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CRYSTALLINE INSOLUBLE ACID SALTS OF TETRAVALENT METALS

XXVII. ION EXCHANGE OF TRIVALENT CATIONS ON IONIC FORMS OF CRYSTALLINE ZIRCONIUM PHOSPHATE WITH LARGE INTERLAYER DISTANCES

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SUMMARY

It is known that, at room temperature, trivalent cations are taken up by amorphous but not by crystalline zirconium phosphate. This lack of exchange has been ascribed to steric hindrance, and therefore the ion-exchange behaviour of trivalent cations has been investigated on some ionic forms of crystalline zirconium phosphate with large interlayer distances in order to reduce considerably the steric hindrance to the diffusion of the counter ions. It was found that Cr(III), La(III) and Tl(III) are taken up selectively by $Zr(HPO_4)_2 \cdot 6H_2O$ and $ZrHNa(PO_4)_2 \cdot 5H_2O$.

The exchange of polyvalent cations on crystalline zirconium phosphate increases the potential uses of this exchanger in analytical chemistry and opens up new possibilities for its application as a catalyst.

The kinetic and ion-exchange mechanism of trivalent cations on crystalline zirconium phosphate are also reported and discussed.

INTRODUCTION

Trivalent and polyvalent cations are taken up at room temperature by amorphous[1–4] but not by fully crystalline zirconium phosphate (interlayer distance 7.6 Å), and the lack of exchange of highly charged cations on crystalline $Zr(HPO_4)_2 \cdot H_2O$ can be ascribed to steric hindrance. In fact, the maximum size of the windows connecting adjacent cavities in this exchanger is 2.64 Å (ref. 5); therefore, if the diameter of the hydrated polyvalent cation is larger than this value, total or partial dehydration must occur in order to make possible the diffusion of the cation within the layered structure. Part of the energy needed for the dehydration could be recovered, as the polyvalent cation, once inside the exchanger, could be partially rehydrated. However, at room temperature, the high energy for the initial dehydration cannot be supplied by

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increasing the pH of the external solution, owing to the strong tendency of polyvalent cations to give insoluble hydrous oxides. The steric hindrance could be avoided by increasing the temperature, by carrying out ion-exchange experiments in the absence of water (*e.g.*, in molten salts) or by using those ionic forms of crystalline zirconium phosphate which have large interlayer distances.

It was recently found[6–9] that some ionic forms of zirconium phosphate with large interlayer distances, such as $ZrHNa(PO_4)_2 \cdot 5H_2O$ and polyhydrated $Zr(HPO_4)_2$* (interlayer distances 11.8 and 10.4 Å, respectively), are indeed able to exchange several divalent cations that usually cannot be taken up by $Zr(HPO_4)_2 \cdot H_2O$ for steric reasons. It was therefore considered interesting to investigate the ion-exchange behaviour of some trivalent cations on these ionic forms of crystalline zirconium phosphate.

Preliminary data obtained with La^{3+}, Cr^{3+} and Tl^{3+} have confirmed that trivalent cations can be taken up in aqueous medium at room temperature.

In order to obtain some information on the ion-exchange mechanism of trivalent cations on these materials, the uptake of La^{3+} and Cr^{3+} has been investigated by performing both equilibrium and kinetic ion-exchange experiments.

EXPERIMENTAL

Chemicals

$Cr(NO_3)_3 \cdot 9H_2O$, $La(NO_3)_3 \cdot 6H_2O$ (Carlo Erba, Milan, Italy), $Tl(NO_3)_3 \cdot 3H_2O$ and $TlCl_3$ (pro analysi, Merck, Darmstadt, G.F.R.) were used.

Ion-exchange materials

$ZrHNa(PO_4)_2 \cdot 5H_2O$ (indicated as $\overline{HNa} \cdot 5H_2O$) was prepared and stored as previously reported[7]. Zr $(HPO_4)_2 \cdot 6H_2O$, indicated as $\overline{HH} \cdot 6H_2O$ (interlayer distance 10.4 Å), was prepared and stored as discribed in ref. 9.

