

Carbon number-dependent intercalation and interlayer amidation properties of α,ω -alkanediamines for α -titanium (2-carboxyethyl)phosphonate phosphate

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The uptake of α,ω -alkanediamines $H_2N(CH_2)_nNH_2$ ($n = 2-10$) by α -titanium (2-carboxyethyl)phosphonate phosphate, $Ti(O_3PCH_2CH_2CO_2H)_{1.91}(HPO_4)_{0.09}$, has been studied at 25 °C. Each diamine forms one or two intercalated phases in which the amine molecules are arranged as a monolayer with their axes tilted by 54 or 67° relative to the inorganic layer. Diamines with $n \geq 7$ show a tendency to produce the high and low chain-tilt forms depending on the even and odd number of carbon atoms, respectively, but both forms coexist for $n = 6$. For shorter chain diamines, on the other hand, only the low-tilt form occurs for $n = 3, 4$ and 5 and the high-tilt form for $n = 2$. On heating at 150 °C or above the diammonium-exchanged solids were thermally condensed into the amide form with or without any significant release of the amine guest. The amidation temperature shows a tendency to vary up or down depending on whether the carbon number is even or odd.

Much attention has been focused on layered metal organo-phosphates and organophosphonates,¹ including di-,² tri-³ and tetra-valent⁴⁻⁷ metal ions, because of their wide applicability as functional materials such as ion exchangers, molecular sieves and catalysts. The most familiar zirconium and titanium organo derivatives have essentially the same layered structure as those of α -Zr(HPO₄)₂·H₂O or γ -Zr(PO₄)(H₂PO₄)·2H₂O.⁸ Layered zirconium organophosphates with γ -layer structure can be obtained by the topotactic reaction between γ -zirconium phosphate and various organophosphoric or organophosphonic acids, as reported by Yamanaka⁹ in 1976. On the other hand, α -zirconium organic derivatives can be synthesized by the direct reaction of tetravalent zirconium ions with organophosphoric or -phosphonic acids, as first presented by Alberti *et al.*¹⁰ in 1978. This approach has been applied to the preparation of an enormous variety of zirconium organo-phosphates or -phosphonates with α -layer structure containing organic groups such as alkyl, phenyl, carboxyl and sulfonyl.¹¹ Burwell and Thompson¹² extended the method of Alberti *et al.* to prepare amide- and ester-functionalized zirconium phosphonates *via* amine and alcohol intercalation reactions of the acyl chloride compound of α -zirconium phosphonate derived from its carboxylic acid form. We reported a simpler route in which a similar amide-functionalized zirconium phosphonate can be obtained by thermal condensation of the alkanemono-ammonium- or alkanediammonium-exchanged form of a α -carboxyethylated zirconium phosphonate.¹³ It was also found that the interamidation method is applicable to γ -zirconium phosphonate-based systems.¹⁴ A similar condensation of carboxyl with amino groups in the interlayer space of layered systems was observed for α,ω -amino acids or their related compounds intercalated in α -zirconium phosphate¹⁵ and montmorillonites.¹⁶

Recently, Bortun *et al.*¹⁷ reported the synthesis and ion-exchange properties of highly crystalline titanium (2-carboxyethyl)phosphonate, as well as the intercalation of several n -alkylamines. Much less, however, has been published on the intercalation and related properties of layered titanium organo-phosphonates. It is of interest to compare the intercalation properties of titanium and zirconium organophosphonates since the metal oxide layer in the former is structurally more

compact than that in the latter. In this paper we report the intercalation and interlayer amidation properties of α,ω -alkanediamines for layered α -titanium (2-carboxyethyl)phosphonate phosphate.

