

Intercalation of α,ω -Alkyldiamines in Layered α -Zirconium Phosphate and the Inclusion Behaviour of Some of the Intercalates Obtained*

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Abstract. The paper reports a study on the intercalation mechanism of $\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ (with $n = 2, 4, 6, 8, 10$) diamines in layered $\text{Zr}(\text{HOPO}_3)_2 \cdot \text{H}_2\text{O}$, performed by titrating the host with aqueous solutions of amines at 80°C . The intercalation reactions occur stepwise according to the 'moving boundary' model, with the formation of a number of intermediate intercalation compounds of formula $\text{Zr}(\text{HOPO}_3)_2 \cdot x\text{NH}_2(\text{CH}_2)_n\text{NH}_2$ ($0 < x < 1$) before obtaining the fully intercalated ones ($x = 1$). For each diamine the batch titration curve and a diagram of the phases involved in the intercalation reaction are reported. Twenty-two intercalation compounds have been isolated and characterized by their composition, XRD patterns and thermal behaviour, and information on the disposition of the guests within the interlayer region have been derived. At full intercalation the diamines form a monolayer of extended molecules with their axis inclined at 58° to the plane of the sheet. The terminal amino groups are protonated by the $-\text{POH}$ groups of the host, thus each diamine binds adjacent layers and, in a sense, transforms a layered structure into a framework structure that may have an accessible or potentially accessible porosity. The intercalation compound $\text{Zr}(\text{HOPO}_3)_2 \cdot 0.5\text{NH}_2(\text{CH}_2)_8\text{NH}_2$ is indeed able to include polar molecules such as water and short chain alkanols.

Key words. Zirconium phosphate, α,ω -alkyldiamines, intercalation.

1. Introduction

The first investigation [1] on the intercalation properties of α - $\text{Zr}(\text{HOPO}_3)_2 \cdot \text{H}_2\text{O}$ was published in early 1965, shortly after the announcement of the layered structure of the compound [2] and it is remarkable to note that no other work on this topic was published until 1976 [3]. Research efforts were in fact mainly devoted to the syntheses of materials of the zirconium phosphate type, to structural investigations and to the study of ion-exchange and transport properties [4, 5].

More recently attention has turned back to the intercalation chemistry of zirconium phosphate since it has been recognized that this compound is one of the best insulator hosts, among other things because of its high thermal and chemical stability and ion exchange properties. However, apart from recent papers on the intercalation of alkylmonoamines [6] with small carbon chains (C_1 – C_6) and of some heterocyclic compounds [7], there is still a lack of systematic studies on the intercalation reactions involving homologous classes of molecules. In this paper we present a detailed study of the mechanism of intercalation of some α,ω - n -alkyldiamines with an even number of C atoms, in α - $\text{Zr}(\text{HOPO}_3)_2 \cdot \text{H}_2\text{O}$ and the characterization of the intercalation compounds thereby

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obtained. This study was of interest not only for the fundamental aspects but also for the design of new materials. Diamines, in fact, bind phosphate groups belonging to two adjacent layers of the host and, in a sense, transform a layered material into a 'framework' material that may show an accessible or potentially accessible porosity.

2. Experimental

2.1. MATERIALS

C. Erba R.P.E. reagents were used, except for $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ which was a Merck 'pro analysi' product and the diamines which were supplied by Fluka.

Microcrystals of $\alpha\text{-Zr}(\text{HOPO}_3)_2 \cdot \text{H}_2\text{O}$ (referred to as $\text{ZrPH}_2 \cdot \text{H}_2\text{O}$), prepared according to the HF procedure [8], were washed with distilled water up to $\text{pH} \sim 4$ and fractionated with a sedimentation apparatus as described in [9]. The fraction containing flat microcrystals of a size ranging between 3 and 10 μm (estimated from electron micrographs) were recovered, stored over P_4O_{10} and used throughout the work.

2.2. INTERCALATION PROCEDURE

The intercalation reactions were studied by titrating the host, suspended in a solution of diamine hydrochloride, with a standardized diamine solution at room temperature or 80°C . Preliminary experiments were performed with a Mettler DK automatic titrimeter operating in the equilibrium point mode (each addition of 0.050M diamine solution was of 0.02 mL when the change in pH was less than 0.03 pH unit per min.). Final tests were carried out with the batch technique. To a series of samples of 0.500 g of $\alpha\text{-ZrPH}_2 \cdot \text{H}_2\text{O}$, dispersed in $(100-n)$ mL of 0.05M of diammonium hydrochloride, n mL of a 0.050M diamine solution was added in order to have samples with increasing loading in diamine. The equilibrium time was determined by monitoring the change in pH of the supernatant liquid. When no further change in pH was apparent (generally after 1 week) the solid was filtered off and the solution was analyzed for pH value and phosphates, eventually released from $\alpha\text{-ZrPH}_2$ because of hydrolytic attack. The amount of phosphates was always less than 2% and was considered negligible.

The XRD patterns were taken on wet and dried (at room temperature and 75% relative humidity) samples. The intercalation compounds were also characterized by the diamine and water content by means of elementary analysis and TG and DTA measurements. Since ignition (up to 1200°C) of the intercalates always leads to cubic ZrP_2O_7 , it was possible to check the composition in the organic guest from the weight loss at this temperature.

2.3. ANALYTICAL PROCEDURE AND APPARATUS

The concentration of the diamine solutions was determined potentiometrically with standard HCl solution by using a Mettler DK titrimeter. The phosphates were determined spectrophotometrically at 430 nm by the phosphomolybdic method.

The elementary C, H, N analysis of intercalates, previously dried at 150°C , was performed with a C. Erba Model 1106 Analyzer.

Simultaneous TG-DTA curves were taken with a Stanton STA-781 Thermoanalyzer at a heating rate of $5^\circ\text{C}/\text{min}$. in an air-flow. The X-ray diffraction patterns were taken on a computer controlled Philips diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation.

The step scanning procedure (step size of 0.03° for 5 seconds) was employed to obtain accurate values of the interlayer spacing. The area of the XRD peaks, corresponding to the interlayer distance of the intercalates, was obtained by multiplying their height by the width at half height.

