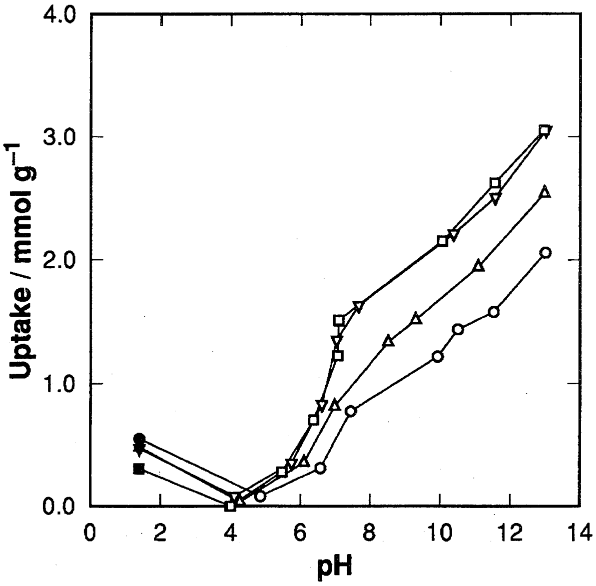

Fig. 1. Uptake curves for Na^+ and Cl^-. m(exchanger amount)/V(solution volume) = 0.06 g/10 cm^3; Initial concentration of each ion: 0.10 mol dm^{-3}. Ion, Open mark: Na^+; Solid mark: Cl^-. Exchanger, ○●: P4; △▲: P6; ▽▼: P8; □■: P10.

Table 1. Particle Size and Some Properties of Sample

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}
P4	169±8	2.32±0.03	1.60±0.02	241±6	0.17±0.01
P6	178±7	2.21±0.03	1.74±0.02	256±4	0.17±0.01
P8	168±7	2.34±0.03	1.65±0.02	242±4	0.15±0.01
P10	165±7	2.39±0.02	1.50±0.02	201±6	0.12±0.01

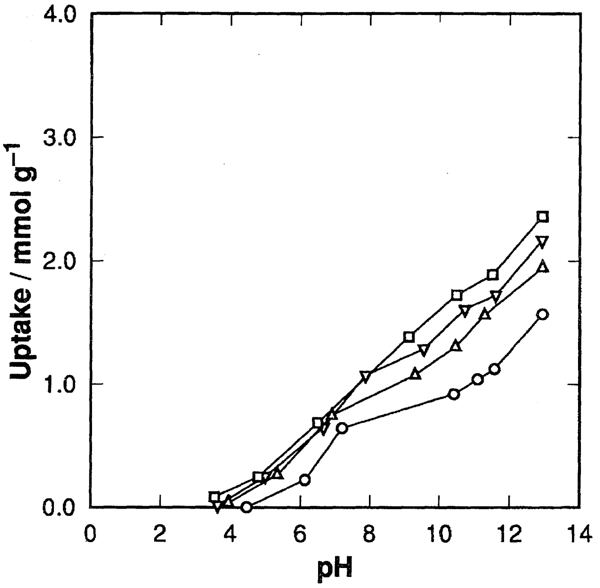

Fig. 2. Uptake curves for Cs^+. Exchanger, ○: P4; △: P6; ▽: P8; □: P10.

of the solution. From these observations, we can consider that these materials differ appreciably from each other in the acid–base property.

When the 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:[6)]

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

where

$$B = \pi^2D/r^2, \qquad (2)$$

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:[7)]

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

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

Figure 3 shows an example of the isotopic exchange rate of Na^+ and Cs^+ between the exchanger and relevant salt solutions of pH 11, indicating that the plots agree well with this expectation on any exchanger. The diffusion coefficients of Na^+ and Cs^+ become progressively greater in the following order; P10<P8<P6<P4, that is, diffusion of ions is faster in the exchanger precipitated at lower pH. The effect of pH of the solution on the isotopic exchange rate in P4 is shown in Fig. 4. The D value of Na^+ increases monotonously with decreasing pH, but that of Cs^+ increases with decreasing pH until pH 9 or 6. This figure also shows that the difference of

