

# Studies on the Colloidization and Stability of Layered M(IV) Phosphates in Aqueous Amine Solutions

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**Abstract.** For the purpose of preparing pillared materials and multifunctional films, the colloidization and hydrolysis of  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -ZrP),  $\alpha$ -Sn(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -SnP) and  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -TiP) in alkylamine and alcohol amine solutions were investigated. The phosphates colloidize at a low level of amine intercalation but recrystallize at high levels of amine uptake. Alcohol amines are more efficient in colloidization of phosphates than alkylamines, and in the same amine solution  $\alpha$ -ZrP and  $\alpha$ -SnP colloidize more readily than  $\alpha$ -TiP. The hydrolytic reaction of the phosphates following the course of intercalation in different amine solutions were studied. The dissolution of the metal ions accompanying the hydrolysis of HPO<sub>4</sub><sup>2-</sup> leads to the destruction of the sheet structure. The strong hydrolytic reaction of  $\alpha$ -TiP causes it to colloidize with difficulty. The phase transformations of the wet amine intercalates during air drying were detected by XRD. The interlayer amine molecules may arrange in monolayer, bilayer or intermediate orientation, depending on the nature and content of the amines.

**Key words:** Layered phosphate, intercalation, colloidization, hydrolysis, sheet stability.

## 1. Introduction

Layered phosphates with well-defined layered structure are used as the substrate for many kinds of novel functional materials, such as pillared phosphate catalysts [1–5], inorganic ion-exchange pellicles [6], and self-assembled functional films [7]. One of the key procedures in the preparation of the above materials is to cause the layered phosphates to exfoliate entirely in solution. Being different from clay minerals, phosphates hardly exfoliate in water due to the high charge density between their sheets. It has been reported [8–11] that organic amines can intercalate into phosphates by reacting with the surface P—OH to enlarge the interlayer distance, and some of them, such as methylamine and *n*-propylamine, can even make the phosphates also completely form a colloidal dispersion. Chromia and alumina pillared phosphates having N<sub>2</sub> surface areas of 180–380 m<sup>2</sup>/g and a narrow pore size distribution have been obtained via colloid manipulation methods by different authors [2–4]. These materials are of interest as catalysts, sorbents and ion exchangers. Besides, it has been found that the interlayer porosity of the pillared

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phosphates is not usually obtained due to crowding of the pillars, therefore a certain degree of hydrolysis is desirable for the success of preparation, but the stability of the sheets is decreased at high degrees of hydrolysis [12].

For the purpose of preparing thermally stable pillared phosphates with high surface area and larger pores more efficiently and economically, the colloidization, hydrolysis and sheet stability of  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O,  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O and  $\alpha$ -Sn(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O in various alkylamine and alcohol amine mediums have been studied in detail and are reported in the present work.

## 2. Experimental

### 2.1. SAMPLE PREPARATION

The crystalline  $\alpha$ -Zr(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -ZrP) samples were prepared by three different methods. Zirconium phosphate gel was prepared by slowly adding a solution containing 25 g ZrOCl<sub>2</sub>·8H<sub>2</sub>O and 150 mL of 2 mol/L HCl to a mixture of 17.5 mL H<sub>3</sub>PO<sub>4</sub>, 10.6 mL HCl and 36 mL water with stirring. The gel was aged overnight and refluxed in 1.2 L of 12 mol/L H<sub>3</sub>PO<sub>4</sub> for 24 h to form  $\alpha$ -ZrP-R crystals [13].  $\alpha$ -ZrP-H was prepared by hydrothermal crystallization of 0.8 g of the above zirconium phosphate gel in 40 mL of 12 mol/L H<sub>3</sub>PO<sub>4</sub> in a stainless steel autoclave lined with glass at 185 °C for 7 d, 5.5 g of ZrOCl<sub>2</sub>·8H<sub>2</sub>O in 80 mL water was added to a mixture containing 4 mL of 40% HF and 46 mL of 85% H<sub>3</sub>PO<sub>4</sub>, and  $\alpha$ -ZrP-F was precipitated after removing HF acid by heating at 80 °C for 7 d under constant stirring [14].

The crystalline  $\alpha$ -Sn(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -SnP-R) was prepared by adding SnCl<sub>4</sub>·5H<sub>2</sub>O to 1 L of 8 mol/L H<sub>3</sub>PO<sub>4</sub> and 3 mol/L HNO<sub>3</sub> solution until the P : Sn ratio reached 30, then refluxing the mixture for 7 d [15]. 25 g of TiCl<sub>4</sub> dissolved in 430 mL of 2 mol/L HCl was slowly added to 400 mL of 1.25 mol/L H<sub>3</sub>PO<sub>4</sub> and a white gelatinous precipitate was obtained. After refluxing this gel in 1.4 L of 10 mol/L H<sub>3</sub>PO<sub>4</sub> for 50 h crystalline  $\alpha$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O ( $\alpha$ -TiP-R) was obtained [16].

### 2.2. INTERCALATION OF AMINE

The phosphate (25 mg) and a calculated amount of 0.1 mol/L amine solution were placed in a polyethylene bottle. Water was then added to keep the total volume to 2.5 mL. The mixture was equilibrated for 5–6 d at 30 °C, and then centrifuged. The colloidization state and interlayer distance of the wet intercalate were determined by XRD. The extent of hydrolysis of the phosphate after intercalation was determined by measuring the amount of HPO<sub>4</sub><sup>2-</sup> and M(IV) (M = Zr, Sn or Ti) in the supernatant solution by colorimetry [17] and the ICP method, respectively.

