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Polyfunctionality of α-Zr(HPO$_4$)$_2$·H$_2$O. Case of H$^+$/Ag$^+$ and H$^+$/Tl$^+$ Ion Exchange Processes[†]

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A detailed investigation of the ion exchange processes of silver and thallium(I) ions on α-$Zr(HPO_4)_2\cdot H_2O$ has been carried out. The H^+/Ag^+ exchange occurs in $AgNO_3$ or CH_3COOAg solution with a single phase transition and leads to $Zr(AgPO_4)_2\cdot H_2O$ (interlayer distance 8.4 Å). The H^+/Tl^+ ion exchange process has been performed by titrating the exchanger with 0.1 M ($TlNO_3+TlOH$) solution, owing to the great ionic size of Tl(I). The titration curve shows essentially a single plateau. In a similar way to that for H^+/Ag^+ exchange, the process takes place with a single phase transition, leading to $Zr(TlPO_4)_2\cdot H_2O$ (interlayer distance 9.0 Å). Since the processes are new examples in which a univalent cation is exchanged with a single phase transition in α-$Zr(HPO_4)_2\cdot H_2O$, the so called "polyfunctionality" of this exchanger has been discussed, considering the high polarizability of Ag^+ and Tl^+ ions. The catalytic potential applications of zirconium phosphate loaded with Ag^+ ions are outlined.

The crystal structure of α-zirconium bis(monohydrogen-orthophosphate) monohydrate, α-$Zr(HPO_4)_2\cdot H_2O$, hereafter referred to as α-HH·H$_2$O[††], has been refined[1)] and the position of the exchangeable hydrogen atoms and water molecule determined by means of powder neutron diffraction data[2)]. From these works it was concluded that: a) the exchangeable hydrogen atoms are covalently bonded to phosphate oxygens; b) the water molecule lies in the center of the cavity formed by the arrangement of the layers and it is hydrogen-bonded to tetrahedral ⩾P–OH groups belonging to the same layer; c) there are no hydrogen-bonds between the layers that are held by van der Waals forces.

Knowledge of the position of the exchangeable hydrogen atoms would help in understanding the so called "polyfunctionality" of α-HH·H$_2$O. It is known that the titration curves of the exchanger with alkali metal hydroxides, in the presence of the respective chlorides, exhibit various steps at different pH values for each cation (*i.e.* 3 steps for Li^+ and Rb^+, 2 steps for Na^+ and K^+, 4 steps for Cs^+; Fig. 3, Ref. 3), as if the hydrogen atoms of α-HH·H$_2$O have different acidities for the different cations. Albertsson *et al.*[2)] suggested that the exchange sites are created by the hydroxide ion, that may freely diffuse in the crystals and reacts with the ⩾POH groups. The energy supplied by this reaction should allow the metal ion to be sorbed by the exchanger as hydrated ions. Troup and Clearfield[1)] attributed the different acidities of the hydrogen atoms to defects of the structure that would lead to a range of hydrogen bond energies and to the shift of the phosphate groups from their normal position. Disorder would thus create exchange sites of different energies. According to Allulli *et al.*[4)] the polyfunctionality of zirconium phosphate is related to the growth of various solid phases.

As a contribution to the knowledge of the exchange behaviour of α-HH·H$_2$O, this paper reports two examples in which monovalent cations having a high polarizability, such as Ag^+ and Tl^+, are taken up by crystalline zirconium phosphate in one step. Furthermore the H^+/Ag^+ ion exchange process provides the first example in which a univalent cation is entirely exchanged at room temperature without addition of hydroxide ions.

Experimental

Chemicals. All reagents, except $ZrOCl_2\cdot 8H_2O$ supplied by "Merck", were R.P.E. "C. Erba". Thallium(I) hydroxide was prepared by adding a Tl_2SO_4 solution to a hot barium hydroxide solution in a closed system filled with nitrogen.

