Intercalation of *n*-Alkylamines in Proton-Type Layered Titanium(IV) Oxide

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Intercalation of proton-type layered titanium(IV) oxides, $H_2Ti_5O_{11}\cdot xH_2O$ (H-TiO_2(A)) and $H_{0.7}Ti_{1.825}O_4\cdot xH_2O$ (H-TiO_2(B)), with *n*-alkylamines were examined for carbon numbers $n_c = 3$–18 in a benzene solution. The amount of intercalated *n*-alkylamines was about 1 mol per 1 mol of H-TiO_2(A) and well-defined X-ray diffraction patterns were observed for $n_c = 4$–14, reflecting the formation of a *n*-alkylamine bilayer between the layered lamellae. The alkyl chain in the bilayer was found to incline 66° against the basal plane. For $n_c = 3$, a fluffy suspended colloid appeared in the reactant solution and the amount of intercalated amines was about 2 mol per 1 mol of H-TiO_2(A), and weak X-ray diffraction peaks suggested the exfoliation and formation of the monolayer or several multilayer sheet of H-TiO_2(A). The size of the exfoliated colloid particles was examined using dynamic light scattering photometry. The scatter angle dependence suggested the shape of the colloid particles was a thin lamella and the average radius was estimated to be about 80 and 210 nm for propylamine and tetrabutylammonium hydroxide intercalation compounds prepared in aqueous solution, respectively. The shape of the colloid particles was rather isotropic and the radius was about 1.0 µm for a propylamine intercalation compound prepared in a benzene solution. The result of dynamic light scattering seems consistent with the exfoliation and following coagulation of layered lamellae of H-TiO_2(A).

Inorganic layered compounds are composed of atomic size thin lamellae that are piled vertically. Each layer is composed of atoms and ions that are combined by rather strong covalent and/or ionic bonds. These thin lamellae are built up through weak interactions such as van der Waals forces to form the layer structure. The layered materials can intercalate various inorganic and organic compounds between the layered lamellae by overcoming the weak interactions. Using the intercalation reaction as well as the acid–base neutralization reaction of the strong solid acid with the basic alkylamine, the authors have reported the solvent effect on the intercalation reaction of layered γ-titanium(IV) and γ-zirconium(IV) phosphates with *n*-alkylamines for $n_c = 1$–18 in different solvents. It was found that a well-defined bilayer of *n*-alkylamines was formed between the layered lamellae and the interlayer distance increased in proportion to the increase in the number of carbon atoms especially in nonpolar organic solvents such as benzene.[1]

On the other hand, it was found that the layers of α-zirconium(IV) phosphate exfoliated to form a dispersed monolayer colloid on occasion of the intercalation of propylamine in an aqueous solution and a flexible inorganic membrane was formed due to the reverse coagulation of the dispersed monolayers.[2] The authors have successfully intercalated enzymes of large molecular weight using the exfoliation phenomenon.[3,4] Proton-type layered titanium(IV) oxide of lepidocrocite form[5] is a weak solid acid and was also found to be exfoliated by the intercalation of tetrabutylammonium hydroxide to form colloidal nano-sheets.[6]

The intercalation reaction of alkylamines with layered titanates(IV) has been reported previously.[7–9] Exfoliation phenomenon as well as the solvent effect, however, have not been revealed satisfactorily. This study deals with the intercalation reaction of layered proton-type titanium(IV) oxide with various *n*-alkylamines in a benzene solution. The role of exfoliation was examined using dynamic light scattering photometry.

Experimental

Reagents. The reagents used in this study were all reagent grade. Deionized water was prepared using ion-exchange resins and a filtering system (Puric Model-R, Japan Organo Co., Ltd., Japan).

