

Intercalation of Phenylethyamines into α -Zirconium Phosphate and Characterization of Intercalates

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Abstract. The intercalation of phenylethyamines into α -zirconium phosphate has been investigated by the pH titration method. *dl*-1-Phenylethylamine (*dl*-PEA) is taken up in two stages. New phases were obtained: $\text{Zr}(\text{HPO}_4)_2(\text{dl-PEA}) \cdot \text{H}_2\text{O}$ in the first, and $\text{Zr}(\text{HPO}_4)_2(\text{dl-PEA})_{4/3} \cdot \text{H}_2\text{O}$ in the second stage. 2-Phenylethylamine (2-PEA) also is loaded in two stages, but the first end point is not observed clearly. A new phase, $\text{Zr}(\text{HPO}_4)_2(2\text{-PEA})_2 \cdot \text{H}_2\text{O}$ has been formed at the second stage. The new phases have been characterized by elemental analysis, X-ray diffractometry, thermal analysis and IR spectroscopy.

Key words. α -zirconium phosphate, phenylethylamine, intercalation.

1. Introduction

α -Zirconium phosphate, which has a layered structure, behaves not only as an inorganic ion-exchanger, but also as a host for intercalation reactions [1]. The intercalation behavior depends on the size and polarity of the organic guest compound. Usually, the intercalate obtained has an interlayer distance larger than that of α -zirconium phosphate, and it is expected that the intercalate will show good selectivity for the ion exchange of a large cation [2].

Primary alkylamines have been studied as intercalants and the relationship between the alkyl chain length and the interlayer distances of the products has been discussed [3, 4]. However, few amines incorporating a cyclic structure have been investigated [5]. Previously, it was found that cyclohexylamine could be accommodated between the interlayer region of α -zirconium phosphate, and the cyclohexylamine was easily replaced with Ni(II) ion in solution [6]. These facts indicate that the cyclohexylamine was present as a cyclohexylammonium ion in the solid.

During the course of the study on the application of α -zirconium phosphate as a catalyst, catalytic activity was found in a probable condensation reaction of *dl*-1-phenylethylamine (α -phenylethyamine, referred to here as *dl*-PEA) [7]. Since many layered compounds are expected to catalyze a reaction in their interlayer region, the behavior of *dl*-PEA in respect of a catalytic mechanism and its chirality is interesting.

Since amines are biologically and medically important, some workers have

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reported their intercalation reaction towards α -zirconium phosphate. Kijima *et al.* [8] have investigated the uptake of some amino-acids and Costantino *et al.* [9] selected heterocyclic compounds incorporating an imidazole ring as guest molecules. It is known that many derivatives of 2-phenylethylamine (phenethylamine) (2-PEA), have physiological and psychological effects. Since their biochemical effects may be ascribed to the structural similarities of the compounds, the intercalation of 2-PEA is also of interest. However, the intercalation reaction of this compound into α -zirconium phosphate has not been studied hitherto.

In this work the intercalation behavior of phenylethylamines was investigated in aqueous media, and the resultant compounds were characterized by means of elemental analysis, X-ray diffractometry, thermal analysis, and infrared spectroscopy.

2. Experimental

2.1. PREPARATION OF α -ZIRCONIUM PHOSPHATE

α -Zirconium phosphate was prepared by the modified direct precipitation method according to the literature [10]. Identification was made by means of X-ray diffractometry, thermal analysis, and the loss on ignition. The α -zirconium phosphate used had a median size (D_{50}) of 3 μm . (The particle size distribution was measured with a Shimadzu centrifugal particle size analyzer SACP-3.)

Phenylethylamines (Tokyo Kasei Co. Ltd.) were used without further purification. A weighted amount of phenylethylamine was added to distilled water degassed by boiling for 5–10 min. *dl*-1- and 2-Phenylethylammonium chloride solution were prepared as follows: a weighted amount of PEA was titrated with hydrochloric acid to the equivalence point, and then the required amount of water was added.

2.2. pH TITRATION

Titration was carried out batchwise in two ways. In the first titration only the amine solutions were employed. The total concentrations of amine and its chloride solution used were 0.1 mol/l and their molar ratio was varied from 0 to 8 (or 10 in the second case). The weight of α -zirconium phosphate was 100 mg and the total volume of solution was 10.0 mL. The mixture was shaken continuously at 25°C for a specified period of time. The titration with 2-PEA also was carried out under the following conditions; the concentration of solutions 0.02 mol/l, total volume 50.0 ml, and α -zirconium phosphate 100 mg.

To prepare the new phase, a slight excess of phenylethylamine relative to the ion-exchange capacity of α -zirconium phosphate was added to a weighed amount of the exchanger. The mixture was shaken at 25°C for at least 96 h, and then the solid phase was centrifuged and air-dried at room temperature.

2.3. ANALYTICAL PROCEDURE

After the uptake reaction, the solid phase was separated by centrifugation. The pH value of the supernatant was measured with a pH meter. Structural change in the

solid phase was measured by X-ray diffractometry using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.542 \text{ \AA}$) (Geigerflex Rad 2B, Rigaku Denki Co. Ltd.).

The carbon, hydrogen, and nitrogen content of phases newly obtained was determined by elemental analysis.

Thermogravimetric (TG) and differential thermal analysis (DTA) data were obtained with a Thermoflex TG-DTA (Rigaku Denki Co. Ltd.) at the heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in a nitrogen stream (about $100 \text{ mL}/\text{min}$). The infrared (IR) spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer.

