The Intercalation of *n*-Alkylamines into Layered Transition Metal Phosphates-Solvent Effect

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The intercalation of *n*-alkylamines (carbon number 1—18) into γ-titanium phosphate and γ-zirconium phosphate was examined in aqueous, methanol, and benzene solutions. The interlayer spacings increased with an increase in the carbon number of alkylamines, showing the formation of bilayers of alkylamines in a similar manner to that in previous reports. The intercalation reaction depended on the solvents used to dissolve the alkylamines. For example, an anomaly was observed regarding intercalation in ethanol solutions. The interlayer spacings decreased when the carbon number exceeded 14—16, indicating a distortion or the monolayer formation of alkylamines. The rate of intercalation was also seriously affected by the kind of solvents. Intercalation occurred almost instantaneously in aqueous solutions. The rate of the intercalation reaction was generally faster in benzene solutions than that in ethanol solutions. The formation of bilayers was also more perfect in benzene solutions, and resulting interlayer spacings were slightly larger than those prepared in ethanol solutions. The anomaly in ethanol was attributed to a disturbance due to the cointercalation of methanol molecules. The solvent effect was also accountable due to the dielectric constant, or dipole moment, of solvents.

γ-Titanium phosphate ($Ti(HPO_4)_2 \cdot 2H_2O$: γ-TiP) and γ-zirconium phosphate ($Zr(HPO_4)_2 \cdot 2H_2O$: γ-ZrP) are known to have a layered structure with interlayer spacings of around 1.2 nm.[1,2] They can be compared with the corresponding α-phosphates, the interlayer spacings of which are about 0.76 nm.[3] These layerd compounds are insoluble acid salts and are known to be typical inorganic ion exchangers.[4] They can also intercalate various alkylamines or organic bases as host materials; their interlayer spacing increases corresponding to the geometric size of the guest intercalants. Among them, the intercalation of *n*-alkylamines has been examined extensively for intercalated alkylamine molecules forming well-established bilayers within the layered compond[5] similar to those of biological cell membranes.[6]

The procedure for the intercalation of alkylamines seems to have been definitely established according to previous studies.[5,7] However, such studies reported so far have treated the intercalation reaction too much ideally, and structural considerations of the final products have been of major interest. The detailed mechanisms for the intercalation reaction of alkylamines have not yet been clarified. For example, the roles of the acid-base reaction, ion exchange, and van der Waals forces acting on the Langmuir-type monolayer, etc. have not been treated properly. This paper mainly deals with the solvent effect on the intercalation reaction of *n*-alkylamines into γ-type transition metal phosphates, while discussing the mechanisms of the intercalation reaction in detail.

Experimental

Layered Materials. γ-TiP was prepared according to a procedure reported by Kobayashi et al.[1] Amorphous titanium phosphate prepared from phosphoric acid and titanium(IV) chloride was heated hydrothermally in 10 M phosphoric acid (1 M=1 mol dm^{-3}) for 24 h at 280 °C; a well crystallized H^+ form of γ-TiP was thus obtained (Fig. 1a). The crystal was carefully washed with de-ionized water and stored in a saturated NaCl desiccator. Two types of γ-ZrP (sodium ion form) were used in this study. One was obtained from Dai-ichi Kigenso Kogyo Co. Ltd., which was prepared under atmospheric pressure. The other was prepared hydrothermally at about 190 °C for 1 week according to a procedure by Yamanaka et al.[2] The H^+ form γ-ZrP was prepared by treating the Na^+ form of γ-ZrP with 1 M HCl untill free of sodium ions. After drying, the H^+ form of γ-ZrP was stored in a saturated NaCl desiccator. The empirical formula of the H^+ form of γ-TiP could be represented by $Ti(HPO_4)_2 \cdot 1.7—1.8H_2O$. γ-ZrP also had a similar content of the water of crystallization.

Intercalation of Alkylamines. *n*-Alkylamines with carbon numbers (C_n) from 1 to 18 were dissolved in water, methanol, benzene, etc. and were used for intercalation. The concentrations of *n*-alkylamines were 0.1 M (M=mol dm^{-3}) for C_n=1 to 10 and 0.05 M for C_n=14 to 18. Intercalation was carried out by immersing 3.6×10^{-4} moles of phosphates (0.1 g for γ-TiP and 0.117 g for γ-ZrP) in 20 ml of each *n*-alkylamine solution. The reaction time was varied from 0.5 h to 4 d (96 h) and the temperature was kept at 30±0.1 °C unless otherwise stated. The amount of intercalated amines was determined by acid-base titration with 0.1 M HCl methanol solution. The indicator used was a (bromocresol green+methyl red) mixture.

X-Ray Diffraction. The intercalation compounds were characterized using X-ray diffractometer with Mn filtered Fe-*Kα* radiation. *d*-Values of up to 7 nm (λ=0.193736 nm, 2-$\theta \geqq 1.5°$) were successfully measured with sufficient accuracy. The interlayer spacings (*d*-spacings) were determined by averaging the *d*-values of the integral sequence of hexagonally approximated (00*n*) planes.