Crystalline zirconium phosphate was prepared according to the method of slow decomposition of zirconium fluorocomplexes in the presence of phosphoric acid.[3)] The microcrystals were sedimented in a countercurrent apparatus[5)] and the various fractions were stored over P_4O_{10}. The fraction with a mean radius of particles of 3—5 μm was used throughout the experiments.

Ion Exchange Procedure. In order to attain different percentages of Ag^+-exchange, several samples of α-HH·H$_2$O (1 g) were equilibrated with increasing volumes of 0.100 M $AgNO_3$ or 0.050 M CH_3COOAg solutions at 25±1 °C. The thallium-uptake, as a function of pH, was obtained from the batch titration performed by contacting several samples of α-HH·H$_2$O (0.500 g) with 100 ml of 0.100 M ($TlNO_3+TlOH$) solutions. After equilibration (4 d) the solid samples were filtered off and their X-ray diffractograms recorded, the clear solutions being analyzed for their pH value and metal ion content. Kinetic experiments were performed as reported.[6)]

Analytical Procedure. Silver ion was determined with a Perkin-Elmer A.A. spectrophotometer. Thallium was titrated with standard potassium bromate at 60 °C. Hydration water content was obtained by the percent-weight loss at 180 °C of the samples, previously conditioned over a NaCl saturated solution ($P/P_0\approx 0.7$). X-Ray powder diffraction patterns were obtained with a General Electric diffractometer using Ni-filtered Cu $K\alpha$ radiation.

Results

Ag^+-uptake. The ion-exchange mechanism of Ag^+ on HNa·5H$_2$O suggests that in acidic media Ag^+ might replace the protons of HH·H$_2$O obtained from the partial regeneration of the monosodium

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[††] The ionic forms of α-$Zr(HPO_4)_2\cdot H_2O$ will also be indicated by their counter-ions and water content.

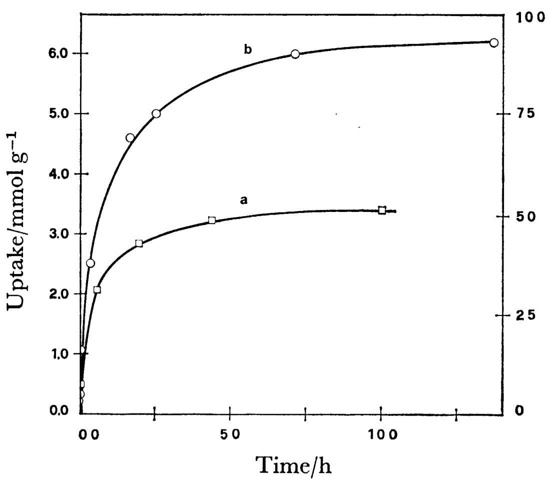

Fig. 1. Ag^+-uptake on α-$HH \cdot H_2O$ as a function of time.
Conditions: 1 g of ecxhanger equilibrated with 200 ml of 0.100 M $AgNO_3$ solution (curve a) or with 200 ml of 0.050 M CH_3COOAg solution (curve b), $t=25 \pm 1$ °C.

form.6) For the sake of confirmation an attempt was made to convert the zirconium hydrogen phosphate into silver form by contacting the exchanger with $AgNO_3$ or CH_3COOAg solutions. Figure 1 shows the Ag^+-uptake of 1 g of $HH \cdot H_2O$, as a function of time, when the exchanger is equilibrated at 25 ± 1 °C with 200 ml of 0.100 M $AgNO_3$ solution (curve a) or with 200 ml of 0.050 M CH_3COOAg solution (curve b). In nitrate media the uptake suddenly slows down after 20 h of equilibration, because of the accumulation in solution of the protons replaced by silver ions (after 70 h the pH was ≈ 1.8). Maximum Ag^+-conversion of 50% was obtained.