3. Results and Discussion

3.1. *dl*-1-PHENYLETHYLAMINE

To determine the equilibration time, the change in pH values was measured at a given period of time. The amine content of the solution was equal to $6 \text{ meq}/\text{g}$ α -zirconium phosphate (abbreviated meq/g for simplicity). The equilibrium was attained within 2 days. In the following work, a reaction time of 4 days was employed.

Figure 1 shows the titration curves of α -zirconium phosphate with *dl*-PEA. *dl*-1-Phenylethylamine was taken up at relatively low pH values in the interlayer region of α -zirconium phosphate. The reaction proceeded in two stages. In the first stage the end point corresponded to 50% of the total ion-exchange capacity of α -zirconium phosphate. Further, one-third mol of *dl*-PEA was taken up at higher pH values by one mol of α -zirconium phosphate.

The low pH values of loading indicate the high selectivity of α -zirconium

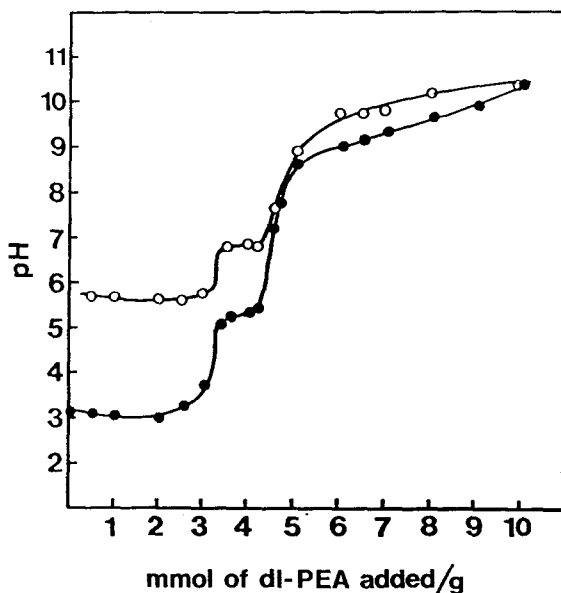


Fig. 1. Titration curves with *dl*-1-phenylethylamine: ●: $0.1 \text{ mol}/\text{l}$ amine-chloride; ○: $0.1 \text{ mol}/\text{amine}$ only.

phosphate to *dl*-PEA. The titration curves show that the two phosphate protons behaved bifunctionally, and that their acidity was apparently different from each other. The observations corresponded to the acidity of $-\text{POH}$ groups in α -zirconium phosphate [11]. This titration behavior was similar to that for lithium ion [12], but not for cyclohexylamine [6].

Two reactions, ion exchange and intercalation, will proceed in the solution. The pH values of the solution is determined by the former. The pK_b value of *dl*-PEA is 4.92 according to the literature [13]. That is, *dl*-PEA is a weaker base than ammonia ($pK_b = 4.65$) and cyclohexylamine ($pK_b = 3.36$). If an ion-exchange reaction is governed only by the basicity of the species involved, the pH values will be the lowest in the titration with cyclohexylamine. Of the three, the lowering of pH values was the largest in the system of *dl*-PEA. This means that a factor other than basicity of a guest is involved in the reaction.

α -Zirconium phosphate and its salt have a layered structure [14, 15]. Since the interlayer distances of these compounds depend on a size of an existing cation or molecules between the layers, it affords a good tool to observe the change in the interlayer distance in order to trace the up-take process. The basal spacing (the interlayer distance) can be seen in the lowest region of an X-ray powder diffraction pattern.

Figure 2 shows typical X-ray powder diffraction patterns obtained during the

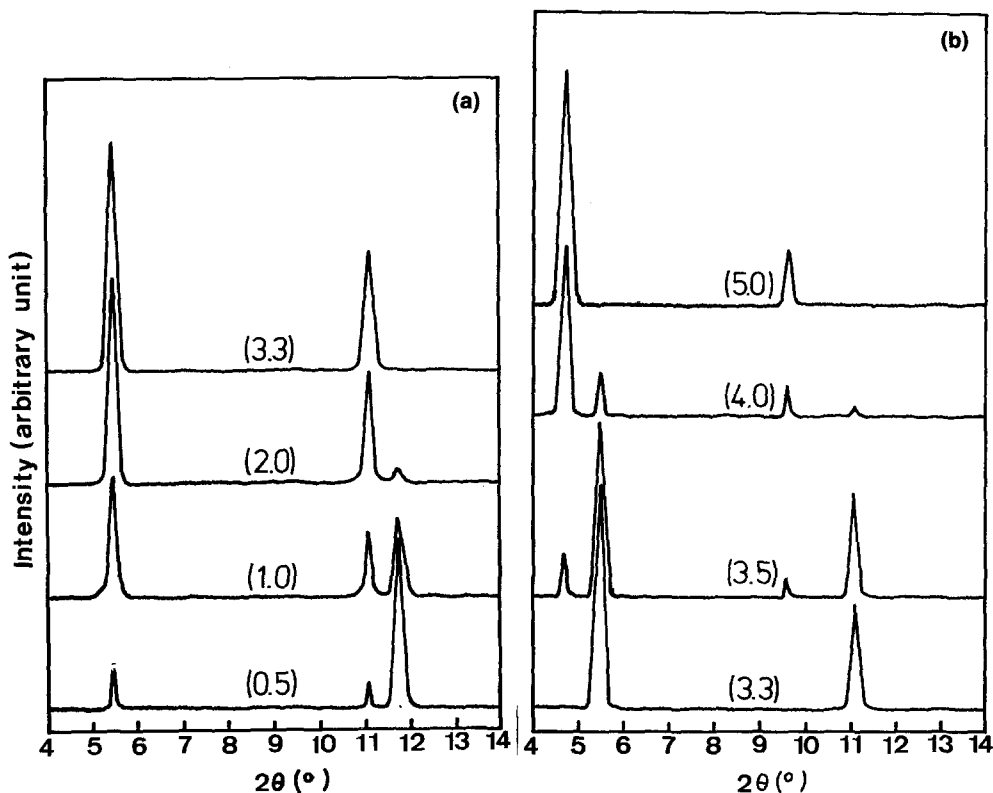


Fig. 2. Typical X-ray powder patterns of solid phase. The numerals in parentheses correspond to those in the abscissa in Fig. 1.