Proton-Type Titanium Oxide (H-TiO_2). Two kinds of lepidocrocite-type layered cesium titanium(IV) oxides was prepared in advance.[5] The first cesium titanium(IV) oxide, $Cs_2Ti_5O_{11}$, was prepared from a mixture of Cs_2CO_3 and rutile-type TiO_2, the ratio being 2.0:5.0. The second one, $Cs_{0.7}Ti_{1.825}O_4$, was prepared from a mixture of Cs_2CO_3:TiO_2 = 0.7:1.825. These mixtures were heat treated at 800 °C for 48 h in an air atmosphere. The cesium titanium(IV) oxide powder thus prepared was dipped in 1.0 mol dm^{-3} aqueous HCl and stirred for 24 h to exchange Cs^+ with H^+. After removing the supernatant solution, the precipitate was treated again by 1.0 mol dm^{-3} HCl and the treatment was repeated twice. The amount of extracted cesium ions was assayed using an atomic absorption spectrophotometer (Model 170-30, Hitachi Ltd., Japan) and the formation of proton-type titanium(IV) oxide was confirmed. The amount of water molecules accommodated in the product was examined by thermogravimetry (Model TAS 200, Rigaku, Japan). The typical composition of the resultant proton-type titanium(IV) oxides was $H_2Ti_5O_{11}\cdot 0.8H_2O$ (abbreviated to H-TiO_2(A), fw: 431.9) and $H_{0.7}Ti_{1.825}O_4\cdot 2.6H_2O$ (abbreviated to H-TiO_2(B), fw: 198.9), respectively.[5] The former has a stoichiometric composition and the latter is non-stoichiometric, having a titanium(IV) vacancy of 0.175, i.e., $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot 2.6H_2O$

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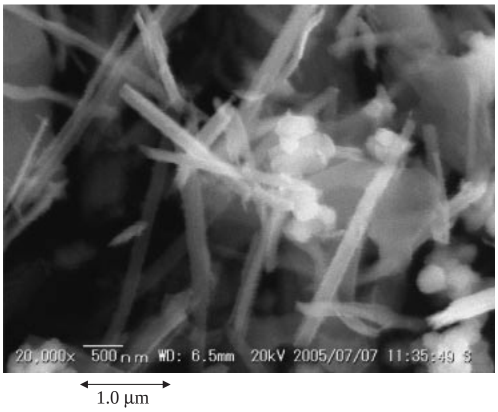

Fig. 1. SEM photograph of $H_2Ti_5O_{11} \cdot 0.8H_2O$ prepared by acid treatment of $Cs_2Ti_5O_{11}$.

where □ means vacancy. The hydrated water will be ignored from the chemical formula in the following discussion. A SEM photograph of H-TiO_2(A) is shown in Fig. 1.

Intercalation Reaction. It was found that the *n*-alkylamine bilayer was formed in γ-titanium(IV) phosphate more regularly in a benzene solution than in an aqueous solution.[1] Thus, the benzene solution was also used in this study and *n*-alkylamines with a carbon number, n_c, of 3, 4, 6, 10, 14, 16, and 18 were used. The concentration of *n*-alkylamines was 0.1 mol dm^{-3} for $n_c = 3$–10 and that of *n*-alkylamines with $n_c = 14$–18 was 0.05 mol dm^{-3}. The volume of the *n*-alkylamine-benzene solution was 10 cm^3. The mole ratio of *n*-alkylamine to H-TiO_2(A) was 4.4:1.0 in the former case, and 2.2:1.0 in the latter. The reaction time examined was 3 h to 2 weeks. The reaction temperature was 37 °C.

The amount of intercalated *n*-alkylamines was estimated by acid–base titration from the residual amount of amines in the supernatant solution. The titration was carried out using hydrochloric acid dissolved in ethanol and the indicator used was a bromocresol green and methyl red mixture.

Characterization. Cesium- and proton-type titanium(IV) oxides were characterized by an X-ray diffractometer (Model MO3X-HF, Bruker AXS Co., Ltd., Japan) equipped with Cu Kα ($\lambda = 0.154$ nm). The precipitation of the intercalation compounds with *n*-alkylamines prepared was developed on a glass plate. After drying, the sample was subjected to the X-ray diffraction analysis with Cr Kα ($\lambda = 0.229$ nm) for the intercalation compounds with a large interlayer distance.

Dynamic Light Scattering. A dynamic light scattering photometer (ALV Laser Vertriebsgesellschaft, m.b.H., Germany) was used to measure the average particle size and particle shape. H-TiO_2(A) powder was added in 0.1 mol dm^{-3} propylamine or 0.1 mol dm^{-3} tetrabutylammonium hydroxide aqueous or benzene solution and kept for 1 week at room temperature. After centrifugation at about 15000 rpm, 30000 G, the supernatant part was separated, and then measured. A Nd-YAG laser with $\lambda = 532$ nm was used as an incident light source.

