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Sodium Isotopic Exchange Rate between Disodium Zirconium(IV) Bis(orthophosphate) Trihydrate and Aqueous Solutions

Yasushi Inoue* and Yoshimune Yamada

Department of Nuclear Engineering, Faculty of Engineering, Tohoku University, Aramaki-aza-Aoba, Sendai 980

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The sodium isotopic exchange rate between the large crystals of disodium zirconium(IV) bis(orthophosphate) trihydrate and aqueous solutions was determined radiochemically. The exchange proceeded quickly up to 5% of the total, followed by a slow process. The first step was attributed to the instantaneous attainment of the equilibrium between the imperfect surface layers of the crystals and the solution, and the second step was found to be controlled by the diffusion of sodium ions along the direction perpendicular to the layers consisting of zirconium atoms. The diffusion constant, D, was calculated with the equation obtained by Fick's diffusion law under the conditions of slab geometry and infinite solution volume. From the dependence of D on temperature, the activation energy for the diffusion was evaluated to be 101 kJ mol^{-1}.

Although the investigation of ion-exchange kinetics is very important for understanding the ion-exchange mechanism of crystalline zirconium(IV) bis(hydrogenphosphate) monohydrate (ZP), there has been only a little information up to date.[1–8] The measurement of the isotopic exchange rate of cations between the corresponding salt forms of ZP and aqueous solutions is especially interesting because it would provide the fundamental data which are useful for elucidating ion-exchange kinetics.

One of the outstanding studies made on this subject is that of Costantino *et al.*[8] They determined the isotopic exchange rate of sodium and potassium ions between the corresponding salt forms of powdered ZP, $M_2Zr(PO_4)_2 \cdot 3H_2O$ (M=Na and K), and aqueous solutions and analyzed the data by the particle-diffusion mechanism. They assumed that the particles of the exchanger were spherically symmetrical, and succeeded in describing the rate law by one diffusion constant. In principle, however, the rate depends on the direction of diffusion because the crystal is not isomorphous, since it has a layered structure. Their assumption, therefore, is an approximation suitable for microcrystalline powders.

When large crystals having crystals shaped like thin platelets are used, the assumption made by Costantino *et al.* will be no longer valid. Hence, if macrocrystals, which have uniform in size are used and the rate is measured as a function of particle size, we can get a deeper insight into the isotopic exchange rate. This induced us to establish the conditions for preparing ZP with a large and uniform crystal size[9] and to obtain the information of phase stability of its disodium forms,[10] as reported previously. This information enables us to carry out the rate study more elaborately than before.

This paper deals with the results of the radiochemical experiments undertaken to measure the isotopic exchange rate of sodium ions between large crystals of $Na_2Zr(PO_4)_2 \cdot 3H_2O$ and concentrated solutions of sodium salts.

Experimental

Preparation of $Na_2Zr(PO_4)_2 \cdot 3H_2O$ Spiked with ^{22}Na. The crystals of $Na_2Zr(PO_4)_2 \cdot 3H_2O$ prepared by the method recommended previously[9] were classified into four particle sizes: 48—70, 70—100, 100—145, and 145—250 mesh, by using Japan Industrial Standard sieves. The size of each fraction was then made more uniform by the sedimentation method with the equipment of Aly and Latimer.[11] The fraction of each uniform size was collected, dried in a desiccator over a saturated NaCl solution, and the particle size was measured with an optical microscope. The average size of each fraction is given in Table 1. $Na_2Zr(PO_4)_2 \cdot 3H_2O$ thus obtained was then labeled with ^{22}Na by equilibrating 1 g of the sample with 10 cm^3 of 0.1 mol dm^{-3} NaOH solution containing ^{22}Na for two weeks at 40 °C. After being washed with distilled water, it was dried again to a constant weight over saturated NaCl solution. The product was verified to be homogeneously labeled at about 40 μCi/g (1 Ci=3.7×10^{10} Bq) and was used for the determination of the isotopic exchange rate.

Apparatus. The apparatus used for the measurements of the isotopic exchange rate is shown in Fig. 1. The sample is placed in a stainless steel cage fitted with a 400 mesh stainless steel screen on the openings at the side wall and the bottom. The cage was designed by modifying the device developed by Kressman and Kitchner;[12] the upper base of

Table 1. Particle size of the samples

No.	Mean crystal size/μm		
	Length	Width	Thickness
1	413±31	333±40	16±5
2	286±44	238±32	16±3
3	190±24	159±15	16±2
4	127±16	111±23	16±2