uptake reaction. Assuming that the intensity of the peak in an X-ray pattern is proportional to the amount of each phase present, the ratio of phases can be approximately estimated. The change in the ratio of each phase is shown in Figure 3. Only α -zirconium phosphate was present at the beginning of the titration. The interlayer distance increased from 7.6 to 15.6 Å. Two phases, α -zirconium phosphate and a new phase (Phase H), coexisted up to 3 meq/g addition, at which value only Phase H was present. In the following region two phases, Phase H and Phase A having an interlayer distance of 18.0 Å, were present. Over 4 meq/g only Phase A was observed. The ratio of Phase H to the α -phase, and of Phase A to Phase H increased linearly with an increase in the loading of *dl*-PEA.

3.2. CHARACTERIZATION OF PHASES H AND A

The *d*-values of Phases H and A are shown in Table I. After the reaction products were stood on an X-ray sample holder for several hours at room temperature, the X-ray powder diffraction patterns did not change. Also, the sample dehydrated in TG-DTA analysis showed no change in the interlayer distance (see the section on thermal analysis). These facts indicate that rather than the water molecule, *dl*-PEA itself acts as a 'pillar' and mainly contributes to the expansion or maintenance of the interlayer distance of Phases H and A.

The interlayer distances of the two phases obtained in this study are smaller than that of the benzylamine form (19.2 Å) or the cyclohexylammonium form (18.4 Å)

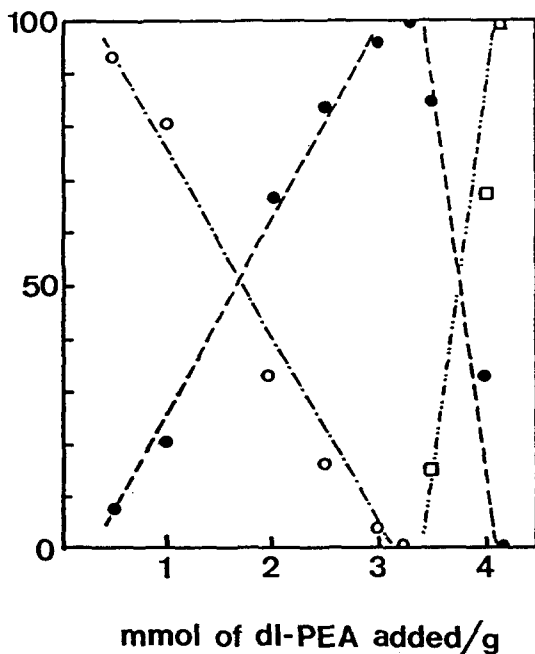


Fig. 3. Approximate ratio of the phases present during the pH titration. \circ : α -zirconium phosphate; \bullet : Phase H; \square : Phase A.

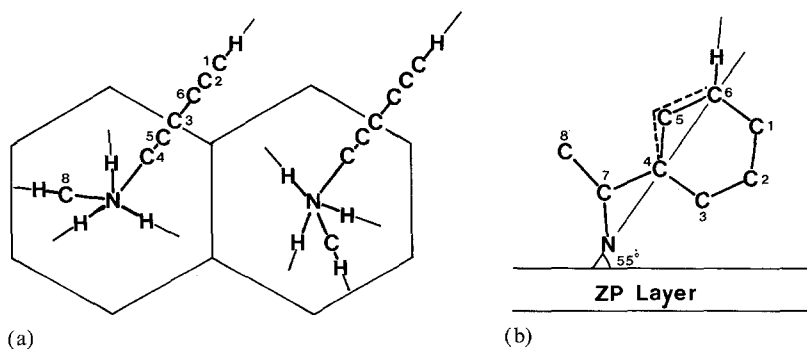
Table I. *d*-values of Phase H and Phase A

Phase H <i>d</i>	<i>I</i> / <i>I</i> ₀	Phase A <i>d</i>	<i>I</i> / <i>I</i> ₀
15.6	100	18.00	100
7.81	30	9.01	13
5.20	1	6.01	5
4.66	*	4.12	2
4.55	3	3.93	1
4.45	*	3.81	1
4.15	4	3.68	2
4.06	3	3.48	1
3.90	1	3.36	*
3.66	5	3.24	*
3.55	2	3.14	*
3.51	1	2.65	*
3.27	*	2.63	*
3.15	1		
3.07	1		
2.82	*		
2.73	1		
2.67	*		
2.64	1		

“*” means that the intensity is less than unity.

[1, 6]. It is possible to relate the interlayer distance of Phases H and A with the molecular size of a guest.