Results and Discussion

The experimental data on the intercalation reaction of H-TiO_2(A) and H-TiO_2(B) will be discussed comparing with those of γ-titanium(IV) and γ-zirconium(IV) phosphates; the former is a weak acid and the latter a strong acid.

Intercalation Rate and Amount of Intercalated Amine. The intercalation rate of *n*-alkylamine was examined to learn the equilibrium state of the intercalation reaction. Figure 2 shows the amount of intercalated amines vs reaction time. The intercalation rate of *n*-alkylamines with $n_c = 4$ and 6 was rather fast and reached equilibrium within 6 h. The reaction reached equilibrium within 24 h for $n_c = 10$, 14, and 16. In total, the intercalation rate in H-TiO_2 was slower than those in γ-phosphates, presumably because of the weak acidity of H-TiO_2, Fig. 5 in Ref. 1.

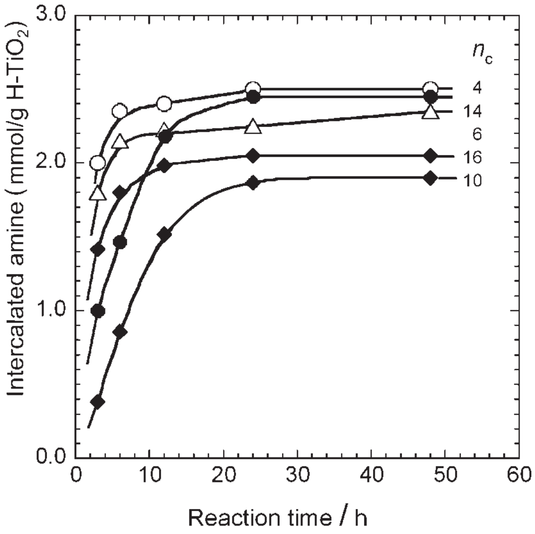

Fig. 2. Time dependence of the amount of intercalated *n*-alkylamines in benzene solution (in mmol/g H-TiO_2(A)).

Table 1. Amount of Intercalated *n*-Alkylamines at the Reaction Time of 24 h in H-TiO_2(A) and H-TiO_2(B) Prepared in a Benzene Solution for Carbon Numbers $n_c = 3$–18 (in mmol/g Each H-TiO_2)[a)]

n_c	3	4	6	10	14	16	18
H-TiO_2(A)	4.35	2.55	2.35	1.90	2.45	2.10	2.00
H-TiO_2(B)	4.75	1.75	1.00	1.00	1.50	1.25	1.00

a) The values were almost similar at the reaction time of 2 weeks.

Table 1 shows the amount of intercalated amines (in mmol/g H-TiO_2) at the reaction time of 24 h, at which the intercalation reaction almost reached equilibrium and the values were almost similar to those measured at the reaction time of 2 weeks. The amount of intercalated amines in H-TiO_2(A) was about two times as much as that in H-TiO_2(B) nominally, i.e., in mole ratio. The amount decreased with increasing the carbon number and showed a minimum at about $n_c = 10$ or a small maximum at $n_c = 14$ in both H-TiO_2 although the reason was not clear. Figure 3 shows the amount of intercalated amines (in mol/mol H-TiO_2). The amount of intercalated amine with $n_c = 3$ was estimated to be (amine/$H_2Ti_5O_{11}$) $= 2$ in mol ratio, suggesting the dibasic behavior of $H_2Ti_5O_{11}$. The amount was almost constant and the value was about (amine/$H_2Ti_5O_{11}$) $= 1$ for $n_c \geqq 4$. The value indicated that about 1/2 mol of H^+ in $H_2Ti_5O_{11}$ exchanged with one mole of amine, suggesting the monobasic behavior of $H_2Ti_5O_{11}$. These results indicated a rather stoichiometric acid–base reaction in both cases. The apparent minimum at $n_c = 10$ was accounted for