Experimental

Reagents and materials

The α -titanium (2-carboxyethyl)phosphonate phosphate sample used in this study was prepared in a manner similar to that reported by Bortun *et al.*¹⁷ A 0.5 M aqueous TiCl₃ solution (15 cm³) was added to a 1.0 M aqueous HO₂CC₂H₄PO(OH)₂ solution (30 cm³) and then refluxed at 97 °C for 5 d. The reaction product was filtered off, washed with distilled water, and then freeze-dried. The resulting solid exhibited an infrared absorption band at 1710 cm⁻¹ attributable to the C=O stretching of the CO₂H group, and the thermogravimetric curve up to 1000 °C for the solid showed no weight loss at temperatures below 350 °C. The carbon and hydrogen contents of the phosphonate solid were 6.39 and 2.53% (w/w) within an error of $\pm 0.5\%$, respectively. On heating at 1000 °C for 1 h the solid was totally converted into TiP₂O₇. On the basis of the above data, the composition of the titanium (2-carboxyethyl)phosphonate sample was $Ti(O_3PCH_2CH_2CO_2H)_{1.91}(HPO_4)_{0.09}$ **1**.

Intercalation reaction

A 0.05 g sample of compound **1** was mixed with an aqueous alkanediamine solution (5 cm³) at a fixed ratio [amine]: [Ti] = 2:1, followed by stirring at 25 °C for 3 d. The resulting mixtures were centrifuged, fully washed with water, and freeze-dried.

Sample characterization

Thermogravimetry (TG) was carried out with a Seiko-Densi instrument at a heating rate of 10 °C min⁻¹ in air. X-Ray diffraction measurements were made on a Shimadzu diffractometer with Cu-K α radiation using tetradecan-1-ol as an external standard. Infrared absorption spectra were measured by the KBr-pellet method using a Nippon Bunko spectrometer.

