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SELF-DIFFUSION OF THE SODIUM ION IN THE MONOSODIUM AND DISODIUM FORMS OF α- AND γ-ZIRCONIUM PHOSPHATE

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SUMMARY

α- and γ-zirconium phosphate are layered exchangers that differ both in their structures and the packing sequence of the layers. In γ-zirconium phosphate the structure of the layer is more compact and the interlayer distance is greater than in α-zirconium phosphate. These compounds are therefore good models for studying the effect of the distance between the fixed charges and of the interlayer distance on the transport properties of layered exchangers. The self-diffusion processes of $^{24}Na^+$ in the monosodium and disodium forms of α- and γ-zirconium phosphate were therefore investigated. In the first stages of the processes, the rate seems to be controlled by fast interfacial isotopic exchange reactions, whereas in the last stages the rate is particle diffusion controlled. The self-diffusion constants and hence the activation energies were calculated by using an approximate equation valid for long diffusion times. The activation energies for self-diffusion increase in the order γ-Zr(NaPO$_4$)$_2 \cdot$5H$_2$O (33 kJ/mole) $< \alpha$-ZrHNa(PO$_4$)$_2 \cdot$5H$_2$O (42 kJ/mole) $< \gamma$-ZrHNa-(PO$_4$)$_2 \cdot$3H$_2$O (53 kJ/mole) $< \alpha$-Zr(NaPO$_4$)$_2 \cdot$3H$_2$O (69 kJ/mole) and the self-diffusion constants, at 25°C, correspondingly decrease. It seems, therefore, that the activation energies are lower and the self-diffusion rates faster in the compounds that possess a greater interlayer distance and have a shorter distance between the $\equiv$P–O$^-$ fixed charges lying on the faces of the layers.

INTRODUCTION

Crystalline zirconium phosphate has been obtained in two layered modifications (α- and γ-ZrP) whose ion-exchange behaviour is strongly correlated with their crystalline structures and with the degree of crystallinity[1,2]. In α-Zr(HPO$_4$)$_2 \cdot$H$_2$O, the structure of which is well known[3], each layer consists of a plane of zirconium atoms bridged through tetrahedral phosphate groups located alternately above and below this plane; the distance between the exchangeable protons, located on the faces of the layer, is 0.53 nm. The layers are staggered in such a way as to create a close-packed structure and the interlayer distance is 0.76 nm. Within two faced layers, zeolite-type cavities, one for each zirconium atom, are present.

The structure of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ is unknown, but experimental evidence[4–6] suggests that the structure of the γ-layer is more compact than that of the α-form, the mean distance between the exchangeable protons present on the faces of the layer being evaluated[7] as 0.40–0.44 nm. The interlayer spacing is 1.22 nm and this high value could arise for a packing sequence of the layers in which the monohydrogen phosphate groups belonging to two adjacent layers are aligned opposite one another and hydrogen bonded by water molecules[8]. Thus, γ-ZrP possesses a larger interlayer distance and a more compact structure of the layers than α-ZrP. Accordingly, in γ-ZrP a lower steric hindrance to the diffusion of the counter ions, within the interlayer space, and a lower activation energy for the jump of the counter ions from one exchange site to neighbouring sites are expected. It was therefore of interest to compare the rates and the activation energies for the self-diffusion of cations in salt forms of α- and γ-zirconium phosphate.

In this work the self-diffusion constants of Na^+ in the monosodium and disodium forms of γ-zirconium phosphate and the activation energies have been determined. These values have been compared with those relative to the self-diffusion processes of Na^+ in α-$ZrHNa(PO_4)_2 \cdot 5H_2O$ and α-$Zr(NaPO_4)_2 \cdot 3H_2O$ previously investigated[9,10].

EXPERIMENTAL

Ion-exchange materials

γ-Zirconium phosphate was prepared according to the procedure described by Clearfield et al.[11]. The compound was stored in a vacuum desiccator containing a sodium chloride-saturated solution ($P/P_0 \approx 0.7$) and both its X-ray powder diffraction patterns and its water content were similar to the values previously reported[8,11]. The monosodium and disodium forms were obtained by titrating γ-$Zr(HPO_4)_2 \cdot 2H_2O$ suspended in 0.2 M sodium chloride solution with 0.1 M sodium hydroxide solution using the end-point titration method up to pH = 5.0 and 10.0, respectively. These salt forms were dried to constant weight over a barium chloride-saturated solution ($P/P_0 \approx 0.9$).

