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Intercalation of Methylene Blue into Layered Phosphates in the Presence of Butylamine and Function of Alkylamine in the Intercalation Reaction

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The intercalation of methylene blue (MB) into layered phosphates was examined in the presence of butylamine (BA) in order to clarify the mechanism of this reaction and the function of alkylamine, such as BA in the intercalation reaction. MB was not directly intercalated into layered phosphates, but could be intercalated in the presence of BA. The intercalation of MB was strongly influenced by the amount of BA used; that is, it was accelerated by the presence of BA, but inhibited by the presence of too much BA. Moreover, in the procedure which BA was previously intercalated into layered phosphates, it was found that the intercalation of MB can be achieved by removing BA from the interlayer region when BA is formed a monolayer in the phase, and depends on the orientation of BA in the interlayer region when BA forms a bilayer.

Layered phosphates of Zr, Ti, and Al are insoluble acid salts with a layered structure,[1,2] and can intercalate various organic molecules including alkylamines,[3,4] amino acids,[5] and protonated alcohols.[6] In addition, layered phosphates are known as an inorganic ion-exchanger and ion exchange of not only metal ions, but also quaternary ammonium ions, such as phospholipid.[7] The metal ion-exchange properties of layered phosphates have been described in detail by Clearfield et al.,[1] and the mechanism of the intercalation of quaternary ammonium ions was reported in our previous paper.[8]

Some organic cations, such as quaternary ammonium ions, cannot be readily intercalated into layered phosphates, due to the weak electrostatic force and steric hindrance around the active site of the cation. In such a case, the use of alkylamine intercalation compounds has been proposed as means for the intercalation of other guest compounds which are not directly intercalated.[1] Practically, the intercalation of enzymes with large molecular weights was achieved by using this method.[9] The mechanism of this intercalation reaction has been based on the phenomenon that delamination occurs in the reaction of zirconium bis(hydrogenphosphate) monohydrate $Zr(HPO_4)_2 \cdot H_2O$ or γ-titanium phosphate $Ti(PO_4)(H_2PO_4) \cdot 2H_2O$ with an aqueous propylamine solution, and gives a colloidal solution of phosphate.[10] In Kanzaki's paper,[9] the success of the intercalation by two procedures was reported. One involves a procedure in which enzymes are reacted with a colloidal solution of γ-titanium phosphate, which was prepared in an aqueous propylamine solution; the second is that γ-titanium phosphate is reacted with a mixed solution of enzyme and propylamine. However, even butylamine, which didn't give a colloidal solution, contributed to the intercalation of guest compounds, being not able to be intercalated into the layered phosphate. Although it has been considered that this is due to an expansion of the interlayer distance of the layered phosphate, the detailed mechanism of this reaction has not yet been clarified. Clarifying the process of the intercalation in this system and the function of alkylamine other than propylamine in the intercalation reaction is very interesting and significant for the practical application of this method.

In the present study, the intercalation of methylene blue as a guest compound into layered phosphates was examined in the presence of butylamine. Methylene blue is a typical thiazine dye, and is well used as a stain in bacteriology, an oxidation–reduction indicator, and a disinfectant. Hence, the intercalation of methylene blue into inorganic host materials may lead to new functional materials with antibacterial action and good thermal stability.

Experimental

Chemicals. Layered phosphates, zirconium bis(hydrogenphosphate) monohydrate $Zr(HPO_4)_2 \cdot H_2O$ (abbreviated as α-ZrP), α- and γ-titanium phosphates $Ti(HPO_4)_2 \cdot H_2O$ (α-TiP) and $Ti(PO_4)(H_2PO_4) \cdot 2H_2O$ (γ-TiP), and aluminum dihydrogentriphosphate dihydrate $AlH_2P_3O_{10}\cdot 2H_2O$ (AlP), were prepared according to procedures described in previous papers.[4,11—13] Methylene blue (MB) was of reagent grade from Chroma Gesellschaft Schmid & Co. All other chemicals were of guaranteed reagent from Wako Chemical Industries Ltd. (Osaka, Japan).

Intercalation Procedures. The direct intercalation of MB into layered phosphates was not successful. Therefore, the following two procedures with butylamine (BA) were employed.

Procedure [1]: Prior to the intercalation of MB, BA was preintercalated into a layered phosphate. BA intercalation compounds were obtained by reactions of layered phosphates (5.0 g) with 0.1 dm^3 of 0.02, 0.04, 0.1, 0.2, and 0.3 mol dm^{-3} aqueous BA solution, that is, 0.4, 0.8, 2.0, 4.0, and 6.0 mmol BA were added per g of layered phosphate, and the suspended solution was stirred at room temperature for 5 h.

Procedure [2]: The reactions of the layered phosphates with MB were carried out in the presence of 0.4—6.0 mmol BA per g of layered phosphate similarly to Procedure [1].

In both procedures, 5.0 g of the host compound (the BA intercalation compound in Procedure [1] or layered phosphate in Procedure [2]) was suspended in 0.1 dm^3 of a 1 wt% aqueous MB solution in an Erlenmeyer flask, and a suspension was stirred at 70 °C for 5 h. The resultant product (called Products [1] and [2] in Procedures [1] and [2], respectively) was filtered, washed with distilled water, and dried in air.