In acetate media, owing to the presence of the Brönsted base, CH_3COO^-, the pH of the solution remains higher than 4. The H^+/Ag^+ exchange seems to proceed in only one step, a maximum Ag^+-conversion of $\approx 95\%$ being reached within 150 h.

X-Ray diffractograms of the sample withdrawn from the nitrate solution showed the presence of a not exchanged $HH \cdot H_2O$ phase and a new phase having an interlayer distance of 8.4 Å; the one withdrawn from the acetate solution showed the presence of only the 8.4 Å phase. In order to obtain further information on the ion-exchange mechanism, equilibrium experiments were carried out by contacting several samples (1 g) of $HH \cdot H_2O$ with increasing volumes of $AgNO_3$ or CH_3COOAg solution.

Figure 2 shows the millimoles of Ag^+ taken up by 1 g of exchanger against the millimoles of Ag^+ initially present in the equilibrating 0.100 M $AgNO_3$ solution (curve a) or 0.050 M CH_3COOAg solution (curve b). The following comments are given.

i) Up to 80—90% Ag^+-conversion the H^+/Ag^+ ion-exchange process seems to take place in a single step both in acetate and nitrate media; after this value of conversion the selectivity of exchanger towards Ag^+ ions strongly decreases and higher volumes of equilibrating solutions are needed to obtain the full Ag^+-phase.

ii) In the acetate medium, in the range 0—85% Ag^+-conversion the exchanger shows a high selectivity for silver ions and virtually all the added Ag^+ ions are taken up. As expected from the constancy of the H^+/Ag^+ rational selectivity coefficient, in the nitrate medium much greater amounts of silver ions (larger volumes of equilibrating solution) must be added to the exchanger in order to reach a Ag^+-conversion identical to that attained in the acetate medium.

X-Ray diffraction patterns of samples having the same Ag^+-conversion but obtained from the nitrate and acetate equilibrating solutions were found to be similar, confirming the view that the same ion exchange mechanism holds in both cases.

X-Ray powder patterns of samples at various Ag^+-loading (Fig. 3a) show that a new phase with interlayer distance 8.4 Å is present already at 10% Ag^+-conversion. This phase and the original $HH \cdot H_2O$ (7.6 Å) phase are present up to 85% Ag^+-conversion, the latter being transformed into the former as the conversion proceeds. After this value of conversion is reached, only the 8.4 Å phase is present and 100% of Ag^+-conversion is obtained without appreciable change in the X-ray diffractograms.

The water content of several samples with increasing Ag^+-loading was also determined (Fig. 4). It can be seen that the water content of the exchanger remains practically equal to one mole per mole of exchanger in all the range of composition. X-Ray powder patterns of hydrated and anhydrous silver forms are given in Table 1.

Tl^+-uptake. Preliminary experiments showed that, in constrast to silver ion, Tl^+ can not diffuse

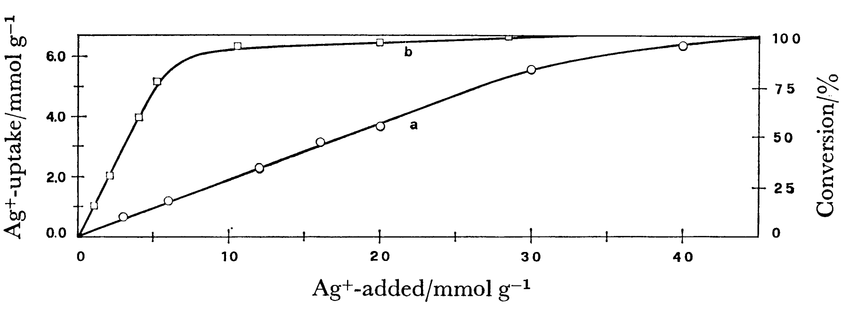

Fig. 2. Ag^+-uptake on α-$HH \cdot H_2O$ as a function of the m·moles of Ag^+ initially added.
Conditions: 1 g of exchanger equilibrated with increasing volumes of 0.100 M $AgNO_3$ solution (curve a) or 0.050 M CH_3COOAg (curve b).