Self-diffusion experiments

A weighed amount of the sodium form of γ-ZrP, containing 5 mmole of Na^+ counter ions, was equilibrated with constant and vigorous stirring, in order to reduce the film diffusion process, with 200 ml of 0.050 M sodium chloride solution labelled with $^{24}Na^+$ (as NaCl). The pH of these solutions was brought to 5 for the γ-monosodium and 10 for the γ-disodium form, in order to avoid further H^+–Na^+ exchange or the hydrolysis of the fully exchanged form, respectively. The attainment of isotopic equilibrium was followed by the procedure described earlier[9]. The average radius of the crystallites, assumed to be spheres, was evaluated by means of a Zeiss ET type electron microscope, and was found to be 2 μm.

Apparatus

The titration of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ in the pH-stat mode was performed with a Radiometer automatic titrimeter. The water content of the salt forms was calculated from the TG, DTG and DTA curves, obtained with a MOM derivatograph. X-ray

diffraction patterns were taken with a Dron 1.5 diffractometer using Ni-filtered $CuK\alpha$ radiation. An NE Scalar Ratemeter SR 3 was used as a γ-counter to follow the decrease in the specific activity of the solution.

RESULTS

Sodium-exchanged materials

The H^+–Na^+ ion-exchange process of γ-$Zr(HPO_4)_2 \cdot 2H_2O$ has been investigated by Clearfield et al.[8] and Allulli et al.[6]. The process was found to occur in two steps, in which first the monosodium form [γ-$ZrHNa(PO_4)_2 \cdot 3H_2O$; $d = 1.16$ nm] and then the disodium form [γ-$Zr(NaPO_4)_2 \cdot 3H_2O$; $d = 1.26$ nm] were obtained.

On the basis of their results, the appropriate conditions for the preparation of large batches of these sodium forms were chosen. Chemical and X-ray analysis confirmed that the monosodium form obtained was identical with that already reported in the literature, whereas a more hydrated disodium form was obtained for our γ-ZrP. The water content for three different preparations was found to range between 4.5 and 6 mole of water per formula weight of exchanger, and the first diffraction maxima in the X-ray diffractograms, corresponding to the interlayer distance, was very broad and located at d values ranging from 1.3 to 1.4 nm. The discrepancy between these data and those previously reported may be explained with the aid of some considerations concerning the exchange of alkali metal ions in γ-ZrP, recently reported by Clearfield and Garces[8]. According to these authors, in the fully alkali metal-exchanged phases a "crowding of cations" in the interlayer space of γ-ZrP must occur and water molecules are inserted between the cations to overcome the electrostatic repulsions. As a consequence, the interlayer distance increases and the lattice becomes less ordered. Owing to these effects, differences in the X-ray patterns and in the water content of these salt forms may arise from slight changes in the preparation or drying conditions.

The composition of the γ-disodium form used in the self-diffusion experiments was $Zr(NaPO_4)_2 \cdot 5H_2O$ ($d = 1.35$ nm, broad), and Fig. 1 shows the TG, DTG and DTA curves for this sample.

Treatment of self-diffusion data

In previous work[9] the kinetic curves relative to the self-diffusion of Na^+ and K^+ in α-$Zr(NaPO_4)_2 \cdot 3H_2O$ and α-$Zr(KPO_4)_2 \cdot 5H_2O$ were interpreted with a model describing the diffusion into a sphere of known radius from a well stirred solution of limited volume, and the following equation[12] valid for a single process, particle diffusion controlled, was used:

$$1 - \frac{W_t}{W_\infty} = \sum_{i=1}^{\infty} A_i e^{-K_i t} \tag{1}$$

where $A_i = \dfrac{6\lambda(\lambda+1)}{9 + 9\lambda + q_i^2 \lambda^2}$, $K_i = q_i^2 \cdot \dfrac{D}{r^2}$ and $\lambda = \dfrac{VM}{vm}$. In this equation W_t / W_∞

represents the fractional attainment of isotopic equilibrium, q_i are the non-zero roots of the equation $3q_i/3 + \lambda q_i^2 = \tan q_i$, r is the radius of the particles, D are the diffusion constants and VM and vm are the product of the molarity and the volume of the solution and of the solid, respectively.