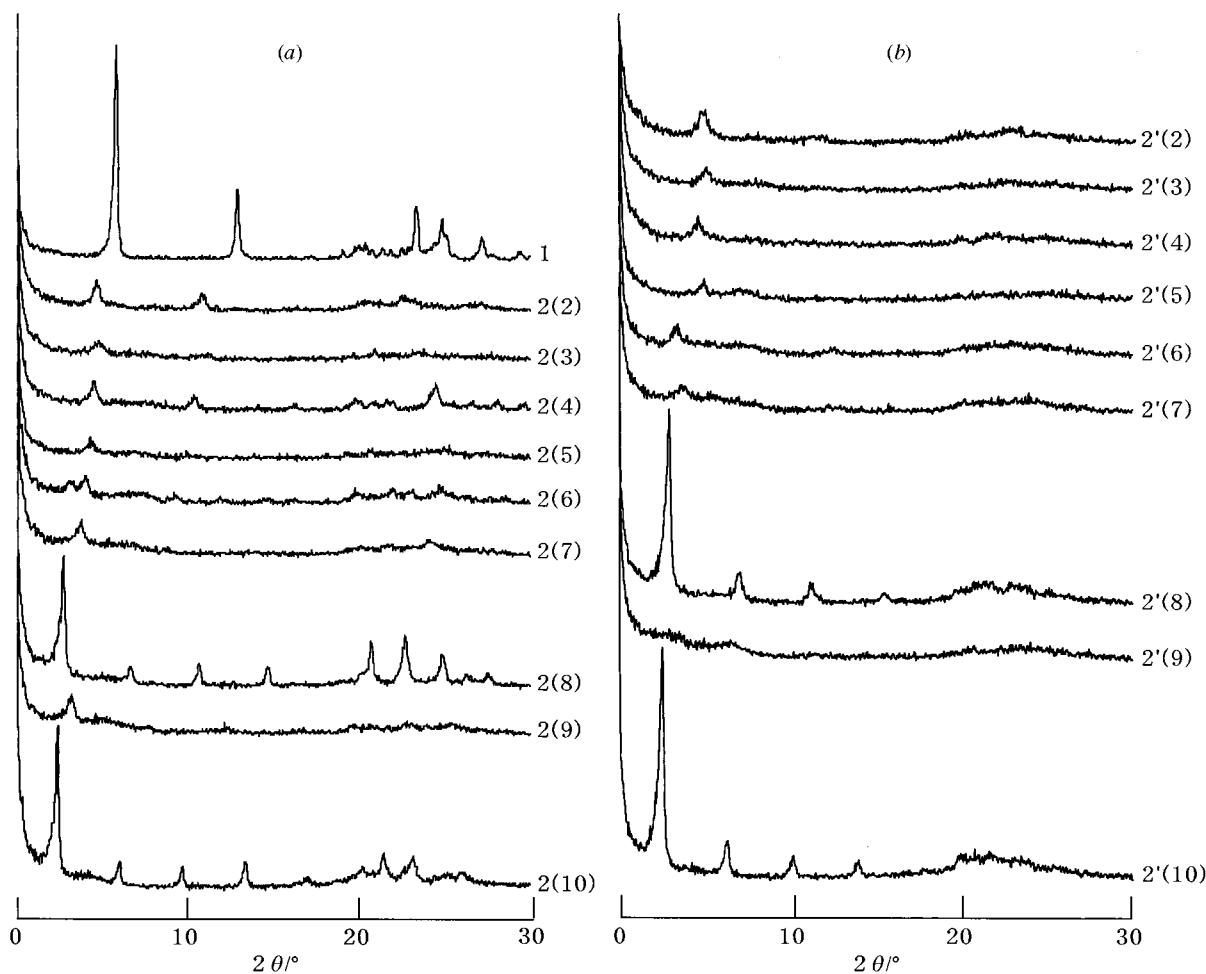


Fig. 1 X-Ray diffraction patterns of (a) compounds **1** and **2**(*n*) and (b) **2'**(*n*), where *n* is the number of carbon atoms of the intercalated amines. Compounds **2'**(*n*) are formed after heating **2**(*n*) at 200 °C for 1 h

Results and Discussion

The products of reaction of compound **1** with α,ω -alkanediamines $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ ($n = 2-10$), **2**(*n*), were primarily characterized by their X-ray diffraction patterns, as shown in Fig. 1(a). The X-ray data reveal that octane-1,8-diamine ($n = 8$) and decane-1,10-diamine ($n = 10$) form one intercalated phase indicating markedly sharp diffraction peaks and having an interlayer spacing longer than 15.4 Å for the host phosphonate, whereas the other diamines react with the host phase to yield one or two intercalated phases indicative of highly decreased peaks. The extremely sharp X-ray diffraction peaks for the $n = 8$ and $n = 9$ products suggest that the host phosphonate and intercalant layers are highly ordered, as observed for the $n = 9$ and $n = 10$ intercalates in the zirconium-based system.^{13b} The interlayer spacings of the intercalated phases were determined from the first and/or second maximum *d* value in the X-ray diffraction patterns (Table 1).

The IR absorption spectra of the diamine-intercalated solids are shown in Fig. 2(a). On addition of alkanediamine, a new single- or double-peaked band near 1530–1620 cm^{-1} due to the $\text{CO}_2^-\text{NH}_3^+$ group appears along with a broad band centred near 2920 cm^{-1} due to the CH stretching of the CH_2 group, while the absorption band at 1710 cm^{-1} attributable to the C=O stretching of the CO_2H group disappears for $n = 8$ and 10 or decreases appreciably in intensity for the other amines. This finding suggests that the intercalation of alkanediamine molecules proceeds *via* proton transfer from CO_2H to NH_2 groups.