Table I. Colloidization of  $\alpha$ -ZrP-R in different media.

Amine*	Amount of amine added (mol/mol $\alpha$ -ZrP)		Interlayer distance after reordering (nm)
	Colloidization	Reordering	
MA	0.3–2.8	>2.8	1.63
EA	0.3–1.8	>1.8	1.67
PA	0.3–1.0	>1.0	1.74
BA	non-colloidal	–	1.89
EOA	0.3–3.0	–	–
POA	0.3–3.0	>3.0	1.80
BOA	0.3–2.0	>2.0	1.96

\*MA = Methylamine, EA = Ethylamine, PA = *n*-Propylamine, BA = *n*-Butylamine, EOA = Ethanolamine, POA = 3-Amino-1-propanol, BOA = 4-Amino-1-butanol.

### 2.3. CHARACTERIZATION

XRD patterns were recorded on a Rigaku D/Max-IIA X-ray diffractometer with  $\text{CuK}\alpha$  radiation at 40 kV and 20 mA. IR spectra were obtained on a Perkin-Elmer 983G spectrometer. The samples were diluted in a ratio of 1 : 200 with KBr and pressed into a self-supporting wafer. TG experiments were carried out on a Rigaku Thermoflex instrument in flowing air. The SEM images were obtained with a Hitachi S-520 microscope. ICP analysis was performed on a Baird PS6 instrument.

## 3. Results and Discussion

### 3.1. $\alpha$ -ZrP

The intercalation of  $\text{C}_1$ – $\text{C}_4$  alkylamines and  $\text{C}_2$ – $\text{C}_4$  alcohol amines into  $\alpha$ -ZrP-R was studied. As the amount of amine, except *n*-butylamine, exceeds 0.3 mol/mol  $\alpha$ -ZrP-R, the phosphate swells completely, giving rise to a colloidal dispersion. The colloidal dispersion remains within a certain amine concentration range. Beyond this range any further addition of amine causes reordering or recrystallization of the intercalate. The (002) peak on the XRD patterns of the wet precipitate shows the presence of the recrystallized intercalate phase and gives its interlayer distance. The results obtained with different amines are summarized in Table I.

The colloidal range and the interlayer distance of the reordered intercalate depend on the nature of the amine added. It has been suggested that swelling occurs when the amine molecules assume an upright position but are sufficiently separated to allow entry of the water [18]. When the amount of amine added is in excess of 3 mol/mol  $\alpha$ -ZrP-R, all the intercalates start to recrystallize because of the lowering of the water activity due to the presence of free amines, its conjugated acids and the phosphate salt generated by hydrolytic attack. The wet precipitates formed at this stage still contain some disordered phase, as indicated by the enlarged interlayer

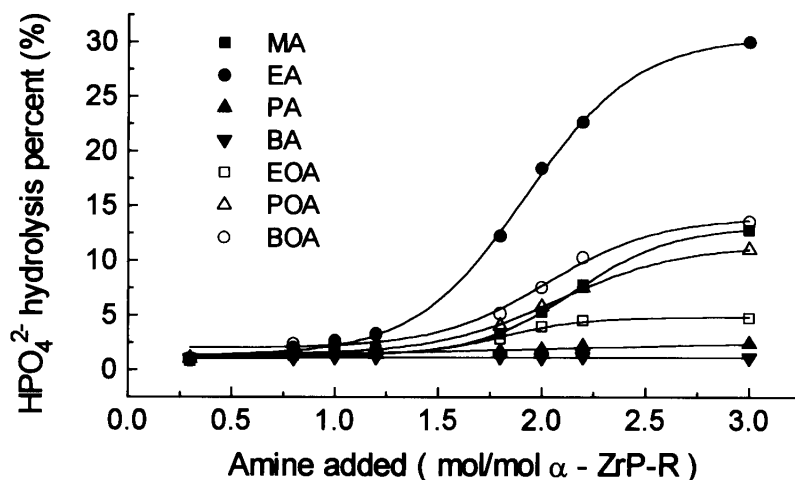


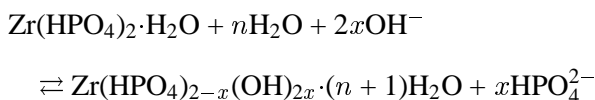
Figure 1. Extent of hydrolysis of  $\alpha$ -ZrP-R vs. amount of amine added.

distances compared with the theoretical values (see Table IV). Colloidization of the phosphate does not take place in *n*-butylamine solution, because a straightforward rearrangement of the amine molecules may occur in the system.

It is interesting to note that the alcohol amine systems are easier to handle than the alkylamine systems in the preparation of a colloidal dispersion because the phosphate colloidizes faster in alcohol amine solutions and their colloidal ranges are wider. This may be explained by the effect of the hydrophilic character of the terminal —OH groups in the alcohol amine molecules.

The hydrolysis of phosphates is favored in alkaline medium, so a hydrolytic loss of  $\text{HPO}_4^{2-}$  groups and a partial destruction of the phosphate sheet structure have been observed during colloidization. However, a controlled degree of hydrolysis has been reported to be advantageous to the formation of pillared phosphates [12]. The hydrolysis of  $\alpha$ -ZrP-R following the course of intercalation in various media are shown in Figure 1. The extent of hydrolysis of the phosphate increases with the amount of amine added and rises dramatically when the ratio of amine/ $\alpha$ -ZrP-R goes beyond 1.5 ~ 1.7. The hydrolytic ability of the amines decreases in the order ethylamine > 4-amino-1-butanol > methylamine > 3-amino-1-propanol > ethanolamine > *n*-propylamine > *n*-butylamine.

