

Intercalation of Aminomethylcrowns into α -Zirconium Phosphate

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Abstract. The intercalation of (\pm)-2-aminomethylcrowns into α -zirconium phosphate has been investigated by the batch method and followed by X-ray diffractometry. The reaction was dependent on the solvent, and 1-propanol was employed as a solvent. (\pm)-2-Aminomethyl-12-crown-4 and -15-crown-5 were taken up in two and three stages, respectively, while the uptake process of (\pm)-2-aminomethyl-18-crown-6 was complicated. Monolayers and bilayers of aminomethylcrowns might be formed when inserted into the interlayer space. ^{31}P CPMAS-NMR and IR spectra of the intercalates suggest that the amino group is protonated by a proton of the phosphate group and/or proton transfer from the phosphate group to the amino group occurred.

Key words: intercalation, α -zirconium phosphate, (\pm)-2-aminomethyl-12-crown-4, (\pm)-2-aminomethyl-15-crown-5 and (\pm)-2-aminomethyl-18-crown-6.

1. Introduction

The intercalation chemistry of α -zirconium phosphate has been extensively investigated because of interest in its fundamental aspects and applications [1, 2]. Many organic compounds have been employed as guests. Generally, the intercalation of organic compounds is restricted by their size as well as their basicity. Solvent also affects the intercalation reaction [3]. In a previous paper we reported the uptake of quinoline into α -zirconium phosphate using solvents such as ethanol, acetone, and carbon tetrachloride [4]. This suggested that an organic compound having a large dimension can intercalate into the interlayer region of α -zirconium phosphate under certain conditions.

Polyethers, such as crown ethers and related compounds have been studied, because crown ethers are able to coordinate to many cations, especially alkali cations [5]. The intercalation compounds of crown ethers can give rise not only to a new class of materials having selectivity to a specific cation, but also to a precursor to accommodate other macrocyclic organic compounds. Recently, covalently bonded aza-18-crown-6 in γ -zirconium phosphate was reported [6].

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This work describes the intercalation of the following aminomethylcrowns into α -zirconium phosphate using some 1-alkanols as solvent; (\pm)-2-aminomethyl-12-crown-4 (AM12C4), (\pm)-2-aminomethyl-15-crown-5 (AM15C5) and (\pm)-2-aminomethyl-18-crown-6 (AM18C6).

2. Experimental

2.1. REAGENTS

All chemicals used were reagent grade. Aminomethylcrowns were purchased from Aldrich Co., and used as supplied. Data could not be obtained for AM12C4 as it is no longer available commercially. α -Zirconium phosphate was prepared by the direct precipitation method [7]. The α -Zirconium phosphate used had a median size (D_{50}) of 3 μm [4].

2.2. INTERCALATION PROCEDURE

The reaction was carried out by the batch method. A weighed amount of aminomethylcrown was added to α -zirconium phosphate (30 mg) in an ampoule. The amount of aminomethylcrown was equivalent to about 0.15 ~ 1.8 of the exchangeable protons in α -zirconium phosphate. Then 3 mL of a solvent was added, and the ampoule was sealed. To select a solvent, the intercalation of AM12C4, AM15C5 and AM18C6 were tried in ethanol, 1-propanol and 1-butanol. After being mixed with an ultrasonic vibrator, the mixture was placed in an air-oven regulated to 60 °C, and shaken intermittently. After a given period of time (seven days), the solid phase was separated by centrifugation, and air dried at room temperature. To determine the amount of aminomethylcrown taken up, the supernatant was titrated with hydrochloric acid, using methyl red as an indicator.

2.3. ANALYSIS

The change in the interlayer distance of crystallites was recorded with a Rad 2C Diffractometer (Rigaku Denki Co.) using Ni-filtered Cu $K\alpha$ radiation. All X-ray powder patterns were measured after complete air drying. The infrared (IR) spectra of KBr discs were recorded on a FT-IR-8000 Spectrophotometer (JASCO). ^{31}P cross polarization magic angle spinning nuclear magnetic resonance (^{31}P CPMAS-NMR) spectra were obtained on a Varian Unity 300 NMR operating at a frequency of 121.4 MHz. Samples were packed into 7-mm silicon nitride rotors and spun at 3 kHz in a Doty supersonic CPMAS probe. Chemical shifts are reported in ppm using $\text{NH}_4\text{H}_2\text{PO}_4$ ($\delta = 1.0$ ppm) as reference.

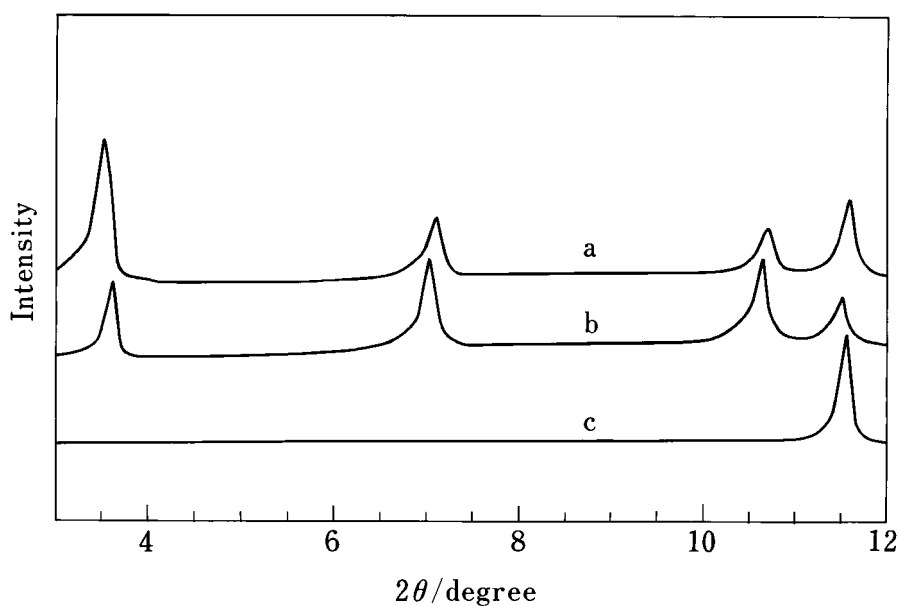


Figure 1. Effect of solvent on the intercalation of AM15C5. Solvent: a: 1-butanol; b: 1-propanol; c: ethanol. Reaction temperature: 60 °C; reaction time: 7 days. Amount of AM15C5 (mmol) added to 1 g of α -zirconium phosphate: a: 11.6; b: 9.46; c: 11.7.