Equilibrium and kinetic experiments

The ion-exchange isotherms were obtained at 25 ± 1° by equilibrating several samples (1.00 g) of $\overline{HNa} \cdot 5H_2O$ with different volumes of 0.100 or 0.010 *N* chromium(III) nitrate, lanthanum(III) nitrate or thallium(III) chloride solution on a mechanical shaker. The solids were separated by centrifugation and the supernatant solutions were analyzed for their pH value and metal ion content. X-Ray diffractograms were obtained for both wet and air-dried samples.

Kinetic experiments, performed with the purpose only of obtaining information on the ion-exchange mechanism under the usual conditions for batch ion-exchange experiments, were carried out by the procedures described by Alberti *et al.*[8].

Analytical procedures

Na^+ and Cr^{3+} were analyzed by using a Perkin-Elmer Model 305 atomic-absorption spectrophotometer. La^{3+} and Tl^{3+} were titrated with standard EDTA solution using xylenol orange as indicator.

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* The water content of this material is 6 ± 1 H_2O molecules per molecule (ref. 9); in this paper, for the sake of brevity, it will be indicated simply as $Zr(HPO_4)_2 \cdot 6H_2O$.

Thermogravimetric curves and approximate water contents of the samples were first determined with a Fisher-Cahn thermobalance. More accurate data on the water of hydration were obtained by drying in an oven, at the appropriate temperature, samples that had previously been brought to constant weight ($\approx 75\%$ relative humidity).

X-ray diffraction patterns were obtained with a General Electric diffractometer using nickel-filtered copper Kα radiation. Approximate percentages of the coexistent solid phases were determined by measuring the area on the characteristic peaks of the various phases in the X-ray diffractograms.

RESULTS AND DISCUSSION

Uptake of chromium(III)

In order to acquire information on the equilibrium time, 1.00 g of $\overline{\text{HNa}}\cdot 5H_2O$ was contacted, with stirring at 25°, with 200 ml of 0.100 N chromium nitrate solution (initial pH 2.75) and the uptake of Cr^{3+} and release of Na^+ were followed as a function of time (Fig. 1).

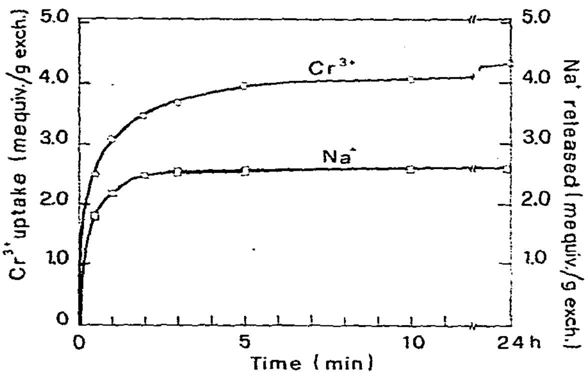

Fig. 1. Uptake of Cr^{3+} on $\overline{\text{HNa}}\cdot 5H_2O$ as a function of time. Conditions: 1 g of $\overline{\text{HNa}}\cdot 5H_2O$ contacted with 200 ml of 0.100 N chromium(III) nitrate solution at 25 ± 1°.

The protons released into the solution are not reported as it was very likely that a certain amount of them were consumed by the hydrolyzed species of Cr^{3+} initially present in the chromium(III) nitrate solution. This fact was confirmed experimentally by adding a known amount of nitric acid to 200 ml of the initial solution. It was found, by pH measurements, that 1.2 mequiv. of the added nitric acid were consumed in *ca.* 24 h. Fig. 1 shows that a conversion of Cr^{3+} of *ca.* 50% was reached quickly but a relatively slower process followed; nevertheless, a conversion of Cr^{3+} higher than 80% was reached after a few minutes. It can also be seen that all of the Na^+ initially in the exchanger was replaced in *ca.* 2 min.