According to the overall hydrolytic reaction of  $\alpha$ -ZrP

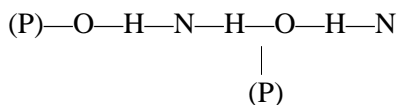


the hydrolytic ability of the amines should increase with their basicity. However, the basicity of alcohol amines is in general weaker than that of alkylamines, but the extents of hydrolysis of  $\alpha$ -ZrP-R in  $\text{C}_2 \sim \text{C}_4$  alcohol amines are higher than those

in *n*-butylamine and *n*-propylamine. The higher degree of hydrolysis of  $\alpha$ -ZrP-R in alcohol amines is caused by a deeper exfoliation of the phosphate sheets, which undoubtedly improves the contact between the sheets and the alkaline aqueous medium.

The hydrolysis of  $\text{HPO}_4^{2-}$  is accompanied by the dissolution of Zr(IV) to a lesser degree, leading to a partial destruction of the phosphate sheet structure. The dissolution of Zr(IV) and sheet stability of  $\alpha$ -ZrP-R in the strongest hydrolytic ethylamine medium are shown in Table II. At a ratio of 3 mol/mol  $\alpha$ -ZrP-R the amount of Zr(IV) lost is less than 10%, so the sheet stability, in the sense of chemical analysis, is more than 90%, indicating that  $\alpha$ -ZrP-R is rather stable in all the amine solutions. The dissolved Zr(IV) probably exists in the form of soluble amine Zr(IV) complexes.

The colloidalized samples are unstable on drying. XRD data of samples with amine/ $\alpha$ -ZrP-R ratios equal to 1, 2 and 3 after exposure to air for 4 h and 8 d are shown in Table III. The wet intercalates may experience a series of phase transformation during air drying until a stable phase is formed after 8 days. According to the structural model of amine intercalates proposed by Clearfield [8]



assuming that the hydrogen bonding is formed with a bond distance of 0.28 nm for  $\text{O—H} \cdots \text{N}$  and a  $180^\circ$  angle, the interlayer distances of intercalates loaded with amine monolayer and bilayer were calculated and are compared with the experimental results in Table IV. For most of the amine intercalates, the experimental values are approximately the same as the theoretical ones. When the amine/ $\alpha$ -ZrP-R ratio is 1, at the beginning of reordering the interlayer amine molecules tend to form a sole monolayer or a blend of monolayer and bilayer, and when the ratio is larger than 2 the bilayer arrangement is predominant. After drying for 8 d the stable phases of the methylamine and ethylamine intercalates display a monolayer orientation as a result of deintercalation of the amines, but those of all the other amine intercalates are still orientated in bilayers. For *n*-propylamine and *n*-butylamine systems several unstable phases with intermediate interlayer distances have been observed, which may mean that the chains of the amine molecules incline at lesser angles to the sheets, or that phases with different degrees of hydration are formed.

The dried stable methylamine and ethylamine intercalates were kept in a vessel saturated with water or amine vapor at  $30^\circ\text{C}$  for 1 d. The interlayer distances of the samples in water vapor remain unchanged, whereas those of the samples in amine vapor increased to 1.28 and 1.40 nm again. This reveals that the intercalated amines may slowly be lost in air, but the intercalation process is reversible. Elemental analysis results show that the methylamine or ethylamine intercalates dried for 4 h contain nearly 2 mol amine/mol  $\alpha$ -ZrP-R and the final air-dried samples contain

Table II. Sheet stability of phosphates in ethylamine solution.

EA/ $\alpha$ -MP-R* (mol/mol)	$\alpha$ -ZrP-R			$\alpha$ -SnP-R			$\alpha$ -TiP-R		
	HPO <sub>4</sub> <sup>2-</sup> lost (%)	Zr(IV) lost (%)	Sheet stability (%)	HPO <sub>4</sub> <sup>2-</sup> lost (%)	Sn(IV) lost (%)	Sheet stability (%)	HPO <sub>4</sub> <sup>2-</sup> lost (%)	Ti(IV) lost (%)	Sheet stability (%)
0.2	<1.0	<1.0	>99.0	7.1	1.1	98.5	10.0	1.8	98.2
0.4	1.2	<1.0	>99.0	12.2	2.8	97.2	19.1	5.2	94.8
0.6	1.8	<1.0	>99.0	16.0	5.5	94.5	28.3	12.0	88.0
0.8	2.0	<1.0	>99.0	21.0	8.6	91.4	37.4	21.2	78.8
1.0	2.4	<1.0	>99.0	26.5	13.6	86.4	46.5	31.5	68.5
1.2	3.3	<1.0	>99.0	36.5	20.0	80.0	55.7	43.0	57.0
1.5	12.7	1.5	98.5	43.0	30.7	69.3	69.0	61.2	38.8
2.0	18.1	4.3	95.7	65.4	53.0	47.0	93.8	90.0	10.0
3.0	27.2	7.2	92.8	100	100	0	100	100	0

\* EA/ $\alpha$ -MP-R: ratio of the amount of ethylamine added to phosphates.

Table III. Phase transformation of amine/ $\alpha$ -ZrP-R intercalates.