3. Results and Discussion

The intercalation of diamines in α -ZrPH₂ may be considered as an acid base topotactic solid state reaction between a layered acid host and Brönsted-base guests according to the scheme:



A simple way to drive the intercalation reaction to completeness consists in titrating the host, suspended in a solvent (generally water) with a standardized solution of alkyl-diamine. If a significant amount of alkyldiammonium cations are present, the intercalation also proceeds by means of the ion exchange $\text{H}^+/\text{R}(\text{NH}_3)_2^{2+}$ process.

Indeed the intercalation reactions turn out to be more complex than is expressed by scheme 1 since they occur stepwise with discontinuous changes in the interlayer distance and formation of intermediate phases in which not all the active sites – the PO_3OH groups – are engaged in a bond with the guest species.

Furthermore they are often affected by the strong steric hindrance created by the stacking of the layers of the host and by the low mobility of the diamines within the interlayer region. It may be recalled that the crystal structure of α -ZrPH₂ arises from the packing of layers, each layer being constituted by zirconium atoms lying nearly in a plane ($\pm 0.25 \text{ \AA}$) capped by phosphate groups (see Figure 1). The stacking of the layers is such that there is

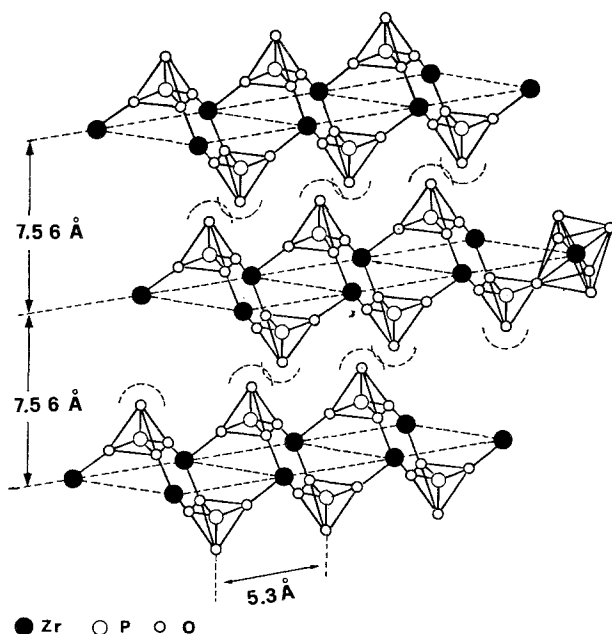


Fig. 1. Schematic view of the α -Zr(HOPO₃)₂·H₂O structure, showing the stacking of three adjacent layers. Hydrogen atoms and water molecules are not shown.

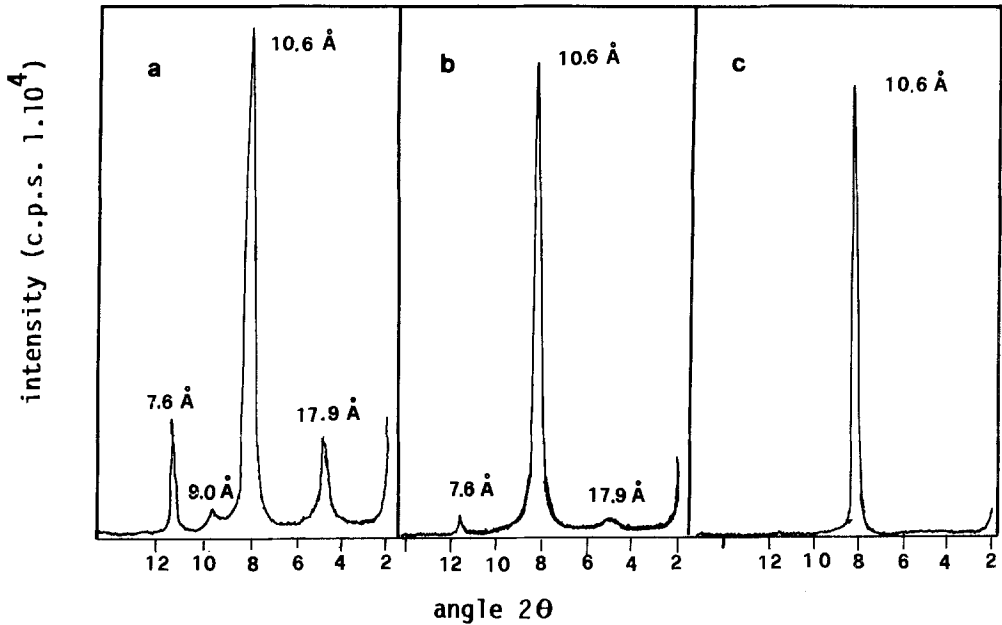


Fig. 2. Evolution as a function of time of the XRD powder patterns of a sample of α -ZrPH₂ titrated with 0.2 mol of n -C₈H₁₆(NH₂)₂ per mol of Zr. XRD pattern taken after two hours (a); two days (b); 20 days (c).

a partial interpenetration of the OH group of phosphates belonging to two adjacent layers and free access to the interlayer region is regulated by windows [2] with a critical dimension of 2.6 Å. Alkyldiamines, whose thickness is estimated to be 4.8 Å, cannot freely diffuse and activation energy is required to spread the layers apart. Once the guest diamine has penetrated the interlayer region further diffusion towards the core of crystallites is a very slow process since each elementary jump requires a concerted double deprotonation and reprotonation of the terminal amino groups.

Preliminary experiments showed that the above mentioned effects give rise to marked supersaturation phenomena, that is before a given intercalated phase is obtained, a new phase with higher diamine content is formed at the edges of the crystallite. From this situation of disequilibrium the system reaches equilibrium with a slow solid state reaction. As an example Figure 2 shows the evolution, as a function of time, of the XRD powder patterns of a sample of α -ZrPH₂ titrated at room temperature with the calculated amount of n -C₈H₁₆(NH₂)₂ to get the intercalation compound containing 0.2 mol of diamine per mol of Zr and an interlayer distance 10.6 Å. It can be seen that initially a small amount of a phase with a higher content of diamine and an interlayer distance of 17.9 Å is formed at the expense of the 10.6 Å phase before the original ZrPH₂ phase (7.6 Å) has been completely consumed. With time the system reaches the equilibrium composition.