In regard to methylamine and 1,4-butanediamine, which were used instead of BA, 5.0 g of α-ZrP was reacted with a 0.1 dm^3 of 1 wt% aqueous MB solution in the presence of 2.0 mmol amine per g of α-ZrP according to Procedure [2].

Analytical Procedures. X-Ray diffraction patterns were measured with a Rigaku Geigerflex 2011 using Ni-filtered Cu *Kα* radiation to monitor all new phases and to determine their interlayer spacings. A Rigaku Denki Differential Thermogravimetric Analyzer (TG 8110), was used for DTA and TG measurements with a platinum–rhodium pan in an air flow. Elemental analyses of C and N in the cointercalation compounds were performed by a Sumigraph NC-90A.

A Bruker MSL-200 spectrometer operating at 81.0 MHz for the ^{31}P nucleus and at 50.3 MHz for the ^{13}C nucleus was used to measure the solid state NMR of the intercalation compounds. A single-pulse sequence with a $\pi/2$ pluse of 2 μs was used to obtain ^{31}P MAS with ^{1}H high-power decoupling. For the ^{13}C CP/MAS spectra a recycle time of 4 s and the accumulation of up to 2400 scans were used. The Magic Angle Spinning (MAS) rate was 3—4 kHz. The chemical shifts for ^{13}C and ^{31}P were measured in comparison with tetramethylsilane and 85% orthophosphoric acid, respectively.

Results

Effect of BA on the Intercalation of MB. Direct intercalations of MB into layered phosphates (α-ZrP, α-TiP, γ-TiP, and AlP) were not successful. Consequently, the intercalation of MB was attempted by using BA in both Procedures [1] and [2]. Although the colors of the products obtained without BA were pale blue, those of the products with BA were deep blue, presuming that the latter contained more MB than the former.

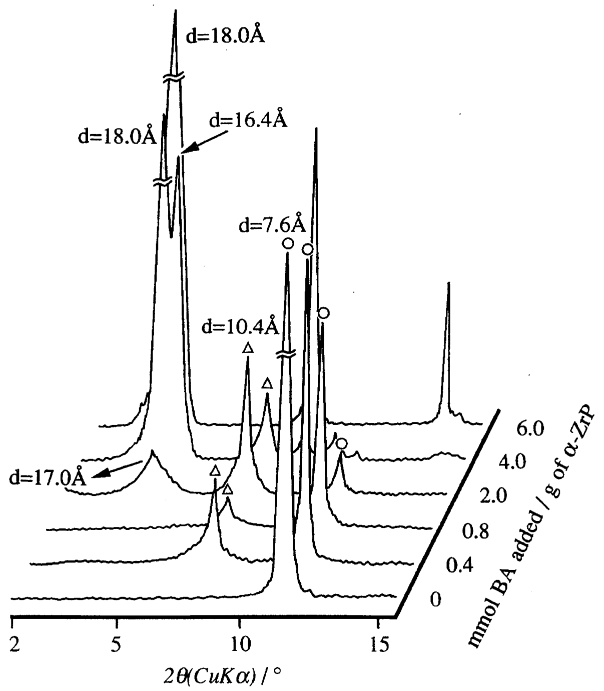

Fig. 1. X-Ray diffraction patterns of BA intercalation compounds of α-ZrP prepared by the Procedure [1].

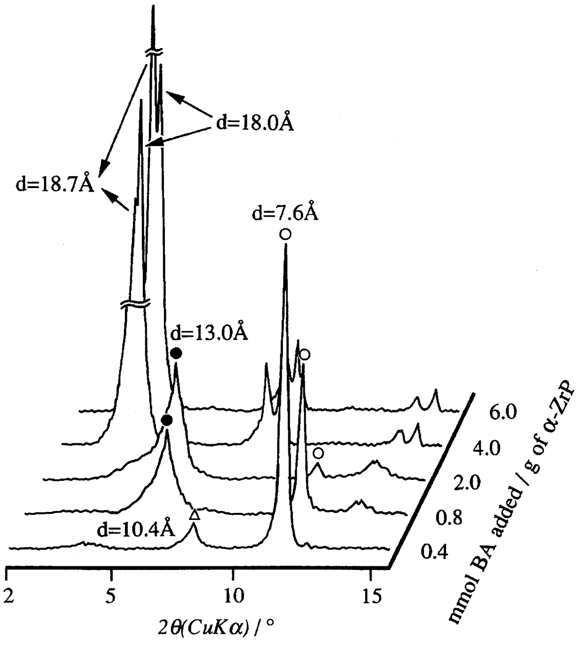

Fig. 2. X-Ray diffraction patterns of MB-BA cointercalation compounds of α-ZrP prepared by the Procedure [1].

