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# Exchange of Alkaline Earth Cations with the Butylamine Intercalate of $\alpha$-Zirconium Phosphate

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**Abstract.** The ion uptake behavior of the butylamine intercalate of $\alpha$-zirconium phosphate, $Zr(HPO_4)\cdot H_2O$, towards alkaline earth cations has been examined. The rates of uptake are in the order $Sr^{2+} \approx Ca^{2+} > Ba^{2+} >> Mg^{2+}$. Because of the high pH afforded by the amine intercalate, the exchanged phase is always the fully exchanged one, $ZrM(PO_4)_2 \cdot nH_2O$. The values of $n$ were found to be 4 for $Mg^{2+}$ and $Ca^{2+}$, 3 for $Sr^{2+}$ and 2 for $Ba^{2+}$. Uptake of ions is quantitative to about 6 meq/g loading when no excess amine is present. Sharply reduced loadings occur in the presence of excess of free amine. A solution containing equal amounts of $Ca^{2+}$ and $Mg^{2+}$ yields a new solid solution phase with a 12.6 Å spacing.

**Key words:** Zirconium phosphate, ion exchange, butylamine intercalate, alkaline earth exchange.

## 1. Introduction

$\alpha$-Zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$, is a layered compound which behaves as an ion exchanger [1, 2]. Both protons are exchangeable; but the small interlayer spacing, 7.6 Å, serves to exclude large hydrated ions. This is evidenced by the exchange behavior of alkaline earth cations with $\alpha$-ZrP (shorthand notation for crystalline $Zr(HPO_4)_2 \cdot H_2O$). Magnesium and barium ions were found to exchange very slowly, or not at all [3, 4], whereas calcium and strontium formed only the half exchanged phases in the presence of base [5–7]. Extremely slow addition of base can result in higher uptakes of these ions [6, 8], but more rapid addition leads to precipitation of the alkaline earth phosphate [5]. In order to avoid this precipitation, Clearfield and Hagiwara used metal acetates to effect the exchange [9]. Boiling of the solutions was necessary in order to complete the exchange reaction. $Ca^{2+}$ and $Sr^{2+}$ formed both half and fully exchanged phases, whereas $Mg^{2+}$ and $Ba^{2+}$ only formed the latter type.

Another way to effect exchange of large cations is to first expand the $\alpha$-ZrP interlayer spacing. This can be done in several ways: (i) by first preparing $ZrNaH(PO_4)_2 \cdot 5H_2O$ which has an 11.8 Å interlayer spacing [10], (ii) by washing out the sodium ion with acid to obtain a higher hydrate of $\alpha$-ZrP (sometimes referred to as $\theta$-ZrP) with an interlayer spacing of 10.4 Å [11] and (iii) by using an amine intercalate [12]. The third method has not been previously tried with alkaline earth cations and forms the subject of this report.

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## 2. Experimental

### 2.1. REAGENTS AND ANALYTICAL METHODS

The alkaline earth chlorides were all reagent grade (either Fisher Certified or Baker Analysed). Solutions were prepared with distilled, deionized water and filtered before using. $Mg^{2+}$, $Ca^{2+}$ and $Sr^{2+}$ were determined by EDTA titrations using Eriochrome Black-T, a saturated aqueous solution of murexide, or 0.1% *o*-cresolphthalein complexone as indicators [13, 14]. $Ba^{2+}$ was also determined by EDTA titration in which an excess of EDTA is used and back titrated with $Mg^{2+}$ (Eriochrome Black-T as indicator).