Amine	Interlayer distance (nm)					
	1 : 1		2 : 1		3 : 1	
	4h	8d	4h	8d	4h	8d
MA	0.96	0.96	1.28	0.96	1.28	0.96
EA	1.42(15) + 1.09(85)	1.06	1.40	1.06	1.40	1.06
PA	1.47(80) + 1.30(10)	1.48(80) + 1.32(10)	1.73(60) + 1.63(40)	1.62	1.73	1.63
	+ 1.09(10)	+ 1.10(10)				
BA	1.82(85) + 1.64(15)	1.82	1.89(60) + 1.82(40)	1.89(60) + 1.82(40)	1.89	1.89
EOA	1.00	1.00	1.47	1.47	1.45	1.47
POA	1.64(5) + 1.21(95)	1.64(10) + 1.22(90)	1.64	1.64	1.67	1.64
BOA	1.84(20) + 1.24(80)	1.84(20) + 1.24(80)	1.88	1.88	1.88	1.88

\*The numbers in parenthesis represent the relative intensities of the (002) diffraction peaks.

Table IV. Calculated and experimental interlayer distances of intercalates (nm).

		MA	EA	PA	BA	EOA	POA	BOA
Monolayer	Calculated	0.92	0.97	1.12	1.17	1.12	1.17	1.32
	Experimental	0.96	1.06	1.10	–	1.00	1.22	1.24
Bilayer	Calculated	1.21	1.31	1.61	1.71	1.60	1.71	2.01
	Experimental	1.28	1.40	1.63	1.89	1.47	1.64	1.88

only 1 mol amine/mol  $\alpha$ -ZrP-R. These data are consistent with the XRD results in Table III.

Crystalline  $\alpha$ -ZrP can be obtained in different ways. To compare the colloidalization and hydrolysis behavior of  $\alpha$ -ZrP prepared by different methods,  $\alpha$ -ZrP samples were synthesized by refluxing, hydrothermal crystallization and HF precipitation methods. XRD, SEM and IR results of the  $\alpha$ -ZrP samples are shown in Figures 2–4, showing that the three kinds of  $\alpha$ -ZrP differ significantly in sheet orderliness and crystal size. In Figure 2, all three samples give a sharp (002) peak and three double peaks at ca. 19.9°, 25.1° and 34.0°. The intensity of the (002) peak decreases in the order  $\alpha$ -ZrP-F >  $\alpha$ -ZrP-H >  $\alpha$ -ZrP-R, indicating that the sample from the HF precipitation method possesses the highest sheet orderliness. SEM images (Figure 3) show that the crystal sizes of  $\alpha$ -ZrP-F,  $\alpha$ -ZrP-H and  $\alpha$ -ZrP-R are in the range of 5–16, 0.7–1.3 and 0.4–0.8  $\mu\text{m}$ , respectively. IR spectra (Figure 4) of the three samples are similar to those in the literature [11, 18]. The broad band at 1000–1200  $\text{cm}^{-1}$  and the band at 1250  $\text{cm}^{-1}$  are attributed to the vibrations of  $\text{PO}_4$  and P—OH, respectively. A clear triple peak in the range of 1000–1200  $\text{cm}^{-1}$  is observed in the spectrum of  $\alpha$ -ZrP-H, showing the different environments around the  $\text{PO}_4$  groups. This may imply that the sheet structure of  $\alpha$ -ZrP-H is more highly ordered than the other two samples, resulting from the high hydrothermal crystallization temperature.

The colloidalization and hydrolysis data of the three  $\alpha$ -ZrP samples are listed in Table V. In many cases the lower limit of the colloidalization range is increased with the size and orderliness of the  $\alpha$ -ZrP crystal, i.e. under the same experimental conditions more amine is needed to colloidalize  $\alpha$ -ZrP-F than the others. This phenomenon fits the moving boundary theory [19], which claims that the intercalation of amine proceeds from the boundary to the center of a crystal, so to exfoliate a larger crystal either more amine or more time and stronger stirring are required. It was surprising to find that  $\alpha$ -ZrP-F can colloidalize in *n*-butylamine solution within a very narrow amine concentration range, suggesting that the rearrangement of the *n*-butylamine molecules in  $\alpha$ -ZrP-F is not as straightforward as in the others. The degree of  $\text{HPO}_4^{2-}$  hydrolysis of  $\alpha$ -ZrP-H is much lower than that of the other two samples, revealing a distinctly higher sheet stability.



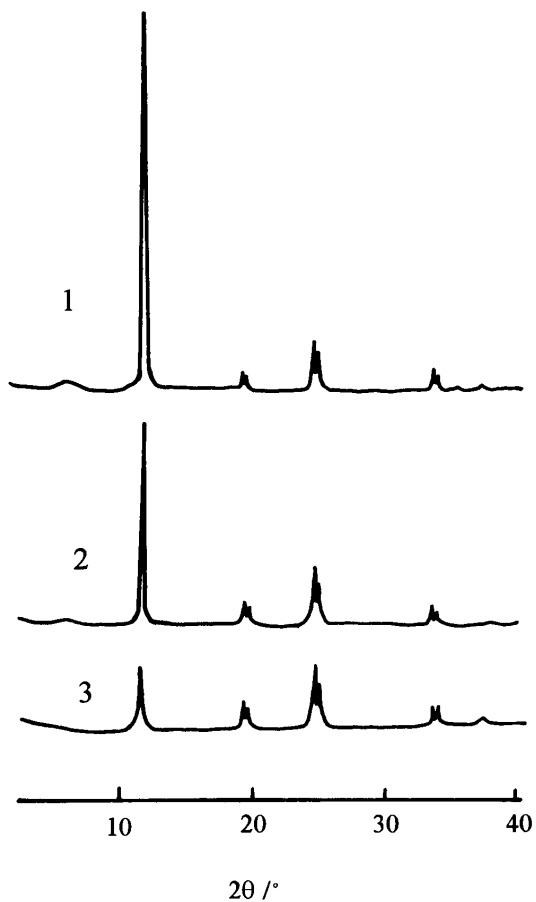


Figure 2. XRD profiles of  $\alpha$ -ZrP samples. 1.  $\alpha$ -ZrP-F, 2.  $\alpha$ -ZrP-H, 3.  $\alpha$ -ZrP-R.