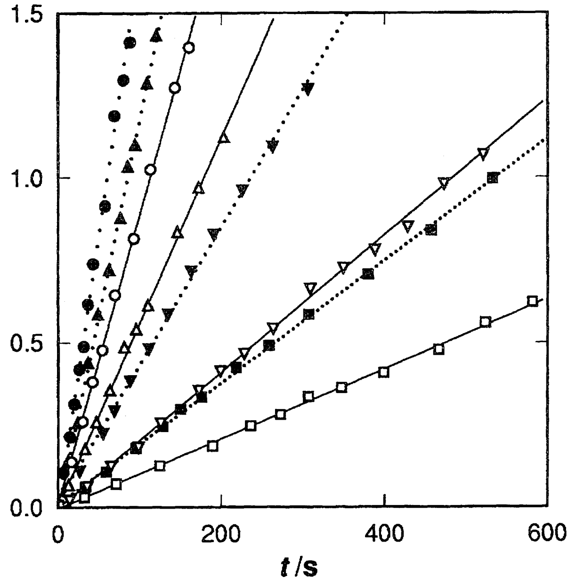

Fig. 3. Isotopic exchange rates of Na^+ and Cs^+. Temperature, 10.0 °C; Concentration of metal ions, 0.1 mol dm^{-3}; pH of solutions, 11.0. Ion, Open mark: Na^+; Solid mark: Cs^+. Exchanger, ○●: P4; △▲: P6; ▽▼: P8; □■: P10.

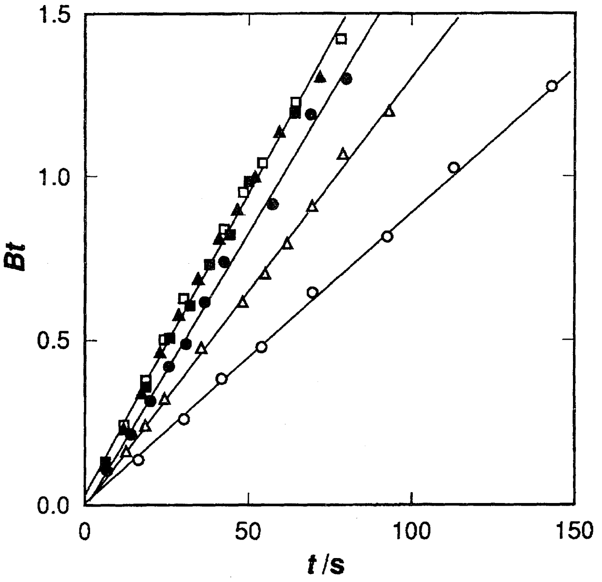

Fig. 4. Effect of pH on the isotopic exchange rate on P4. Temperature, 10.0 °C; Concentration of metal ions, 0.1 mol dm^{-3}. Ion, Open mark: Na^+; Solid mark: Cs^+. pH of the solutions, ○●: 11.0; △▲: 9.0; □■: 6.0.

D between Na^+ and Cs^+ decreases with decreasing pH. The dependency of D of Na^+ and Cs^+ in other exchangers on the pH is similar to P4.

Figure 5 shows the plots of the diffusion coefficient as a function of the amount of ions taken up on the exchanger, which is obtained from Fig. 1. The D value decreases with increasing density of the dissociated ion-exchange sites. This observation can be understood by considering that the increase of frequency of the electrostatic interaction between ions and dissociated sites slows down the movement of

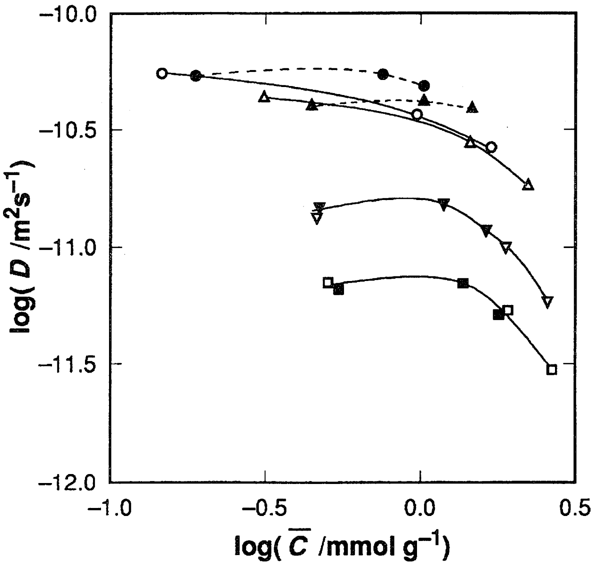

Fig. 5. Relation between amount of ion taken up ($\overline{C}$) and diffusion coefficient (D). Temperature, 10.0 °C; Concentration of metal ions, 0.1 mol dm^{-3}. Ion, Open mark: Na$^+$; Solid mark: Cs$^+$. Exchanger, ○●: P4; △▲: P6; ▽▼: P8; □■: P10.