### 2.2. PREPARATION OF EXCHANGER AND EXCHANGE REACTIONS

$\alpha$-ZrP was prepared by refluxing a gel in 12M $H_3PO_4$ for 300 h. Details have been given previously [1, 15]. Approximately 0.3 g of $\alpha$-zirconium phosphate was weighed into a polyethylene bottle and a precalculated amount of about 0.2 N solution of butylamine (BA) was added to give the required butylamine-exchanger ratio, 6.4 meq/g. Water was added to yield a solution to $\alpha$-ZrP ratio of 50 ml/g, and the whole was shaken at 25 °C for 24 h to obtain the complete intercalation of the amine. Exchange rates were determined by adding 6 meq of the desired cation per gram of $\alpha$-ZrP to the above dispersion of amine intercalate, and the whole diluted to 100 mL. The containers were shaken at a constant temperature of $25 \pm 0.1$ °C for a fixed period of time and then the solids were immediately filtered off, dried in air and their X-ray diffractograms obtained. The filtrates were analysed for $M^{2+}$ in solution by the EDTA method. In some cases the uptake of cation was also determined by digesting the exchanger with acid, filtering and determining the amount of recovered $M^{2+}$.

A series of equilibrium experiments were also carried out in which from 1–7 meq of $M^{2+}$ per g of $\alpha$-ZrP was added to the amine intercalates. The mixtures were equilibrated at $25 \pm 0.1$ °C for times determined by the rate experiments – about 24 h for $Ca^{2+}$, $Sr^{2+}$ and $Ba^{2+}$, but at least 3 days for $Mg^{2+}$.

### 2.3. INSTRUMENTAL

pH values were measured with a Fisher Accumet pH meter model 144 fitted with a Fisher microprobe combination electrode. A Cahn electrobalance in the thermogravimetric mode was used to obtain weight loss data. The heating rate was 5°/min. A Seifert-Scintag PAD-II X-ray Diffractometer was used to obtain powder patterns for phase identification, Cu$K\bar{\alpha}$ radiation ($\lambda = 1.5418$ Å) was used and the scan rate was 2°/min.

## 3. Results

X-ray powder patterns showed that the starting phase of the exchanger was the one containing a bilayer of butylamine and possessing an 18.6 Å interlayer spacing [16]. Figure 1 gives the rate of uptake of the 4 alkaline earth cations. The exchange reaction may be formulated as

$$Zr(CH_3(CH_2)_3NH_3^+)_2(PO_4)_2 + M^{2+}(Aq.) \rightleftharpoons ZrM^{2+}(PO_4)_2 \cdot nH_2O + 2CH_3(CH_2)_3NH_3^+ \qquad (1)$$

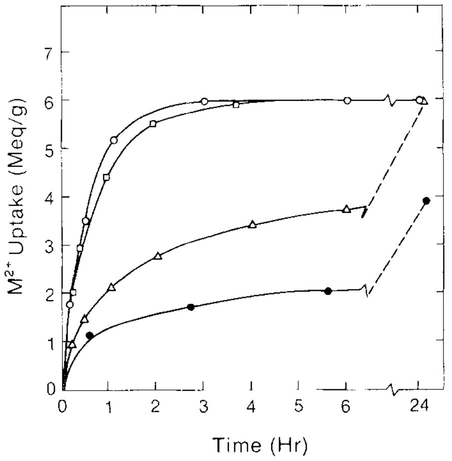

Fig. 1. Alkaline earth ion uptake as a function of time: $Mg^{2+}$, ●; $Ca^{2+}$, □; $Sr^{2+}$, ○; $Ba^{2+}$, △.

It is seen that the rate of ion uptake is in the order $Sr^{2+} \approx Ca^{2+} > Ba^{2+} >> Mg^{2+}$. About 6 h was required for $Sr^{2+}$ and $Ca^{2+}$ exchange to reach equilibrium as compared to 24 h for $Ba^{2+}$ and 48 h for $Mg^{2+}$. Portions of the solid removed at different times, in all cases, showed the presence of two solid phases; the fully exchanged alkaline earth phase, $ZrM^{2+}(PO_4)_2 \cdot nH_2O$, and the 18.6 Å amine intercalate. X-ray powder patterns for the alkaline earth exchanged phases, used for comparison, have been given previously [9]. Half exchanged phases were not obtained because the pH was high enough to bypass these intermediate stages of exchange.