The thermogravimetric curves for the solids **2**(*n*) indicated three or four steps over the temperature range 20–700 °C, as shown in Fig. 3. The first weight loss at below 100 °C is due to

Table 1 Interlayer spacing as a function of the carbon number of the diamine, *n*, for the diammonium-exchanged form of compound **1** prepared by precipitation at the reactant ratio [diamine]:[Ti] = 2.0:1, **2**(*n*), and the amide form prepared by heating **2**(*n*) at 210 °C for 1 h, **2'**(*n*)

<i>n</i>	Interlayer spacing/Å	
	Diammonium form, 2 (<i>n</i>)	Diamide form, 2' (<i>n</i>)
2	15.6	15.0
3		14.5
4		15.7
5		14.7
6	20.5	20.1
7		18.3
8	23.6	22.2
9		19.3
10	25.9	24.6

desorption of interlayer water. The second slight weight loss near 200 °C as well as the weight losses at higher temperatures are mostly due to loss of the interlayer organic moiety and partly to condensation of the hydrogenphosphate groups. On heating at 1000 °C for 1 h the solids except for those with $n = 8$ and 10 were totally converted into $\text{Ti}_2\text{O}(\text{PO}_4)_2$, indicating release of nearly half the phosphorus due to decomposition of the host phase during the reaction with amine solution. This is consistent with the X-ray observations for these unpyrolysed solids suggesting a considerable decomposition of the host phase with loss of phosphorus. The solids with $n = 8$ and 10, on the other hand, were converted by the same heat treatment mostly into the major phase of TiP_2O_7