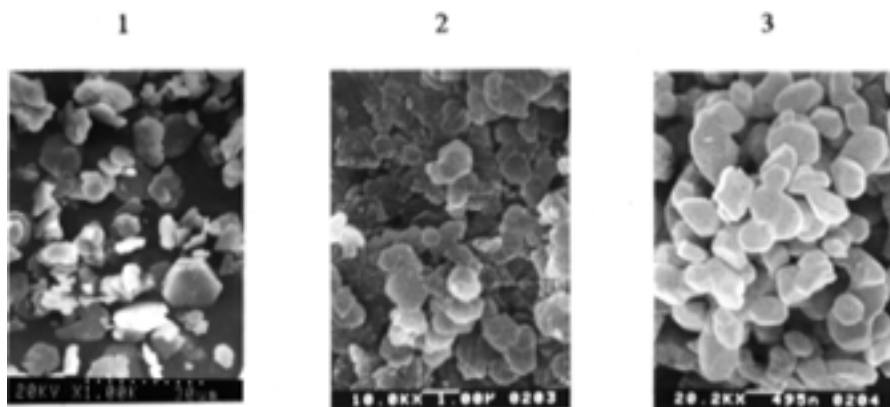


Figure 3. SEM images of  $\alpha$ -ZrP samples. 1.  $\alpha$ -ZrP-F, 2.  $\alpha$ -ZrP-H, 3.  $\alpha$ -ZrP-R.

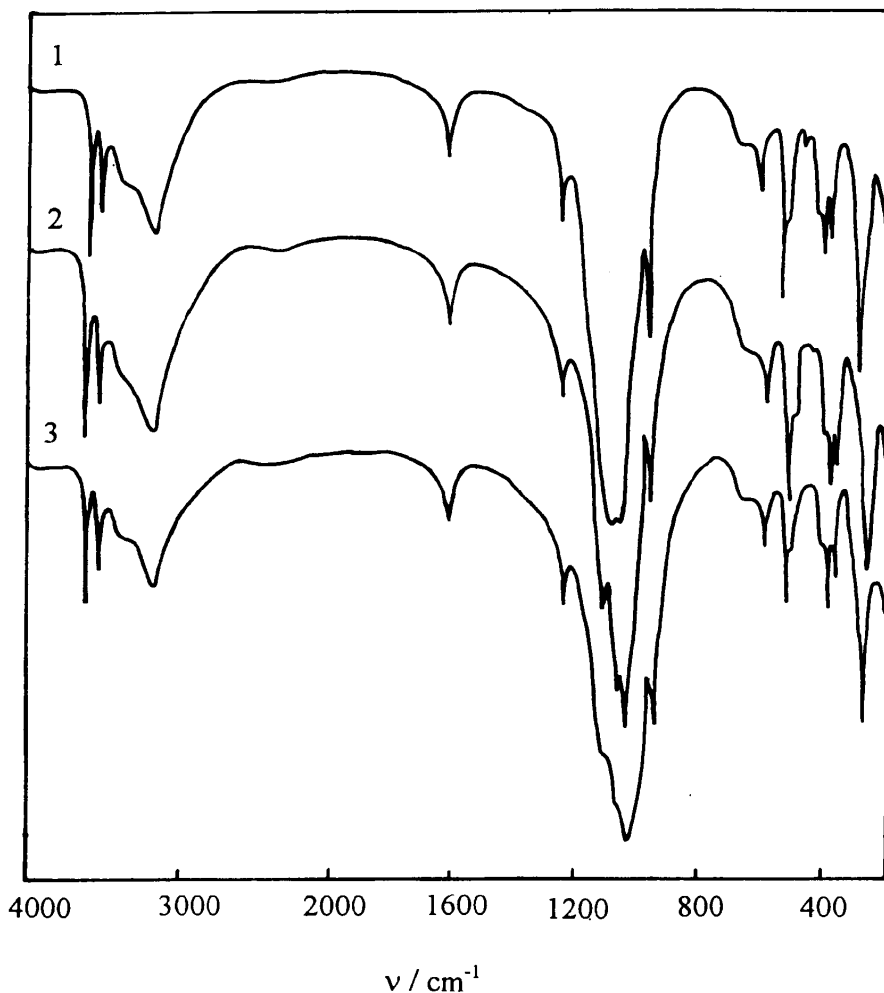


Figure 4. IR spectra of  $\alpha$ -ZrP samples. 1.  $\alpha$ -ZrP-F, 2.  $\alpha$ -ZrP-H, 3.  $\alpha$ -ZrP-R.