However, it was found that the points given by eqn. 1 did not fit the experi-

mental points well: for short times of the self-diffusion process the experimental W_t/W_∞ values were higher than the calculated values, whereas the reverse occurred for long times[9]. The kinetic curves relative to the self-diffusion of Na^+ in the γ-sodium forms show a similar behaviour. It is as if the diffusion constant decreases with time. To take into account this effect, in the previous paper[9] we introduced into eqn. 1 a function of distribution of the radii of the particles, determined experimentally by the conifuge method. The equation obtained gave W_t/W_∞ values in agreement with the experimental values but its use is complicated and time consuming.

The discrepancies observed between the experimental and calculated values of W_t/W_∞ may also be explained by assuming that in the first stages of the self-diffusion process the rate is controlled by the superposition of faster interfacial isotopic exchange processes (surface mass reactions, salt adsorption on the crystal, etc.) and a slower particle diffusion process in the bulk of the crystals, whereas in the last stages of isotopic exchange the rate is only particle diffusion controlled. It may be observed that many heterogeneous isotopic exchange reactions [*i.e.*, those between insoluble salts and ions in solution[13-15], such as $BaSO_4$–Ba^{2+}, CaC_2O_4–Ca^{2+}, ZnO–Zn^{2+}, or those between CaY and Ce(III)Y zeolites and the corresponding ions[16]] have been found to be controlled by the superposition of a fast interfacial and slow particle diffusion processes.

For sufficiently long diffusion times, the slower process predominates, and under these conditions an approximate equation, derived from eqn. 1 describes well the change of W_t/W_∞ with reaction time. In particular, it has been found[17,18] that for long diffusional times and high values of W_t/W_∞ the following equation, similar to Mackey's equation, holds:

$$\ln\left(1 - \frac{W_t}{W_\infty}\right) = -\frac{Dq_1^2}{r^2} \cdot t + A_1 \tag{2}$$

Thus, if the kinetic data are plotted as $\ln(1 - W_t/W_\infty)$ *vs. t*, the graph is a straight line at high values of W_t/W_∞, from the slope of which the diffusion constant can be calculated, once one knows the radius of the particles and q_1, tabulated for the chosen geometrical model of self-diffusion and for the experimental λ value[12].

In this work the above method was used. Figs. 2 and 3 show the kinetic curves at various temperatures (a) and the corresponding Mackey plots (b), relative to the self-diffusion of Na^+ in γ-$ZrHNa(PO_4)_2 \cdot 3H_2O$ and γ-$Zr(NaPO_4)_2 \cdot 5H_2O$, respectively. Although eqn. 2 requires the intercepts A_1 of the straight lines in Figs. 2b and 3b to be the same, as A_1 is independent of temperature, in our work the values of the intercepts changed slightly with temperature. This fact may be considered as support to the hypothesis that, in the first stages of the attainment of isotopic equilibrium, there is the superposition of two different processes that have different activation energies. A detailed discussion of this effect, and of the method for the determination of the rate constants of the faster processes, will be reported elsewere[10].