Weight loss curves shown in Figures 2 and 3 indicate the following values of $n$: 4 in the cases of $Mg^{2+}$ and $Ca^{2+}$, 3 for $Sr^{2+}$ and 2 for $Ba^{2+}$. Only the strontium value differs from previous results [9] where the formula $ZrSr(PO_4)_2 \cdot 2.5H_2O$ was proposed.

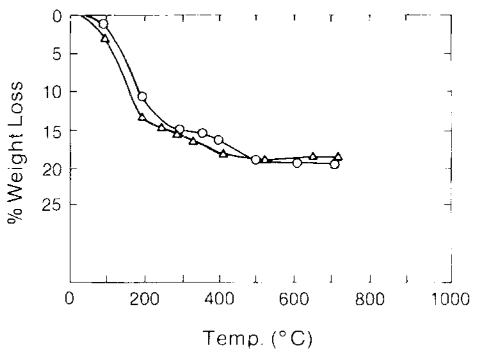

Fig. 2. Weight loss data for magnesium (○) and calcium (△) exchanged $\alpha$-zirconium phosphate.

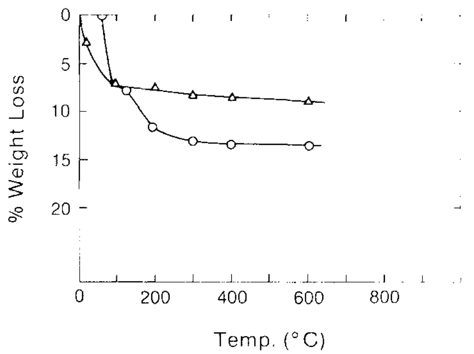

Fig. 3. Weight loss data for strontium (○) and barium (△) exchanged $\alpha$-zirconium phosphate.

Figures 4–7 show the alkaline earth ion uptake as a function of the amount of cation added. Points on the solid lines indicate quantitative ion uptake. Quantitative uptake occurred for each ion when no excess amine was used in the intercalation step. In fact a slight deficiency, 6.4 meq/g added versus 6.62 meq/g required for saturation, was used. It is seen that up to about 6 meq/g of added ion the uptake is quantitative, but beyond that, the points deviate from the straight line. The uptake corresponds to about 95% of theoretical uptake for $Mg^{2+}$, $Sr^{2+}$ and $Ba^{2+}$. That is, all the amine originally intercalated (6.4 meq/g) was replaced by cations according to Equation (1). However, for $Ca^{2+}$ the uptake was very nearly 100% (6.6 meq/g). pH values as a function of loading are also shown in Figures 4–7. The large drop in pH at high loadings of $Sr^{2+}$ and $Ba^{2+}$ may be due to the liberation of some of the protons

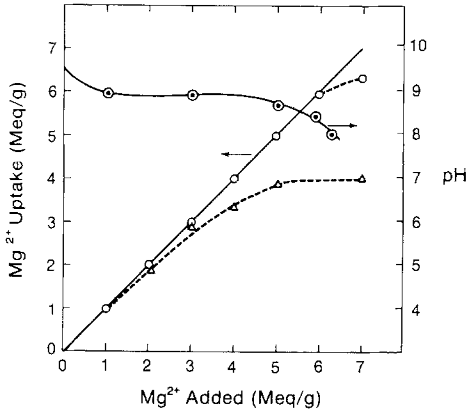

Fig. 4. Magnesium ion uptake as a function of total magnesium ion added (○) using 6.4 Meq BA/g of α-ZrP, (△) using 7.0 Meq BA/g of α-ZrP. The curve at the top represents the pH as a function of ion uptake.