To partly overcome these supersaturation phenomena, a more detailed discussion of which is reported in [7], intercalation was performed by titrating the host, suspended in the chlorohydrate of the diamine at 80°C, with the 'batch' procedure. Each addition of the free base was made with the pH stat technique at pH values higher than those necessary to form a given intercalate and, where possible, lower than the threshold of formation of the subsequent one.

The batch procedure provides a series of samples, with increasing guest content, whose XRD patterns give information on the nature of the crystalline phases present and on their relative amounts, since the area of the X-ray diffraction maxima, corresponding to the interlayer distance, is roughly proportional to the amount of phase. A plot of the approximate phase percentage versus the mol of diamine intercalated can be employed to follow the various steps of the intercalation process. In the following, each of the investigated systems will be discussed with the aid of the titration curve and the diagram of the phases identified.

3.1. SYSTEM α -ZrPH₂-1,2 DIAMINOETHANE (EDA)

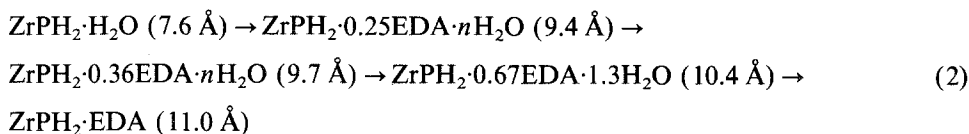
This system showed itself to be the most complicated of those investigated; the rate of diffusion of the guest in the host lattice is so slow, even at 80°C, that it was not possible to avoid supersaturation phenomena and obtain, as pure compounds, all the intermediate phases of the intercalation process.

Figure 3a reports the batch titration curve obtained by adding increasing amounts of base to the host suspended in EDA – hydrochloride at 80°C, and leaving each sample to be equilibrated for 30 days.

The shape of the curve with two plateaux (the first one at pH ~ 2.1, indicating that some replacement of protons of the host with ethylenediammonium ions has taken place, and the other at pH ~ 7) seems to suggest that the process occurs in two steps.

XRD patterns of samples with different degree of intercalation (see Figure 3b) indeed show that four different intercalated phases are involved. Two of them have been isolated and characterized as Zr(HOPO₃)₂·0.67EDA·1.3H₂O (10.4 Å) and Zr(HOPO₃)₂·EDA (11.0 Å); the composition of the other two has been deduced by taking into account the total amine content and the approximated percentage of the phases present in selected samples.

On the basis of these results the intercalation should occur according to the following reaction scheme:



Here and after, the composition of the intercalates is given without considering the solubility of the guest species in the already formed phase. Slightly different values may be obtained especially when the range of solubility is appreciable. Plots, like that of Figure 3b, are also useful to explicitly show up the solubility ranges.

A sequence of phases similar to that described in (2) was found by Clearfield and Twinda [10] who titrated α -ZrPH₂·H₂O suspended in water with EDA at room temperature but the effects of supersaturation phenomena were much more relevant than in the present case.

3.2. SYSTEM α -ZrPH₂-1,4 DIAMINO BUTANE (BuDA)

The intercalation of BuDA turned out to be a slow process at room temperature but is significantly fast at 80°C thus avoiding the formation of more than two intercalation compounds in the same crystallite. Figures 4a and 4b show the batch titration curve at this temperature and the relative diagram of the phases involved. The titration curve consists

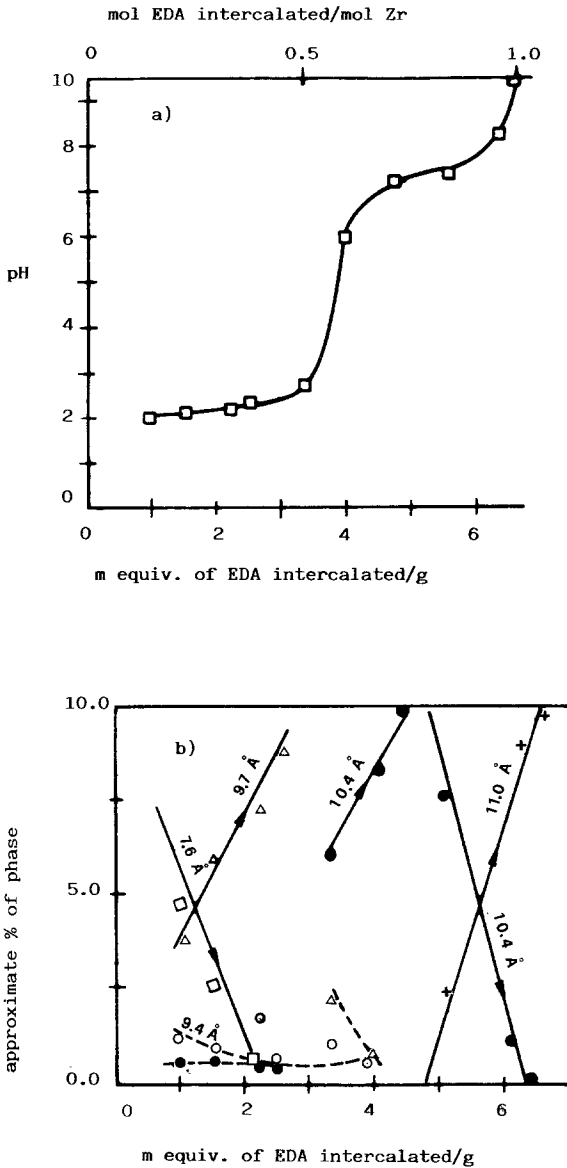
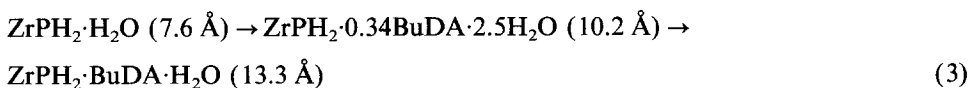


Fig. 3. (a) Batch titration curve of α -Zr(HOPO₃)₂·H₂O with 0.050M 1,2-Diaminoethane solution, performed at 80°C. (b) Approximate percentage of the phases present in the various stages of the batch titration.