As shown in Scheme 1(a), where C(1)—C(6) are carbons in the benzene ring and some of the hydrogens are omitted for simplicity, the terminal —NH₃⁺ and adjacent methyl group cover an area of one —POH anion present in the *ab* plane of α -zirconium phosphate. The interlayer distance of Phases H and A can be compared with that of the butylamine intercalate of α -zirconium phosphate, if the orientation of the R—NH₃⁺ ion with respect to the layers of zirconium phosphate is similar to that of *n*-alkylamines. The C(7)—C(4)— dashed line represents the orientation of butylamine (see Scheme 1(b)). It can be expected that the interlayer distances will be nearly equal to those of the butylamine forms. The interlayer distance of 18.8 Å



was that of a fully intercalated form [5]. Since α -zirconium phosphate did not form a half-converted form with butylamine [5], the interlayer distance of Phase H has no reference. Assuming that a half-converted form could be prepared, its interlayer distance is estimated as the sum of that of propylamine and the difference of the distance of propylamine and ethylamine cited in the literature [3], that is, 15.4 Å. These values agree well with those found experimentally.

The molar ratio of guest to host (loading ratio) can be determined with the free volume (V_f) created in the interlayer region. V_f is calculated with the following equation:

$$V_f = 24.3 \times (d - 6.3) - 37 \times n \quad (1)$$

where 24.3 Å² is the area covered by one $-\text{POH}^+$, d is the interlayer distance of an intercalate, 6.3 Å is the thickness of the α -zirconium phosphate macroanion, 37 Å³ is the volume of a hydrated water molecule, and n is the hydration number.

Assuming that *dl*-PEA is arranged in the interlayer region as shown in Scheme 1(b), the volume of *dl*-PEA is represented as follows:

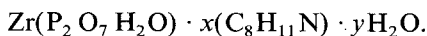
$$V_\alpha = V_b + V_m + V_a$$

where V_b is the volume occupied by a benzene ring and calculated as a rectangular solid having dimensions 3.4 × 6.44 × 6.06 Å, V_m is the volume of a methyl group and estimated as a column having a radius of 2.1 and a height of 2.3 Å, V_a is the volume of an $-\text{NH}_3^+$ group and determined as a column having a radius of 1.85 and a height of 2.1 Å. Thus, V_α is equal to about 187 Å³.

Since Phase H has the interlayer distance of 15.6 Å and one hydration water, V_f is the 189 Å³ according to Equation (1). This indicates that one mole of *dl*-PEA can be accommodated in the interlayer region of Phase H. Phase A has an interlayer distance of 18.0 Å and one mole of hydrated water. V_f is then estimated to be 247 Å³. The loading ratio is 1.32. The experimental value agrees well with that calculated.

Table II shows the results of elemental analyses. A portion of *dl*-PEA was decomposed during the analysis and a small amount of residue was left (presumably carbon). Assuming that the amount of residue can be neglected, the molar ratio of carbon to nitrogen is calculated. It should be noted that the molar ratio of carbon to nitrogen was equal to 8 in both phases, indicating that *dl*-PEA was taken up without decomposition.

The hydrogen content originates from *dl*-PEA, water of hydration, and the condensation of $(-\text{HPO}_4)_2$ to P_2O_7 . Since the ratio of hydrogen to nitrogen was more than 13, two phases should contain water of hydration. The chemical formula of Phases H and A can conveniently be represented as follows;



Then the ratio is $8x(\text{C}):(2 + 11x + 2y)(\text{H}):x(\text{N})$, that is, C 8:H (2 + 11x + 2y)/x :N1. Since the value of x is unity and the molar ratio of hydrogen to nitrogen was 15 in Phase H (see Table II), y is estimated to be 1. Since the value of x was 4/3 and the ratio of H to N was 13.8 in Phase A, y is calculated to be unity. This means that Phases H and A contained one mole of water per formula.

Table II. Chemical composition of Phase H and Phase A

	C(%)	Phase H		ignition loss (%)
		H(%)	N(%)	
exp.	21.42	3.40	3.15	36.1
calcd.*	22.75	3.58	3.32	37.2
mole ratio	7.93	15.0	1.00	—
	C(%)	Phase A		ignition loss (%)
		H(%)	N(%)	
exp.	26.31	3.81	3.83	42.1
calcd.**	27.68	4.47	4.04	42.8
mole ratio	8.01	13.8	1.00	—

*: The chemical formula of Phase H was postulated as $Zr(HPO_4)_2(dl\text{-PEA}) \cdot H_2O$.

** : The chemical formula of Phase A was postulated as $Zr(HPO_4)_2(dl\text{-PEA})_{4/3} \cdot H_2O$.

3.3. THERMAL ANALYSIS

Figures 4 (a) and (b) show the thermal analysis curves of Phases H and A. Thermal decomposition occurred at three steps for Phase H in the temperature range 80–300°C. In the first stage dehydration took place. Then *dl*-PEA was evolved and

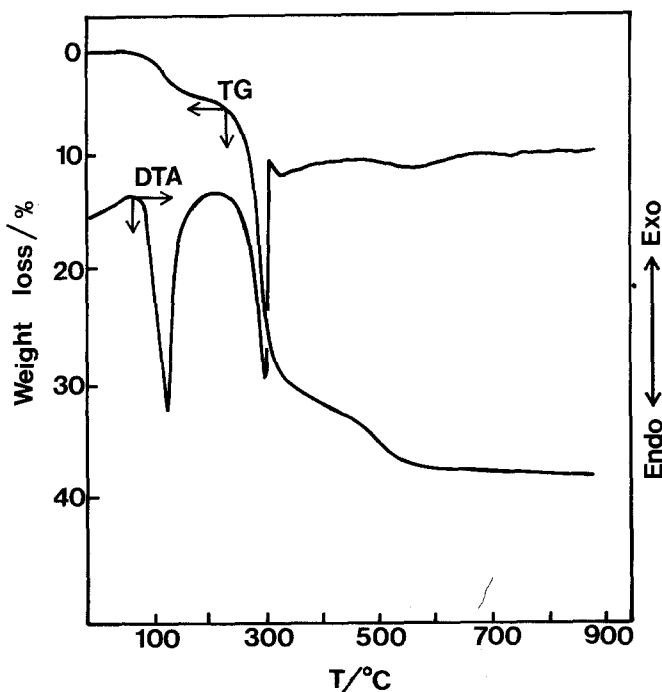


Fig. 4a. TG and DTA curves of Phase H.