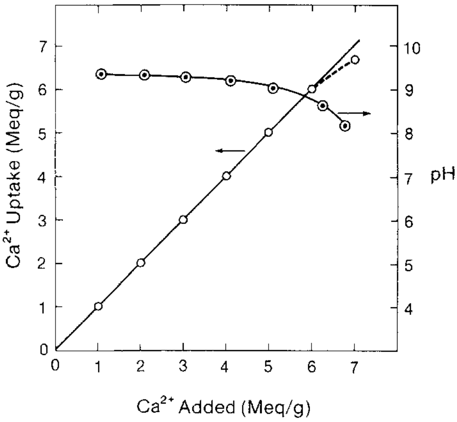

Fig. 5. Calcium uptake as a function of total calcium added.

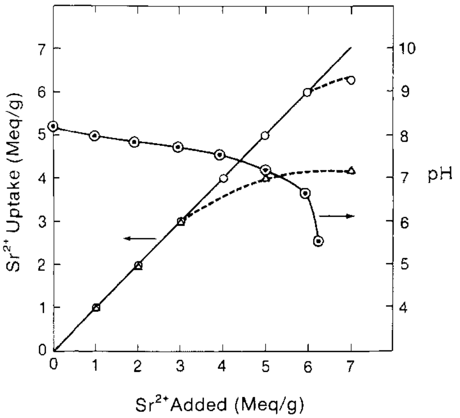

Fig. 6. Strontium ion uptake as a function of total strontium ion added (○) using 6.4 Meq BA/g of α-ZrP; (△) using 7.0 Meq BA/g of α-ZrP.

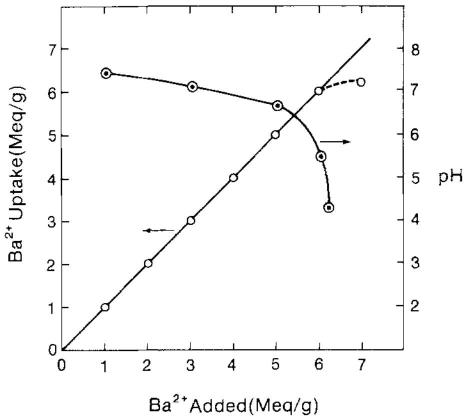

Fig. 7. Barium uptake as a function of total barium added.

for which insufficient amine is present to compensate. Alternatively, somewhat less amine may have been intercalated than the full 6.4 meq added.

The larger dashed curves in Figures 4 and 6 result when excess amine ($\approx$7 meq/g) was used for the intercalation reaction. When this was done, about 0.4 meq of butylamine per 100 ml of solution remained unintercalated and remained in solution setting up an amine-alkyl ammonium ion buffer system. This introduces additional equilibria as shown below:

$$RNH_2 + H_2O \rightleftharpoons RHNH_3^+ + OH^- \tag{2}$$

$$M^{2+} + OH^- \rightleftharpoons (MOH)^+ \tag{3}$$

Both reactions (2) and (3) tend to drive the exchange reaction [Equation (1)] to the left and this is illustrated graphically in Figures 4 and 6.

In carrying out separations of ions with zirconium phosphate a mixture of cations needs first to be exchanged onto the solid exchanger. It was therefore of interest to determine the nature of the uptake reaction of the butylamine intercalate. Therefore, a 50–50 mole % mixture of $Ca^{2+}$ and $Mg^{2+}$ ions was equilibrated with the intercalate in the same way as for the individual ions. The results are shown in Figure 8. The uptake was quantitative up to about 4 meq/g of added ions but then deviated substantially from the ideal value. The maximum uptake was 5.84 meq/g at 7 meq added. Mostly magnesium ion remained in solution and a portion of the solid phase remained in the amine intercalate form. However, only a single alkaline earth phase of zirconium phosphate was obtained. This phase consisted of a solid solution of the two alkaline earth cations with an interlayer spacing of 12.6 Å. A similar situation was observed when a mixed $Cu^{2+}$—$Ni^{2+}$ solution was contacted with the butylamine intercalate.