The intercalation of MB into a layered phosphate was proved by X-ray diffraction pattern, NMR spectra, a differential thermal analysis (DTA), and an elemental analysis. In the X-ray diffraction patterns of Products [1] and [2] from α-ZrP, a new peak due to the formation of a MB-BA cointercalation compound was observed (Figs. 1, 2, and 3). Details are described later. In Products [1] and [2] from γ-TiP, a slight low-angle shift in the diffraction peak was recognized, suggesting the intercalation of MB into γ-TiP. On the other hand, for α-TiP and AlP, the intercalation of MB could not be clearly proved from the X-ray diffraction pattern, due to the formation of an amorphous phase.

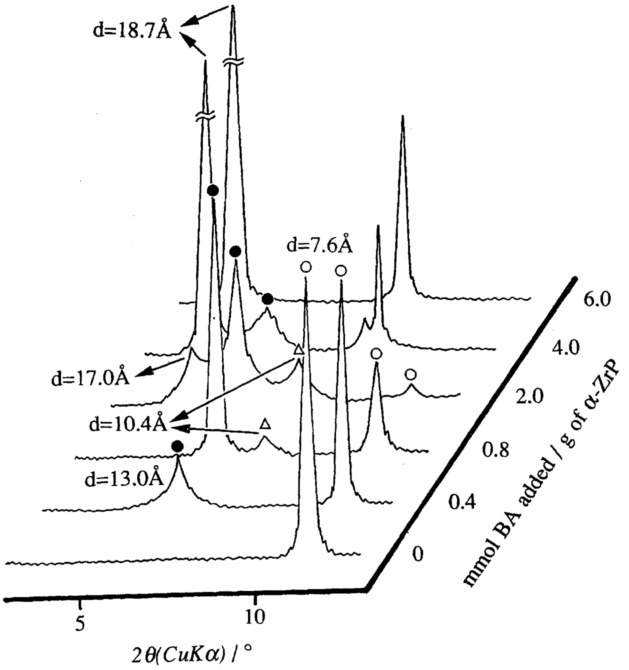

Fig. 3. X-Ray diffraction patterns of MB-BA cointercalation compounds of α-ZrP prepared by the Procedure [2].

The DTA curves of Products [1] and [2] differed from those of the BA intercalation compounds of layered phosphates. Figure 4 shows DTA and TG curves for the MB-BA cointercalation compound of α-ZrP prepared by Procedure [2]. In the DTA curve of α-ZrP (Fig. 4a), two endothermic peaks due to the dehydration on the water of crystallization appeared at about 150 and 200 °C, and an endothermic peak due to the dehydration of structural water appeared at 590 °C.1)

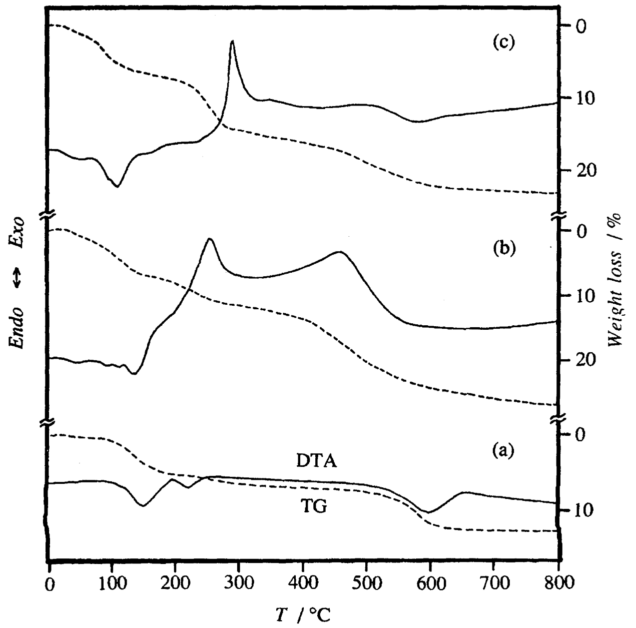

Fig. 4. DTA and TG curves of α-ZrP, MB-BA cointercalation compound of α-ZrP, and BA intercalation compound of α-ZrP prepared by the Procedure [2]. (a) α-ZrP, (b) MB-BA cointercalation compound, (c) BA intercalation compound.

A large exothermic peak appeared at about 290 °C in the DTA curve of the BA intercalation compound (Fig. 4c), suggesting that the BA which intercalated into α-ZrP was decomposed at this temperature. On the other hand, in the DTA curve of MB-BA cointercalation compound, as shown in Fig. 4b, two exothermic peaks appeared at about 250 and 460 °C. These peaks must be ascribable to the thermal degradation of MB and BA intercalated in α-ZrP. Similar results were obtained for Porduct [1] from α-ZrP and products from the other layered phosphates, except for AlP. These imply that MB was able to be cointercalated into α-ZrP, α-TiP, and γ-TiP in the presence of BA.