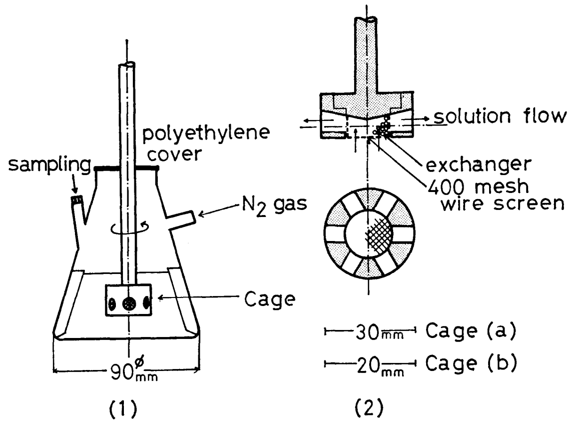

Fig. 1. Apparatus for the measurement of the isotopic exchange rate.

the inner surface was tapered and grooved so that no air might stay in the cage. This ensures the intimate contact of the exchanger with the solution. The cage is connected to the shaft of a stirrer and dipped into the solution in a conical beaker. The lower part of its wall is indented at three places to prevent the surface of the solution from becoming paraboloid when the solution is vigorously agitated by the stirrer. As it is rotated in the solution, the cage draws liquid from the bottom screen and discharges it through the side screen into the bulk of the solution; thus a very rapid stream of the solution passes through the sample placed inside the cage. The frequency of revolution was measured with a Yokogawa Model 2607 Photo Tachometer.

Measurements of the Isotopic Exchange Rate. All the experiments were performed in nitrogen atmosphere. A portion of 400 mg of the sample was placed in the cage and immersed into 200 cm^3 of the test solutions while the cage was rotated. The solution had been adjusted in advance to a constant temperature within ±0.1 °C (below 50 °C), or within ±0.2 °C (above 50 °C). Aliquots of the solution (about 0.2 cm^3) were taken out at appropriate time intervals in order to measure the radioactivity. A well-type NaI(Tl)scintillation counter (Fuji Denki Model NHS-2) was used for the measurement of radioactivity. The time of contact of the solution with the exchanger was taken as the time elapsed between the immersion of the cage and the withdrawal of an aliquot of the solution.

The fractional attainment of equilibrium, $F=C_t/C_\infty$, 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 the equation, $C_\infty=CM/(M+m)$, where C is the initial total radioactivity of the exchanger, and m and M are the total amounts of Na$^+$ ions in the exchanger and in the solution, respectively.

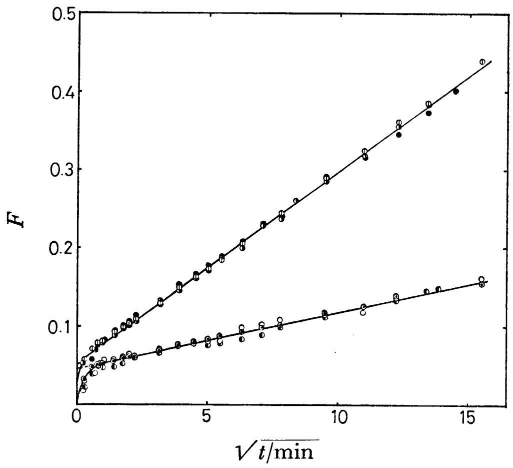

Fig. 2. Effect of anions on the isotopic exchange rate (sample 3).
T, 44.9 °C. ⦶: 5 mol dm^{-3} NaNO$_3$ (pH 11), ◑: 5 mol dm^{-3} NaCl (pH 11), ●: 5 mol dm^{-3} NaOH. T, 24.1 °C. ⊙: 0.5 mol dm^{-3} NaNO$_3$ (pH 11), ○̲: 0.5 mol dm^{-3} NaCl (pH 11), ◐: 0.5 mol dm^{-3} NaOH.

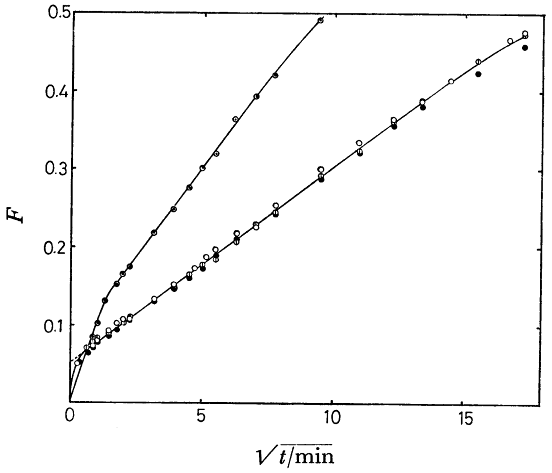

Fig. 3. Effect of Na$^+$ ion concentration on the isotopic exchange rate (sample 3).
pH 11. ⊙: 0.01 mol dm^{-3} NaNO$_3$, ○: 0.5 mol dm^{-3} NaNO$_3$, ⦶: 5 mol dm^{-3} NaNO$_3$, ●: saturated NaNO$_3$.