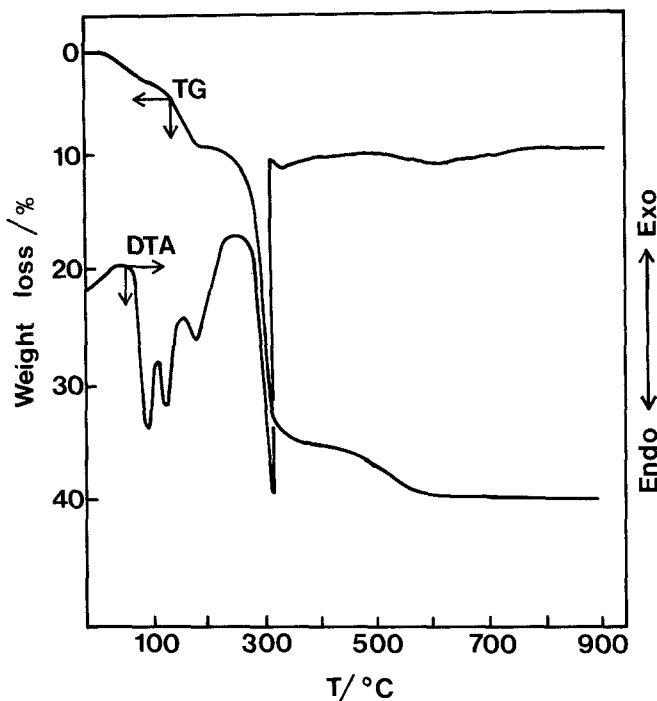


Fig. 4b. TG and DTA curves of Phase A.

a part of it decomposed to a small amount of residue, seen by the fact that a sample in a platinum pan was grayish black. The reaction occurred mainly at 200–310°C. The decomposition temperature was equal to that observed for the cyclohexylammonium form and slightly higher than that for the ammonium form of α -zirconium phosphate [6]. These facts may reflect the basicity of *dl*-PEA.

The decomposition continued gradually in the third step. Slow oxidation of the residue will proceed throughout this stage. An endothermic reaction at 500–600°C was caused by the dehydration associated with the condensation of $-(\text{HPO}_4)_2$ to P_2O_7 .

Phase A was decomposed thermally in five steps. The weight loss occurred continuously in three steps. The first and second step corresponded to the dehydration, indicating that two kinds of water were present in Phase A. A part of the *dl*-PEA was evolved without decomposition at the third step. Then, another *dl*-PEA was removed leaving a black residue. The fifth step was identical to the third step of Phase H.

Figure 5 shows the IR spectra of Phases H, A and α -zirconium phosphate. The IR spectra of Phases H and A were almost identical with the composite spectra of *dl*-PEA and α -zirconium phosphate.

The absorptions due to the stretching of $-\text{NH}$ and $-\text{OH}$ were observed in the region of $3600\text{--}2800\text{ cm}^{-1}$. The bands near 3500 cm^{-1} were assigned to hydrated water in α -zirconium phosphate [16]. These were sharp in the spectra of Phase H and broad in Phase A. This suggests that the water molecules will be more strongly hydrogen-bonded in Phase A than in Phase H.

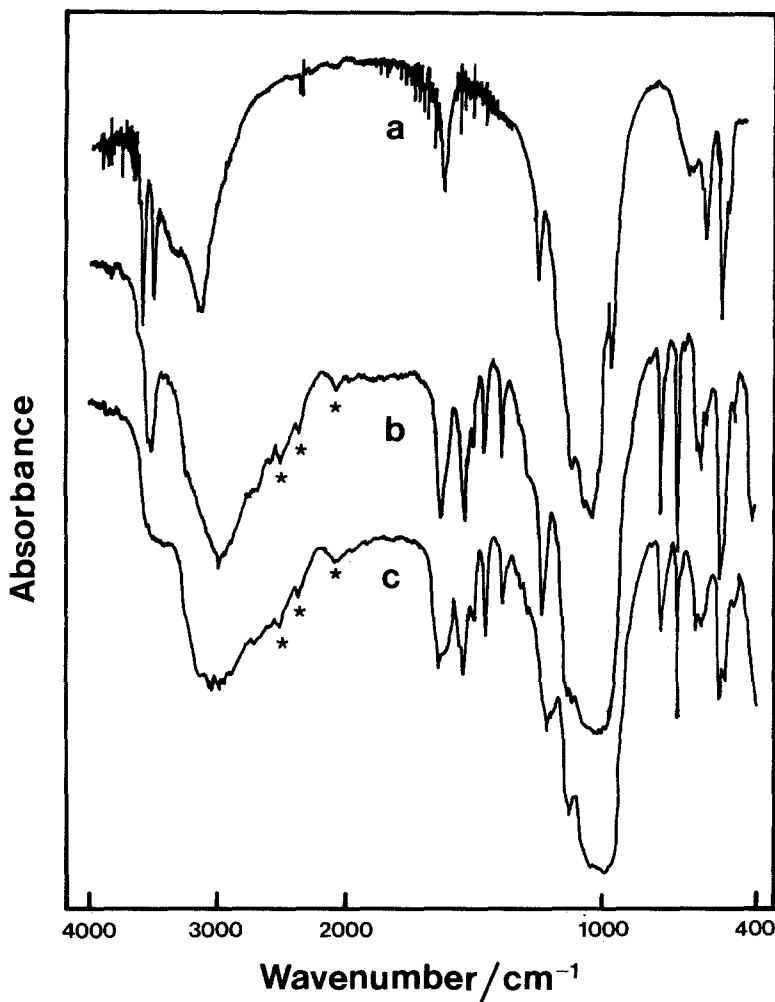


Fig. 5. IR spectra of (a) α -zirconium phosphate, (b) Phase H and (c) Phase A.