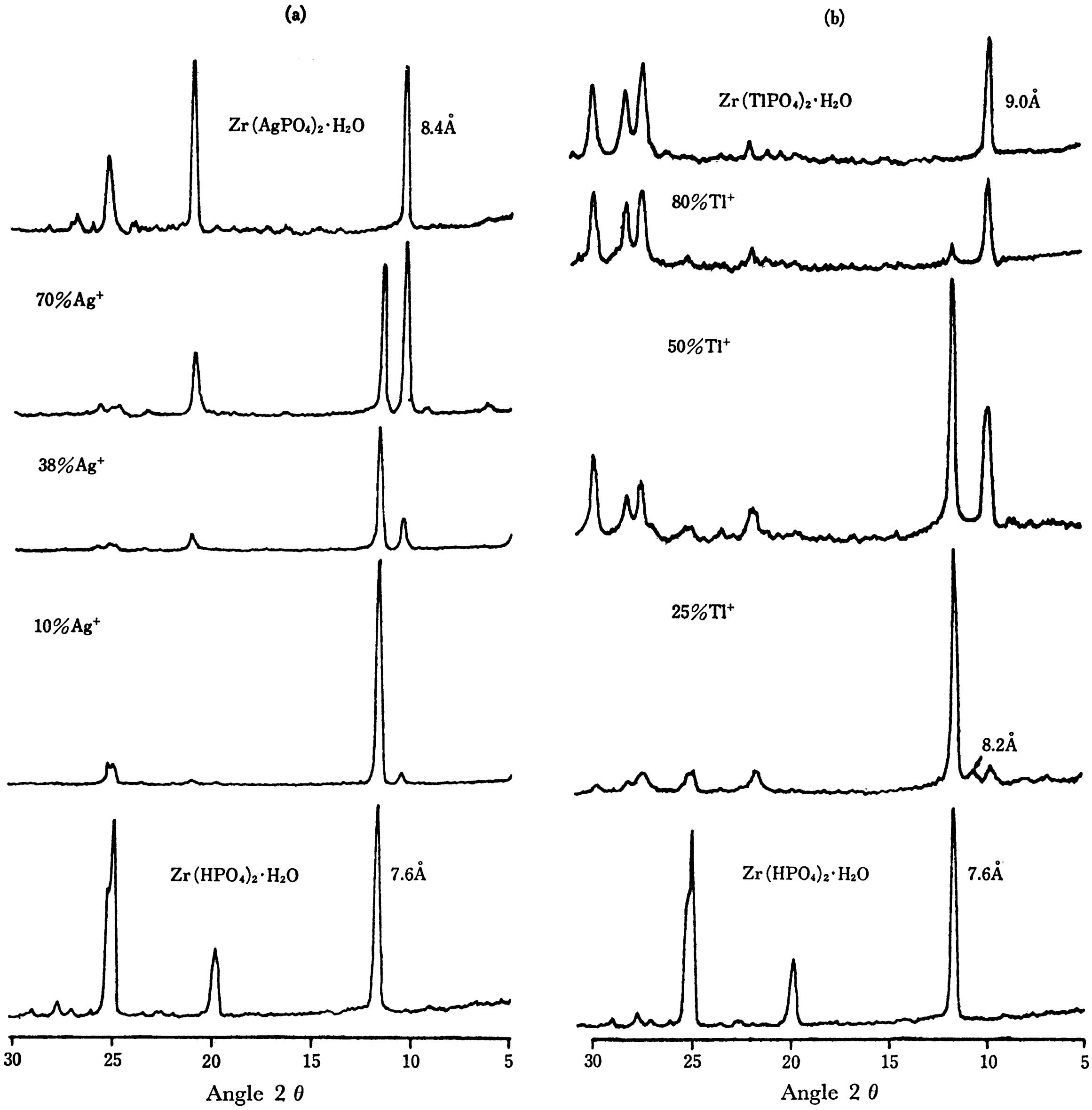

Fig. 3. Some X-ray diffractograms relative to H^+/Ag^+ (a) or H^+/Tl^+ (b) ion exchanges on α-HH·H_2O.