The contents of MB in the products were determined by elemental analyses of C and N to further clarify the intercalation of MB and to compare Procedures [1] and [2]. Table 1 shows the contents of MB in the products (2.0 mmol BA added/g of layered phosphate). Although the contents of MB in the products obtained without BA were nearly zero, those with BA increased appreciably. In the intercalation of MB into AlP, however, BA was not effective. The contents of MB in Products [1] and [2] of AlP were as few as those in the other layered phosphates without BA. In comparing Products [1] and [2], few differences in the contents of MB in the MB-BA cointercalation compounds were found, except for α-TiP. The content of MB in Products [2] from α-TiP was about three-times as large as that in Product [1]. The reason has not yet been clarified.

In addition, the contents of BA in the MB-BA cointercalation compounds are also listed in Table 1. Surprisingly, the intercalation of BA was inhibited by the presence of MB. In Procedure [1], BA once intercalated into the layered phosphates (the contents of BA in the BA intercalation compounds used as host are listed on the right column in Table 1) was extruded based on the intercalation of MB.

Intercalation of MB into α-ZrP in the Procedure [1]. In order to clarify the process of the above-mentioned intercalation reaction, the intercalation of MB into α-ZrP in Procedures [1] and [2] was examined in detail by varying the amount of BA added.

Figure 5 shows the contents (wt% for layered phosphate)

Table 1. Contents of Methylene Blue (MB) in the Intercalation Compounds

Phosphate	Content/mmol g^{-1}			
	MB			
	wihtout BA	with BA[a)] Procedure (1)	with BA[a)] Procedure (2)	BA
α-Zr(HPO$_4$)$_2$·H$_2$O	0.03	0.57 (1.04)	0.49 (1.24)	1.81
α-Ti(HPO$_4$)$_2$·H$_2$O	0.07	0.23 (0.12)	0.60 (0.44)	1.12
γ-Ti(HPO$_4$)$_2$·2H$_2$O	0.01	0.56 (0.77)	0.63 (1.19)	1.62
AlH$_2$P$_3$O$_{10}$·2H$_2$O	0	0.09 (1.11)	0.10 (0.42)	1.40

a) ( ) shows the contents of BA in the MB-BA cointercalation compounds.

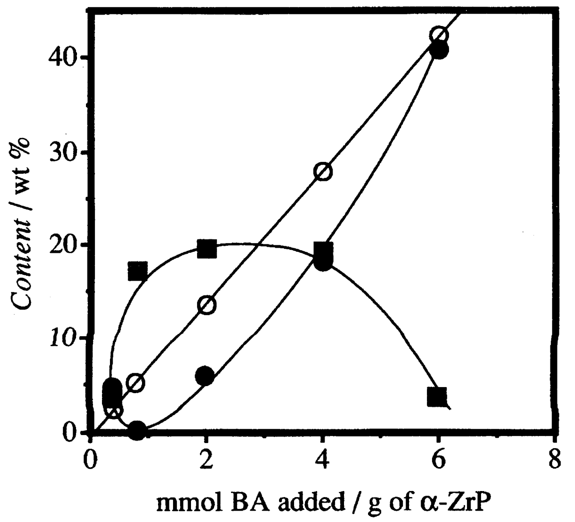

Fig. 5. Relationship between an amount of BA added and contents of (○) BA in the BA intercalation compound α-ZrP, and (■) MB and (●) BA in the MB-BA cointercalation compound of α-ZrP, in the Procedure [1].

of BA in the BA intercalation compounds, as well as those of BA and MB in the MB-BA cointercalation compounds obtained by Procedure [1]. The content of BA (opened circle) in the BA intercalation compound used as the host linearly increased with increasing the amount of BA added. On the other hand, in the MB-BA cointercalation compound, the content of MB (closed quadrate) increased once and then decreased, and the content of BA (closed circle) approximately agreed with that in the BA intercalation compound.

These facts were also observed based on the ^{13}C NMR spectra. Figure 6 shows the ^{13}C CP/MAS spectra of BA intercalated into α-ZrP, and of the BA-MB cointercalation compound. For BA intercalated into α-ZrP the peaks due to the CH_3– and –CH_2– groups appeared from 10 to 40 ppm. The intensity of these peaks increased linearly with increasing the amount of BA added. In addition to these peaks, extra peaks due to MB appeared between 100 and 150 ppm, and another peak was recognized at 43 ppm for BA-MB cointercalation compounds. The intensity of these peaks assigned to MB was approximately constant at 0.8, 2.0, and 4.0 mmol of BA added, and decreased at 6.0 mmol of BA added. Comparing the spectra with and without MB, the