The weak bands marked with * in the figure appeared, as did strong bands at about 750 and 700 cm^{-1} , on forming Phases H and A. According to the literature the IR spectra of *dl*- and 2-PEA are almost identical [17]. When 2-PEA formed a hydrochloride, new bands appeared in the region of $2400\text{--}2000\text{ cm}^{-1}$. Also, the broad band near 800 cm^{-1} disappeared, while sharp absorptions are present at 782 , 743 , and 695 cm^{-1} . Hence, these bands could be assigned to —NH_3^+ .

A medium intensity peak at 970 cm^{-1} was observed in the spectra of α -zirconium phosphate. This band disappeared when the hydrogen ions were ion-exchanged with ammonium or potassium ions [10, 16]. Similar phenomena were found in the spectra of Phases H and A. These facts indicate that *dl*-PEA was present as a *dl*-phenylethylammonium ion between the layers of zirconium phosphate.

3.4. 2-PHENYLETHYLAMINE

To determine the reaction time, the change in pH values was measured at a given period of time for the 3 and 6 meq/g amine additions. Since it took 1 day to reach equilibrium, an equilibration time of 4 days was chosen.

Figure 6 shows the titration curves of α -zirconium phosphate with 2-PEA. The reaction took place in two stages. The end point of the first stage was not observed clearly, but it would correspond to 50% of the ion-exchange capacity of α -zirconium phosphate. A large jump in the pH value was apparent at the end of the second stage.

The titration curves show that the acidity of the two phosphate protons was nearly equal towards the amine, because the pH values were almost constant during the titration process with 2-PEA only, and also the pH jump was small for the titration with the mixture of 2-PEA and its chloride solution.

Titration curves also show that 2-PEA was selectively taken up by α -zirconium phosphate. 2-Phenylethylamine has a pK_b of 4.17 [18] and is a stronger base than *dl*-PEA, but weaker than cyclohexylamine. Since 2-PEA was taken up at low pH, factors other than basicity will be involved in the reaction.

3.5. STRUCTURAL CHANGE

The interlayer distance of the exchanger expanded with the uptake of 2-PEA. Figure 7 shows typical X-ray diffraction patterns observed during the titration, and Figure 8 shows the ratio of phases present.

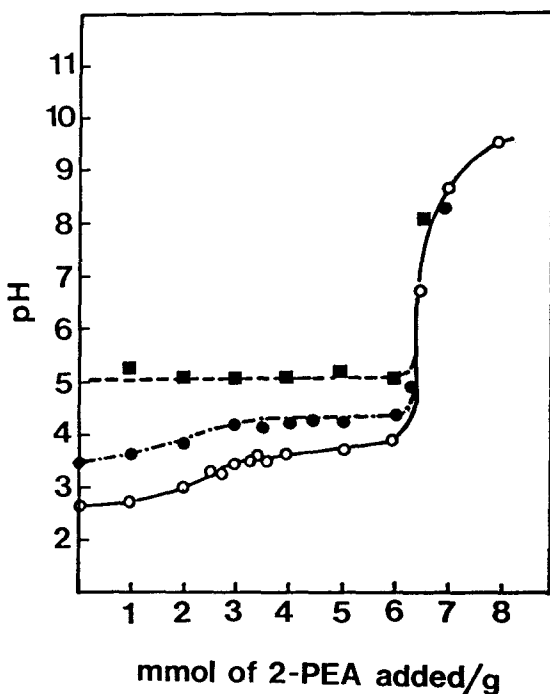


Fig. 6. Titration curves with 2-phenylethylamine ○: 0.1 mol/l amine-chloride; ●: 0.02 mol/l amine-chloride; □: 0.1 mol/l amine only.

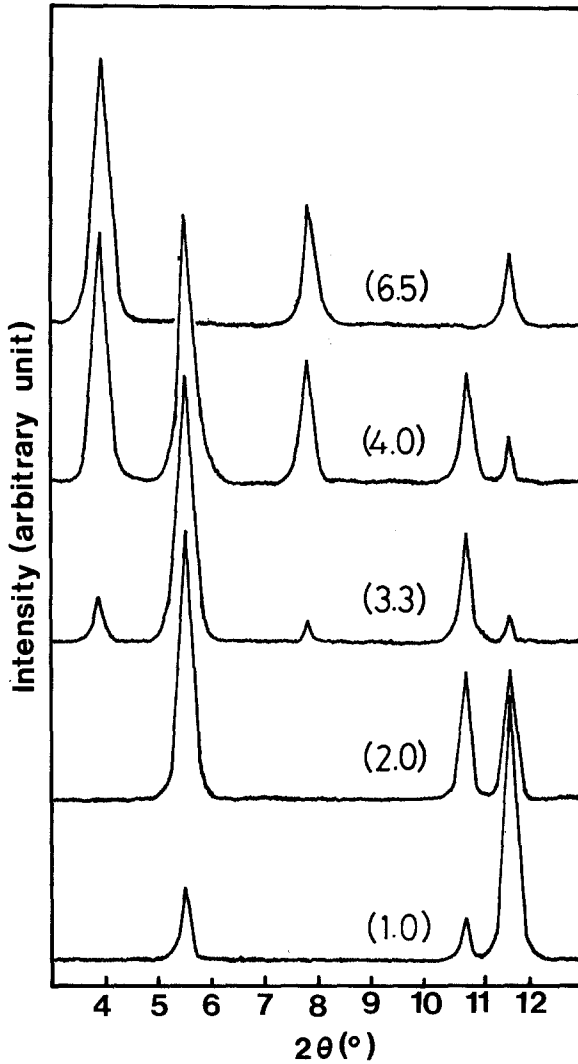
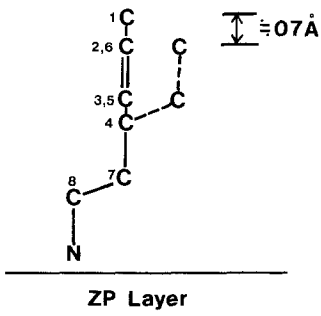