The uptake of Cr^{3+} in equilibrium experiments with 0.010 N and 0.100 N chromium(III) nitrate solutions was also studied. The results obtained with a 0.010 N solution acidified to pH 2.75 (in order to have the same hydrolysis pH as the 0.100 N solution) are shown in Fig. 2. It can be seen that nearly all of the Cr^{3+} added was

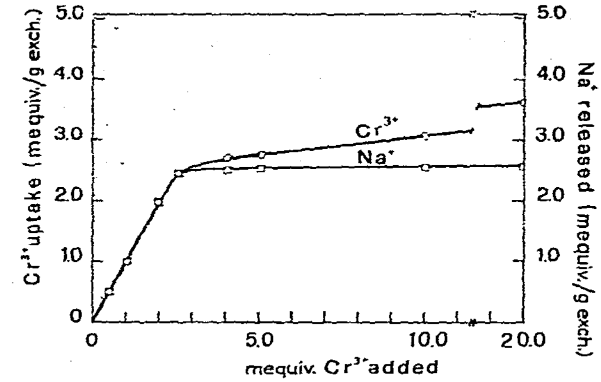

Fig. 2. Ion exchange of Cr^{3+} on $\overline{\mathrm{HNa}}\cdot 5H_2O$. Conditions: 1 g of $\overline{\mathrm{HNa}}\cdot 5H_2O$ equilibrated with different volumes of 0.010 *N* chromium(III) nitrate solution at 25 ± 1°.

taken up by the exchanger until a conversion of Cr^{3+} of *ca.* 50% was reached; three Na^+ ions were released in to the solution for each Cr^{3+} ion taken up, thus confirming that chromium was exchanged as a trivalent cation.

The selectivity of the exchanger for Cr^{3+} was found to decrease above a conversion of Cr^{3+} of 50% and a conversion of about 75% was obtained by using large volumes of chromium(III) nitrate solution.

X-Ray analyses of samples at various conversions of Cr^{3+} showed that, in the range 0–50%, three solid phases with interlayer distances of 11.8, 11.6 and 10.6 Å, respectively, were co-existing and that, in the range 50–75%, the 10.6 Å phase is converted into the 11.6 Å phase. The approximate percentages of these solid phases, as a function of the conversion of Cr^{3+}, are shown in Fig. 3. The water content of the 75% Cr^{3+} form was 4 mole per formula weight of exchanger.

On the basis of these results, we suggest that the following process takes place in the range of conversions of Cr^{3+} of 0–50%:

$$\underset{(11.8\ \text{Å})}{3\overline{\mathrm{HNa}}\cdot 5\mathrm{H_2O}} + \mathrm{Cr^{3+}} \rightarrow 2\ \underset{(11.6\ \text{Å})}{\overline{\mathrm{H_{0.5}Cr_{0.5}}}\cdot 4\mathrm{H_2O}} + \underset{(10.6\ \text{Å})}{\overline{\mathrm{HH}}\cdot 6\mathrm{H_2O}} + 3\mathrm{Na^+} + \mathrm{H_2O} \quad (1)$$

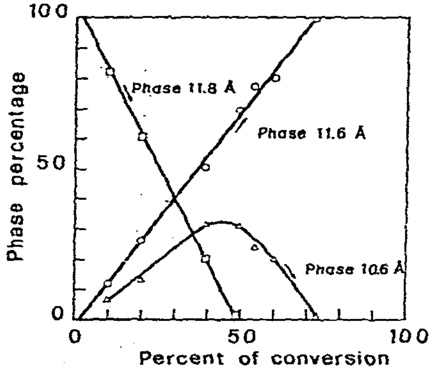

Fig. 3. Approximate percentage of the solid phases as a function of conversion found in the uptake of Cr^{3+} on $\overline{\mathrm{HNa}}\cdot 5H_2O$.