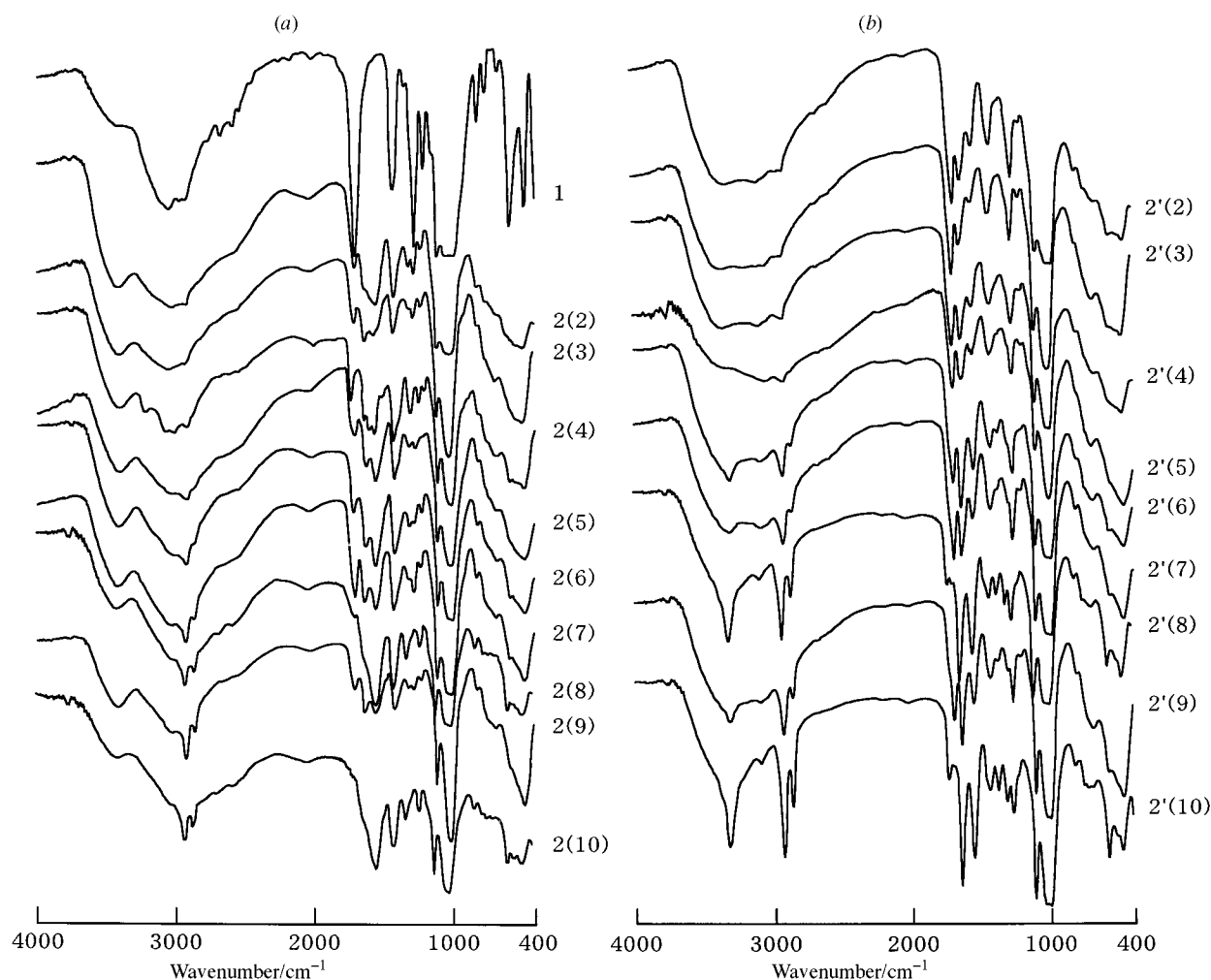


Fig. 2 Infrared spectra of (a) compounds **1** and **2**(*n*) and (b) **2'**(*n*)

expected from the composition of the host phase as well as the minor phase of $\text{Ti}_2\text{O}(\text{PO}_4)_2$. This observation reveals that the formation of highly crystalline intercalates with octane- and decane-diamines is accompanied by only a slight decomposition of the host phosphonate. The compositions of these two solids diammonium-exchanged without dephosphonation were approximately evaluated by a combination of the thermogravimetric data for these solids and **1** assuming their deorganized forms to be TiP_2O_7 . In harmony with the X-ray observations, the diamine contents for the $n = 8$ and 10 products thus obtained were 0.21 and 0.30 mol per mol of the host phosphonate, respectively. These two values are much less than 0.38 and 0.74 for the zirconium-based analogues,^{13b} due to the difference in structural compactness between both the phosphonates as discussed below.

Fig. 4 shows a plot of the interlayer spacing (d) against the number of CH_2 units (n) in the alkyl chain for the crystalline phases formed as the major or minor phases in the resulting solids. These are two straight lines with high and low slopes. The slopes of these lines were evaluated from data for $n = 2, 6, 8$ and 10 and those for $n = 3-7$ and 9 , being 1.03 and 1.17 Å per CH_2 , respectively. These values are less than the typical methylene repeat distance of 1.27 Å per CH_2 for an all-*trans* extended-chain conformer. It is therefore most likely that alkanediamines form two groups of intercalated phases in which the diamine molecules are arranged as a monolayer with their axes tilted by 54 or 67° relative to the inorganic layer, as illustrated for the $n = 7$ and $n = 8$ systems in Fig. 5. These observations show that the diamines with $n \geq 7$ produce the high and low chain-tilt forms depending whether the carbon number is

even or odd, respectively, whereas shorter chain diamines except for $n = 2$ give only the low chain-tilt form. Both forms coexist for one intermediate member, $n = 6$.

The α -carboxyethylated zirconium phosphonate-alkanediamine system also yielded two similar groups of intercalates with different chain orientations, for which the two tilt angles of 59 and 19° are slightly or appreciably lower than those observed for the present system.^{13b} It was also observed that such an even/odd effect occurs for short chain diamines with $n \leq 7$, whereas longer chain diamines yield only the high chain-tilt form and both forms coexist for intermediate members with $n = 4, 6, \text{ or } 7$. Fig. 6 summarizes the phase diagrams for the titanium- and zirconium-based (carboxyethyl)phosphonate-alkanediamine systems. The striking contrast between the carbon number dependence of the phase relation for the two systems could be explained as follows. In the zirconium-based phosphonate the phosphorus atoms bearing 2-carboxyethyl groups are located in a pseudo-hexagonal fashion with a distance of 5.3 Å as in α -zirconium phosphate, while those in the titanium-based phosphonate are likely situated in a similar manner but with a shorter distance of 5.0 Å as in α -titanium phosphate.⁸ The zirconium- and titanium-based structures give values of 24.0 and 21.6 Å² for the free area associated with each phosphorus on the plane, respectively, indicating that the latter structure is 10% more compact than the former. Both ammonium termini of alkanediammoniated molecules with their *trans* zigzag conformation are in *trans* and *cis* directions according to the even and odd numbers of carbon atoms, respectively. The observations on the zirconium-based system were reasonably explained by assuming that the two ammonium termini of even carbon