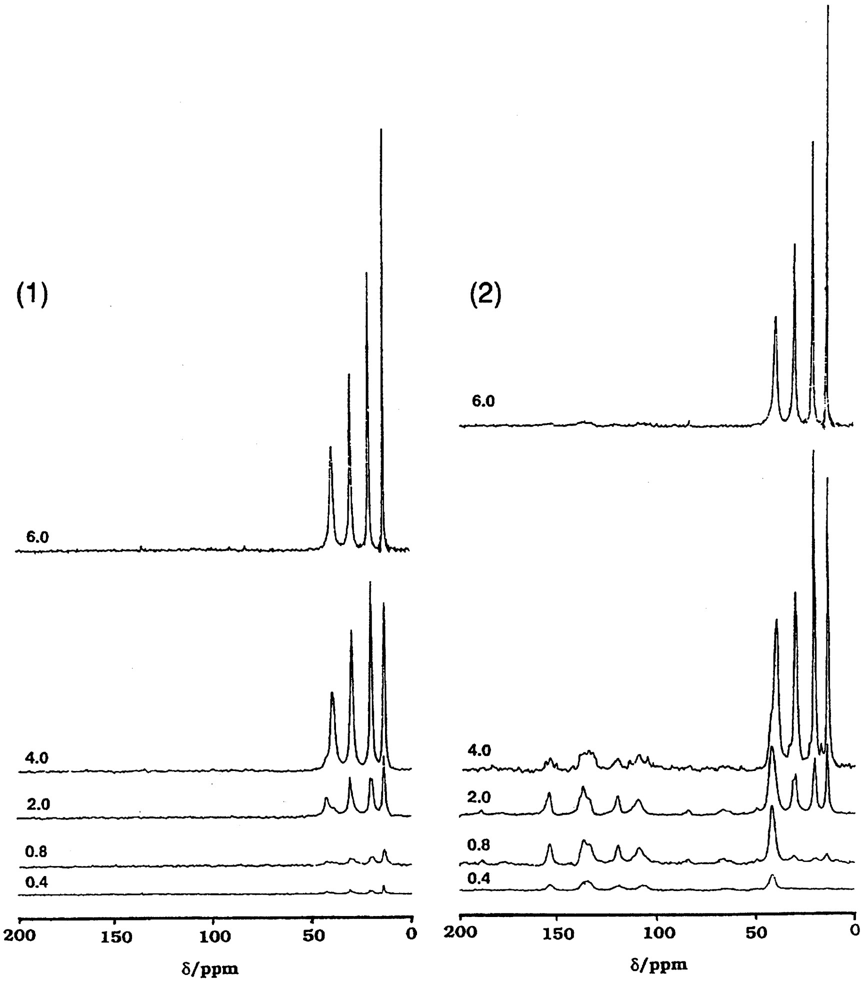

Fig. 6. ^{13}C CP/MAS NMR spectra of (1) BA intercalated into α-ZrP and (2) BA-MB cointercalation compound. Numbers in the figure show the amount of BA added (mmol) per g of α-ZrP.

addition of MB to the system resulted in a decrease in the peak intensity of BA. This tendency is obvious at 0.4 and 0.8 mmol of BA added.

These results suggest that the intercalation of MB is accelerated by using the BA intercalation compound as a host, but is inhibited by containing too much BA; also, BA once intercalated into the layered phosphate is extruded by the intercalation of MB.

Further, a variation of the phases existing in the above samples was observed based on the X-ray diffraction patterns (Figs. 1 and 2). The phases in the BA intercalation compounds were varied by changing the amount of BA added (Fig. 1). With an increase in the amount of BA, the peak for α-ZrP ($d=7.6$ Å, opened circle) gradually decreased in intensity, and new other peaks appeared. Taking account of each interlayer distance, the peaks at $d=10.4$ (opened triangle) and 16.4—18.0 Å must be due to the BA intercalation compounds in which BA forms a monolayer and bilayers in the interlayer region, respectively.[14]

Figure 2 shows the X-ray diffraction patterns of MB-BA cointercalation compounds prepared by Procedure [1]. In the higher content of MB (0.8—4.0 mmol BA added/g of α-ZrP), the peaks ($d=10.4$, 16.4, and 17.0 Å) due to the BA intercalation compound disappeared. These phases were converted into other phases with different interlayer distances by insertion of MB. In 0.8 and 2.0 mmol BA added per g of α-ZrP, a phase with $d=13.0$ Å was formed. In this phase, a part of BA which previously formed a monolayer was extruded from the interlayer region, and MB coexisted with residual BA while maintaining a monolayer structure, by taking account of the results from Fig. 5. In 4.0 mmol of added BA, since a peak at $d=13.0$ Å did not appear, MB should be present in those phases with $d=18.0$ and/or 18.7 Å. In 6.0 mmol, a phase with $d=18.7$ Å appeared in addition to that with $d=18.0$ Å. The states of MB and BA in the phase can be closely confirmed by investigating the ^{13}C CP/MAS spectra of BA and by measuring the ^{31}P MAS spectra.

According to the solution NMR data, the ^{13}C isotropic chemical-shift values of alkylamines varied along with the protonation.[15] Figure 7 shows the ^{13}C CP/MAS spectra of the BA intercalation compound. The ^{13}C isotropic chemical-shift values of BA depended on its concentration. At a higher concentration (> 2.0 mmol) of BA, δ (^{13}C) values of α (40.6 ppm), β (29.9 ppm), γ (20.3 ppm), and δ (14.3 ppm) carbons corresponded to those of protonated BA from the solution NMR data. At a lower concentration (< 2.0 mmol), the δ (^{13}C) values of α (42.1 ppm), β (36.2 ppm), γ (21.1 ppm), and δ (14.8 ppm) carbons coincided with those of the base BA of the solution NMR data. Therefore, the bilayer structure contains protonated BA, whereas the monolayer structure has non-protonated BA. This tendency was the same for a BA-MB cointercalation compound.