This is followed by H^+/Cr^{3+} exchange on the polyhydrated dihydrogen form, *viz*:

$$\underset{(10.6\ \text{Å})}{\overline{HH}\cdot 6H_2O} + 0.5\,Cr^{3+} \rightarrow \underset{(11.6\ \text{Å})}{\overline{H_{0.5}Cr_{0.5}}\cdot 4H_2O} + 1.5H_3O^+ + 0.5\,H_2O \qquad (2)$$

Preliminary experiments performed with $Zr(HPO_4)_2\cdot 6H_2O$ and 0.010 *N* chromium(III) nitrate solutions confirmed that H^+/Cr^{3+} exchange occurs according to eqn. 2. The peak at 10.6 Å probably was due to a polyhydrated dihydrogen form containing some solubilized Cr^{3+}. This hypothesis is supported by the interlayer distance of the anhydrous phases. When a sample with a conversion of Cr^{3+} of 50% was dried at 180°, two peaks, at 7.6 and 8.2 Å, were obtained, the former being much weaker than the latter. Now, the peak at 7.6 Å could also be obtained by drying the hydrated dihydrogen forms, while the peak at 8.2 Å was obtained by drying the 75% converted Cr^{3+} form.

The formation of the polyhydrated dihydrogen form in eqn. 2 could be ascribed to the fact that, under the experimental conditions chosen, a fraction of the Na^+ present in the monosodium form was replaced by protons coming from the sites occupied by Cr^{3+} ions according to the process

$$\overline{HNa}\cdot 5H_2O + H_3O^+ + (n-6)\,H_2O \rightarrow \overline{HH}\cdot nH_2O + Na^+$$

If this hypothesis is true, the formation of the polyhydrated dihydrogen form should be prevented by increasing the Na^+ concentration in order to avoid the regeneration of the monosodium form. Experiments performed with large volumes of solution [0.1 *N* $Cr(NO_3)_3\cdot 9H_2O$–0.1 *N* $NaClO_4$] at an initial pH of 2.75 showed that the 10.6 Å phase was not formed in appreciable amounts and that the process taking place under these conditions was essentially

$$\overline{HNa}\cdot 5H_2O + Cr^{3+} \rightarrow \overline{H_{0.5}Cr_{0.5}}\cdot 4H_2O + 0.5H_3O^+ + 0.5H_2O + Na^+$$

i.e., analogous to eqn. 1 without added $NaClO_4$.

The results of equilibrium experiments performed with 0.100 *N* chromium(III) nitrate solution are shown in Fig. 4. In our opinion, these results could be explained by considerations similar to those made for the 0.010 *N* solution. However, owing to the higher Cr^{3+} concentration, the remaining protons from $ZrH_{0.5}Cr_{0.5}(PO_4)_2\cdot 4H_2O$ can be replaced with the formation of a solid solution. By using large volumes of 0.1 *N* chromium(III) nitrate solution, conversions ranging from 80 to 90% were obtained. The X-ray diffraction patterns of a hydrated and an anhydrous 85% Cr^{3+}-converted sample are shown in Table I, columns (a) and (b).

Uptake of lanthanum(III)

Kinetic experiments performed with 0.100 *N* lanthanum(III) nitrate solution (Fig. 5) showed that the uptake of La^{3+} was considerably slower than that of Cr^{3+}. A relatively fast conversion of La^{3+}, up to about 30%, was followed by a very slow process and a conversion of about 60% was reached only after equilibration for 45 days. X-ray patterns of samples at various conversions of La^{3+} showed that the decrease in the monosodium phase was proportional to the amount of Na^+ ions