number chains can be brought into a position favourable for binding to the carboxyl groups of any two adjacent phosphonate layers, but those with odd carbon number chains cannot be bound to any carboxyl group without changing their conformation. The behavior of odd but long chain diamines yielding the high chain-tilt form was attributed to their high chain flexibilities. In the titanium-based system, on the other hand, the intercalation behavior of diamines exhibits a more explicit dependence on the structural character of the host phospho-

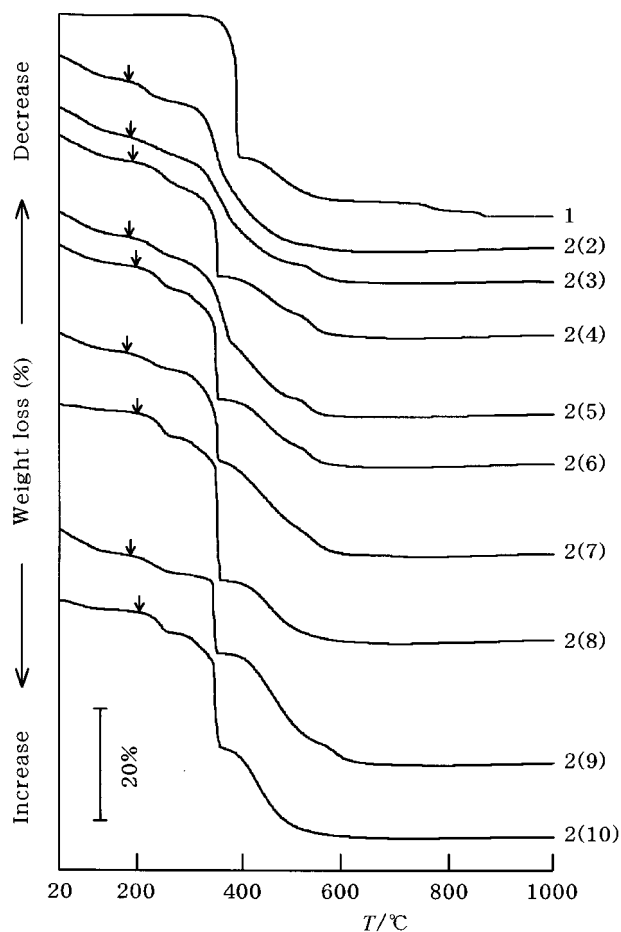


Fig. 3 Thermogravimetric curves for compounds 1 and 2(*n*) with a heating rate of 10 °C min⁻¹ in air

nate. Owing to the compact structure of the host, short chain diamines would have to change their conformation to bind to the carboxyl groups of any two adjacent phosphonate layers, whereas longer chain diamines could attain a situation capable of binding to any carboxyl group without any significant change of their conformation. Such a marked host effect would be responsible for the extremely narrow range for the high and low chain-tilt forms to coexist (*n* = 6), compared to their coexistence for *n* = 4, 6, or 7 in the zirconium-based system. A similar effect would be valid for the highly ordered arrangement of the host phosphonate and intercalant layers for the long and even carbon number (*n* = 8 or 10) products in the titanium-based system, in striking contrast to the zirconium-based system in which long chain (*n* = 9 or 10) diamines form a highly crystalline intercalate independent of the even or odd character of *n*.^{13b} The exceptional behavior of ethane-1,2-diamine (*n* = 2) with a short chain length yielding the high chain-tilt form could be attributable to the even carbon number effect coupled with its extremely low chain flexibility, as also observed