The binding state between amine and phosphate can also be confirmed by the ^{31}P MAS NMR. The ^{31}P MAS NMR

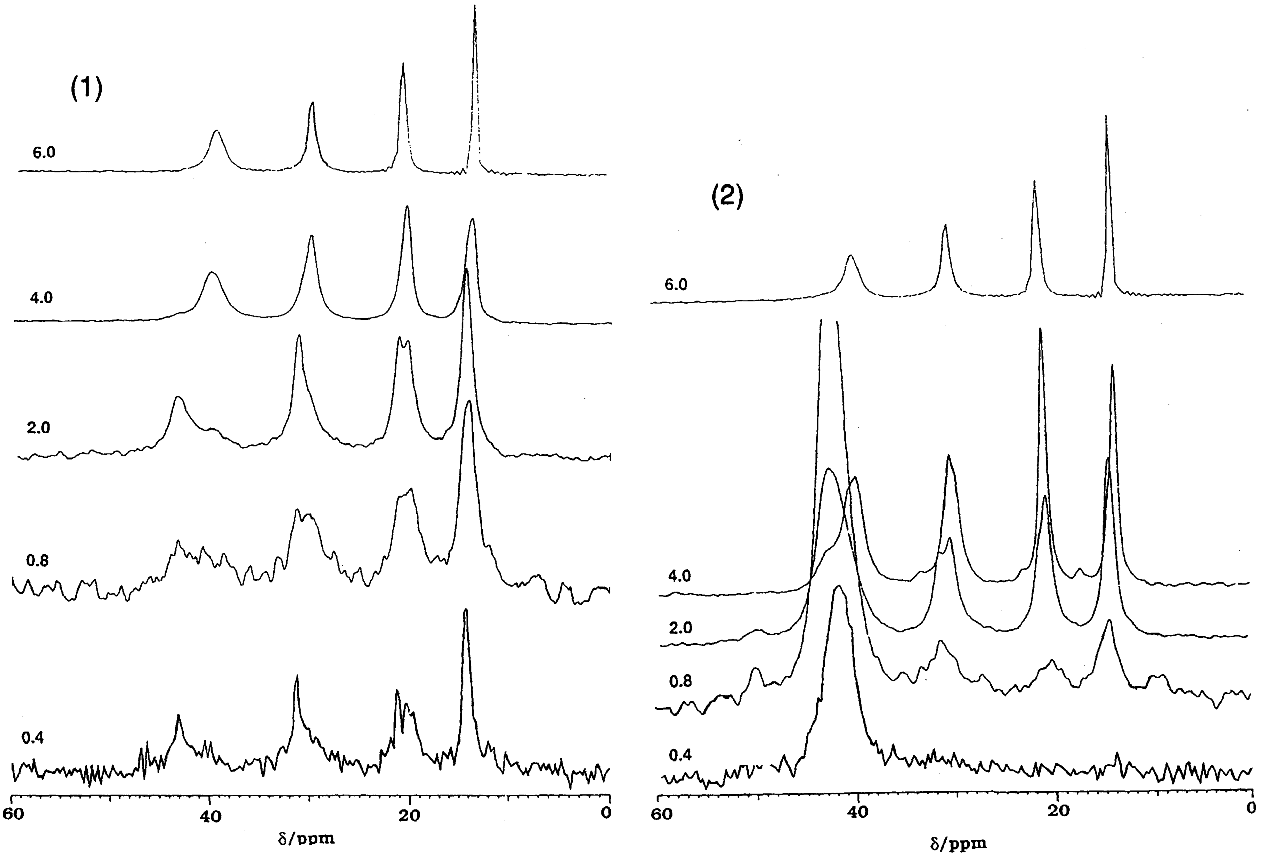

Fig. 7. ^{13}C CP/MAS NMR spectra of (1) BA intercalated into α-ZrP and (2) BA-MB cointercalation compound in the range between 0 and 60 ppm. Numbers in the figure show the amount of BA added (mmol) per g of α-ZrP.