Results

Table 1 shows crystallographic data of γ-type phosphates. Figure 1 (a—d) shows SEM photographs of

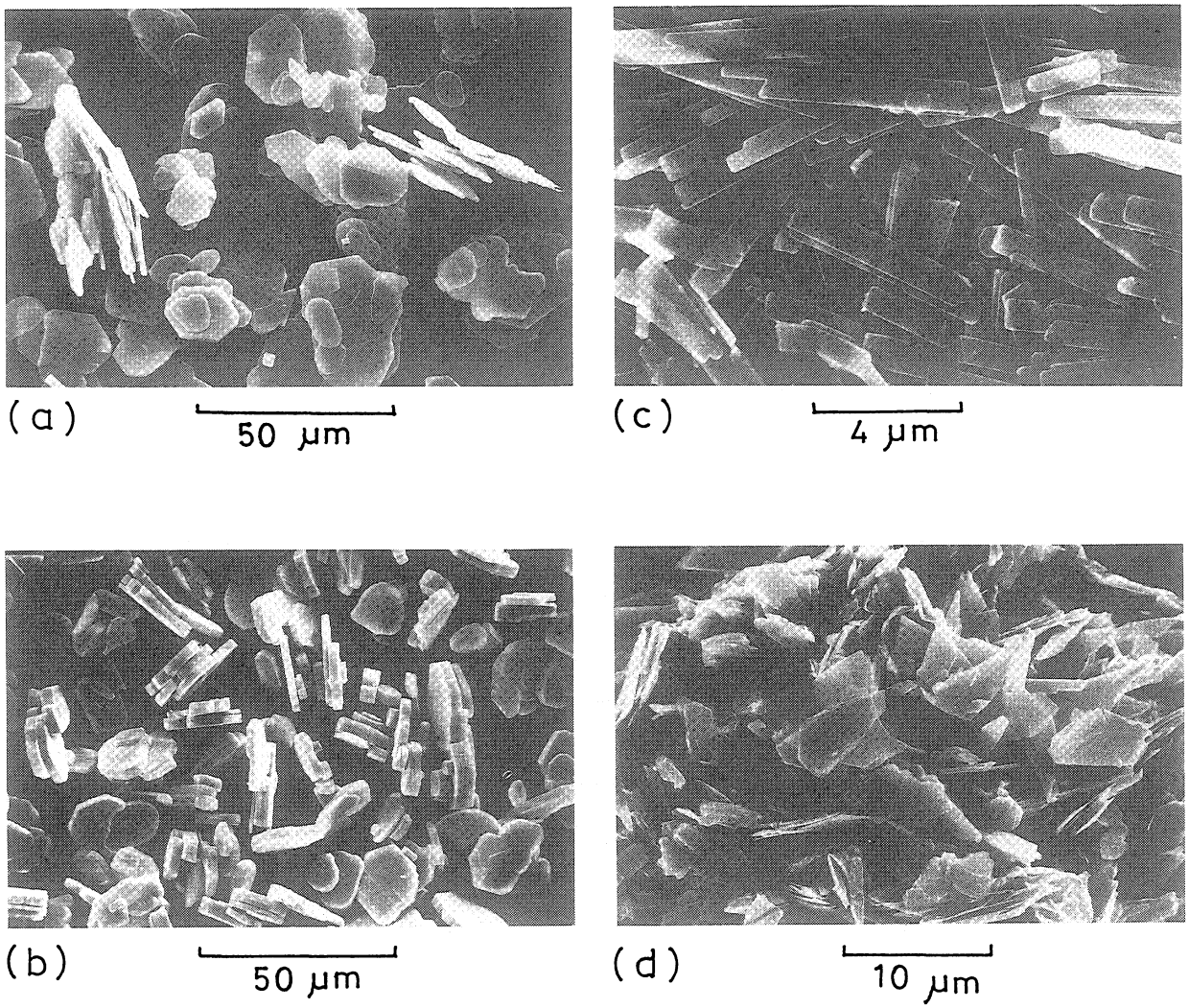

Fig. 1. SEM photographs of γ-TiP (a), octadecylamine intercalated (bilayer) γ-TiP (b), hydrothermal γ-ZrP (c), γ-ZrP supplied from Dai-ichi Kigenso Kogyo Co., Ltd. (d).