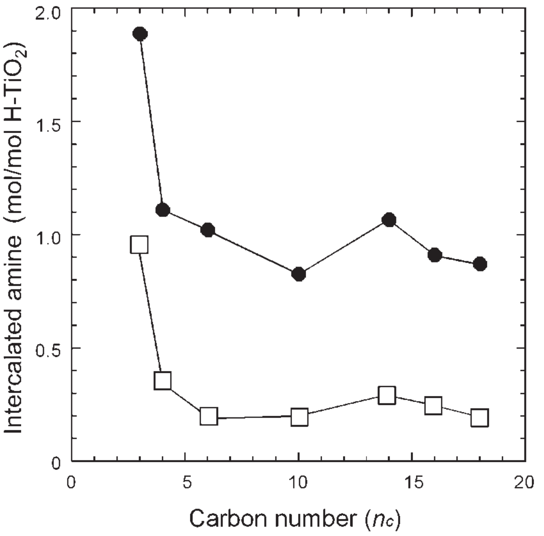

Fig. 3. Amount of intercalated n-alkylamines at the reaction time of 24 h in H-TiO$_2$(A) [●] and H-TiO$_2$(B) [□] prepared in a benzene solution (in mol/mol each H-TiO$_2$).

as follows. The van der Waals forces among alkyl chains increased with increasing carbon number and the most suitable number is 16–18 when the natural lipid bilayer of cell membranes of a living body is taken into account. On the other hand, the intercalation reaction should decrease with increasing the molecular weight due to the steric hindrance. The minimum of the intercalated amount as well as the reaction rate at $n_c = 10$ was attributable to such competitive properties. In the case of γ-titanium(IV) phosphate or γ-zirconium(IV) phosphate, the (amine/H$^+$ in γ-phosphates) ratio was non-stoichiometric 1.2–1.4 in the benzene solution, Table 2 in Ref. 1. In the case of γ-phosphates, the upper limit of the amount of intercalated amines must be controlled by the spatial density to form a rigid arrangement of alkyl chains in the interlayer gallery space, i.e., the intercalated amount was limited by steric hindrance.

In the case of H-TiO$_2$(B), 0.20($n_c = 6$)–0.35($n_c = 4$) mol of amine was exchanged with one mole of $H_{0.7}Ti_{1.825}O_4$, i.e., 0.29–0.50 mol amine was intercalated vs 1.0 mol of H$^+$ reflecting the non-stoichiometric property of the host layered compound.

X-ray Diffraction Analysis. X-ray diffraction patterns of two proton-type H-TiO$_2$ were similar and are shown in Fig. 4a. The interlayer distance was 0.936 nm. The lattice parameter as well as the diffraction pattern were consistent with those reported previously.[3]

The X-ray diffraction patterns of n-alkylamine intercalated H-TiO$_2$(B) were rather broad, especially for carbon numbers $n_c \leqq 10$, and suggested the formation of amorphous compounds. On the other hand, the X-ray diffraction patterns of H-TiO$_2$(A) showed well defined peaks as shown in Fig. 4. Accordingly, the results on H-TiO$_2$(A) will be explained mainly in the following discussion. Typical X-ray diffraction patterns for $n_c = 3$–16 are shown in Figs. 4b–4e for the reaction time of 24 h. The reaction time was enough to reach equilibrium. A single phase X-ray diffraction pattern was always observed for $n_c = 3$–10. On the other hand, two phases with different interlayer distances appeared occasionally in $n_c = 14$ and always appeared in $n_c = 16$ and 18 as shown in Fig. 4e, Phase *I* and Phase *II*.

The product for $n_c = 3$ showed a single phase; however, the suspension contained a fluffy suspended colloid. The X-ray diffraction peak was very weak and suggested the coexistence of the amorphous state (Fig. 4b). Thus, the suspended colloid suggested the exfoliation and following coagulation of the host layered lamellae to form a dispersed monolayer or nano-sheet in the benzene solution.