Results and Discussion

In order to determine the efficiency of agitation, the effect of the stirring rate and the size of the cage on the half-exchange time was examined for solutions of pH 11 having different NaNO$_3$ concentrations. In solutions as dilute as 0.01 mol dm^{-3} NaNO$_3$, the time required for half-exchange became shorter as the revolution rate increased, and became constant at 1000 min^{-1}. In more concentrated solutions, it was almost independent of the rate of revolution. This observation was irrespective of the diameter of the base screen of the cages used (17 and 12 mm): that is, the constant exchange rate is not due to the limiting hydrodynamic efficiency of the stirring. Furthermore, it was confirmed that no crystals were broken down during the agitation. From these results a revolution rate of 1400 min^{-1} was adopted throughout the subsequent experiments.

To make clear the rate controlling steps of the isotopic exchange, a plot of F against the square root of contact time t, was made for different experimental conditions. Figure 2 shows the comparison of the isotopic exchange rates in solutions of different sodium salts, indicating that no difference was observed in the rates for different anions in the solution. Figure 3 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 sodium-ion concentration, and a linear relation between F and $\sqrt{t}$ held in the F range smaller than about 0.4, except for the initial portion of these plots. When the sodium-ion concentration was 0.01 mol dm^{-3}, however, the rate was much faster than that obtained for the solutions of higher concentrations than 0.5 mol dm^{-3}; in addition, linearity between F and $\sqrt{t}$ did not hold.

The observations that the exchange rate is not affected by the revolution rate of the cage, by the kind of anions, or by the sodium-ion concentration, mean that the rate is controlled by the process within the particles. Moreover, the linearity of F *vs.* $\sqrt{t}$ in the F range smaller than 0.4 indicates that the particle diffusion is rate-controlling, and that the infinite solution-volume approximation is closely obeyed in this range, although the method of the rate measurement is for the limited solution-volume condition. The deviation from the linearity means that the assumption of the infinite solution-volume condition is no longer

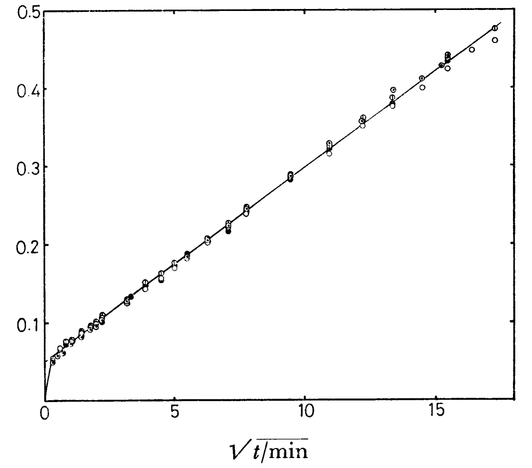

Fig. 4. Effect of particle size on the isotopic exchange rate.
T, 44.9 °C, 5 mol dm^{-3} $NaNO_3$. ⊙: Sample 1, ○: sample 2, ⦶: sample 3, ●: sample 4.

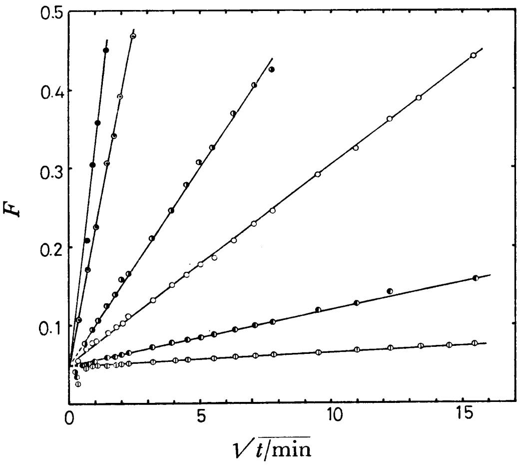

Fig. 5. Effect of temperature on the isotopic exchange rate (sample 3).
pH 11, 5 mol dm^{-3} $NaNO_3$. ●: 91.4 °C, ⊙: 79.8 °C, ◑: 57.9 °C, ○: 44.9 °C, ◐: 24.1 °C, ⦶: 4.6 °C.

effective.