Fig. 7. Typical X-ray powder patterns of solid phases. The numerals in parentheses correspond to those in the abscissa in Fig. 6.



Scheme 2.

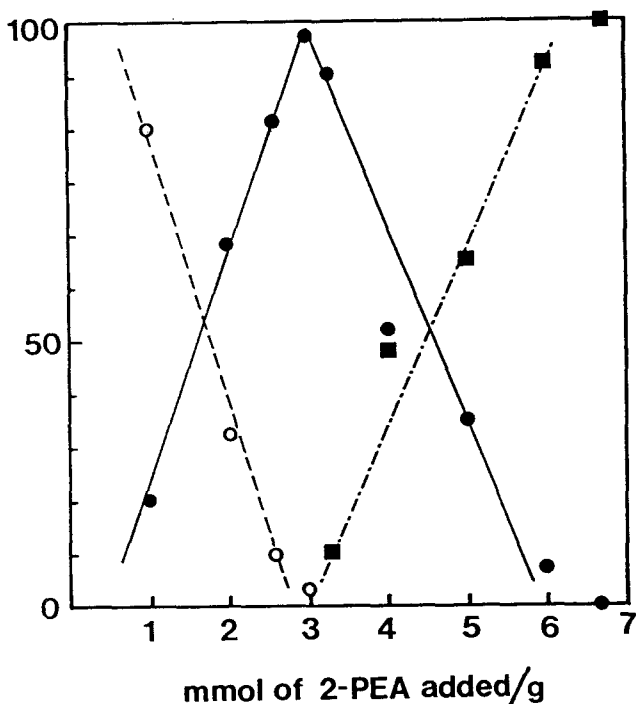


Fig. 8. Approximate ratio of the phases present during the pH titration. \circ : α -zirconium phosphate; \bullet : Phase I; \blacksquare : Phase II.

At the beginning of the titration the phase having the interlayer distance of 16.3 Å (Phase I) appeared. A new phase having the interlayer distance of 22.4 Å (Phase II) was observed at 3 meq/g. Three phases coexisted in the region of 3–4 meq/g. Two phases, Phase I and II, were present over 4 meq/g, and only Phase II near the second end point.

3.6. CHARACTERIZATION OF PHASE II

Table III shows the interplanar spacings of Phase II. The largest distance was 22.4 Å corresponding to (002) of the compound. The interlayer distance may be compared with that of pentylamine, having an interlayer distance of about 21 Å (see Scheme 2) [3]. The d value found is slightly larger than that expected.

Assuming the 2-PEAs are arranged in the interlayer region as shown in Scheme 2, the volume of 2-PEA can be estimated as follows:

$$V_{\beta} = V_b + 2 \times V_m + V_c + V_a$$

where V_b = the volume of the benzene ring as a rectangular solid, V_m = the volume of a methyl group, 17 Å³ [19], V_c = the volume around C(7)—C(8) as a column having a radius of 1.7 Å and height of 1.54 Å, and V_a = the volume of an $-\text{NH}_3^+$. Thus, V_{β} is estimated to be 173 Å³. Since Phase II has an interlayer distance of 22.4 Å and one mole of hydration water, V_f is 354 Å³ according to Equation (1). The loading ratio is about 2. This agrees well with the experimental result.

Table III. d -values of Phase II

d	I/I_0	d	I/I_0
22.4	100	3.88	*
11.2	18	3.58	1
7.48	9	3.53	*
5.10	*	3.23	*
4.59	*	3.18	*
4.50	1	2.92	*
4.27	*	2.65	*
4.23	*	2.64	*
3.93	1		

“*” means that the intensity is less than unity.

Table IV shows the C, H and N content found by elemental analysis. The ignition loss was determined separately. When Phase II was ignited for a long time in a platinum crucible, the carbon was burned off completely and the resultant solid was colorless. Taking account of the residue in the elemental analysis, the analytical values agree well with the theoretical ones within experimental errors.