Interlayer Distance. It is well known that n-alkylamines intercalated in inorganic layered materials form bilayers in the gallery space between the layered lamellae. Figure 5 shows the interlayer distance of n-alkylamine intercalation compounds of H-TiO$_2$(A) vs the number of carbon atoms of the alkyl chain. The plot of open circles (Phase *I*) gives a linear relation with the exception of $n_c = 18$. The R value was estimated to be 0.9991 and the slope 0.2326 nm/n_c. If the alkyl chains formed a regular bilayer and were arranged with an angle θ relative to the basal plane, the interlayer distance d is shown by

$$d = d_o + 2 \times 0.127 n_c \sin\theta \quad \text{(in nm)}, \tag{1}$$

where d_o is the interlayer distance of the original layered compound and n_c is the carbon number of n-alkylamine.[10]

The value $(d - d_o)$ indicates the gallery space for each n-alkylamine bilayer between the host H-TiO$_2$ layers. The observed d_o was 0.758 nm and it must be consistent with the thickness of the host lamella. On the other hand, the interlayer distance of the host H-TiO$_2$ is 0.936 nm as shows in Fig. 4a. The difference between 0.758 and 0.936 is accountable as follows. The difference seems consistent if the size of the water molecule is taken into account because the host H-TiO$_2$ accommodates water molecules with the near monolayer.

The slope of the n-alkyl chain against the basal plane was able to be estimated from the slope of the d vs n_c plot in Fig. 5; the value was about 66° against the basal plane. In the case of γ-phosphates, the slope was near 90°. The difference may be attributed to the affinity of the basic amino group and an acidic lamella surface. The strong affinity with γ-phosphates could establish a more perpendicular orientation. Sasaki et al. reported the interlayer distance of the n-alkylamine intercalation compounds of lepidocrocite $H_{1.07}Ti_{1.73}O_4$ prepared in a water–ethanol mixed solvent.[8] The interlayer distance of $n_c = 5$–10 prepared in the water–ethanol mixed solvent was 0.1–0.5 nm smaller than those prepared in a benzene solvent and suggested that n-alkylamines were arranged in a monolayer or in a seriously distorted bilayer due to the co-intercalated water or ethanol molecules. In addition, they found the absence of layer stacking regularity for $n_c = 8$–10 and showed the formation of an irregular bilayer in the water–ethanol mixed solvent.

Dynamic Light Scattering Study. It was found from Table 1 that the amount of propylamine intercalated was two times as large as that of other n-alkylamines with a carbon number larger than 3 and showed near dibasic behavior. The colloidal dispersion appeared only in a propylamine solution when H-TiO$_2$(A) powder was added. On the other hand, a transparent solution appeared in other n-alkylamine solutions. The dibasic behavior in the propylamine solution and the