Fig. 4 shows the change of the self-diffusion constants as a function of the reciprocal of the absolute temperature for the monosodium and disodium forms of α- and γ-zirconium phosphate. The diffusion constants relative to the self-diffusion of Na^+ in α-$ZrHNa(PO_4)_2 \cdot 5H_2O$ and in α-$Zr(NaPO_4)_2 \cdot 3H_2O$ were calculated from the slopes of the $\ln(1 - W_t/W_\infty)$ *vs. t* straight lines obtained by using our previous data[9,10] for the fractional attainment of isotopic equilibrium. The plots of $\ln D$ against $1/T$ show reasonable linearity and the activation energies for the self-diffusion
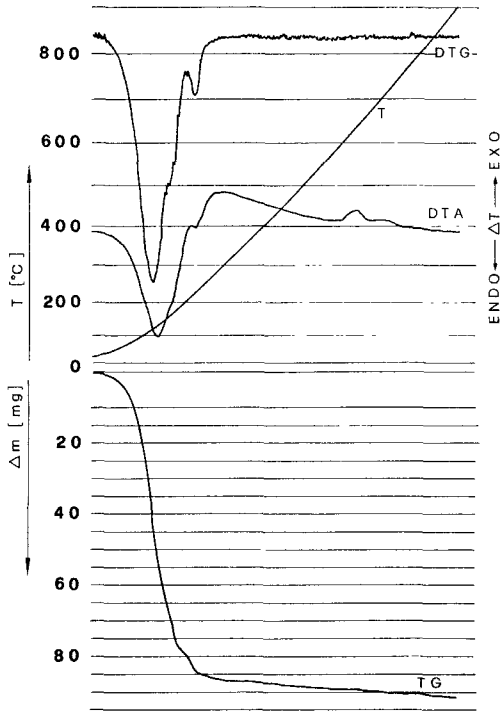
Fig. 1. TG, DTG and DTA curves for the disodium form of γ-ZrP. Initial weight of the sample: 403.7 mg.
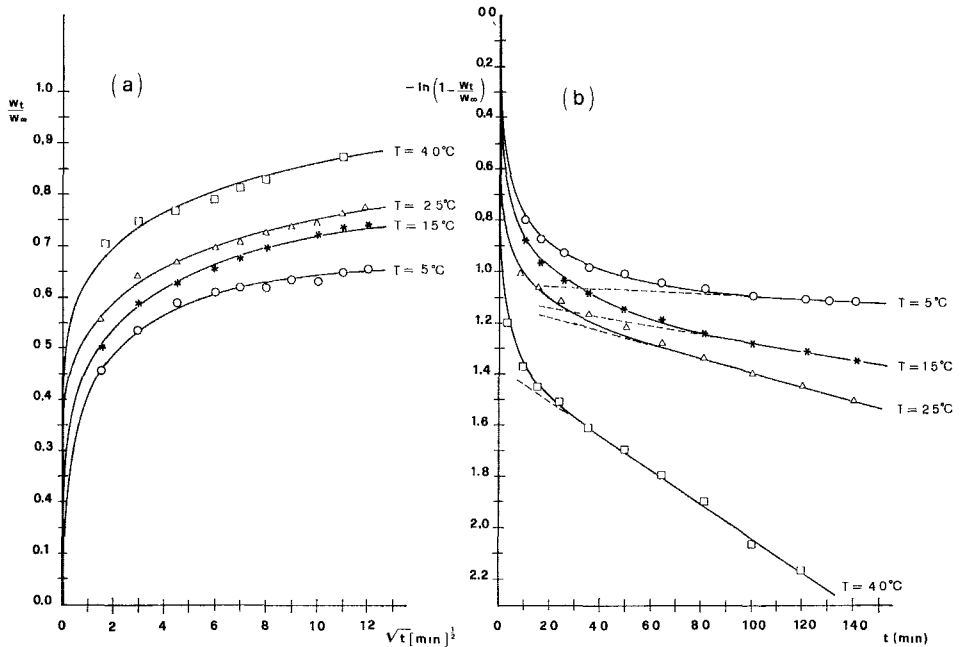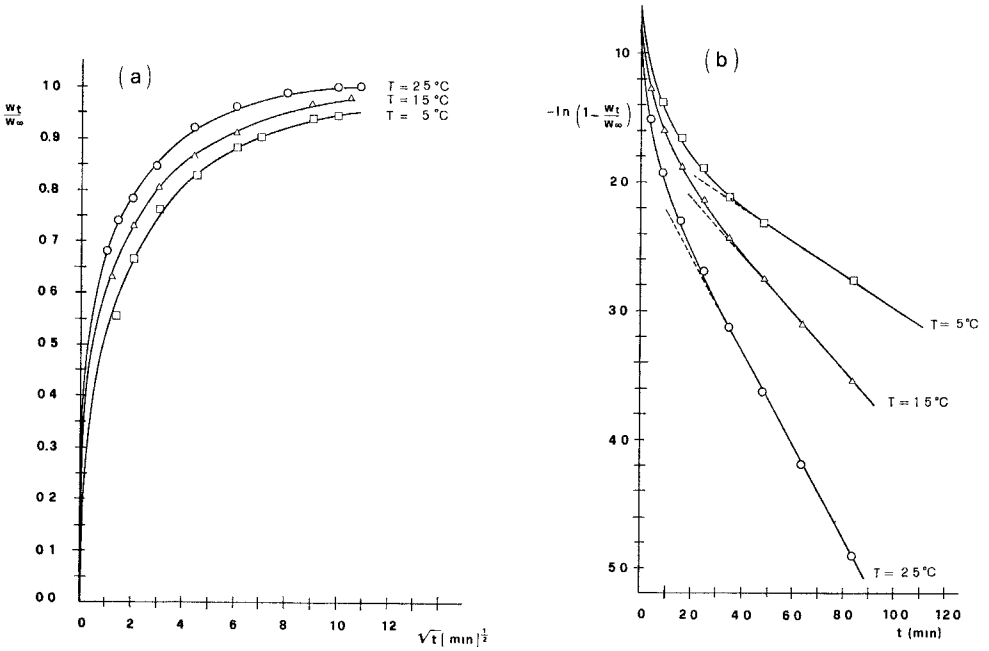