of two well defined plateaux, one at pH ~ 2.3 and the other at pH ~ 7.3. Along the first plateau α -ZrPH₂ is transformed into an intercalate containing 0.34 mol BuDA per mol of host, while in the second this is converted into the fully intercalated phase. Thus the process is described by the following scheme of reaction:



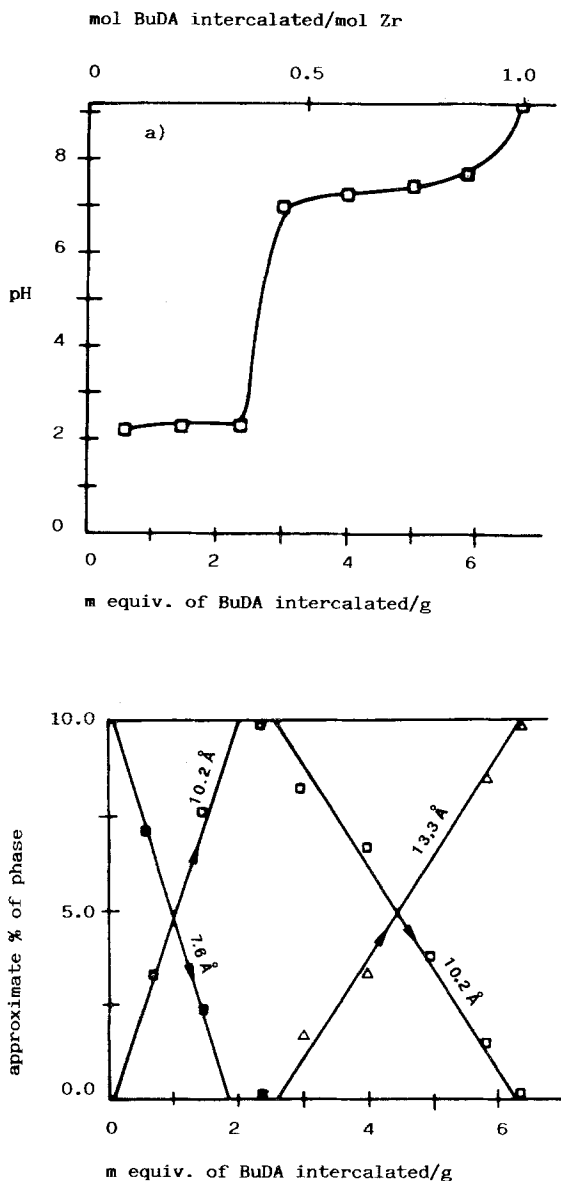


Fig. 4. (a) Batch titration curve of α -Zr(HOPO₃)₂·H₂O with 0.050M 1,4-Diaminobutane solution, performed at 80°C. (b) Approximate percentage of the phases present in the various stages of the batch titration.

3.3. SYSTEM α -ZrPH₂·H₂O-1,6 DIAMINOHEXANE (HeDA)

This base may be intercalated at room temperature; the titration curve, with the relative phase diagram, is shown in Figure 5a and 5b respectively.

The process is accompanied by three phase transitions; two of them occur at low pH ($\sim 2, 5$), the other at pH ~ 7 . The pure intercalation compounds were isolated and found to be ZrPH₂·0.2HeDA·2.5H₂O (10.7 Å), ZrPH₂·0.5HeDA·1.5H₂O (12.6 Å) and ZrPH₂·HeDA·H₂O (15.4 Å).

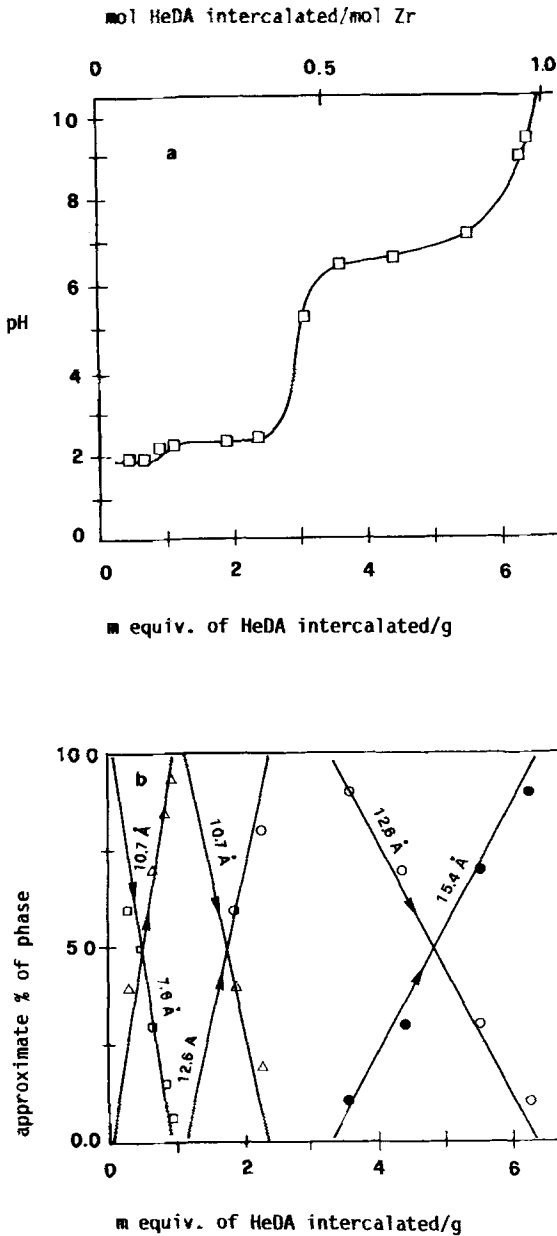


Fig. 5. (a) Batch titration curve of α -Zr(HOPO₃)₂·H₂O with 0.050M 1,6-Diaminohexane solution, performed at room temperature. (b) Approximate percentage of the phases present in the various stages of the batch titration.