3. Results and Discussion

3.1. INTERCALATION AND CHANGE IN THE INTERLAYER DISTANCE

Preliminary studies showed that crowns without the amino group could not be intercalated into the interlayer region of α -zirconium phosphate under the experimental conditions employed.

Figure 1 shows that the interlayer distance of the host was varied by uptake of AM15C5, and that 1-butanol was a better solvent than ethanol or 1-propanol. Similar phenomena were observed for the intercalation of AM12C4 and AM18C6. It has been reported that neat alkylalcohols can be intercalated thus expanding the interlayer distance of α -zirconium phosphate. The change in the interlayer distance was dependent on the length of the alkyl chain [8, 9]. These facts mean that the alcohols expanded the interlayer distance of α -zirconium phosphate and then the aminomethylcrowns intercalated into the interlayer region, that is, the alcohols co-intercalated in a solvent. As the interlayer distances of the 1-butanol, 1-propanol and ethanol-intercalates are 18.6 Å, 16.5 Å and 14.1 Å, respectively, the intercalation of aminomethyl crowns took place more easily in 1-butanol or 1-propanol than in ethanol [9]. 1-Propanol was thus employed as a solvent, because 1-propanol was removed more quickly by drying in air than 1-butanol.

Figures 2 and 3 show the uptake curves during intercalation of AM15C5 and AM18C6 into α -zirconium phosphate at 60 °C. Intercalation of AM15C5 and

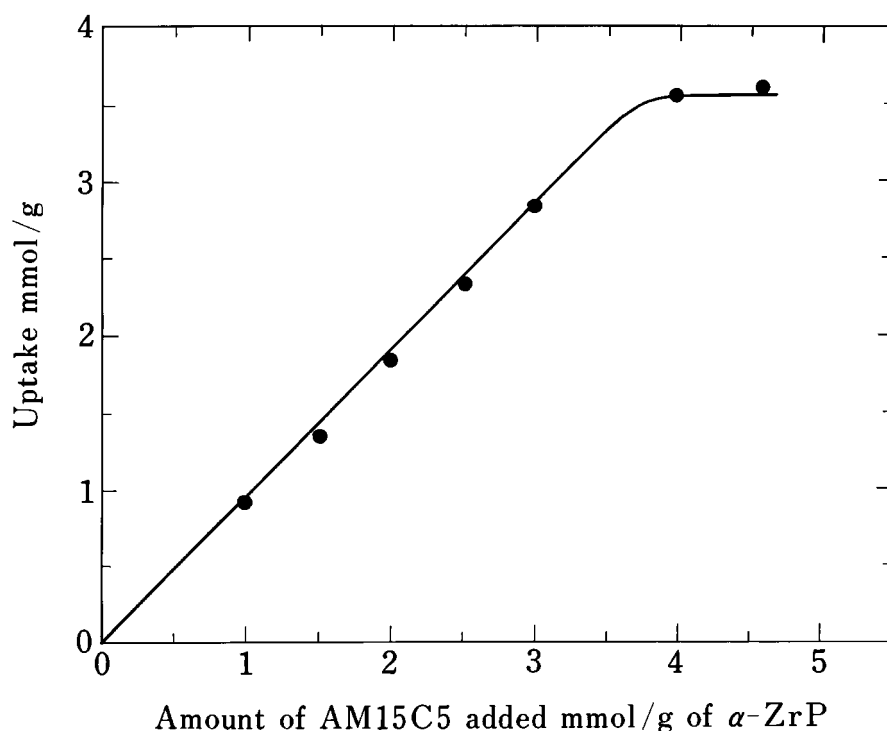


Figure 2. Uptake curve of AM15C5 by α -zirconium phosphate at 60 °C.

AM18C6 occurred completely at low concentration, but uptake curves showed a plateau at about 3.7 mmol of AM15C5 and AM18C6 added per gram of α -ZrP (hereafter abbreviated to mmol/g). The maximum uptake at 60 °C for AM15C5 was 3.5 mmol/g; that is, the final composition was represented formally as $\text{Zr}(\text{HPO}_4)_2(\text{AM15C5})_{1.05}$ (see Figure 2), while that for AM18C6 was 3.3 mmol/g; corresponding to a chemical formula of $\text{Zr}(\text{HPO}_4)_2(\text{AM15C5})_{0.99}$ (Figure 3). The maximum uptake of AM18C6 is slightly lower than that of AM15C5, probably because of the larger molecular size.

Figure 4(a) shows that the intercalation of AM12C4 took place simply in two steps. The interlayer distance of the host expanded from 7.6 Å (Phase α) to 14.9 Å (Phase 1), and then to 23.4 Å (Phase 2).