### 3.2. $\alpha$ -TiP AND $\alpha$ -SnP

$\alpha$ -TiP-R and  $\alpha$ -SnP-R hydrolyze in amine media much more readily than  $\alpha$ -ZrP-R. Figure 5 depicts the degree of hydrolysis of these two phosphates in relation to the amount of amines added. It is evident that the hydrolysis stability of the phosphates in all the amine solutions decreases in the order  $\alpha$ -ZrP-R >  $\alpha$ -SnP-R >  $\alpha$ -TiP-R, whereas the sequence of the hydrolytic ability of different amines for  $\alpha$ -TiP-R and  $\alpha$ -SnP-R is the same as that for  $\alpha$ -ZrP-R, i.e. ethylamine > ethanolamine > *n*-propylamine > *n*-butylamine. Following the addition of amines, the pH value of the  $\alpha$ -ZrP-R system increases from ca. 5.0 (0.3 mol amine/mol  $\alpha$ -ZrP-R) to 11.0 (3.0 mol amine/mol  $\alpha$ -ZrP-R). The final pH value is close to that of the pure

Table V. Colloidization and hydrolysis of different  $\alpha$ -ZrP samples.

Amine	Amount of amine added (mol/mol $\alpha$ -ZrP)			HPO <sub>4</sub> <sup>2-</sup> hydrolysis (2 mol amine/mol $\alpha$ -ZrP) (%)		
	$\alpha$ -ZrP-R	$\alpha$ -ZrP-H	$\alpha$ -ZrP-F	$\alpha$ -ZrP-R	$\alpha$ -ZrP-H	$\alpha$ -ZrP-F
MA	0.3 ~ 2.8	0.3 ~ 3.0	0.3 ~ 3.0	5.3	2.7	5.5
EA	0.3 ~ 1.8	0.3 ~ 3.0	1.2 ~ 3.0	18.4	4.9	17.3
PA	0.3 ~ 1.0	0.3 ~ 1.2	0.6 ~ 1.2	1.8	0.7	1.2
BA	non-colloidal	non-colloidal	0.3 ~ 0.5	1.1	0.6	1.2
EOA	0.3 ~ 3.0	0.6 ~ 3.0	0.6 ~ 3.0	5.6	3.6	7.6
POA	0.3 ~ 3.0	0.6 ~ 3.0	0.6 ~ 3.0	5.6	3.6	7.6
BOA	0.3 ~ 2.0	0.6 ~ 2.0	0.6 ~ 2.2	7.5	3.1	7.7

amine solutions. By contrast, the pH values of the amine solutions after reacting with  $\alpha$ -TiP-R or  $\alpha$ -SnP-R increase very slowly with the addition of amines and eventually falls below 7.5, indicating that a large amount of amine is consumed in the hydrolytic reaction. At the same time, it has been noticed that the amount of  $\alpha$ -SnP-R or  $\alpha$ -TiP-R intercalate after centrifugation is reduced due to the destruction of the sheets.

The ethylamine system was again chosen as a representative to study the sheet stability of  $\alpha$ -TiP-R and  $\alpha$ -SnP-R. The extent of HPO<sub>4</sub><sup>2-</sup> hydrolysis and the amount of M(IV) dissolved from  $\alpha$ -TiP-R and  $\alpha$ -SnP-R are much larger than those of  $\alpha$ -ZrP-R, as shown in Table II. The sheet stability of the phosphates decreases in the order  $\alpha$ -ZrP-R  $\gg$   $\alpha$ -SnP-R >  $\alpha$ -TiP-R. At the equivalent point (2 mol amine/mol  $\alpha$ -MP-R), the sheet stabilities of  $\alpha$ -ZrP-R,  $\alpha$ -SnP-R and  $\alpha$ -TiP-R are 95%, 47% and 10%, respectively. For all three systems the atomic ratio of P/M(IV) in solution is far above 2 at first, and decreases gradually with the addition of amine to 2; in such case the phosphates are completely dissolved and a clear solution is obtained. This again proves that hydrolysis of HPO<sub>4</sub><sup>2-</sup> takes place before the dissolution of M(IV) and the destruction of the sheets probably occurs after the dissolution of M(IV) to form soluble amine M(IV) complexes in the solution. Experimental results in Table II and Figures 1 and 5 show that the extent of hydrolysis of the phosphates can be controlled as desired by varying the kind and amount of amine added to the specific system.

The ethylamine intercalates of the three types of phosphates were acidified with HCl to convert them to hydrogen form phosphates. XRD patterns of the acidified samples are shown in Figure 6. As the HPO<sub>4</sub><sup>2-</sup> hydrolysis percent is increased, the (002) peak of the sample becomes lower and wider, showing that the sheet structure of the phosphate is compromised by hydrolysis. XRD results are consistent with those of chemical analysis.

The colloidization and phase transformation of intercalates of  $\alpha$ -TiP-R and  $\alpha$ -SnP-R in different amine media were investigated, while keeping the extent of