It is interesting to note that when ZrPH₂·0.2HeDA·2.5H₂O is dehydrated at 150°C a mixture of two phases, ZrPH₂ (7.41 Å) and ZrPH₂·0.2HeDA (10.4 Å), is obtained. The dehydration of ZrPH₂·0.5HeDA·1.5H₂O leads instead to a single phase with an interlayer distance of 10.8 Å. These dehydrated phases, dipped in water, regain the water molecules lost and the initial intercalation compounds are reobtained.

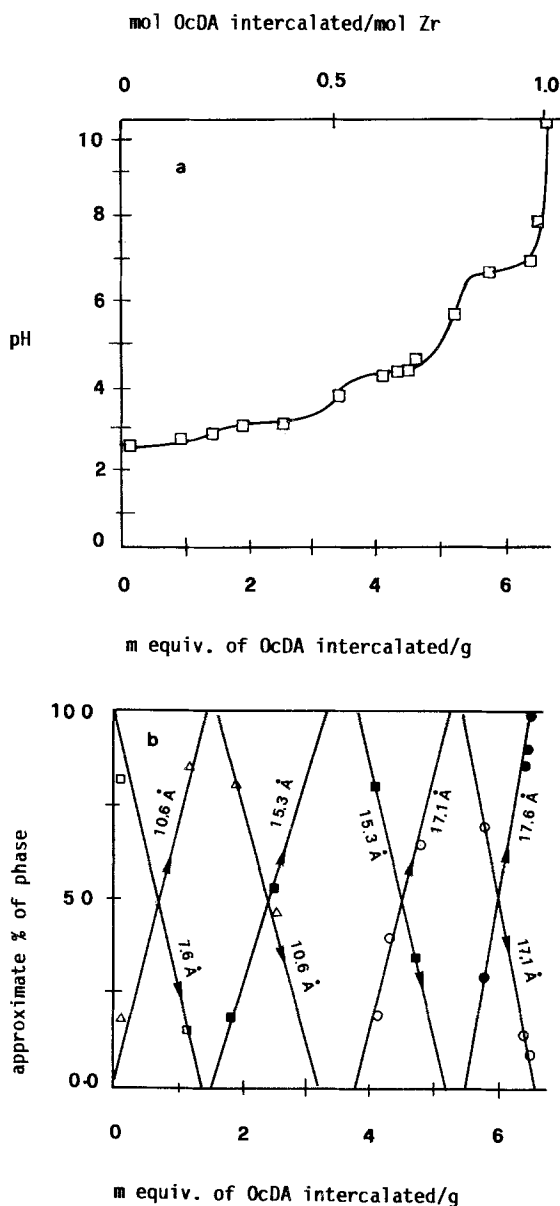


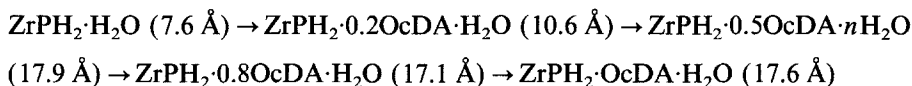
Fig. 6. (a) Batch titration curve of α -Zr(HOPO₃)₂·H₂O with 0.050M 1,8-Diamine Octane solution, performed at 80°C. (b) Approximate percentage of the phases present in the various stages of the batch titration. The 15.3 Å phase comes from the 17.6 Å one (see text).

3.4. SYSTEM α -ZrPH₂·H₂O-1,8 DIAMINOCTANE (OcDA)

Again the intercalation reaction occurs very slowly at room temperature. A good separation between the intermediate stages of the process was obtained at 80°C.

The batch titration curve, shown in Figure 6a, shows four plateaux, three of them at pH below 4 and the fourth around pH 7; to each plateau is associated a phase transition as pointed out in Figure 6b. A knowledge of the composition of the pure intercalated phase

allows us to describe the process according to the following scheme:

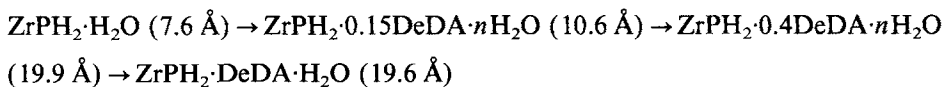


The behaviour of the phase containing 0.5 mol of OcDA per mol of Zr was found to be rather puzzling. When the XRD patterns are taken on the sample, immediately after the separation from the warm supernatant liquid at 80°C, the interlayer distance is found to be 17.9 Å, i.e. very similar to that of the $\text{ZrPH}_2 \cdot \text{OcDA} \cdot \text{H}_2\text{O}$ complex. If the wet sample is left to cool at room temperature the interlayer distance is 15.3 Å and the same value is found for the sample dried at room temperature over a saturated solution of BaCl_2 (r.h. 92%). When the sample is dried at room temperature and relative humidity less than 75%, the XRD patterns show the simultaneous presence of four phases with $d = 7.6$; 10.6; 15.3 and 17.6 Å respectively. Upon dehydration at 150°C the XRD pattern is typical of an amorphous compound. This material, as well as the one dried in air, rehydrates when dipped in water and the XRD patterns of the wet materials are those of the original 17.9 Å phase. Finally, it is of interest to note that the dehydration at 150°C of the phase containing 0.2 mol of OcDA per mol of Zr, leads to a mixture of anhydrous ZrPH_2 (7.4 Å) and a phase with interlayer distance 17.1 Å.

3.5. SYSTEM ZrPH_2 -1,10 DIAMINODECANE (DeDA)

The intercalation reaction of this base is, in many respects, similar to that of OcDA. Figures 7a and 7b show the titration curve performed at 80°C and the relative phase diagram. The titration curve consists of a short plateau at $\text{pH} \sim 2.2$ and a long one at $\text{pH} \sim 3$. In the 0–2.5 meq/g uptake range three phases coexist, the original $\text{ZrPH}_2 \cdot \text{H}_2\text{O}$ and two new ones with interlayer distances of 10.6 Å and 19.9 Å, respectively. Along the remaining part of the plateau at $\text{pH} \sim 3$, the 19.9 Å phase is transformed into the fully intercalated one with an interlayer distance of 19.6 Å. The 19.9 Å phase behaves in a manner similar to the one already described for the $\text{ZrPH}_2 \cdot 0.5\text{OcDA}$ (17.9 Å) compound. The interlayer distance drops to 17.0 Å when the sample is left to cool at room temperature. Attempts to obtain the 10.6 Å phase as a pure intercalation compound were unsuccessful, while it was possible to prepare near-pure samples of the 19.9 Å (17.0 Å at room temperature) phase (see Figure 7b).