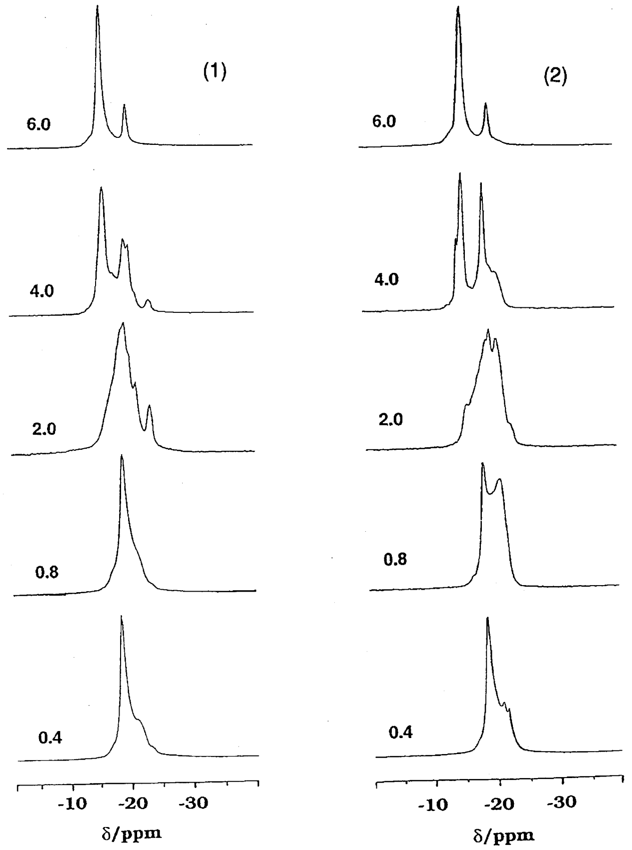

Fig. 8. ^{31}P MAS NMR spectra with ^{1}H high power decoupling of (1) BA intercalation compound and (2) BA-MB cointercalation compound of α-ZrP. Numbers in the figure show the amount of BA added (mmol) per g of α-ZrP.

spectra of the BA intercalation compound and the BA-MB cointercalation compound are shown in Fig. 8. These spectra were very complicated due to the superimposed spectra of BA intercalation compounds with the bilayer and monolayer structures, the BA-MB cointercalation compound, and non-reacted α-ZrP. Although it is difficult to assign all of the peaks unambiguously, MacLachlan et al.[14,16)] investigated the ^{31}P MAS NMR spectra of the BA intercalation compound of α-ZrP in detail. From their analysis, the peak at -15.0 ppm at a concentration above 4.0 mmol can be assigned to a BA intercalation compound with the bilayer structure, where only this structure phase is seen in the X-ray diffraction pattern. In the intermediate region (2.0 mmol) of the concentration it is very hard to assign broad peaks correctly, because of the presence of the mixture phases. The broad peak at around -20 ppm in Fig. 8-(1) might be due to the phosphate of the monolayer structure. In the case of the BA-MB cointercalation compound, a new peak of phosphate appeared at -21.3 ppm. Therefore, it is found that the peaks of BA intercalation compounds with the bilayer and monolayer structures shifted by +3.7 ppm and -1.3 ppm from the peak of α-ZrP (-18.7 ppm), respectively, and that the peak of the BA-MB cointercalation compound shifted by -2.6 ppm. According to an investigation of the effect of the deprotonation of HPO_4^{2-}, the ^{31}P MAS spectra move to a low field on deprotonation.16) Thus, HPO_4^{2-} in the BA intercalation compound with the bilayer structure shows deprotonation, whereas the HPO_4^{2-} sites in the monolayer structure and the BA-MB cointercalation compound show no deprotonation. These ^{13}P MAS data were consistent with the results based on the ^{13}C CP/MAS spectra.

Intercalation of MB into α-ZrP in the Procedure [2]. Figure 9 shows the contents of BA and MB in the MB-BA cointercalation compounds obtained by Procedure [2]. These results are approximately similar to those based on Procedure [1] (Fig. 5). The intercalation of MB is accelerated by the coexistence of BA, but inhibited by too much BA.

Figure 3 shows the X-ray diffraction patterns of the MB-BA cointercalation compounds obtained by Procedure [2]. The peak at $d = 13.0$ Å, which is obviously different from those of the BA intercalation compound, must be due to the formation of the MB-BA cointercalation compound similarly to that in Procedure [1]. On the other hand, the phase at $d = 10.4$ Å, where BA forms a monolayer in and disappeared in the Product [1], remained in 0.8 and 2.0 mmol BA added/g of α-ZrP, and that at $d = 18.0$ Å which appeared in Product [1], disappeared in 4.0 and 6.0 mmol BA added.

Discussion

Function of Alkylamine in the Intercalation of MB. The function of alkylamine in the intercalation of MB into layered phosphates was examined by using methylamine and 1,4-butanediamine instead of butylamine according to Procedure [2]. The contents of MB in MB-amine cointercalation compounds are summarized in Table 2. As can be seen, 1, 4-butanediamine scarcely accelerated the cointercalation of MB. It is responsible for the arrangement of 1,4-butanediamine in the interlayer region of the layered phosphates. Diamines form a monolayer in the interlayer region of the layered phosphates by bridging between the P–OH groups of the adjacent layers.17) The layers of the diamine intercalation compounds must be more strongly held than those of

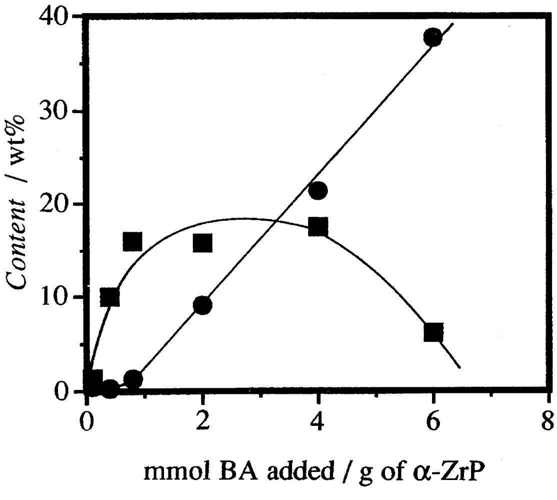

Fig. 9. Relationship between an amount of BA added and contents of (■) MB and (●) BA in the MB-BA cointercalation compound prepared by the Procedure [2].