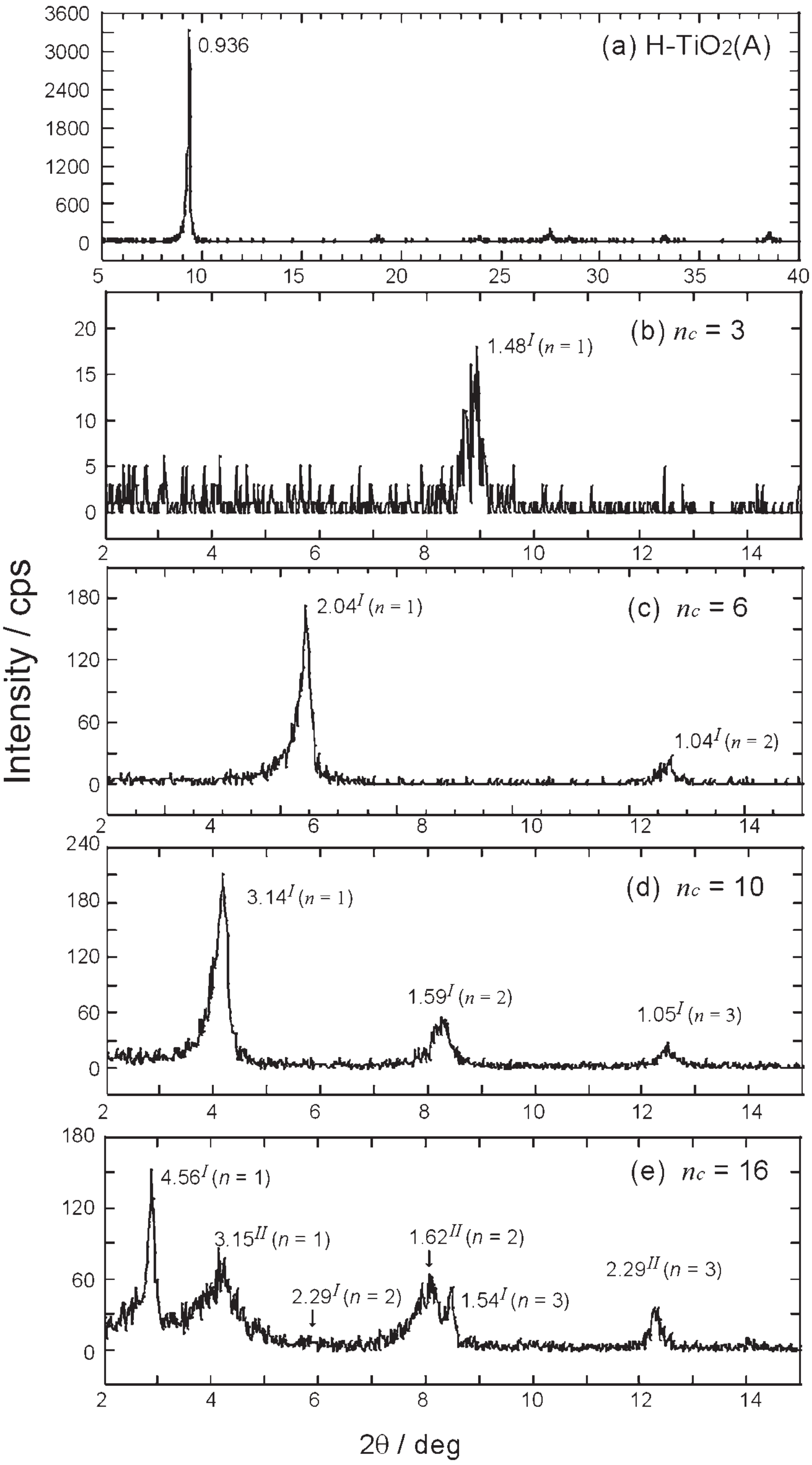

Fig. 4. (a): X-ray diffraction pattern of as prepared H-TiO$_2$(A) (Cu Kα radiation). H-TiO$_2$(B) showed a similar pattern. (b)–(e): X-ray diffraction pattern of *n*-alkylamines intercalated H-TiO$_2$(A) for $n_c = 3$, 6, 10, and 16 (Cr Kα radiation) at the reaction time of 24 h. Numerals with superscript *I* and *II* indicate *d*-parameter in nm. Phase *I* and superscript *I* indicate an intercalation compound with regular bilayer form of *n*-alkylamines with an angle of 66°. Symbol *n* (=1–3) indicates $n\lambda$ sequence in Bragg's relation that is ascribed to a similar plane.

formation of colloidal dispersion must suggest the presence of an exfoliated monolayer or nano-sheet. Thus, the dynamic light scattering was used to measure the size of the H-TiO$_2$(A) colloid. The diffusion coefficient D_{obs} is calculated from the parameter, Γ which is an inverse of the observed correlation time and parameter q that has a dimension of the inverse of

Table 2. Scatter Angle Dependence of Dynamic Light Scattering Photometry for a Colloid of H-TiO_2(A) Prepared in Aqueous Solutions of Propylamine and Tetrabutylammonium Hydroxide, and in a Benzene Solution of Propylamine[a)]

Angle/deg	*n*-Propylamine (aq)			*t*-Butylammonium hydroxide (aq)			*n*-Propylamine (benzene)		
	Γ_{obs}/s^{-1}	$D_{app}/10^{-12}\,m^2\,s^{-1}$	R/nm	Γ_{obs}/s^{-1}	$D_{app}/10^{-12}\,m^2\,s^{-1}$	R/nm	Γ_{obs}/s^{-1}	$D_{app}/10^{-12}\,m^2\,s^{-1}$	R/nm
45	378.0	2.62	82.8	147.9	1.02	211	61.6	0.349	948
60	667.5	2.71	80.1	248.7	1.01	215	97.6	0.324	1022
75	1254.7	3.43	63.1	464.8	1.27	170	150.9	0.338	980
90	2811.0	5.70	38.0	800.6	1.62	133	200.2	0.332	997

a) Observed correlation function Γ_{obs}, apparent diffusion coefficient D_{app}, and averaged particle radius calculated using the Stokes–Einstein equation R.