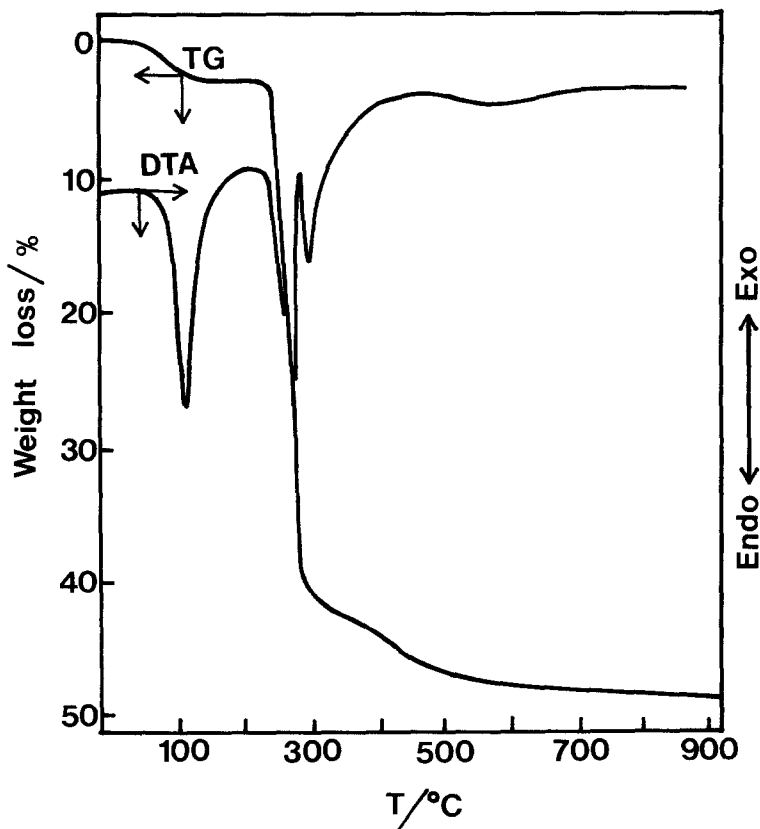


Fig. 9. TG and DTA curves of Phase II.

Table IV. Chemical composition of Phase II

	C(%)	H(%)	N(%)	ignition loss
exp.	34.33	4.46	4.97	50.7
calcd.*	35.35	4.82	5.15	51.2
mole ratio	8.06	12.48	1.00	—

*: The chemical formula of Phase II was postulated as $\text{Zr}(\text{HPO}_4)_2 (2\text{-PEA})_2 \text{H}_2\text{O}$.

3.7. THERMAL ANALYSIS

Figure 9 shows thermoanalytical curves of Phase II. Thermal decomposition occurred in three steps. The first reaction took place endothermically in the temperature region of 80–140°C. Then 2-PEA was evolved continuously, because the DTA curve showed two endothermic peaks. These indicate that the two phosphate protons have almost similar acidity (see Figure 6). Continuous weight

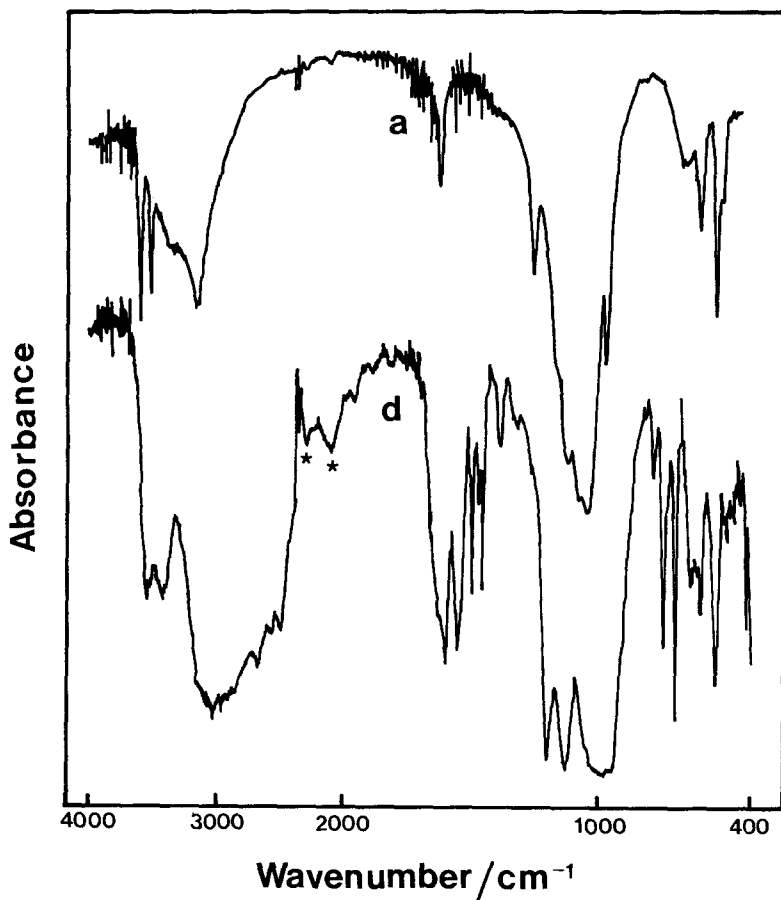


Fig. 10. IR spectra of (a) α -zirconium phosphate, (d) Phase II.

loss followed. At 460–610°C the endothermic reaction was observed. This is due to dehydration accompanied by the condensation of $(\text{HPO}_4)_2$ to P_2O_7 .

Figure 10 shows the IR spectra of Phase II. The bands near 3600 cm^{-1} suggest that free water molecules were present. Two weak bands at 2300 and 2100 cm^{-1} , and strong, sharp bands at 782 , 743 , and 635 cm^{-1} appeared, while a broad absorption near 800 cm^{-1} disappeared. These newly observed bands could be assigned to $-\text{NH}_3^+$, as stated in the section on *dl*-PEA. Also, the medium intensity band at 970 cm^{-1} was not present in the spectra of Phase II.

These facts indicated that 2-PEA was present as 2-phenylethylammonium ions in the solid phase.

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