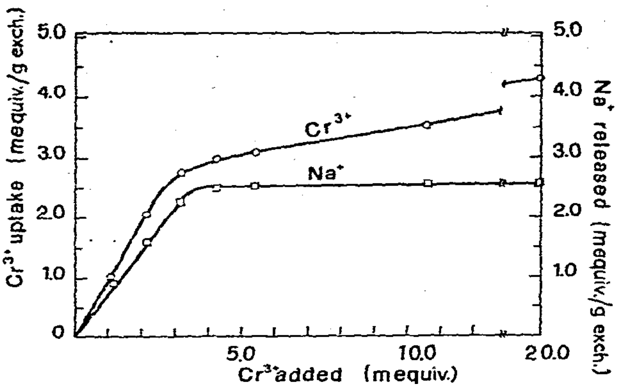

Fig. 4. Ion exchange of Cr^{3+} on $\overline{HNa}\cdot 5H_2O$. Conditions: 1 g of $\overline{HNa}\cdot 5H_2O$ equilibrated with different volumes of 0.100 *N* chromium(III) nitrate solution at 25 ± 1°.

released into the solution. At a conversion of La^{3+} of 60%, a single phase with 4 mole of water and an interlayer distance of 10.3 Å was present. Hence the ion-exchange process seems to be

$$\overline{HNa}\cdot 5H_2O + 0.4\,La^{3+} \rightarrow \overline{H_{0.8}La_{0.4}}\cdot 4H_2O + 0.3H_3O^+ + Na^+ + 0.7H_2O$$

The X-ray pattern of a 60% La^{3+}-loaded sample is reported in Table I, column (c).

However, remembering the results obtained with Cr^{3+}, the sample with a conversion of La^{3+} of 60% was dehydrated at 180°. X-ray analyses showed the presence of two phases with interlayer distances of 7.6 and 8.2 Å. Hence the 60% La^{3+}

TABLE I

X-RAY POWDER PATTERNS OF HYDRATED (a) AND ANHYDROUS (b) 85% Cr^{3+}-LOADED PHASE AND 60% La^{3+}-LOADED PHASE (c) OF CRYSTALLINE ZIRCONIUM PHOSPHATE

Symbols used: s, strong; m, medium; w, weak; v, very.

d (Å)		
(a)	*(b)*	*(c)*
11.6 (vs)	8.8 (vs)	10.3 (vs)
5.75 (m)	4.60 (w)	5.13 (s)
4.61 (vw)	4.46 (m)	4.52 (w)
4.57 (vw)	4.33 (w)	4.45 (w)
4.45 (w)	4.00 (w)	4.29 (m)
4.18 (vw)	3.91 (vw)	3.88 (vw)
3.92 (w)	3.78 (vw)	3.81 (w)
3.78 (s)	3.67 (vw)	3.75 (w)
3.55 (vw)	3.49 (vw)	3.52 (m)
3.49 (vw)	2.65 (w)	3.06 (m)
3.42 (vw)	2.60 (vw)	3.00 (w)
3.24 (w)		2.80 (w)
3.20 (m)		
2.79 (vw)		
2.63 (m)		

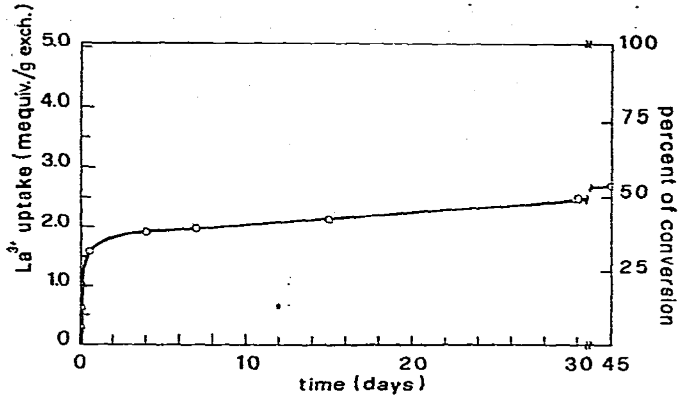

Fig. 5. Uptake of La^{3+} on $\overline{HNa}\cdot 5H_2O$ as a function of time. Conditions: 1 g of $\overline{HNa}\cdot 5H_2O$ contacted with 200 ml of 0.100 *N* lanthanum(III) nitrate solution at 25 ± 1°.

phase was probably not a pure phase but rather a mixture of $ZrH_{0.5}La_{0.5}(PO_4)_2\cdot 4H_2O$ (or a more highly converted La^{3+} phase) with a polyhydrated dihydrogen form (with some proportion of solubilized La^{3+}).