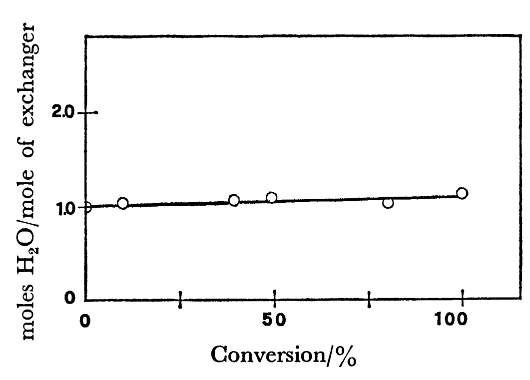

Fig. 4. Water content of α-zirconium phosphate at various stages of Ag^+-conversion.

(or diffuses very slowly owing to its greater ionic radius) within the layers of the exchanger from nitrate solutions.

When the steric hindrance prevents the free diffusion of a counter-ion in the HH·H_2O lattice (in this case the ionic diameter of Tl^+ ion, 3.0 Å, is much greater than the free diameter[1] of the openings connecting the cavities, 2.61 Å) it is possible to force the cations to cross these openings and to enlarge the layers of the exchanger,[3] if sufficient energy is supplied. This energy can be provided by the neutralization of the protons of the exchanger if the soluble cation hydroxide is available.

Figure 5 shows the Tl^+-uptake curve of HH·H_2O obtained by titrating the exchanger with 0.100 M ($TlNO_3$+TlOH) solutions at 25±1 °C. Apart from the sloping regions between 0—20% and 80—100% of Tl^+-conversion, the curve shows a single plateau at pH≈5.

X-Ray diffractograms of samples with increasing Tl^+-conversion (Fig. 3b) show that in the range 0—25% of conversion the phases, with interlayer distance of 7.6, 8.2, and 9.0 Å, are present.

In the approximate range 25—80%, two phases with interlayer distance 7.6 and 9.0 Å, respectively, are co-existent, one transforming into the other. After

Table 1. X-Ray powder diffraction patterns of hydrated and anhydrous Ag^+ and Tl^+ forms of α-zirconium phosphate

$Zr(AgPO_4)_2\cdot H_2O$ d/Å	$Zr(AgPO_4)_2$ d/Å	$Zr(TlPO_4)_2\cdot H_2O$ d/Å	$Zr(TlPO_4)_2$ d/Å
8.4 s	7.78 s	9.0 vs	8.9 vs
5.78 vw	5.33 w	5.86 vw	4.66 vw
5.35 w	4.51 w	5.00 vw	4.05 m
4.64 vw	4.32 vw	4.52 vw	3.58 vw
4.52 w	4.11 w	4.34 w	3.19 s
4.33 vw	3.88 s	4.20 w	2.71 vw
4.19 vs	3.79 m	4.05 m	2.61 w
3.96 vw	3.36 w	3.79 vw	
3.76 w	3.33 m	3.25 s	
3.51 w	3.24 w	3.16 m	
3.44 m	3.18 m	2.99 s	
3.36 w			
3.29 vw			
3.08 vw			

s, Strong; m, medium; w, weak; v, very.