Figure 4(b) shows the fraction of phases as a function of the concentration of AM12C4 in the initial solution. Assuming that the intensity of the peak in an X-ray diffraction pattern is proportional to the amount of each phase present, the ratio of phases can be approximately estimated using the following equation,

$$R(\text{Phase X}) = I(\text{Phase X}) / \{I(\text{Phase}\alpha) + I(\text{Phase 1}) + I(\text{Phase 2})\}$$

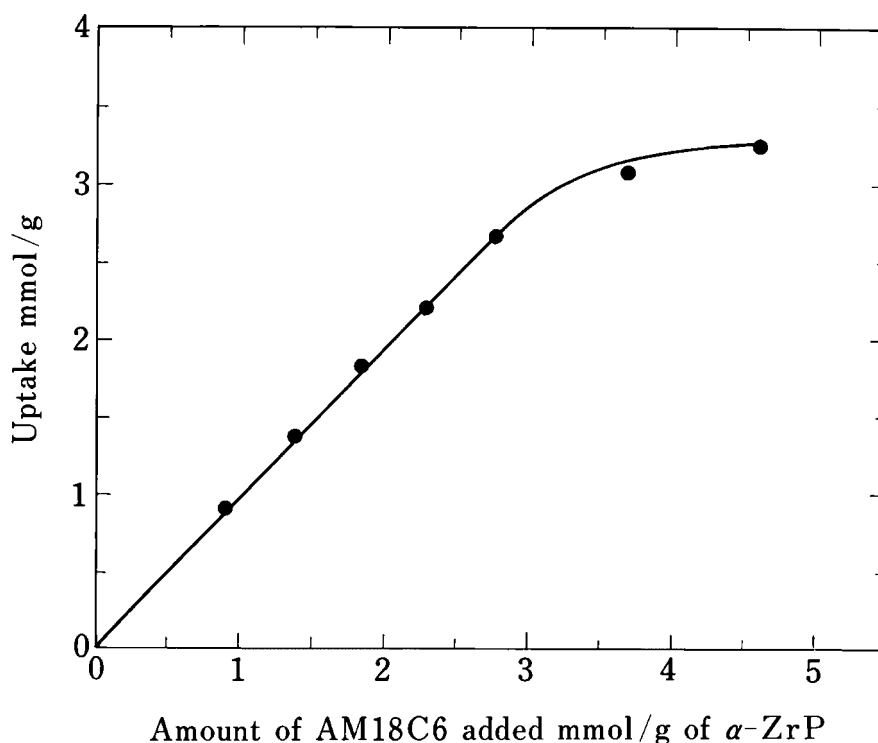


Figure 3. Uptake curve of AM18C6 by α -zirconium phosphate at 60 °C.

where $I(\text{Phase } \alpha)$, $I(\text{Phase 1})$ and $I(\text{Phase 2})$ represent the intensities of the peaks at 7.6 Å, 14.9 Å and 23.4 Å, respectively. The ratio of Phase 1 to Phase (α) and Phase 2 to Phase 1 increased linearly with an increase in the loading of AM12C4.

In the intercalation of AM15C5, the interlayer distance varied from 7.6 Å (Phase α) \rightarrow 14.5 Å (Phase 1) \rightarrow 15.9 Å (Phase 2) \rightarrow 24.7 Å (Phase 3) (see Figure 5(a)). The fractions of phases as a function of the concentration of AM15C5 in the solution are shown in Figure 5(b). The ratio of phases changed linearly.

The change in the interlayer distance upon intercalation of AM18C6 was complicated as shown in Figure 6. The interlayer spacing changed from 7.6 Å (Phase α) \rightarrow 14.6–17.5 Å \rightarrow 20.5 Å \rightarrow 27.1 Å. When the amount of uptake was over 3.0 mmol/g, only the phase at 27.1 Å was present. These changes may result from the structural flexibility of the crown ring of AM18C6. It is hard to express the fractions of phases as a function of the concentration of AM18C6 in the solution, because the change in interlayer distance from 14.6 Å to 17.5 Å is much too complicated.

3.2. STRUCTURAL CONSIDERATIONS

The relation between the interlayer spacing of α -zirconium phosphate intercalation compounds and the molecular size of the intercalants has been discussed in several

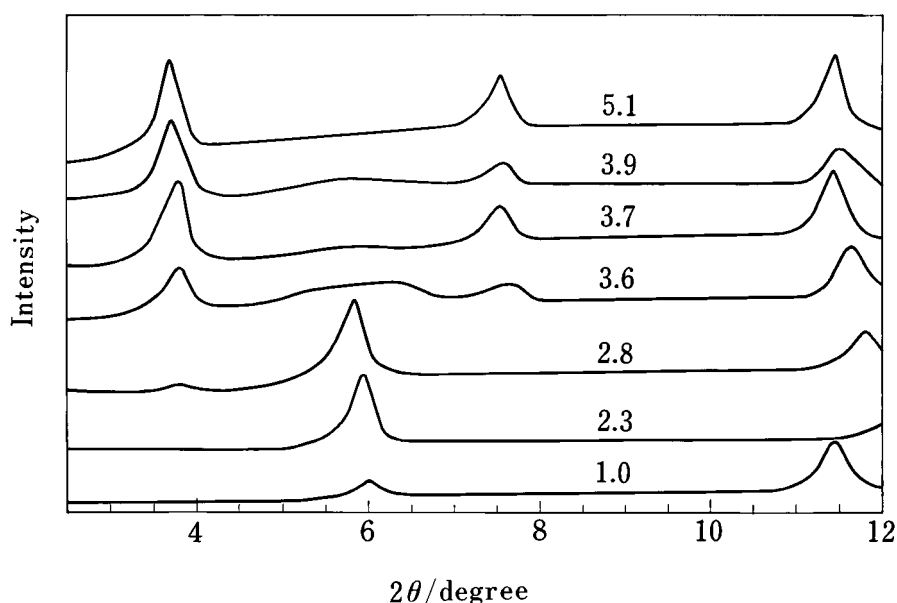


Figure 4a. Change in the XRD patterns of intercalation compounds of AM12C4. Numerals in the figure denote the amount of AM12C4 (mmol) added to 1 g of α -zirconium phosphate.

publications [1, 2]. When aminomethyl crowns are intercalated into α -zirconium phosphate, they can take various conformations between the layers. Bovill and co-workers discussed the conformation of 12-crown-4 and 18-crown-6, and compared them from an energy point of view [10].