Fig. 2. Fractional attainment of isotopic equilibrium *versus* the square root of the reaction time (a) and the corresponding $\ln(1 - W_t/W_\infty)$ *versus* t plots (b) for the self-diffusion of Na+ in γ-ZrHNa(PO$_4$)$_2 \cdot 3$H$_2$O at the indicated temperatures.

Fig. 3. Fractional attainment of the isotopic equilibrium *versus* the square root of the reaction time (a) and the corresponding $\ln (1 - W_t/W_\infty)$ *versus* t plots (b) for the self-diffusion of Na^+ in γ-Zr(NaPO$_4$)$_2 \cdot 5H_2O$ at the indicated temperatures.
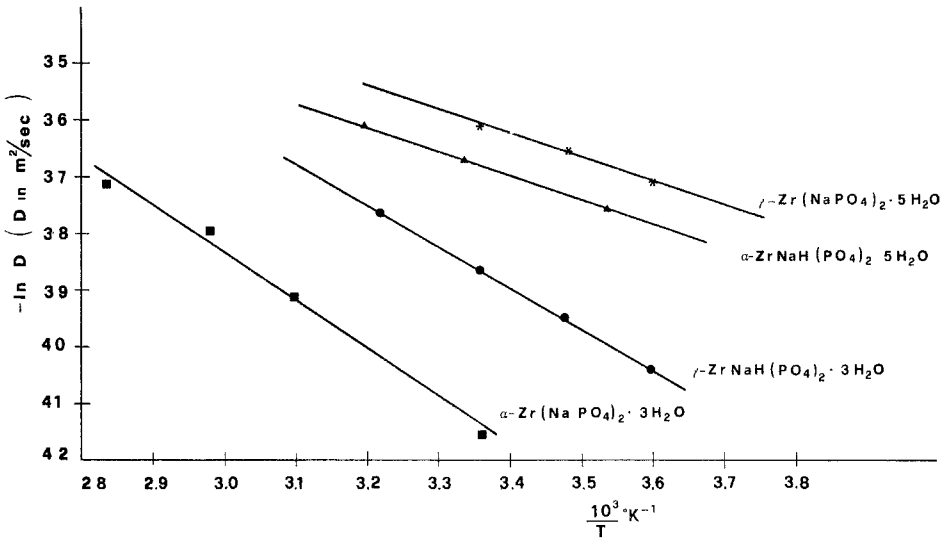

Fig. 4. Plots of $\ln D$ as a function of $10^3/T$ for the self-diffusion of Na^+ in the monosodium and disodium forms of α- and γ-zirconium phosphates.

were calculated from the Arrhenius relationship:

$$\ln D = \ln D_o - \frac{E_a}{RT}$$

Values for the entropy of activation were obtained from the Eyring relationship:

$$D_o = 2.72 \cdot \frac{KT}{h} \cdot d^2 \exp\left(\frac{\Delta S^*}{R}\right)$$

where d is the jump distance. The choice of a value for d was arbitrary. The jump distance was assumed to be equal to the distance between the fixed charges lying on the face of the layers, that is, 0.53 and 0.4 nm for the α- and γ-phases, respectively.

Table I gives the thermodynamic parameters relative to the self-diffusion processes together with the interlayer distances for the samples examined. It is interesting that the activation energies for the self-diffusion of Na⁺ in α-ZrHNa(PO₄)₂·5H₂O and in α-Zr(NaPO₄)₂·3H₂O are very similar to those obtained earlier by using the eqn. 1 corrected for the function of the distribution of the radii of the particles[9,10].