Table 1. Crystallographic Data of γ-Phosphates

	γ-TiP	γ-ZrP
System	Monoclinic[a)]	Monoclinic[b)]
a/nm	0.527	0.5376
b/nm	0.642	0.6636
c/nm	2.429	2.456
β/deg	102.5	93.94
Basal spacing/nm	1.16	1.225
Free area/nm^2	0.166	0.178

a) Ref. 1. b) Ref. 2.

the phosphates used. The appearances of the crystals are quite different from each other, even though they are classified as a monoclinic lattice with similar geometric dimensions. The X-ray diffraction pattern of hydrothermal γ-ZrP was quite similar to that of γ-ZrP prepared under atmospheric pressure, though they look quite different from each other. The γ-ZrP prepared under atmospheric pressure was mainly used for the hydrothermal γ-ZrP sometimes gave X-ray diffraction patterns which indicated the presence of mixed phases.

Solvent Effect on Butylamine Intercalation. Figures 2a and 2b show the time dependence of the uptake of butylamine in three different solvents. Intercalation into γ-TiP occurred almost instantaneously in aqueous and benzene solutions. On the other hand, it took three to four days to reach equilibrium in a methanol solution. The maximum uptake was in the order aqueous>benzene>methanol (Molality of protons in solid γ-TiP: 7.25 mmol g^{-1} and γ-ZrP: 6.27 mmol g^{-1}). The reaction was relatively slow in γ-ZrP, though the apparent solvent effect was similar to that in γ-TiP. The speed of the reaction rate in aqueous solution may be attributed to the (strong) basic property of butylamine in the solvent, which results in a neutralization reaction with strong solid acid γ-TiP.

A similar experiment was carried out for the alkylamines with C_n=1 to 18 in methanol solutions. The

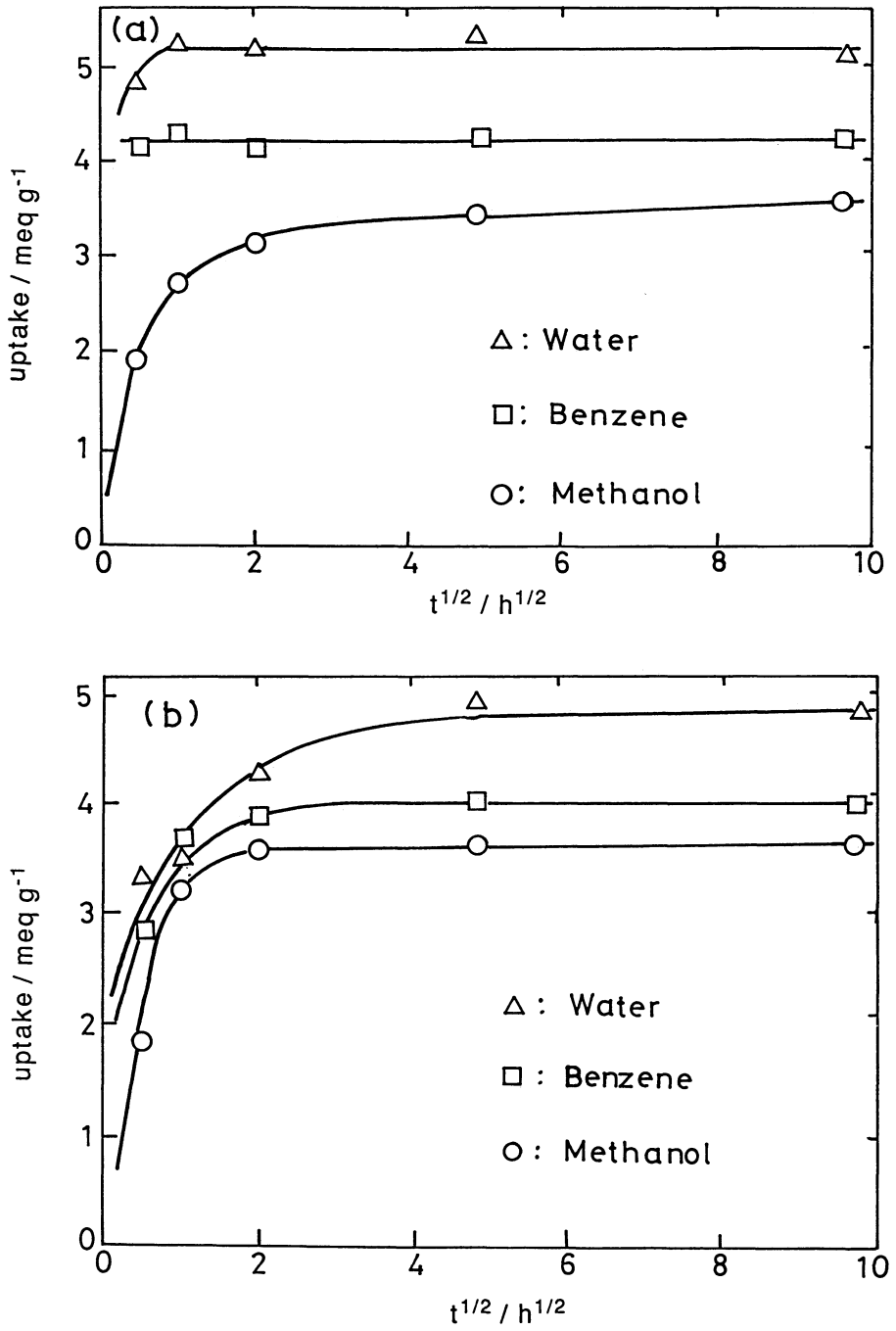

Fig. 2. Uptake of butylamine vs. reaction time in various solvents. (a) γ-TiP, (b) γ-ZrP. Absissa $t^{1/2}$ was taken for convenience and has no chemical significance (same as below).