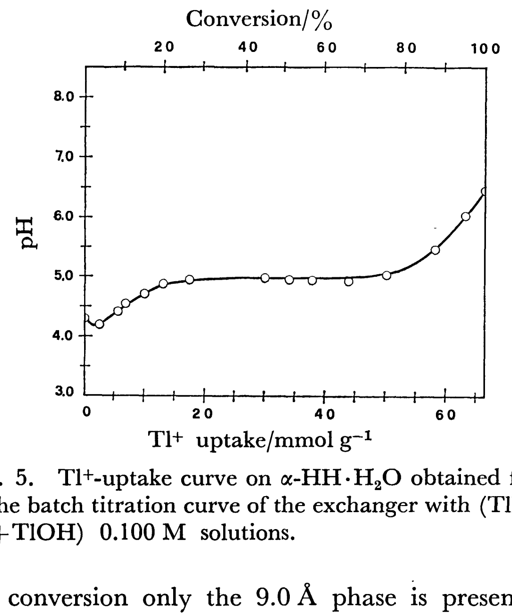

Fig. 5. Tl^+-uptake curve on α-$HH\cdot H_2O$ obtained from the batch titration curve of the exchanger with ($TlNO_3$ +$TlOH$) 0.100 M solutions.

80% conversion only the 9.0 Å phase is present, full conversion being reached without drastic modifications of the X-ray patterns. Determination of the water content of samples having different Tl^+-conversion, shows that as in the case of H^+/Ag^+, the H^+/Tl^+ exchange takes place without changes in water content that remains equal to one mole per mole of exchanger. The X-ray powder patterns of hydrated and anhydrous thallium forms are given in Table 1.

Discussion

The results obtained indicate that the H^+/Ag^+ and H^+/Tl^+ ion exchange processes on α-$HH\cdot H_2O$ occur in a single step with the direct transformation of the dihydrogen phase into the about fully exchanged phase. Thus, without considering the solubility of the Ag^+ ion in the $Ag_{1.7}H_{0.3}\cdot H_2O$ phase or the solubility of Tl^+ in the $Tl_{1.6}H_{0.4}\cdot H_2O$ phase, the ion exchange processes may be schematically described by the reactions:

$$\underset{7.6\,\text{Å}}{\mathrm{HH\cdot H_2O}} + 2\mathrm{Ag^+} \longrightarrow \underset{8.4\,\text{Å}}{\mathrm{AgAg\cdot H_2O}} + 2\mathrm{H^+} \qquad (1)$$

$$\underset{7.6\,\text{Å}}{\mathrm{HH\cdot H_2O}} + 2\mathrm{Tl^+} + 2\mathrm{OH^-} \rightarrow \underset{9.0\,\text{Å}}{\mathrm{TlTl\cdot H_2O}} + 2\mathrm{H_2O}. \qquad (2)$$

Only in the case of H^+/Tl^+ ion exchange process, the weak reflection at d=8.2 Å, present in X-ray diffractograms of samples having a Tl^+-conversion ranging from 5 to 25%, suggests that a small percentage of the HTl phase could be obtained.

In the case of the alkali metal ions, the ion exchange process on $HH\cdot H_2O$ occurs in several steps, thus the H^+/Ag^+ and H^+/Tl^+ are the first examples in which a univalent cation is taken up by α-$HH\cdot H_2O$ with a single phase transition.[†††] This cannot be explained in terms of ionic size, since Ag^+ and Tl^+ have effective ionic radii very similar to those of Na^+ and Rb^+, respectively, involving the difference in polarizability.

If polarizable ions constitute a ionic solid there is a further contribution to the lattice energy and discrepancies are generally found between the calculated and experimental values of lattice energy. The discrepancy is usually attributed to dispersion forces and to the possibility of some covalent bonding. The salt forms of crystalline zirconium phosphate may be considered covalent-ionic solids because the counterions present within the layer are ionically bonded to the macro-anions, constituting the layers themselves, that are of covalent nature.

Thus, it can be assumed that Ag^+ and Tl^+, owing to their polarizability much higher than that of alkali metal ions, give rise to higher interaction energy with the fixed groups of the matrix. Allulli *et al.*[4] found that crystalline zirconium phosphate, in molten salts, strongly prefers Tl^+ to K^+.