The effect of particle size on the rate was then studied. This is shown in Fig. 4, which indicates that the rate was not affected by the particle size of the samples employed. This observation can be explained as follows. The structure of $Na_2Zr(PO_4)_2\cdot 3H_2O$ is a layered one similar to ZP: each layer consists of zirconium atoms lying very nearly in a plane and bridged by phosphate groups situated above and below the plane. Adjacent layers are arranged in such a way as to create zeolite-like cavities; these layers are interconnected by openings.[13)] The diameters of the openings are 0.263 and 0.24 nm along the directions parallel and perpendicular to the layers, respectively. Since the sodium ion is small in size (0.19 nm), it can diffuse along both directions. Here, let us define the diffusion constants along the direction parallel and perpendicular to the layers respectively as D' and D, where D' is considered to be greater than D because of the difference in the diameters of the passages of ions. When D' is supposed to be very much greater than D, the isotopic exchange rate is determined by the diffusion along the direction parallel to the layers; accordingly, it must depend on the particle size of the samples. The experimental data, however, does not support this assumption. By assuming that D' is nearly equal to D, the diffusion along the direction parallel to the layers can be ignored, since the diffusion distance is much longer along this direction than along the direction perpendicular to the layers. As a result, the rate will be determined only by D. The independence of the rate on the particle size can reasonably be explained by this assumption since the thicknesses of the crystals are equal irrespective of the particle size.

The fractional attainment of equilibrium, therefore, can be obtained by solving the equation for diffusion in slabs immersed in a well-stirred solution under the infinite-solution volume condition:

$$F = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2\pi^2} \exp[-\beta(n+1/2)^2\pi^2 t] \qquad (1)$$

where, $\beta = D\, l^{-1}$ and l is the half-length of the crystal in the direction perpendicular to the layers.[14,15)]

When βt is smaller than 0.1, that is, when F is less than about 0.4, Eq. 1 can be approximated by a simpler form:

$$F = \frac{2}{\pi^{1/2}} \sqrt{\beta t} \qquad (2)$$

which holds to a fairly good approximation.

The fractional attainment of equilibrium against square root of time was then studied as a function of temperature, as is shown in Fig. 5. The figure indicates that the slope of the linear relation between F and $\sqrt{t}$ increases with temperature. The straight lines, however, do not pass through the origin and always intersect the F axis at 0.05. This observation can be understood by considering that the defects of the crystal structure exist on the surface of the crystals and that the equilibrium between the surface region of the crystals and the solution is attained rapidly and then the diffusion into the bulk of the crystals proceeds. D was then calculated by taking consideration of the facts that 95% of total sodium ions in the crystals took part in the particle diffusion and that the effective length for diffusion was 95% of the actual crystal size.

When $\log D$ was plotted against $1/T$, good linearity was obtained, as is shown in Fig. 6. From the Arrhenius equation, $D = D_0\exp(-E_a/RT)$, the activation energy E_a and the constant D_0 were determined. The value of E_a was 101 kJ mol^{-1} and $D_0 = 19$ m^2 s^{-1}. The present value of E_a is considerably higher than that given by Costantino *et al.*, 73 kJ mol^{-1}.[8)] One explanation of this discrepancy is as follows. The activation energy of diffusion along the direction perpendicular to the layers is expected to be higher than that along the direction parallel to the layers, because the effective diameter of passage is smaller along the former than along the latter direction. The present value is related to the diffusion along the direction of the highest activation energy while Costantino's value resulted from some average of two diffusion con-

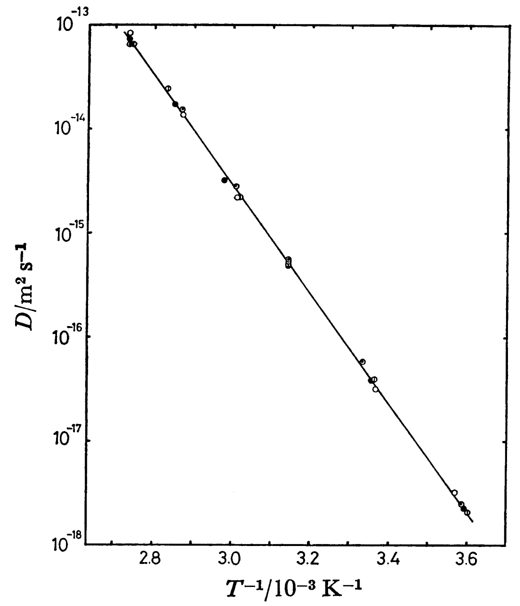

Fig. 6. Arrhenius plot for diffusion constant, D. pH 11, 5 mol dm^{-3} $NaNO_3$. ⊙: Sample 1, ○: sample 2, ⦶: sample 3, ●: sample 4.

stants.

The experiments so far were performed with the dried exchanger which had been stored in a desiccator containing saturated NaCl solution. The same results were also obtained when the experiments were carried out by using the exchanger which had been equilibrated with distilled water. This fact offers a striking contrast between the trihydrate and high-temperature phases. The results for the latter phases will be reported later.

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