results are shown in Figs. 3a and 3b. Generally speaking the rate of intercalation became slower as the alkyl-chain of the amines become longer. The intercalation of octadecylamine did not reach the equilibrium point, even after 4 d. The maximum uptake depends considerably on the length of the alkylamines and no easy finding regularity was observed. This fact may suggest a disturbance due to cointercalated methanol molecules. Figure 4 shows the uptake of butylamine into γ-TiP, which was pretreated (immersed) by pure methanol. It was found that the uptake decreased with increasing pretreatment time with methanol. This result suggested the co-intercalation of methanol[5] and, therefore, a disturbance due to the co-intercalated methanol. Figures 5a and 5b shows the results obtained in each benzene solution. The intercalation reached equilibrium points within two days, even in octadecylamine for either γ-TiP or γ-ZrP. The maximum uptakes were almost independent of alkylamines, suggesting a smaller disturbance due to the solvent molecules, unlike

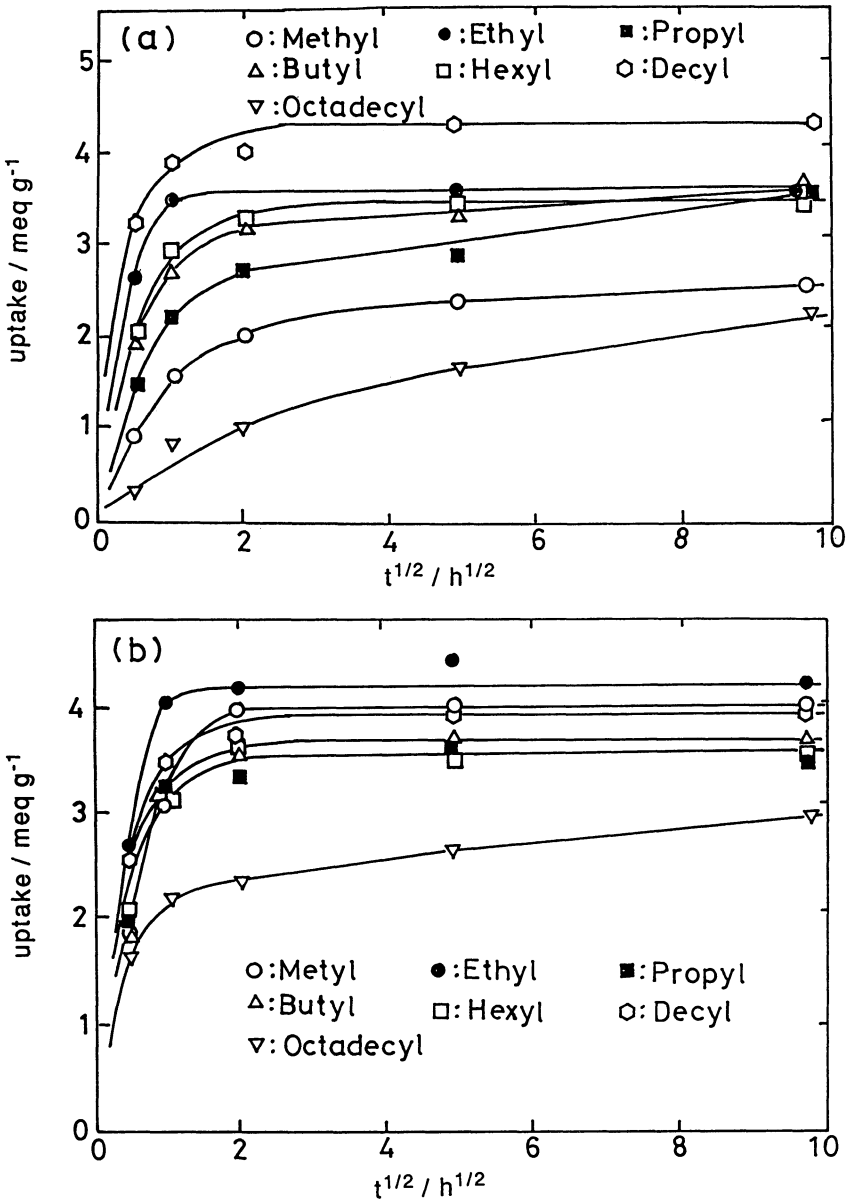

Fig. 3. Uptake of various amines vs. reaction time measured in methanol solutions. (a) γ-TiP, (b) γ-ZrP.