The strong interaction between Ag^+ and Tl^+ and

[†††] It should be recalled that H^+/Li^+ ion exchange on an another layered inorganic ion exchanger, α-$Ti(HPO_4)_2\cdot H_2O$, occurs in a single step.[7,8]

the $\geqslant$P–O$^-$ groups of the exchanger, and thus their low mobility in the crystal lattice, could explain why a single step in the ion exchange processes has been obtained, in a manner similar to that recently outlined for the H^+/K^+ exchange on α-HH·H_2O.[5,9)]

Let us suppose that the energy required for exchanging the proton of the hypothetical, *i.e.* HAg·H_2O, is lower than that furnished by the pH of equilibrating solution, in other words that the eventual second plateau of exchange lies at pH value lower than ≈ 6. In the first stages of the H^+/Ag^+ exchange, both the protons present in each cavity would be replaced by the silver ions. An appreciable amount of AgAg·H_2O is thus formed in the external parts of the crystals. According to the model of co-existing solid phases[3)] in a single crystal of HH·H_2O, a situation similar to that schematically shown in Fig. 6 may occur. The Ag^+ ions of the 8.4 Å phase should have a strong tendency to diffuse into the HH·H_2O phase, arranging themselves in a regular mode. Thus, for each cavity of the exchanger there would be one silver ion, giving rise to the HAg phase. However, if the rate of this internal diffusion is very low and the pH of the external solution remains higher than that required for the exchange of the second proton, other Ag^+ ions would be furnished by the solution, the exchange taking place, with low activation enery, in the region of separation between the AgAg·H_2O and HH·H_2O co-existing phases. In this region the cavities are very likely irregular, and the exchange of both the protons may occur with a rate greater than the diffusion of Ag^+ in the HH·H_2O to give the HAg phase. Thus the exchange process goes on with an advancing phase bondary (Fig. 6). This mechanism requires that, if the exchange is stopped and a crystal of zirconium phosphate, half converted into silver form, is left standing for a long time, it should be transformed into the monosilver phase according to the reaction occurring in the crystal:

$$\underset{7.6\ \text{Å}}{\mathrm{HH{\cdot}H_2O}} + \underset{8.4\ \text{Å}}{\mathrm{AgAg{\cdot}H_2O}} \rightarrow \mathrm{2HAg{\cdot}H_2O}. \qquad (3)$$

A sample half converted into silver form and heated at 180 °C, for 2 d, showed no co-existence of the anhydrous AgAg (7.78 Å) and HH (7.41 Å) phases. Only one phase, with inter-layer distance 7.46 Å, very likely the anhydrous HAg, was detected. This indicates that the rate of the proposed transformation (3) is very low at room temperature. Several other experiments, such as the H^+/Ag^+ exchanges performed in buffered media at different pH values for very long periods, are expected to confirm this point.

Zirconium phosphate loaded with silver ion is considered to be a promising material for catalytic processes. La Ginestra *et al.*[10)] were able to reduce reversibly the silver counter-ions present between the layers of crystalline zirconium phosphate and obtain materials containing dispersed silver atoms in the structure.

The authors thank Prof. G. Alberti for helpful discussions.

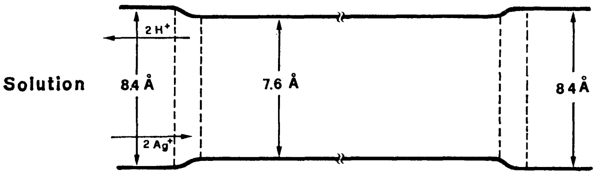

Fig. 6. Schematic representation of the co-existence of $Zr(AgPO_4)_2 \cdot H_2O$ (8.4 Å) and $Zr(HPO_4)_2 \cdot H_2O$ (7.6 Å) in a single crystal of the exchanger. The advancement of the phase bondary during the H^+/Ag^+ ion exchange is shown.

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