Under equilibrium conditions the intercalation process should occur according to the following scheme:



3.6. COMMENTS ON THE INTERCALATION REACTIONS AND ON THE DISPOSITION OF DIAMINES WITHIN THE INTERLAYER REGION

In a previous paper [11], concerning intercalation compounds of α -zirconium phosphate partially loaded by propylamine, it was pointed out that the monoamines are evenly distributed among all the interlayer regions. The data collected in the present paper seem to lead to the same conclusions. In fact, if the intercalation process occurred according to the 'staging' mechanism, then in the half loaded compounds non-intercalated regions

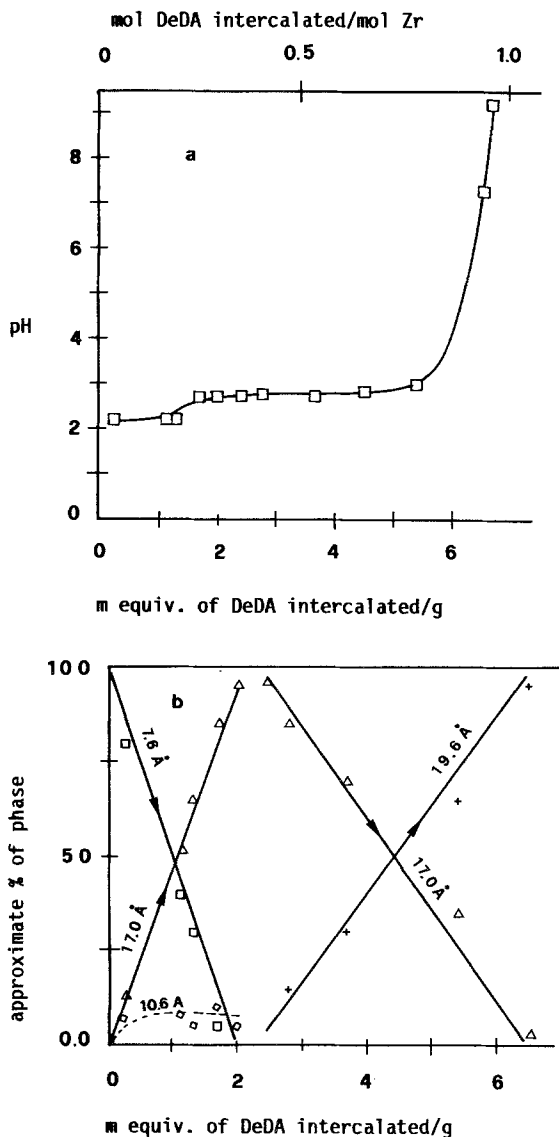


Fig. 7. (a) Batch titration curve of α -Zr(HOPO₃)₂·H₂O with 0.050M 1,10-Diaminodecane solution, performed at 80°C. (b) Approximate percentage of the phases present in the various stages of the batch titration. The 17.0 Å phase comes from the 19.9 Å one (see text).

would alternate with regions fully loaded by diamines. In this case no swelling phenomena should be observed, since neither the hydrogen form of α -ZrPH₂ nor its fully intercalated compounds swell spontaneously in water. This contrasts with the behaviour observed for the half intercalated compounds with OcDA and DeDA.

The general aspects of the intercalation reactions described may be therefore interpreted in terms of the 'moving boundary' model [12], already used to discuss the ion exchange mechanism in α -ZrPH₂.

According to this model, intercalation involves every interlayer region concomitantly. In

the initial stages of the process there is an opening of the interlayer space at the edges of the crystallites to accommodate the incoming diamine molecule and/or diammonium cations and the layers are bent with the formation of a phase boundary between the intercalated part and the original ZrPH_2 phase. Once a perceptible amount of new phase has been formed the process occurs in a faster way in the boundary region (degree of intercalation vs time curves are often S-shaped with a larger or shorter induction period), until all the $\alpha\text{-ZrPH}_2\text{-H}_2\text{O}$ phase has been consumed. The phase rule requires that when two phases coexist (at constant temperature and pressure) the system has no degree of freedom. Thus the process occurs at constant composition of the product and a plateau in the titration curves is observed. When the intercalate is the only solid phase present, the system becomes monovariant and for further addition of the diamine the pH can rise until the threshold of formation of a new intercalation compound is reached. A phase boundary is then again formed, another plateau in the titration curve is obtained and so on until the fully intercalated phase is obtained.

This model provides a good interpretation of the intercalation reaction of BuDA, HeDA and OcDA whose titration curves show well-defined plateaux when two phases are present, and a large change in pH in the presence of a single solid phase.

The titration curve of EDA and, to a lesser extent that of DeDA, do not show well-defined plateaux owing to the presence of more than two phases in a wide range of uptake.

The number of plateaux, and hence of the intercalation compounds obtainable for a given diamine, should correspond to the number of different orientations that the diamine may assume before achieving the one present in the fully intercalated compound. These orientations, in turn, depend on the length of the alkyl chain and the density of P-OH groups in the interlayer region.

It seemed of interest to examine how the arrangement of the diamines in the interlayer region is also driven by the so-called 'space filling' postulate [13], according to which the most probable arrangements should be those in which the most economical use is made of the interlayer space. Table I reports the composition, the interlayer distance and a parameter V_p related to the packing of the diamine (see later) for the intercalation compounds prepared in the present study. If the fully intercalated monohydrate compounds are taken into account, a good correlation between the interlayer distance and the number of carbon atoms in the alkyl chain is observed (see Figure 8). The straight line follows the equation

$$d_{002} = 8.93 + 1.08n_c \quad (r = 0.9998)$$

Since the increment of alkyl chain length, in the *trans-trans* conformation, is estimated to be 1.27 Å for each additional carbon atom, it is reasonable to assume that the diamines are present as a monomolecular layer of extended molecules with their longitudinal axis inclined at an angle of $\arcsin(1.08/1.27) = 58^\circ$ with respect to the plane of the sheet.