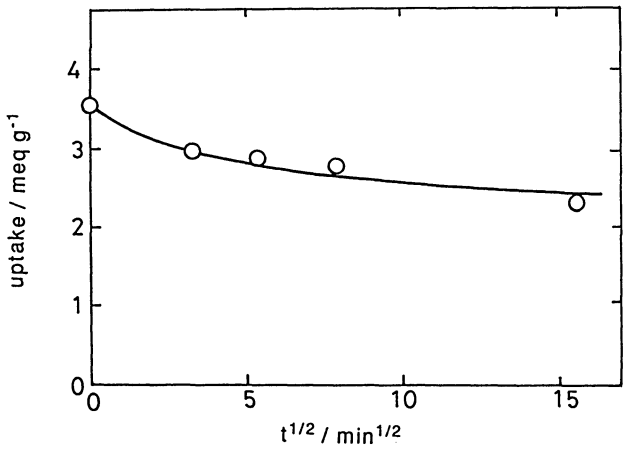

Fig. 4. Uptake of butylamine vs. suspension time in methanol.

those in methanol solutions.

Table 2 shows the amount of intercalated alkylamines [(mole of amine)/(mole of phosphate)] in the products for a reaction time of 4 d. Roughly speaking, the alkylamines intercalated in these phosphates amounted to about 1/2 of the active (or exchangable) protons in the host phosphates. The data obtained by Costantino[5] are listed in the same table for comparison. Our data are in good agreement with those reported by Costantino, except for some combinations (underlined). Small differences between the two data may be attributable to the difference in the preparation procedures of the γ-phosphates. The maximum uptakes were larger in the intercalates prepared in benzene solution than those in methanol solution, corresponding to the reaction rates in both solvents (Figs. 3a, 3b, 5a, 5b).