Assuming that the volume occupied by the crown (V) is calculated as a rectangular solid having dimension $l \times w \times d$, the size of AM12C4, AM15C5 and AM18C6 are summarized in Table I. The size of AM15C5 was estimated by assuming that the 15-crown-5 ring adopts a conformation in which the oxygen atoms are orientated in a plane (see Scheme 1).

Hasegawa and coworkers proposed a method to estimate the molar ratio of the guest to host (loading ratio) for the intercalation of dl-1-phenylethylamine [11]. The loading ratio can be determined by the following equation, since no hydration water was observed in TG-DTA analysis;

$$\text{Loading ratio} = \{24.0 \times (d - 6.3)\} / \text{molecular volume of an intercalant}$$

where 24.0 \AA^2 is the area surrounding one -POH group, d is the interlayer distance of an intercalate and 6.3 \AA is the thickness of the α -zirconium phosphate macroanion taking copenetration of the guest into account. (If the thickness of the macroanion is 9.0 \AA [1], the loading ratio will decrease. The values are shown in parentheses.)

The volume of AM12C4, AM15C5 and AM18C6 can be estimated as an ellipsoidal column having the dimensions shown in Table 1. Thus the loading ratio

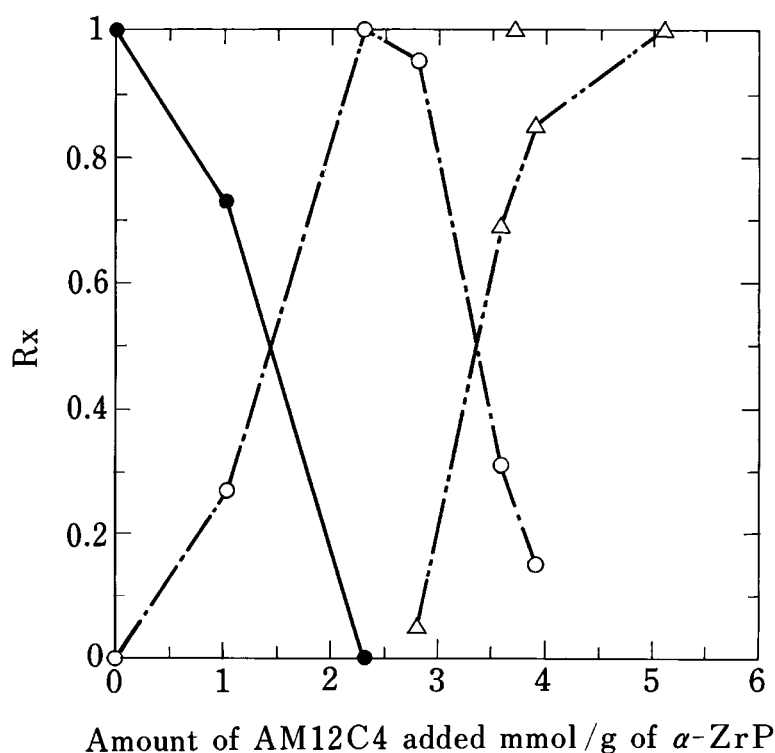


Figure 4b. Approximate ratio of the phases present during uptake of AM12C4. ●; α -ZrP, ○; Phase 1, △; Phase 2.

Table I. The size of aminomethylcrowns.

Compound	Conformation	l (Å)	w (Å)	d (Å)	V (Å ³)
AM12C4	AM12C4-(a)	10.5	8.5	5.4	379
	AM12C4-(b)	11.3	8.5	5.0	377
AM15C5	AM15C5-(a)	12.7	9.0	5.2	467
AM18C6	AM18C6-(a)	14.7	8.5	5.2	510
	AM18C6-(b)	12.5	9.1	5.2	536

The conformation of AM12C4-(a) corresponds to that in the crystal, and AM12C4-(b) to that in a free molecule [10]. The conformation of AM15C5-(a) was assumed to adopt a planar configuration

The conformation of AM18C6-(a) corresponds to that in the crystal, and AM18C6-(b) analogous to that adopted by cyclooctadecane in the crystal. According to the literature, the conformation of AM18C6-(a) is the most stable energetically [10].

is 1.10(0.91) for Phase 2 of AM12C4, 0.50(0.35) for Phase 2 and 0.96(0.81) for Phase 3 of AM15C5 and 0.94 ~ 0.99 (0.81 ~ 0.85) for Phase 3 of AM18C6. These values, which are calculated from the thickness of the macroanion, agree well with

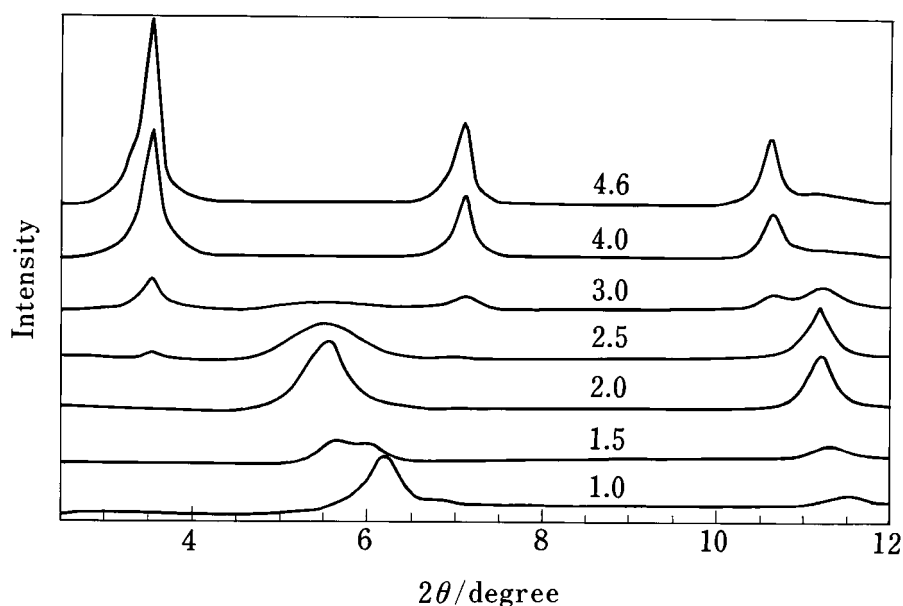


Figure 5a. Change in the XRD pattern of intercalation compounds of AM15C5. Numerals in the figure denote the amount of AM15C5 (mmol) added to 1 g of α -zirconium phosphate.