ions since ions would diffuse in the exchanger particles while interacting with the sites. The D values in P4 or P6 for Na$^+$ and for Cs$^+$, respectively, (1.8—5.5)$\times10^{-11}$ and (3.9—5.5)$\times10^{-11}$ m^2 s^{-1} at 10 °C, are similar to those in other hydrous metals (Nb, Zr, and composite Si–Ti) oxides; (2.3—7.9)$\times10^{-11}$ m^2 s^{-1} for Na$^+$-diffusion and (2.0—5.9)$\times10^{-11}$ m^2 s^{-1} for Cs$^+$-diffusion at 10 °C.[8—10] The D value in a sulfonated polystyrene type resin of 8.6% divinylbenzene also resembles that in P4 or P6; 5.28$\times10^{-11}$ and 8.94$\times10^{-11}$ m^2 s^{-1} at 10 °C, respectively, for Na$^+$ and for Cs$^+$.[11] Diffusion of Na$^+$ and Cs$^+$, however, is much slower in P8 and P10 than in P4 and P6 at a certain concentration of ions in the exchanger. Furthermore, the uptake curves on P8 and P10 are about the same but the D values differ markedly. These facts cannot be explained only by the difference of the density of the dissociated sites.

Not only the density of the dissociated sites but also the acidity may change with pH. Thus we measured the ion-exchange isotherm between Na$^+$ in the exchanger and Cs$^+$ in the solution to discover the relative strength between Na$^+$ and Cs$^+$ to interact with the sites. As shown in Fig. 6, at pH 6 interaction is stronger for Cs$^+$ than for Na$^+$, which is attributable to the dissociation of the sites having strong acidity. Since the dissociation of the weakly acidic sites is increased with increasing pH, the selectivity for Cs$^+$ lowers in higher pH of the solution, as in the case of weakly acidic resin showing affinity stronger for Na$^+$ than for Cs$^+$.[12] The difference of the affinity to the exchanger between two ions is negligible at pH 9, and Na$^+$ is slightly more selective than Cs$^+$ at pH 11.

In general, the relative strength of interaction between ions and sites changes with pH as mentioned above. The selectivity for Na$^+$, however, is slightly stronger in the exchanger