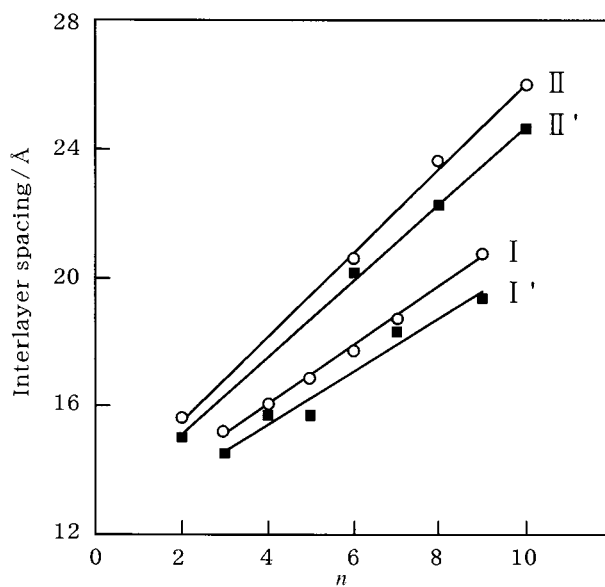


Fig. 4 Interlayer spacings of compounds 2(*n*) and 2'(*n*) as a function of the carbon number of the alkyl chain. The designations I and II and I' and II' denote the low and high chain-tilt forms of the diammonium-exchanged and diamidated solids, respectively

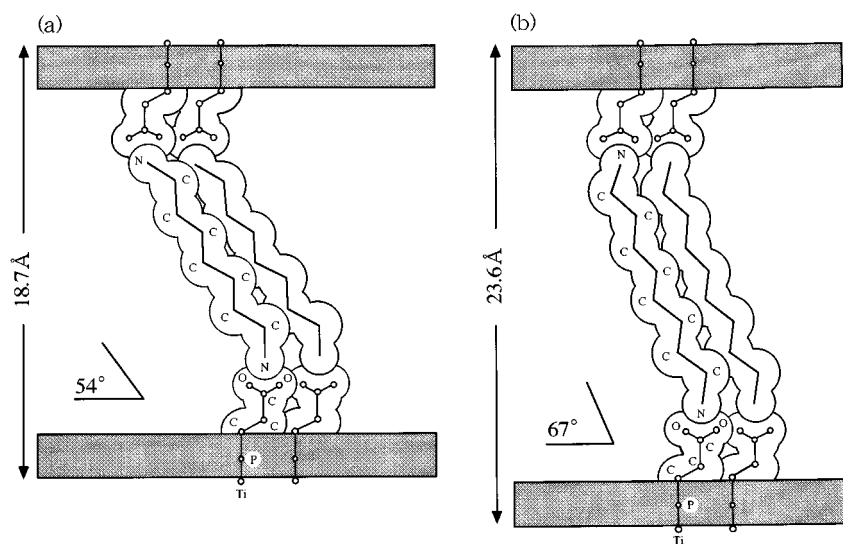


Fig. 5 Models for the arrangement of (a) heptanediammonium (*n* = 7) and (b) octanediammonium (*n* = 8) molecular ions in the interlayer space of compound 1

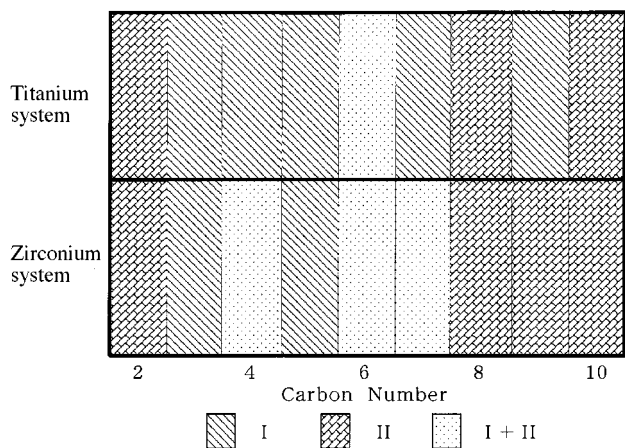


Fig. 6 Phase diagram for the α -zirconium and α -titanium (2-carboxyethyl)phosphonate phosphate-alkanediamine systems. Key as in Fig. 4