the experimental value determined by titration; 0.55 for Phase 2 and 1.05 for Phase 3 of AM15C5 and 0.99 for Phase 3 of AM18C6.

Table II shows the interlayer distance of *n*-alkylamine intercalated α -zirconium phosphate and the length of the *n*-amine in the *trans-trans*-alkyl chain conformation. Tables I and II show that the lengths of AM12C4, AM15C5 and AM18C6 are almost identical to the *trans-trans*-alkyl chain length of *n*-hexylamine, *n*-heptylamine, and *n*-heptylamine or *n*-octylamine, respectively, and that the largest interlayer distance of aminomethylcrown intercalated α -zirconium phosphate (hereafter abbreviated to AMC-ZrP) agrees well with that of the alkylamine intercalates in a bilayer form. The above considerations strongly suggest that the bilayer of aminomethylcrowns is formed in Phase 2 of AM12C4, Phase 3 of AM15C5 and Phase 3 of AM18C6. Moreover, the phases with half of the maximum loading ratio might be built up with a monolayer of aminomethylcrowns; *viz.* Phase 1 of AM12C4, Phase 2 of AM15C5 and Phase 3 of AM18C6.

3.3. SPECTROSCOPIC STUDY

Figures 7 and 8 show the ^{31}P CPMAS-NMR spectra of intercalation compounds of AM15C5 and AM18C6 (AM15C5- and AM18C6-ZrP). At lower loading ratio, both spectra of AM15C5- and AM18C6-ZrP are very similar, but the spectra at higher loading ratio are quite different from each other.

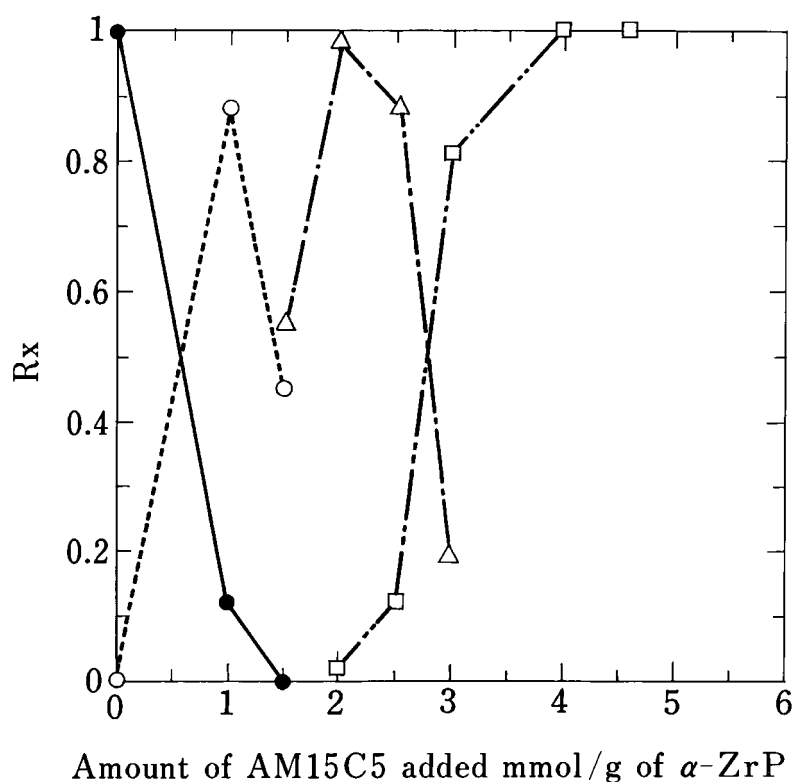


Figure 5b. Approximate ratio of the phases present during uptake of AM15C5. ●; α -ZrP, ○; Phase 1, △; Phase 2, □; Phase 3.

Table II. *trans-trans*-Alkyl chain length and the interlayer distance of *n*-alkylamine intercalated α -zirconium phosphate.

	Chain length (Å)	Interlayer distance of intercalate (Å)
Pentylamine	10.0	20.9
Hexylamine	11.2	22.8
Heptylamine	12.6	26.0
Octylamine	13.8	28.0
Decylamine	16.2	32.1

The interlayer distances, except for heptylamine, are quoted from ref. [18]. For heptylamine ref. [1].

Figures 7(a) and 8(a) show that two peaks were observed in both spectra at -18.9 (sharp) and ca. -21 ppm (broad). The single peak at -18.9 ppm is due to the phosphate group in α -zirconium phosphate despite the presence of two crystallographically non-equivalent phosphorus atoms [12]. The broad peak at ca. -21 ppm might be due to an anhydrous protonated phosphate group [13].