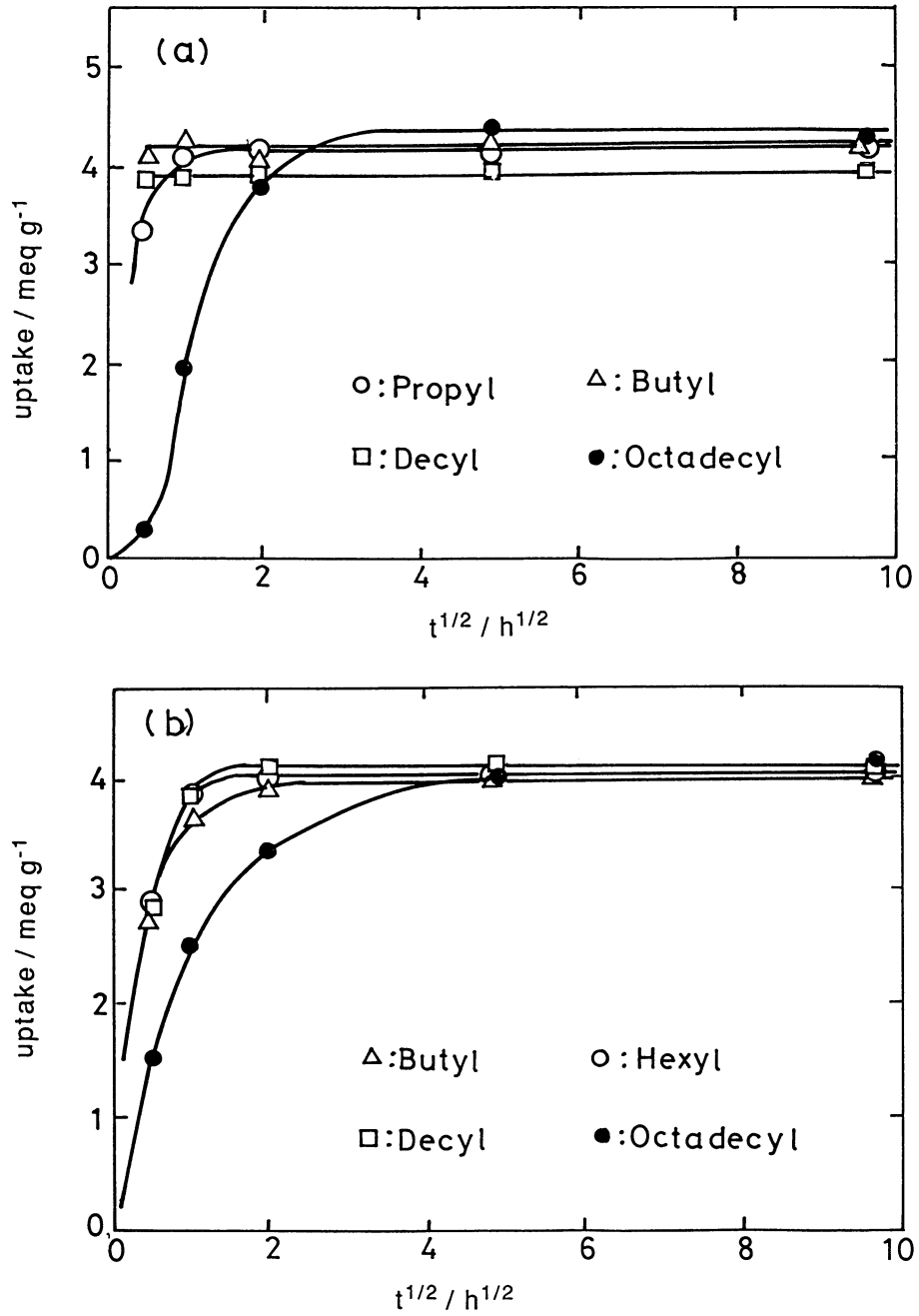

Fig. 5. Uptake of various amines vs. reaction time measured in benzene solutions. (a) γ-TiP, (b) γ-ZrP.

Table 2. Content of *n*-Alkylamine Intercalated in γ-Phosphates (moles/mole of γ-phosphate)

Amines	γ-TiP (Methanol)	γ-TiP (Methanol)[a)]	γ-TiP (Benzene)	γ-ZrP (Methanol)	γ-ZrP (Methanol)[a)]	γ-ZrP (Benzene)
Methylamine	0.71	—[b)]	—	1.26	—	—
Ethylamine	1.08	1.00	—	1.37	1.05	—
Propylamine	0.99	1.08	1.24	1.14	0.95	1.35
Butylamine	0.99	1.02	1.24	1.15	1.00	1.29
Hexylamine	0.95	—	1.15	1.16	—	1.31
Decylamine	1.14	0.93	1.17	1.28	1.05	1.34
Tetradecylamine	1.30	0.67	1.27	1.28	1.33	1.40
Hexadecylamine	1.25	0.58	1.25	1.04	1.33	1.31
Octadecylamine	0.60	0.64	1.24	0.96	1.33	1.33

a) U. Costantino, *J. Inorg. Nucl. Chem.*, **43**, 1895 (1981). b) Not measured.