The packing of the alkyl chains may be expressed by the parameter $V_p = V_c/V_i$, where V_c is the volume occupied by the alkyl chains and V_i is the volume available to them in the interlayer space.

V_i can be calculated by subtracting from the interlayer spacing the thickness (d') of the region occupied by the α -layer, the crystallization water and the terminal $-\text{NH}_3^+$ groups; referred to 1 cm² of layer, V_i is

$$V_i(\text{cm}^3) = d_{002} - d'$$

d_{002} and d' being expressed in cm.

Table I. Interlayer distance (d), water content ($n_{\text{H}_2\text{O}}$) and packing parameter (V_p) for intercalation compounds of α -zirconium phosphate containing x molecules of diamine per unit formula; numbers within brackets refer to V_p values calculated taking into account the volume of water (see text).

Diamine	x	$n_{\text{H}_2\text{O}}$	$d(\text{\AA})$	V_p
$\text{C}_2\text{H}_4(\text{NH}_2)_2$	0.25	n	9.4	1.04
	0.36	n	9.6	1.05
	0.67	1.3	10.4	0.88 (0.98)
	1.0	—	11.0	0.94
$\text{C}_4\text{H}_8(\text{NH}_2)_2$	0.34	2.5	10.2	1.04 (1.62)
	0.34	—	9.4	—
	1.0	1.0	13.3	0.89
$\text{C}_6\text{H}_{12}(\text{NH}_2)_2$	0.2	2.5	10.7	0.66 (1.08)
	0.5	1.5	12.6	0.80 (0.86)
	0.5	—	10.8	—
	1.0	1.0	15.4	0.90
$\text{C}_8\text{H}_{16}(\text{NH}_2)_2$	0.2	1.0	10.6	0.93
	0.5	1.0	15.3	0.61
	0.5	n	17.9	0.43
	0.8	1.0	17.1	0.76
	1.0	1.0	17.6	0.90
$\text{C}_{10}\text{H}_{20}(\text{NH}_2)_2$	0.15	n	10.6	0.87
	0.4	1.2	17.0	0.48 (0.49)
	0.4	n	19.9	0.35
	1.0	1.0	19.6	0.91

Assuming that the interpenetration of the $-\text{NH}_3^+$ groups within the layer surface is independent of n_c , d' is equal to the value of d_{002} for $n_c = 0$, i.e. 8.93×10^{-8} cm.

The cross section area of a *trans-trans* alkyl chain, deduced from the a and b unit cell dimensions [14] of crystalline $\text{C}_{29}\text{H}_{60}$, is $a \cdot b/2 = 18.6 \times 10^{-16}$ cm²; the volume of an alkyl chain containing n_c carbon atoms can be therefore estimated to be $n_c(1.27 \times 10^{-8}) \times (18.6 \times 10^{-16})$ cm³ so that V_c , referred to 1 cm² of layer, is:

$$V_c(\text{cm}^3) = n_c(1.27 \times 10^{-8})(18.6 \times 10^{-16})(4.12 \times 10^{14})$$

where 4.12×10^{14} is the number of unit formulae per square centimeter of α -layers.

From Table I it is seen that V_p values for fully intercalated monohydrate phases are about 0.9 indicating that the packing density is near to that present in the crystalline n -paraffin. Thus, the hypothesis that the diamines are arranged as a monomolecular layer of extended chains seems to be sound.

Taking into account the different diamine loading, a similar calculation can be extended to the partially intercalated monohydrate compounds under the further assumption that the interpenetration of the $-\text{NH}_3^+$ groups within the layer surface is independent of diamine loading (i.e. $V_i = d_{002} - d'$). For compounds containing more than one H_2O molecule, V_i can be roughly estimated by subtracting from $d_{002} - d'$ the volume (V_w) occupied by the excess of water:

$$V_w(\text{cm}^3) = (n - 1)(4.12 \times 10^{14})(1.2 \times 10^{-23})$$

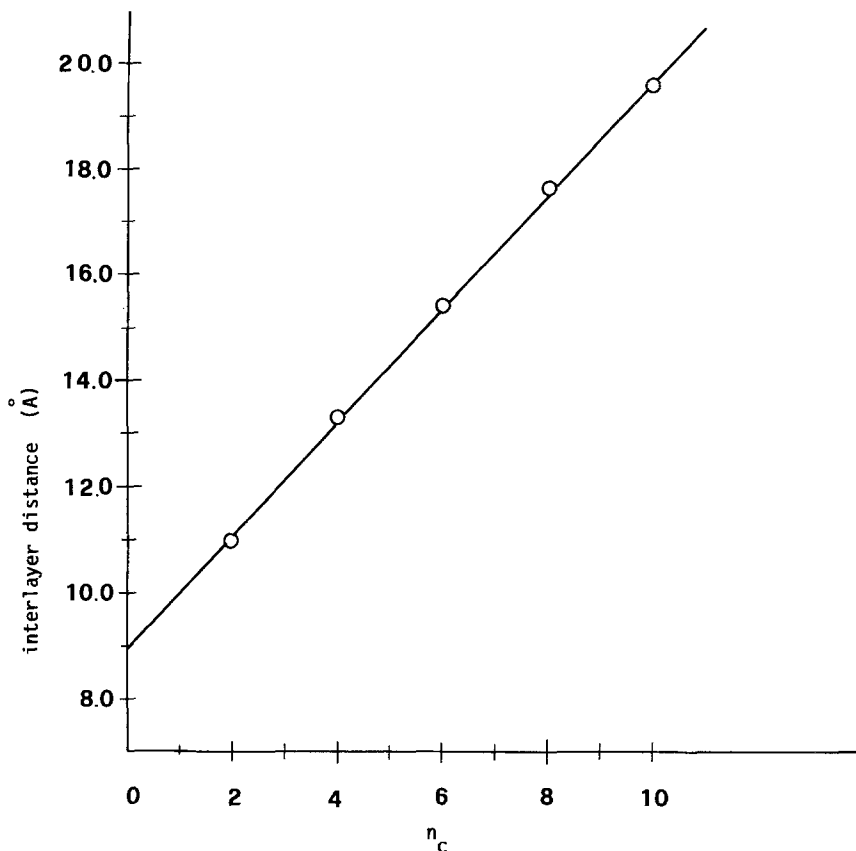


Fig. 8. Interlayer distance (d_{002}) of intercalation compounds of α -Zr(HOPO₃)₂·H₂O with α - ω , n -alkyl diamines containing one mol of diamine per mol of zirconium as a function of the number of carbon atoms in the alkyl chain. The samples were conditioned at room temperature at 75% relative humidity.

where 1.2×10^{-23} is the Van der Waals volume of a water molecule and n represents the moles of water per mole of Zr. The data listed in Table I show that V_p values found for mono- and polyhydrate partially intercalated compounds are in some cases considerably lower than those obtained for the fully intercalated ones.