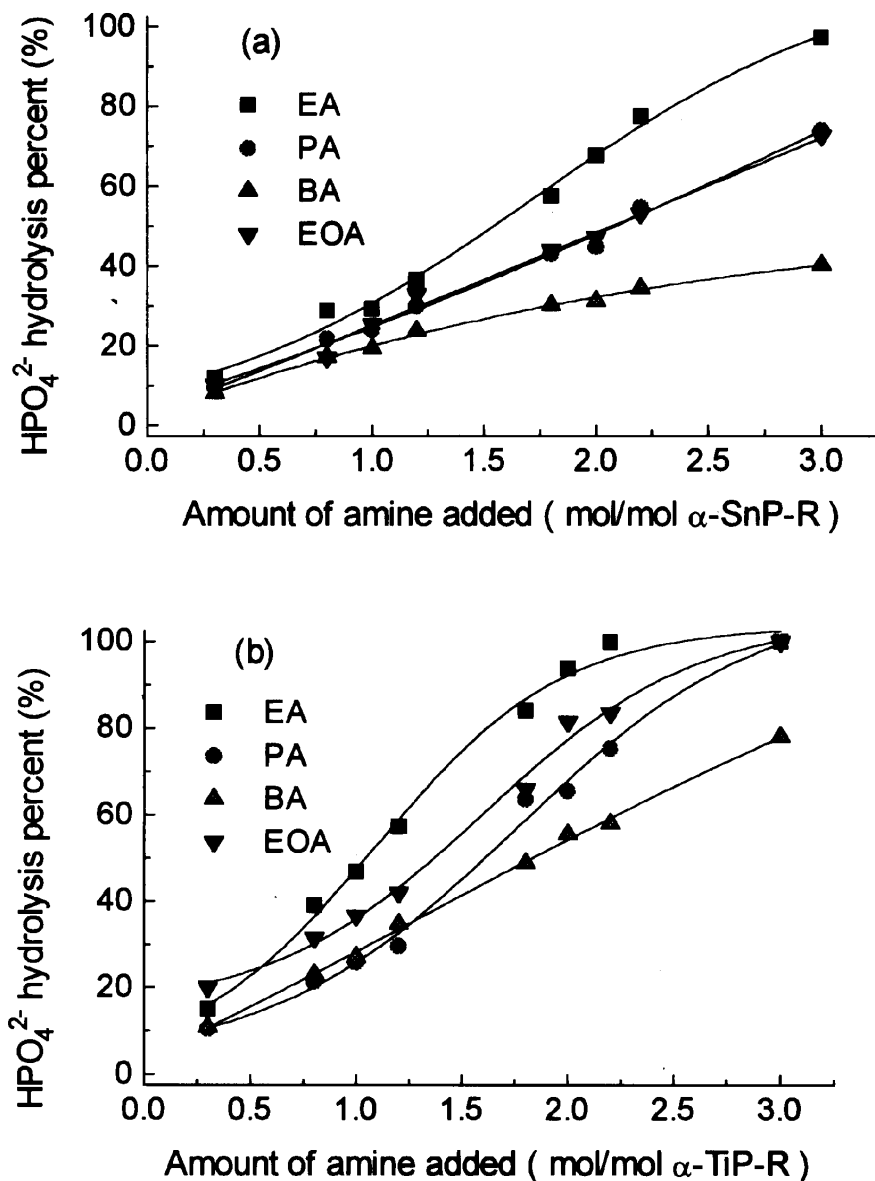


Figure 5. Extent of hydrolysis of  $\text{HPO}_4^{2-}$  vs. amine added. (a)  $\alpha$ -SnP-R, (b)  $\alpha$ -TiP-R.

hydrolysis of the phosphates less than 40% and the sheet stability above 75%. XRD data of the wet and air dried intercalates of the two phosphates are given and compared with those of  $\alpha$ -ZrP-R in Table VI. Like  $\alpha$ -ZrP-R,  $\alpha$ -SnP-R colloidalizes readily in ethylamine, *n*-propylamine and ethanolamine solutions. After air drying for 4 h, the colloidalized sheets are reordered and the (002) peak reappears in the