Table 2. Contents of Methylene Blue (MB) in the Intercalation Compounds

Pillar	pH	MB Content/mmol g^{-1}			
		α-ZrP	α-TiP	γ-TiP	AlP
CH_3NH_2	11.8	0.24	0.50	0.40	0.09
$CH_3(CH_2)_3NH_2$	11.8	0.49	0.60	0.63	0.10
$H_2N(CH_2)_4NH_2$	11.9	0	0.01	0.01	0
without Pillar	2.8	0.03	0.07	0.01	0

alkylamine intercalation compounds. Therefore, diamines are not suitable as an accelerator in the intercalation of MB into layered phosphates. On the other hand, methylamine gave an effect upon the intercalation of MB as much as did butylamine, in spite of the narrower expansion of the interlayer distance of layered phosphate by methylamine than butylamine and 1,4-butanediamine (in the case of α-ZrP, the interlayer distances of the methylamine and 1,4-butanediamine intercalation compounds are 9.6 and 13.6 Å, respectively, and that of the MB-methylamine cointercalation compound is 12.6 Å). Thus, although expanding the interlayer distance of layered phosphate is thought to be one of the important functions of alkylamine, a more important factor which influences the intercalation of MB is the arrangement and flexibility of amine in the interlayer region, rather than the expanded interlayer distance.

Mechanism of Intercalation Reaction in the Presence of BA. We discussed the mechanism of MB-BA cointercalation system in Procedure [1], in accordance with the conception of protonation state and the butylamine orientations for each phase proposed by MacLachlan et al.[14] It was proved that the interlayer phosphates were protonated in the 10.4 Å phase in which BA forms a monolayer, and deprotonated in the other phases in which BA forms bilayers by ^{13}C CP/MAS NMR spectra and ^{31}P MAS NMR. Since BA in the interlayer is regarded as being mobile on the protonated phosphate group, that is, in the 10.4 Å phase, BA was easily extruded from the interlayer region and MB was held in the space constructed by a part of BA leaving. However, even in the phase with deprotonated phosphate, the intercalation of MB occurred. It is possible to be explained by the orientation of BA in each phase. In the 16.4 Å phase, there is comparatively more space in the interlayer region, assuming that BA adopts the orientation proposed in Ref. 14. Further, the orientation of BA can be converted into one that is more convenient than that for the intercalation of another molecule. In the 16.4 Å phase, therefore, MB inserts into the space constructed by BA intercalated previously, and BA reorients in a more stable configuration. In 6.0 mmol BA added, the phase with $d=18.7$ Å appeared in addition to that with $d=18.0$ Å, because of the formation of a stable reorientation of BA in the interlayer region. In these phases, the alkyl chain of BA had an even more upright orientation. Thus, the intercalation of MB into the BA intercalation compound is achieved by removing BA from the interlayer region in the phase in which BA forms a monolayer, and depends on the orientation of BA in the phase in which BA forms a bilayer.

On the other hand, since the reaction in Procedure [2] differs from that in Procedure [1] in the process or speed of intercalation of MB and BA, it is difficult for only these X-ray diffraction patterns to explain the mechanism of the intercalation reaction in Procedure [2]. However, it is thought that MB and BA adopt the most stable arrangement in the presence of each amount of BA, and lead to the MB-BA cointercalation compound having the same structure as that of Product [1].

Conclusion

The intercalation of MB into layered phosphates (α-ZrP, α-TiP, and γ-TiP) was successful by using BA, and Products [1] and [2] contained a similar MB-BA cointercalation phase in the structure of each other. The intercalation of MB was strongly influenced by the amount of BA used; that is, it was accelerated by the presence of BA, but inhibited by the presence of too much BA. Moreover, in Procedure [1], it was found that the intercalation of MB into BA intercalation compound could be achieved by removing BA from the interlayer region in the phase in which BA forms a monolayer, which depends on the orientation of BA in the phase in which BA forms a bilayer. This is because the space which can accommodate the other molecule is different according to the orientation of BA.

Further, we succeeded to intercalate other guest compounds which could not be directly intercalated into layered phosphates. For example, although Rhodamine B, which is a dye with a quaternary ammonium ion structure, was not intercalated into α-ZrP, it could be intercalated into α-ZrP by using BA, leading to Rhodamine B-BA cointercalation compounds ($d=19.6$ Å) in which the contents of Rhodamine B and BA were 0.62 and 0.44 mmol per g of α-ZrP, respectively. Thus, this method will be applied to the intercalation of useful compounds which cannot be directly intercalated into layered phosphates.

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