This means that phases with identical interlayer distances but higher loadings in diamines could be obtained if the molecules were arranged in a more regular way. Very probably, the constraint due to the anchoring of the terminal amino groups at the surface of the layer as well as the low angle that the axis of the alkyl chain makes with the plane of the sheet, does not allow regular filling of the available interlayer space.

3.7. INTERACTIONS OF INTERCALATION COMPOUNDS AT LOW DEGREE OF INTERCALATION WITH POLAR MOLECULES

The data reported in Table I have shown that some intercalation compounds contain a large fraction of empty space. For many compounds this space is not accessible, even to

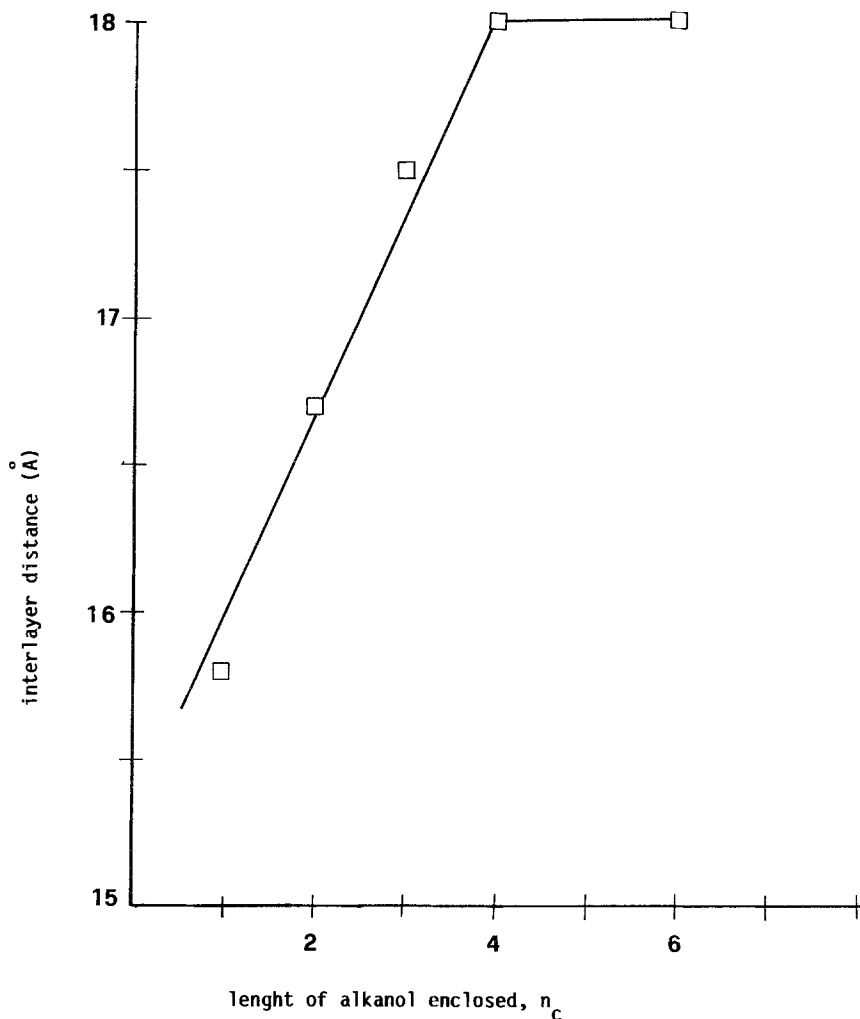


Fig. 9. Interlayer distance (d_{002}) of samples of α -Zr(HOPO₃)₂·0.5C₈H₁₆(NH₂)₂ as a function of the number of carbon atoms of the alkanol included.

water molecules, probably because it is cloistered by the guest diamine. In two cases, ZrPH₂·0.5OcDA and ZrPH₂·0.4DeDA, swelling phenomena have been observed. As described in Sections 3.4 and 3.5, once these materials have been air dried, they have interlayer distances of 15.3 and 17.0 Å respectively (the V_p values are 0.61 and 0.48), but they swell when dipped in pure water and the interlayer distances become 17.9 and 19.9 Å. It is as if the water molecules were able to occupy the potentially available interlayer space as a result of a change in conformation of the long alkyl chain of the diamines. It seemed of interest to check if other polar molecules could be included in the interlayer space with a mechanism similar to that shown by water molecules. The experiments were performed with the intercalate ZrPH₂·0.5OcDA·H₂O (15.3 Å) which was the only one obtained as a pure compound. 1 g of material was equilibrated with 25 mL of methanol, ethanol, propanol, butanol or hexanol for one day.

After centrifuging, the XRDs of the samples, quickly washed with small fractions of acetone, were taken. Figure 9 shows the interlayer distance of the samples as a function of the number of carbon atoms in the alkylchain of the enclosed alkanol. The slope of the straight line is 0.75 Å/carbon atom and the maximum value of the interlayer distance obtainable is the one that corresponds to the presence of extended molecules of OcDA in the *trans-trans* conformation anchored to POH groups belonging to adjacent layers. The amount of alkanol taken up has been found, from TG experiments, to be near to 0.5 mol per mol of Zr. Half of the POH groups not deprotonated by the amino group of the guest diamine thus interacts with molecules of alkanol. This in turn induces, in relation to its length, gradual changes in the conformation of the diamine until the maximum extension of the alkylchain is reached.

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