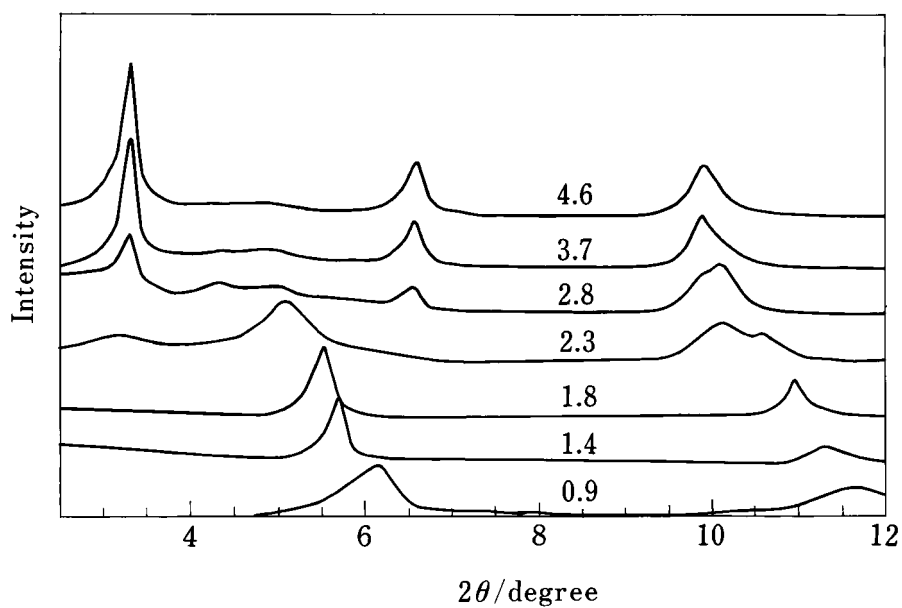
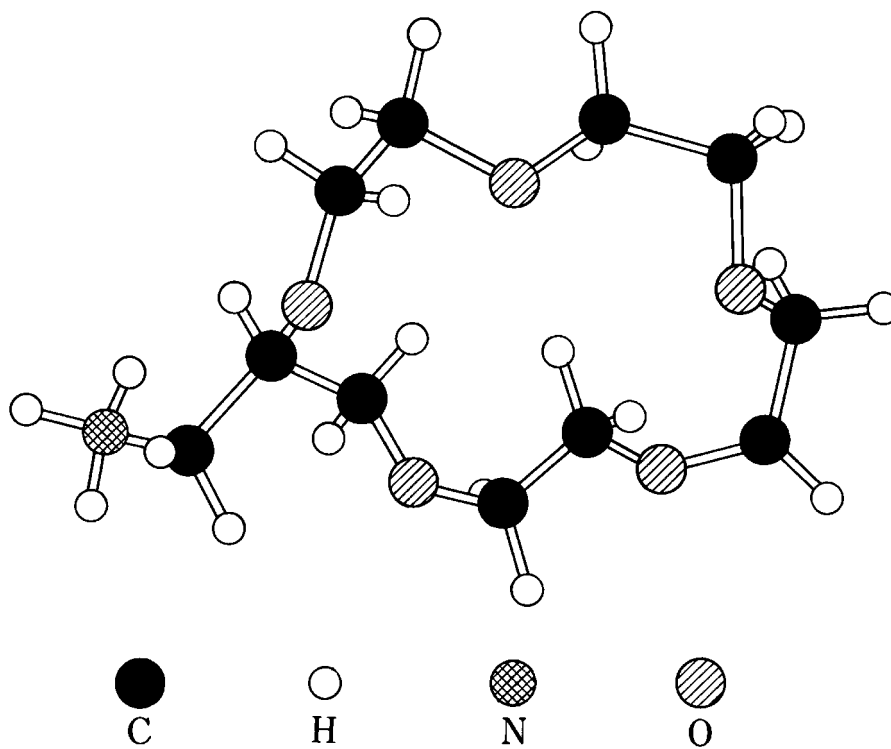


Figure 6. Change in the XRD pattern of intercalation compounds of AM18C6. Numerals in the figure denote the amount of AM18C6 (mmol) added to 1 g of α -zirconium phosphate.



Scheme 1. Conformation of AM15C5.