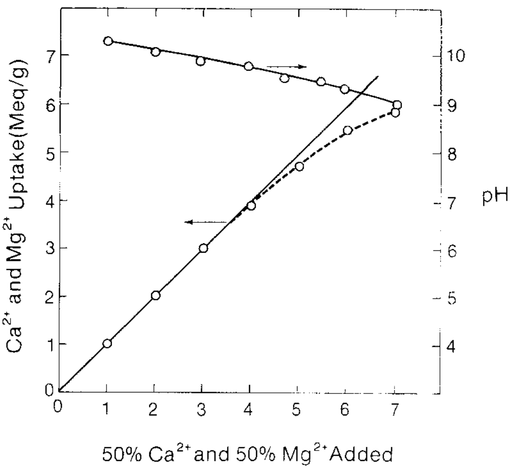

Fig. 8. Calcium and magnesium ion uptake as a function of total cation solution (50% calcium ion and 50% magnesium ion) added.

## 4. Discussion

The interlayer spacing of $\alpha$-ZrP is only 7.6 Å and this restricts the free volume for diffusion into the layers to a sphere of about 1.3 Å radius [17]. Hydrated alkaline earth cations are therefore too large to exchange. Either the layers must expand, or the cations need to shed their hydration shell ($Ba^{2+}$ would still be too large) in order to exchange. However, the hydration energies of divalent cations are too large for the reaction to proceed spontaneously. Addition of base removes protons from the layers allowing them to expand, and at the same time, provides energy for the dehydration process to occur [18]. This procedure works well for alkali metal cations [17, 19], but the exchange reactions with alkaline earth cations are slow and incomplete [4, 5]. Using a weaker base such as acetate ion allows the solutions to be boiled without a significant amount of phosphate hydrolysis which otherwise leads to precipitation of alkaline earth phosphate [9]. An alternative procedure is provided by the amine intercalates. In these intercalates the layers are already far enough apart for the hydrated ions to diffuse into the interior. Thus, the reaction may be visualized as a counter-diffusion of hydrated alkali metal cations and akyl ammonium ions. In order to complete the reaction, lattice oxygens need to displace some of the waters of hydration of the cations.

First row transition elements form exchange phases of composition $ZrM(PO_4)_2 \cdot 4H_2O$ [15, 20]. In these compounds the transition metal cation has been shown to be octahedrally coordinated with two oxygens of the layers forming part of the coordination sphere [21]. Presumably the same situation holds for $Mg^{2+}$ and $Ca^{2+}$, with more water being displaced from $Sr^{2+}$ and $Ba^{2+}$, where the hydration energies are progressively less. Thus, the very slow rate of uptake of aqueous $Mg^{2+}$ relative to the other ions may well result from both its large size and the large energy expenditure required to remove two water molecules from its primary hydration shell. For the same reasons barium ion should diffuse the fastest, but its rate of uptake is slower than $Ca^{2+}$ and $Sr^{2+}$. In this connection we must mention another factor which may influence rates of exchange, namely site binding [6] . These exchange reactions are decidedly irreversible. Once the divalent cations are in place in the layers, they tend to remain fixed. For example, higher uptakes are observed at elevated temperature, but on cooling, the ions do not diffuse back into the solution. Thus in the course of the exchange reaction, a certain number of ions may become immobile or site fixed and further exchange requires that the ions follow longer, more tortuous paths. This may account for the relatively large initial ion uptake followed by a much slower rate.

It is obvious from the preliminary mixed $Ca^{2+}$, $Mg^{2+}$ exchange experiment described in this study that the presence of a second ion in solution greatly alters the exchange reaction. In the case of the alkali metals, a complicated series of phases is obtained depending upon pH and relative concentration of the two ions [22, 23]. However, with divalent ions (a $Ni^{2+}$—$Cu^{2+}$ case will be treated later) a single solid solution phase is obtained. Should this behavior hold for many series of ions, then it may be possible to carry out separations of these ions on the crystalline intercalates.

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