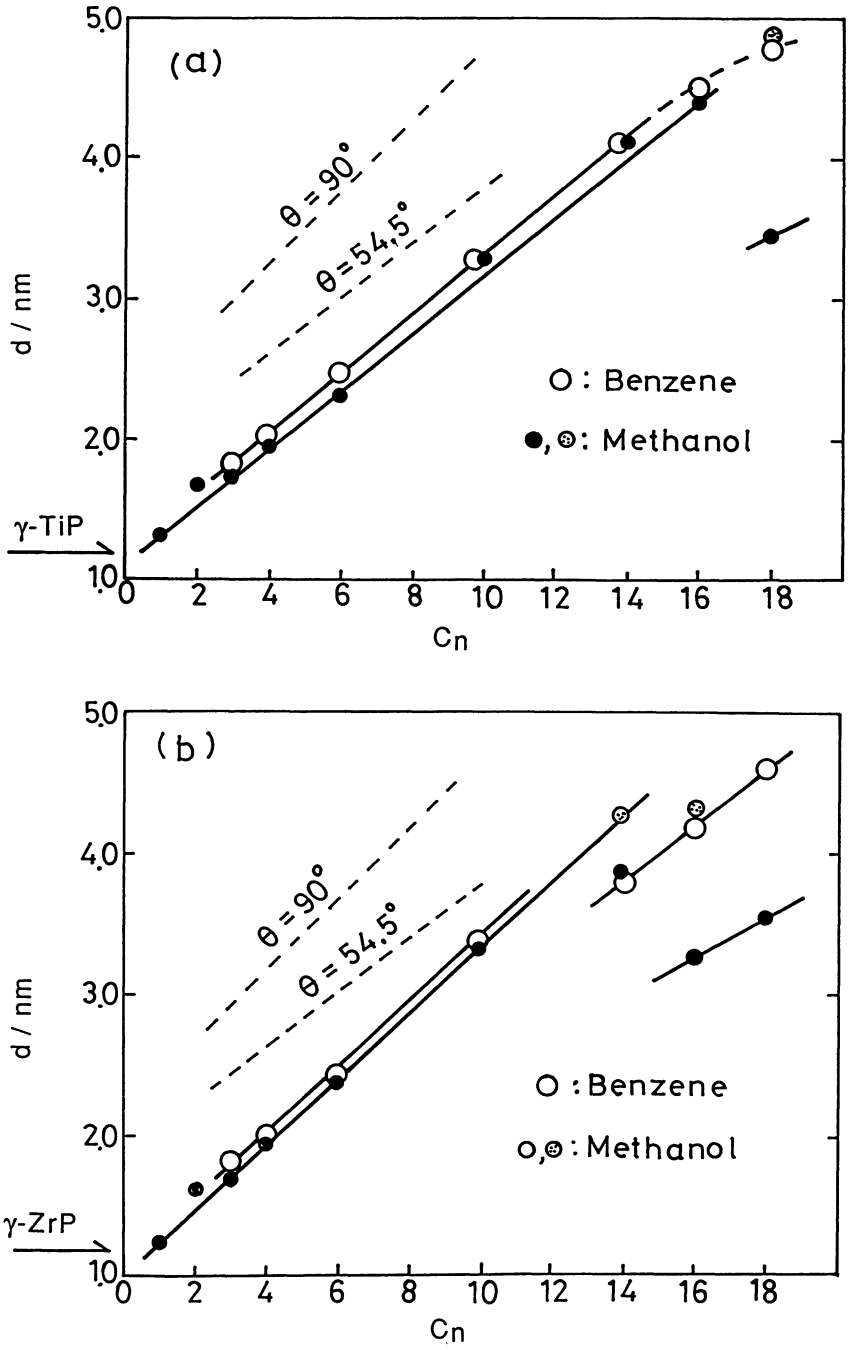

Fig. 6. *d*-Spacing (*d*) vs. number of carbon atom in *n*-alkyl chain (C_n).
(a) γ-TiP, (b) γ-ZrP.

Figures 6a and 6b show the *d*-spacings of the alkylamine intercalates corresponding to those in Table 2. The slope vs. number of carbon atoms (C_n) seems to be almost parallel to the theoretical slope (2×0.127 nm per carbon atom[5] which was estimated by assuming that the alkyl-chains were intercalated in a bilayer just perpendicular to the basal planes, for C_n lower than 10 (γ-ZrP in both solutions) and lower than 16 (γ-TiP, methanol) or 18 (γ-TiP, benzene). Above these carbon numbers, some distortion might have occurred, such as irregular bilayer formation, inclination, and kink-block distortions.[7] The *d*-spacings for the intercalates of γ-ZrP for C_n=16 and 18 prepared in methanol solution may indicate the formation of monolayer of these amines.

The temperature effect of the intercalation of alkylamines with carbon numbers 14, 16, and 18 was examined in order to clarify the cause of the above mentioned distortion. The combinations of γ-TiP with benzene and γ-ZrP with methanol were selected as to be ideal (no distortion) and non-ideal (much distorted) (Fig. 7), respectively. The bilayer products of γ-TiP were obtained in benzene solutions for temperatures ranging

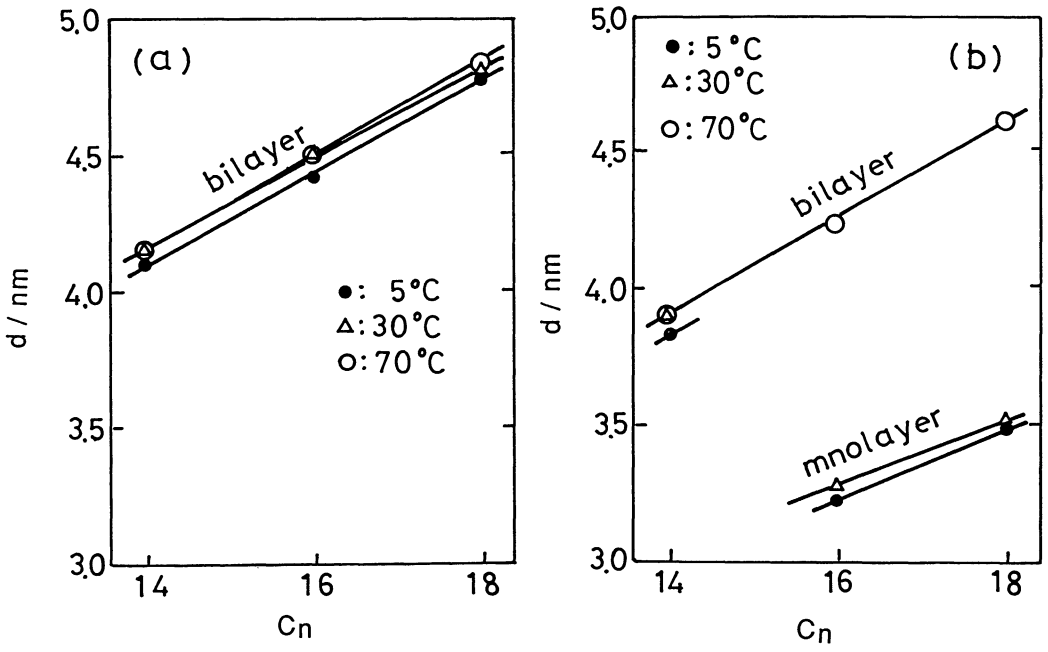

Fig. 7. Temperature dependence of *d*-spacing vs. number of carbon atom in alkyl-chain (C_n). (a) in benzene, (b) in methanol.

between 5 and 70 °C. On the other hand, bilayer products of γ-ZrP for carbon numbers 16 and 18 were obtained in methanol only for a sample prepared at 70 °C. Monolayer products were obtained at lower temperatures. It has been reported that the temperature rise up to this range caused an increase in kink-block distortion, resulting in a decrease in the *d*-spacings.[7] In the present study, however, it was found that the rise in temperature assisted in the formation of more perfect bilayers, presumably due to vibrational motion.