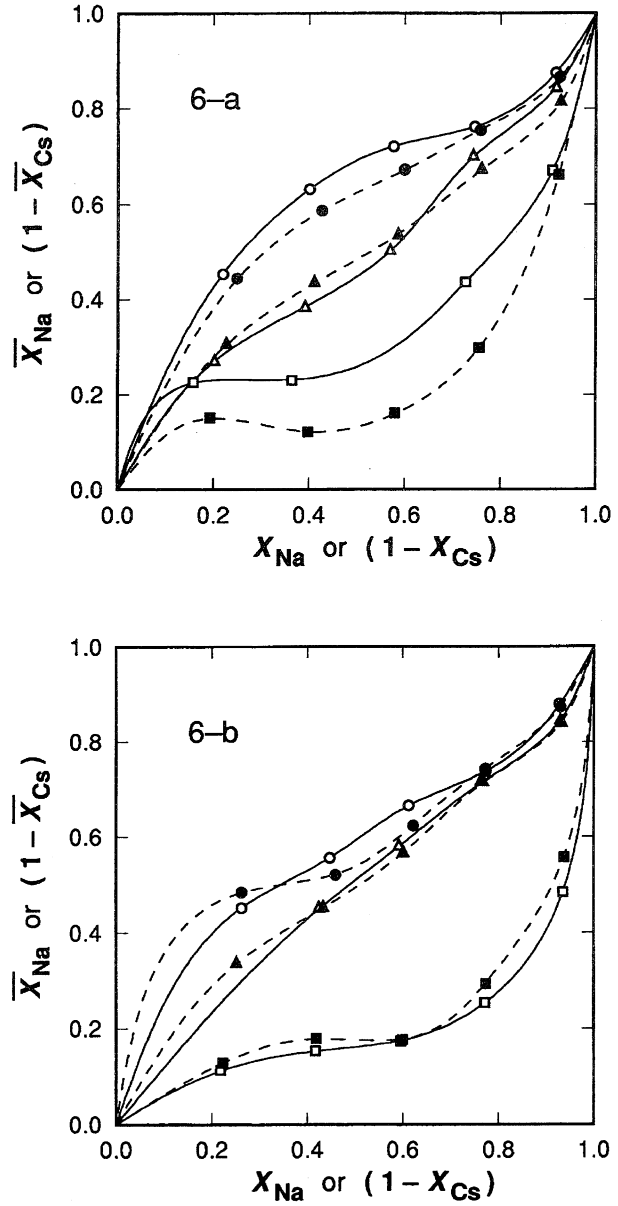

Fig. 6. Ion-exchange isotherm between Na$^+$ and Cs$^+$. X_{Na}: Ionic fraction of Na$^+$ in the solution. $\overline{X}_{\mathrm{Na}}$: Ionic fraction of Na$^+$ in the exchanger. Temperature, 20.0 °C; Concentration of metal ions, 0.1 mol dm^{-3}. pH of the solutions, ○●: 11.0; △▲: 9.0; □■: 6.0. Exchanger, 6-a, Open mark: P4; Solid mark: P6. 6-b, Open mark: P8; Solid mark: P10.

precipitated at low pH than in that precipitated at high pH when we note the affinity to the ions at each pH. This small difference of selectivity cannot account for the difference of the D values among these exchangers but for that between Na$^+$ and Cs$^+$ in an exchanger at a particular pH of the solution. The difference of the D values between two ions is negligible when the uptake is very small (Fig. 5) although the D values in strongly acidic resins and in aqueous solutions at infinite dilution is larger for Cs$^+$ than for Na$^+$ due to hydrated ionic size.[11,13] The strong interaction between Cs$^+$ and sites at low pH of the solution, shown in Fig. 6, should slow down the mobility of ions. The dissociation of the sites

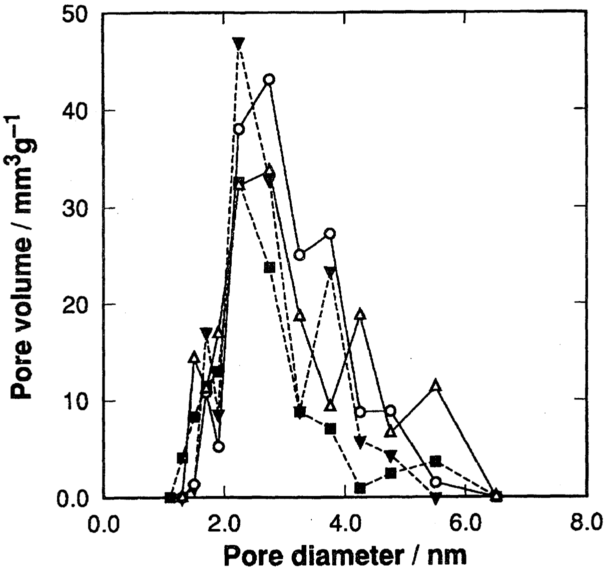

Fig. 7. Pore size distribution curves. Exchanger, ○: P4; △: P6; ▼: P8; ■: P10.

in P8 and P10 increases the frequency and the strength of interaction between Cs^+ and sites because these exchangers include sites having a high affinity for Cs^+ even in higher pH of the solution. Therefore, D values between Na^+ and Cs^+ are not different over a wide range in P8 or P10.

Figure 7 shows the pore size distribution curves. The most probable diameter of pores, irrespective of the kind of exchangers, is around 2.5 nm, which is larger than the diameter of hydrated alkali metal ions (reported to be 0.72 nm for Na^+ and 0.66 nm for Cs^+).[14] These materials, therefore, have paths geometrically large enough to move hydrated alkali metal ions. The fraction of pores of large diameter is greater in P4 and P6 than that in P8 and P10. Retardation in the diffusion of ions is increased with a decreasing fraction of pores with large diameters since the collision of ions themselves and the friction of ions with pore walls may become great. Porosity decreases in the order of P4, P6, P8, and P10, which can be calculated from Table 1. Therefore, the diffusion path is restricted by the solid matrix more in P10 than in the others. As a matter of course, the geometry of the pores is not clearly defined by the measurement of the N_2 adsorption isotherm, but it seems likely that tortuosity and constrictivity of pores may differ from exchanger to exchanger, which is suggested by the variation of the ratio of the specific surface area to the specific pore volume. From these observations, it would be concluded that the difference of the D values between these hydrous titanium(IV) oxides is mainly caused by the difference in the microstructure of the exchangers.

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