TABLE I

THERMODYNAMIC PARAMETERS RELATIVE TO THE SELF DIFFUSION OF ²⁴Na⁺ IN THE MONOSODIUM AND DISODIUM FORMS OF α AND γ-ZIRCONIUM PHOSPHATES
The composition and the interlayer distance of the samples are also reported.

Sample	Interlayer distance (mm)	$D_{25}°C$ (m^2/sec)	E_a ($kJ/mole$)	D_0 (m^2/sec)	$\triangle S^*$ ($J/mole \cdot °K$)
α-ZrHNa(PO₄)₂·5H₂O	1.18	$1.1 \cdot 10^{-16}$	42	$2.2 \cdot 10^{-9}$	-63
γ-ZrHNa(PO₄)₂·3H₂O	1.16	$1.8 \cdot 10^{-17}$	53	$3.7 \cdot 10^{-8}$	-36
α-Zr(NaPO₄)₂·3H₂O	0.90	$8.6 \cdot 10^{-19}$	69	$1.1 \cdot 10^{-6}$	-11
γ-Zr(NaPO₄)₂·5H₂O	1.35 (broad)	$2.0 \cdot 10^{-16}$	33	$1.3 \cdot 10^{-10}$	-84

DISCUSSION

Although the locations of the counter ions and of the water molecules in the interlayer space of α- and γ-ZrP are unknown, the data in Table I and the known structural differences between these exchangers outlined in the Introduction enable us to make some comments. For example, it is reasonable to suppose that the Na⁺ counter ions are present between the layers of the exchangers as a film of hydrated cations. In the monosodium forms, the sodium–sodium distance may be assumed to be equal to the distance of the fixed charges belonging to a face of the layer, that is, 0.53 and 0.4 nm for the α- and γ-phases, respectively. In the disodium forms the cation–cation distance will be much lower than the mentioned values, as double the number of sodium ions are now present in the interlayer space. Clearfield and Kulberg[19] estimated the sodium–sodium distance in α-Zr(NaPO₄)₂·3H₂O as 0.38 nm. An even lower value must be expected for the γ-disodium form. To a first approximation, it may be thought that, by assuming that the enthalpies for the formation of the defects are the same for the α- and γ-compounds, the overall activation energy for the self-diffusion will be lower for the γ-forms than for the α-forms, owing to the lower jump distance in the former compounds. However, the water content of the salt forms seems to play an important and complementary role. In highly hydrated compounds the water molecules are less structured, as has recently been confirmed from dielectric measurements[20], and more diffusion paths will be present within the layers. This effect is also indicated by the high negative ΔS^* values associated with the self-diffusion in highly hydrated forms (see Table I).

The effect of the hydration of the cations may exceed the effect of the closeness of the counter ions. The activation energy for the self-diffusion of Na^+ in α-ZrHNa-$(PO_4)_2 \cdot 5H_2O$ (42 kJ/mole) is in fact lower than that found for γ-ZrHNa$(PO_4)_2 \cdot 3H_2O$ (53 kJ/mole). In the disodium forms both the effect of the hydration and the effect of the closeness of the fixed charges seem to enhance the self-diffusion rates of Na^+ in γ-Zr(NaPO_4)_2 \cdot 5H_2O$ with respect to those in α-Zr(NaPO_4)_2 \cdot 3H_2O$, and the activation energy in the γ-form (33 kJ/mole) is about half that found in the α-form (69 kJ/mole). Further, the activation energy for γ-Zr(NaPO_4)_2 \cdot 5H_2O$ is lower than that found for α-ZrHNa(PO_4)_2 \cdot 5H_2O$. However, as the γ-disodium form has a very low degree of crystallinity in comparison with that of the other sodium forms examined, enhancement of the self-diffusion rate due to the disorder of the structure may not be excluded. Without considering the effect of the degree of crystallinity, which requires further work, is seems that the ion-exchange rates and the mobility of counter ions in layered exchangers of the zirconium phosphates type will be faster in those compounds which possess a larger interlayer distance and a shorter distance between the fixed charges lying on the faces of the layers. Recent data on the ionic conductance[20] of salt forms of γ-titanium phosphate and α-zirconium phosphate are in agreement with this, and similar conclusions have been recently drawn by Dyer and Yusof[21] in a study of the Na^+–Cs^+ ion exchange mechanism in α-Zr(HPO_4)_2 \cdot H_2O$.

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