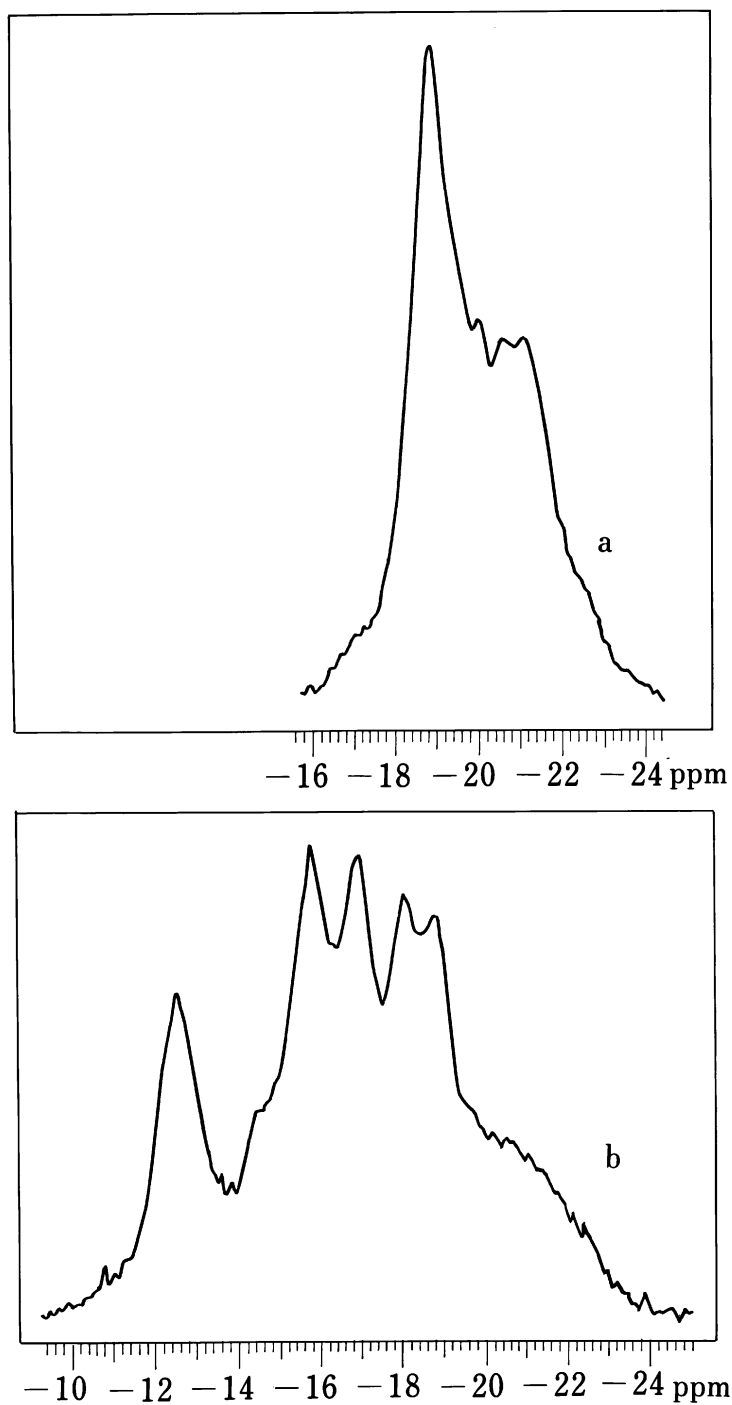


Figure 7. The ^{31}P CPMAS-NMR spectra of intercalation compounds of AM15C5. The loading ratios are 0.27 for (a) and 1.05 for (b).

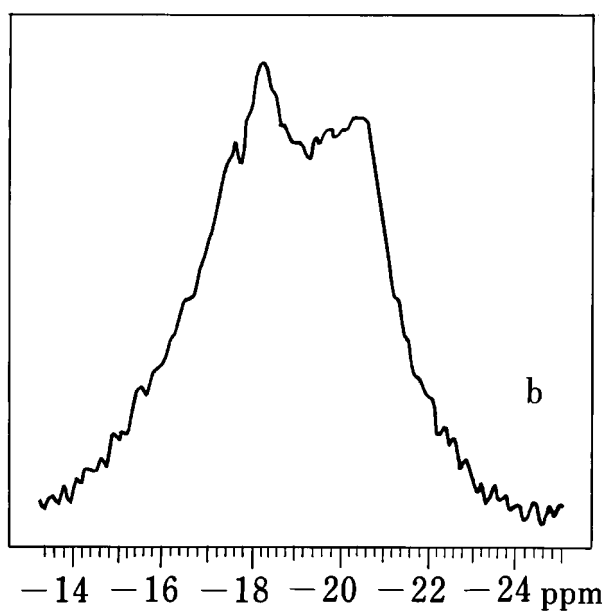
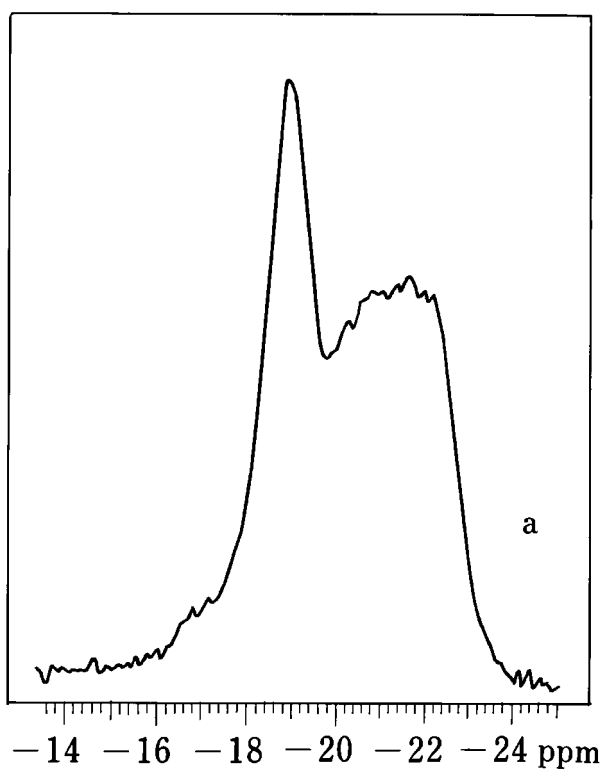


Figure 8. The ^{31}P CPMAS-NMR spectra of intercalation compounds of AM18C6. The loading ratios are 0.28 for (a) and 0.97 for (b).