It is likely that the low rate of uptake of La^{3+} was due to steric hindrance owing to its large hydrated ion. When equilibration studies were performed at 75°, a conversion of La^{3+} of 60% was reached in 4 days.

Finally, preliminary investigations of H^+/La^{3+} exchange on polyhydrated dihydrogen forms showed that a conversion of La^{3+} higher than 50% can be easily obtained, but the ion-exchange kinetics were still slow.

Uptake of thallium(III)

Preliminary ion-exchange experiments were performed with Tl^{3+}. It is well known that this cation is strongly hydrolysed in aqueous medium and for this reason it was not possible to employ thallium(III) nitrate solution as it gives a low pH at which the monosodium form was regenerated to the dihydrogen form. Using 0.100 *N* thallium(III) chloride solution, an acceptable pH (*ca.* 2.8) was obtained; however, in this instance, it was known that the predominant species in solution are $TlCl_2^+$ and $TlCl_4^-$ complexes[10] and therefore, owing to the low Tl^{3+} concentration, very slow ion-exchange kinetics could be anticipated. By equilibrating 1.00 g of the monosodium form with 200 ml of 0.100 *N* thallium(III) chloride solution, a 50% Tl^{3+}-converted form was obtained after 7 days while all of the Na^+ originally present in the monosodium form was found in the solution. X-ray analyses showed that the characteristic peak at 11.8 Å of the monosodium form was completely absent, replaced by an initial peak at 21.5 Å and a broad, intense peak at 10.6 Å. It was possible to show that the peak at 10.6 Å was due to the mixture of a Tl^{3+} form with a polyhydrated dihydrogen form because, on dehydration at 110°, it disappeared, giving rise to peaks at 7.6 Å and 8.3 Å.

It was concluded that the behaviour of Tl^{3+} was similar to that of La^{3+} and phases with similar interlayer distances were obtained. However, the peak at 21.5 Å remains unexplained.

In general, for ionic forms of zirconium phosphate, the first reflexion of a pure phase represents its interlayer Zr–Zr distance. However, in this instance, it seemed very doubtful to consider such a large value as an interlayer distance. Some further experiments were therefore carried out in order to clarify this point. When the 50% Tl^{3+} sample was brought to constant weight over saturated sodium chloride solution, it contained 3.6 mole of water per formula weight and had an initial X-ray diffraction maximum at 19.2 Å. Over P_4O_{10} the first peak decreased to 17.7 Å, while on heating at 160° this reflexion disappeared but, on leaving the sample in air for some time, it reappeared at 19.2 Å. The observed density of the 50% Tl^{3+} sample was 2.8 g/cm³, which seemed to be too high for an interlayer distance of 19.2 Å.

It was interesting that a peak at 15 Å was also found in some ion-exchange experiments with Cr^{3+}. Therefore, the possibility that chloro and aquo cationic complexes of Tl^{3+} or Cr^{3+} are taken up by the exchanger, giving phases with very large interlayer distances, must be considered; this problem deserves further attention.

CONCLUSIONS

Trivalent cations are taken up by ionic forms of zirconium phosphate with large interlayer distance, demonstrating that the lack of exchange on $Zr(HPO_4)_2 \cdot H_2O$ (7.6 Å) is due to steric hindrance. By using appropriate ionic forms of zirconium phosphate, it is likely that this inorganic exchanger can be charged with any polyvalent metal cation and even the uptake of cationic complexes can be anticipated.

Investigations on the reticular positions of polyvalent cation and research on the catalytic activity of zirconium phosphate loaded with polyvalent cations, and also on the practical use of crystalline zirconium phosphate in analytical separations and the removal of polyvalent cations from solutions, are therefore now possible.

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