Comparison with Other Solvents. The facility of bilayer formation in the intercalation corresponding to the study illustrated in Fig. 7 (the rate and *d*-spacings) was examined in other solvents, xylene and propanol. Xylene and propanol showed intermediate properties between Figs. 7a and 7b. Thus, the order of facility for the intercalation of *n*-alkylamines was estimated to be as follows:

Benzene > Xylene > Propanol > Methanol

These results may suggest an effect of the dielectric constant of the solvent or the dipole moment of the solvent molecule in addition to the cointercalation of solvent molecules. The slow, imperfect intercalation reaction observed in methanol solutions suggests a strong solvation of the alkyl chain with polar methanol molecules, which may cause a slow desolvation on the occasion of the intercalation process, in addition to the co-intercalation effect stated above.

Ion Exchange and Acid-Base Reactions. The intercalation reaction of *n*-alkylamines into γ-phosphates is fundamentally an acid-base reaction. The ion-exchange reaction of decylammonium cations was examined in both methanol and aqueous solutions (Table 3). No ion-exchange reaction of decylammonium cations occurred in ethanol solution. This result suggests a poor dissociation of decylammonium chloride in the solvent. The *d*-values for the product by ion-exchange reactions of γ-TiP in aqueous solution were similar to that of decylamine intercalates in methanol, and showed the formation of a bilayer compound. On the other hand, the combination of γ-ZrP with decylammonium cations gave a monolayer inter-

Table 3. Interlayer Spacings of *n*-Decylamine and *n*-Decylammonium Ion Intercalates

Solvent	γ-TiP/nm		γ-ZrP/nm	
	Decylamine	Decylammonium	Decylamine	Decylammonium
Methanol	3.58 (Bilayer)	n.i.[a]	3.53 (Bilayer)	n.i.
Water	—[b] (Insoluble)	3.67 (Bilayer)	— (Insoluble)	2.80 (Monolayer)

a) Not intercalated. b) Intercalant was insoluble.

calate. These results indicate that the intercalation of *n*-alkylamines occurred more easily than did that of *n*-alkylammonium ions with a similar alkyl-chain; the intercalation of alkyl-chain was more accelerated by the acid-base reaction than that in an ordinary ion-exchange reaction.

Discussion

This study was designed to reveal that the intercalation of *n*-alkylamines should not be interpreted as being due solely to crystallographic, or visible, considerations regarding intercalated alkylamines, such as packing sequence, inclination of alkyl chain, and kink-block property. It was found from the present study that the crystallographic properties of *n*-alkylamines intercalated in layered compounds depend strongly on the conditions under which the intercalation reaction is carried out. This means that the crystallographic properties of intercalated alkylamines should not be interpreted only in terms of the final products. The crystallographic considerations reported so far should be reexamined by taking into account how they were prepared.

Packing Sequence. It has been proposed that alkyl chains in γ-phosphates are intercalated with an angle of 54.5°.[5] This study suggests, however, that alkyl-chains are intercalated almost perpendicular to the basal plane in γ-ZrP from carbon number 1 to 10 if the length of the carbon chain is assumed to be 0.127 nm/carbon and alkyl chains are closely packed without any distortion. Above that number, alkyl chains do undergo some distortion and, in some cases, intercalation occurs by forming monolayers. Alkylamines are to some extent inclinated in γ-TiP, though the angle is larger than 54.5°. However, it seems insignificant to determine the angle in detail only from the C_n vs. *d*-spacing curve, since the reproducibility of the *d*-value is rather poor and the error in determining the inclination would be large at high angles (near 90°).

Packing Density. It has been estimated that the free areas of the active site (exchangeable proton) are 0.166 and 0.178 nm^2 for γ-TiP and γ-ZrP, respectively (Table 1). The maximum uptake of alkylamines can not be estimated from the data obtained in ethanol solutions, but can be reasonably be estimated from the data obtained in benzene solutions. The number of alkyl-chains, thus estimated, are 1.22 and 1.33 chains per two active protons for γ-TiP and γ-ZrP, respectively (Table 2). This means that the packing density of the alkyl chains is 0.27 nm^2 (3.7 alkyl-chains per 1 nm^2) in both γ-TiP and γ-ZrP, which approaches the corresponding value 4.17 observed in α-ZrP.[7] It can be concluded, therefore, that the packing density is determined mainly by the cross section of the alkyl chain. The length of the alkyl chain and the free area of the active protons are less important. The kink-block distortion would also be less important if intercalation procedures were settled properly.

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