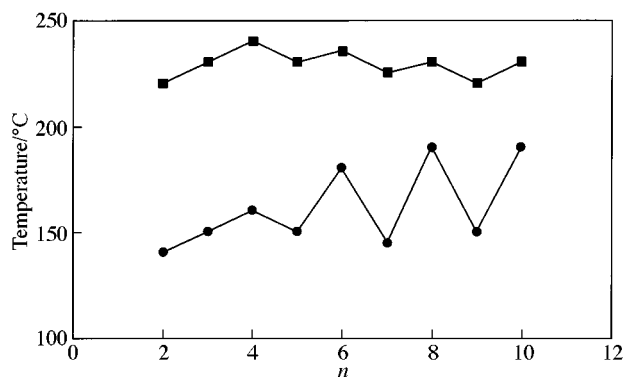


Fig. 7 Plots of the (●) onset and (■) end temperatures for the second weight loss in the thermogravimetric curves of compounds **2**(*n*) as a function of carbon number

for the zirconium-based system.^{13b} This means that such exceptional behavior occurs independently of the structural compactness of the host phosphonates.

Heating of the ammonium-exchanged solids **2**(*n*) at 220 °C for 1 h led to total conversion of the 1680 cm⁻¹ band due to the CO₂⁻NH₃⁺ group into so-called amide-I and -II bands at 1640 and 1550 cm⁻¹, respectively, or partial recovery of the CO₂H band at 1700 and/or 1730 cm⁻¹, as shown in Fig. 2(b). The IR observations indicate that the ionically bonded CO₂⁻NH₃⁺ group in the ammonium-exchanged solids is thermally condensed into the amide CONH form accompanied by partial deintercalation of the diamine guest to leave the regenerated acid host. The X-ray diffraction patterns of the amidated solids are shown in Fig. 1(b), and the interlayer spacings are summarized in Table 1. The *d* vs. *n* plot reasonably implies that the amidation causes an interlayer contraction for both the high and low chain-tilt forms. The second weight loss in the temperature range 150–250 °C on the thermogravimetric curves for all the ammonium-exchanged solids (Fig. 3) is attributable to the interlayer amidation, accompanied by partial deintercalation of the intercalated amine, as suggested from the above IR observations. The amidation reaction would occur in such a manner that the ammonium termini or the whole of the intercalated guest molecules are thermally mobilized to react with the nearby carboxyl groups or partly migrate out of the interlayer space. Here we can define two characteristic temperatures, T_{Gon} and

T_{Gend} , as the beginning and end temperatures for the amidation-related weight losses. These two temperatures were determined from the beginning and end inflection points in the amidation region, respectively, at which the slope of the tangent to each thermogravimetric curve has a minimum, as indicated for T_{Gon} by an arrow on each curve in Fig. 3. The onset and end temperatures, T_{Gon} and T_{Gend} , thus obtained are plotted as a function of carbon number in Fig. 7. The onset temperature exhibits a marked tendency to vary regularly up and down depending on the even or odd number of the carbon atoms, as well as an increasing tendency with increasing carbon number for each even or odd carbon number. The end temperature shows the same but less sensitive odd/even effect over the whole range of *n*. Thus, the present titanium-based system was found to undergo carbon number-dependent interlayer amidation characterized by an odd/even effect, as observed for the α -zirconium (2-carboxyethyl)phosphonate-alkanediamine systems, with or without an accompanying partial deintercalation of the diamine guests.^{13b}

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