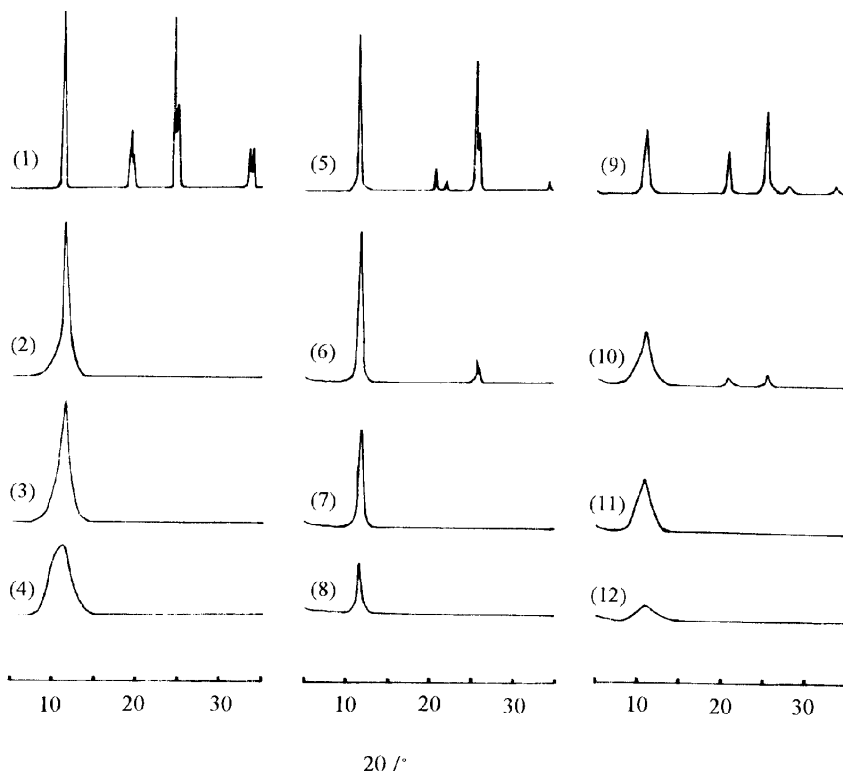


Figure 6. XRD patterns of partially hydrolyzed phosphates. (1)  $\alpha$ -ZrP-R,  $x = 0$ , (2)  $\alpha$ -ZrP-R,  $x = 13$ , (3)  $\alpha$ -ZrP-R,  $x = 18$ , (4)  $\alpha$ -ZrP-R,  $x = 27$ , (5)  $\alpha$ -TiP-R,  $x = 0$ , (6)  $\alpha$ -TiP-R,  $x = 23$ , (7)  $\alpha$ -TiP-R,  $x = 42$ , (8)  $\alpha$ -TiP-R,  $x = 69$ , (9)  $\alpha$ -SnP-R,  $x = 0$ , (10)  $\alpha$ -SnP-R,  $x = 18$ , (11)  $\alpha$ -SnP-R,  $x = 38$ , (12)  $\alpha$ -SnP-R,  $x = 59$ . \* $x = \text{HPO}_4^{2-}$  hydrolysis percent of phosphates.

XRD patterns. With an increase in the amount of amine added, the orientation of the interlayer amine molecules changes from a monolayer to a bilayer arrangement.  $\alpha$ -TiP-R can only colloidalize fully in ethanolamine solution, and a bilayer arrangement of the interlayer amine molecules dominates in all the wet and air dried  $\alpha$ -TiP-R intercalates. The reason for this is that a large part of the amine added is consumed in the hydrolytic reaction of  $\alpha$ -TiP-R and the remaining amine molecules are inadequate to cause colloidal dispersion of the phosphate. In such a case the intercalation of amine proceeds only along the boundary of the crystals and an excess of amine in the region results solely in a bilayer orientation.

#### 4. Conclusions

Colloidal dispersions of  $\alpha$  type zirconium, tin and titanium phosphates can be achieved in aqueous solutions of various alkylamines and alcohol amines. Among these three phosphates  $\alpha$ -ZrP and  $\alpha$ -SnP colloidalize more easily than  $\alpha$ -TiP. The

Table VI. XRD data of the intercalates in different amine solutions.

Amine	Amine $\alpha$ -MP (mol/mol)	$\alpha$ -ZrP-R		$\alpha$ -SnP-R		$\alpha$ -TiP-R	
		Wet	4hr	Wet	4hr	Wet	4hr
EA	0.3	am <sup>a</sup> + $\alpha$ <sup>b</sup>	1.08 <sup>c</sup> + 1.01 + $\alpha$	am + $\alpha$	1.18 + $\alpha$	am + $\alpha$	$\alpha$
	0.8	am	1.08	am	1.45 + 1.18 + $\alpha$	am + $\alpha$	1.45 + $\alpha$
	1.0	am	1.42 + 1.08	am	1.47 + 1.18	–	–
	1.2	am	1.40 + 1.08	am	1.49 + 1.20	–	–
	2.0	am + 1.67	1.40	–	–	–	–
	3.0	am + 1.67	1.40	–	–	–	–
PA	0.3	am + $\alpha$	1.05 + $\alpha$	am + $\alpha$	$\alpha$	1.67 + $\alpha$	1.55 + $\alpha$
	0.8	am	1.47 + 1.09	am	1.40 + $\alpha$	1.67 + $\alpha$	1.58 + $\alpha$
	1.2	1.70 + am	1.47 + 1.30 + 1.09	am	1.42 + $\alpha$	1.67 + $\alpha$	1.58 + $\alpha$
	2.0	1.73 + 1.64	1.73 + 16.3	1.82	1.72	–	–
	3.0	1.74	1.73	–	–	–	–
BA	0.3	1.83 + $\alpha$	1.83 + 1.64 + $\alpha$	1.84 + $\alpha$	$\alpha$	1.84 + $\alpha$	1.69 + $\alpha$
	0.8	1.83 + $\alpha$	1.80 + 1.64 + $\alpha$	1.84 + $\alpha$	1.73 + 1.40 + $\alpha$	1.86 + $\alpha$	1.69 + $\alpha$
	1.2	1.83	1.82	1.86	1.80 + 1.40	1.86 + $\alpha$	1.72 + $\alpha$
	2.0	1.89 + 1.82	1.89+1.82	1.92	1.88	–	–
	3.0	1.89	1.89	1.94	1.92	–	–
EOA	0.3	am	1.02 + $\alpha$	am + $\alpha$	$\alpha$	am + $\alpha$	$\alpha$
	0.8	am	1.01 + $\alpha$	am	1.12 + $\alpha$	am	1.58 + $\alpha$
	1.2	am	1.47	am	1.40	am	1.58 + $\alpha$
	2.0	am	1.47	–	–	–	–
	3.0	am	1.47	–	–	–	–

\*a: amorphous, b: original compound, c: interlayer distance (nm) of intercalates.

use of alcohol amines can be recommended, because the phosphates colloidize more readily in alcohol amine solutions. The hydrolysis of the phosphates can be controlled as desired by varying the type and amount of amine added to the solution. The sheet stability of the phosphates is reduced as their hydrolysis extent is increased. In general, to keep the sheet stability of the phosphates at a level above 80%, the extent of hydrolysis must be less than 35%. The wet colloidal precipitates are unstable. After air drying the sheets will be reordered, and the interlayer amine molecules will display a monolayer, bilayer or intermediate orientation depending on the nature and amount of the amines intercalated.

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