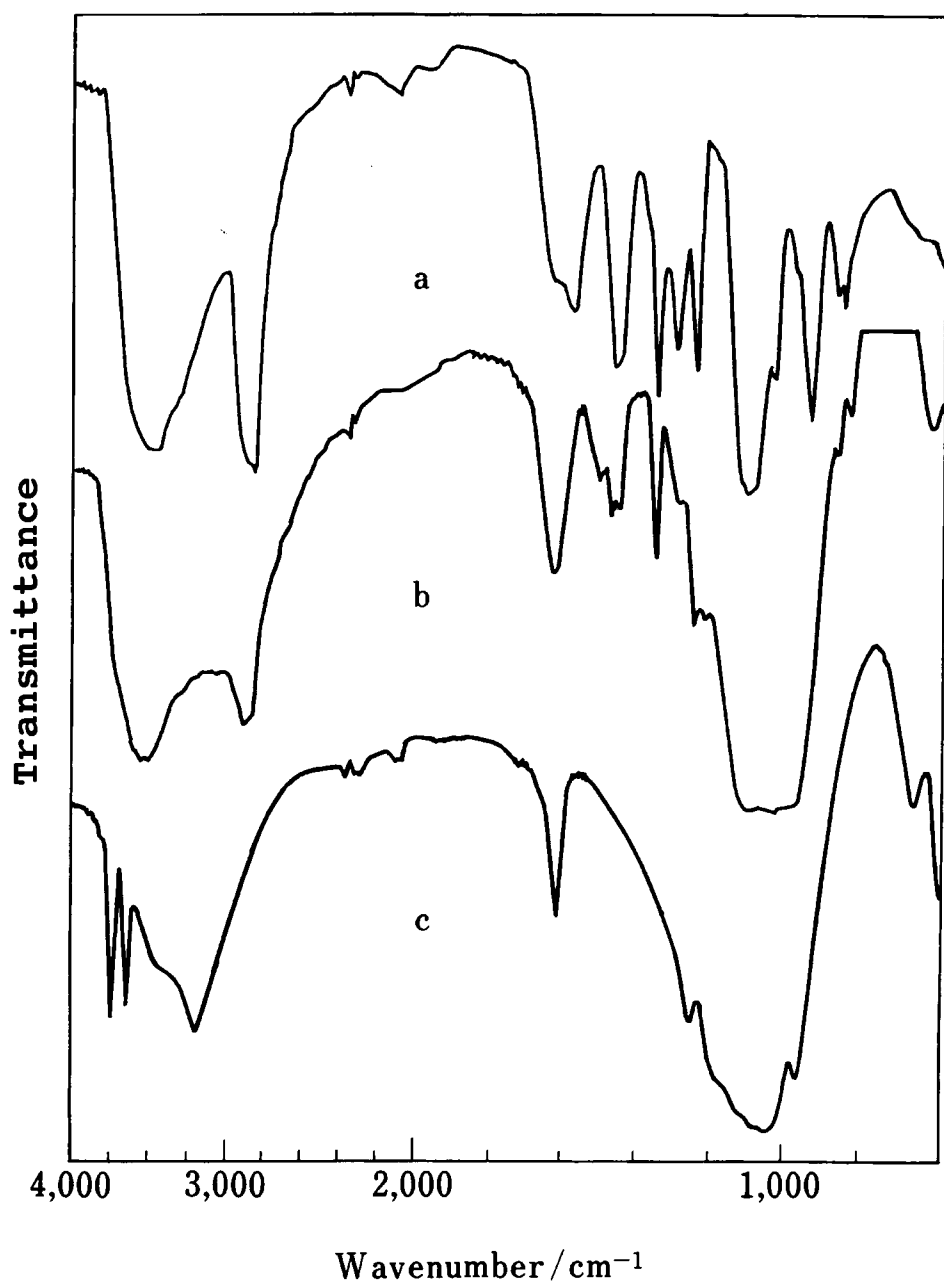


Figure 9. The IR spectra of (a); AM15C5, (b); its intercalation compound, and (c); α -zirconium phosphate.

The spectra of AM15C5-ZrP is complex at the higher loading ratio. Figure 7(b) shows that there are at least 5 sharp peaks in the spectrum. The peak at -18.9 ppm is again due to the monohydrogen phosphate group. The resonances at -12.5 , -15.7 and -16.9 ppm are probably assigned to deprotonated phosphate groups which are hydrogen bonded to the amine. On the other hand, the spectrum of AM18C6 is quite different from that of AM15C5 and has two peaks at -18.3 and -20.4 ppm (see Figure 8(b)). The sharp peak at -18.9 ppm in (a) decreases the relative intensity, and the broad peak at ca. -21 ppm showed a low field shift.

The IR spectra of α -zirconium phosphate, AM15C5-ZrP and AM15C5 are shown in Figure 9. The two sharp bands at 3594 and 3488 cm^{-1} in α -zirconium phosphate are due to asymmetric OH stretching vibrations of the lattice water [14]. The symmetric stretching vibration and the bending vibration of the lattice water are seen at 3146 and 1620 cm^{-1} , respectively. The disappearance of the lattice water from the IR spectra is related to the appearance of the ^{31}P CPMAS-NMR broad peak at -21 ppm.

Figure 9(a) shows the spectra of AM15C5. The absorption bands in the region of 3600 – 3200 and 1650 – 1550 cm^{-1} are assigned to the amino group of AM15C5, while the other peaks are the same as those of 15-crown-5 reported in a previous study [15, 16]. Those peaks were shifted when AM15C5 was inserted into α -zirconium phosphate: $3420 \rightarrow 3453$ (NH stretching vibration), and $1591 \rightarrow 1525$ (NH symmetric deformation mode) cm^{-1} .

These peak shifts result from protonation of the amino group by a proton of the phosphate group and/or proton transfer from the phosphate group to the amino group [17]. The same peak shifts were also observed in AM12C4 and AM18C6: $1638 \rightarrow 1626$ and $1584 \rightarrow 1500$ cm^{-1} in AM12C4; $1636 \rightarrow 1632$ and $1591 \rightarrow 1510$ cm^{-1} in AM18C6.

4. Conclusions

The intercalation of (\pm)-2-aminomethylcrowns into α -zirconium phosphate took place in 1-propanol and 1-butanol, but not in ethanol. The interlayer distances of AMC-ZrP which are strongly suggestive of bilayers of AM12C4, AM15C5 and AM18C6 are 23.4 Å, 24.7 Å and 27.1 Å, respectively.

From IR spectra, it is suggested that the lattice water of the α -zirconium phosphate was lost and at the same time the protonation of the amino group by a proton of the phosphate group and/or proton transfer from the phosphate group to the amino group would occur. The disappearance of the lattice water from the IR spectra is related to the change of the ^{31}P CPMAS-NMR signal. The NMR single peak at -18.9 ppm, which was assigned as the original phosphate group in α -zirconium phosphate, decreased in height and showed a variety of changes in the spectrum depending on the crown at a high loading ratio.

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