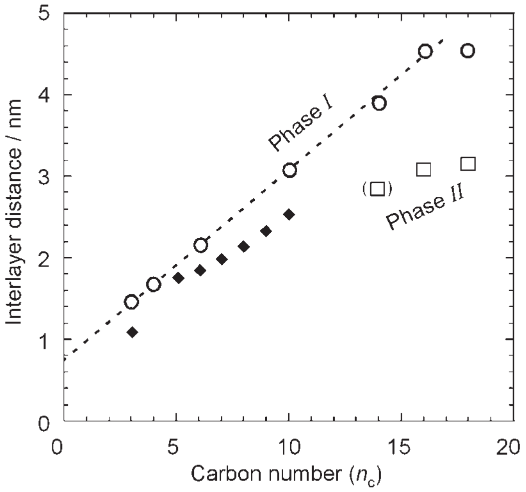

Fig. 5. Relation between interlayer distance and carbon number in the *n*-alkyl chain. Open circles indicate the interlayer distance for the bilayer form of *n*-alkylamines (Phase *I*). Open squares indicate appearance of a second phase (Phase *II*). Open squares (□) indicate irreproducible result. Closed squares indicate those prepared in an ethanol–water mixed solvent using lepidocrocite $H_{1.07}Ti_{1.73}O_4$.[6] Dotted line indicates regression equation for $n_c = 3$–16.

length:

$$D_{obs} = \Gamma/q^2, \tag{2}$$

where q is a function of scattering angle θ:

$$q = (4\pi n/\lambda)\sin(\theta/2), \tag{3}$$

where n is the solution refractive index and λ is the wavelength of the incident light. If the particle is really spherical, D_{obs} indicates the ordinary translational diffusion coefficient and the radius of the spherical particle is calculated using the Stokes–Einstein equation.

In the present study, however, the shape of the colloid particles is expected to be thin lamellae. No theory is available for particles with thin lamellae. If the shape of the particle were a rigid rod instead of thin lamella, the correlation function would be indicated by the following equation:[11]

$$\Gamma = q^2 D_T + 6D_R, \tag{4}$$

where D_T is the translational diffusion coefficient and D_R is the rotational diffusion coefficient caused by the anisotropy. If the shape of the particle is spherical, Γ has no scatter angle dependence and D_R should be diminished, i.e., $D_T = \Gamma/q^2$. The observed data for propylamine in an aqueous solution showed significant scattering angle dependence and suggested the formation of thin lamellae. On the other hand, those observed in the benzene solution showed a steady value and suggested a rather isotropic shape.

The average radius of the particle was estimated first using the Stokes–Einstein equation, Table 2. The size of the colloid particles with a thin lamella shape formed in an aqueous solution was estimated from the apparent diffusion coefficient measured at $\theta = 45°$ because the contribution of rotational motion, D_R in Eq. 3, becomes significant with increasing the scattering angle.[11] The average radii of the colloid particles calculated from Eq. 2 and the Stokes–Einstein equation were about 80 and 210 nm for the colloid in aqueous propylamine and tetrabutylammonium hydroxide solutions, respectively. The formation of the monolayer sheet of H-TiO_2 in aqueous tetrabutylammonium hydroxide has been proved using TEM[6] and AFM.[12] The length of the monolayer plate was 0.25–0.5 µm and the presence of coagulated 2–5 or more multi layers was also observed in the AFM image.[12] If the averaged radius of 210 nm observed in tetrabutylammonium hydroxide solution really corresponded to the exfoliated monolayer or nano-sheet and following coagulated multilayer, the averaged radius of 80 nm observed in the propylamine solution also would suggest the formation of exfoliated monolayer sheets.

In the present study that was carried out in a benzene solution, the shape of colloid particles was rather isotropic. The average size was estimated to be about 1.0 µm and the size of the suspended colloid corresponded to that of the horizontal length of the host H-TiO_2(A) as shown in Fig. 1. The coagulation of monolayer sheets developed rapidly in the benzene solution and formed a fluffy suspended colloid with isotropic shape because the layered lamella is hydrophilic, while benzene is hydrophobic. The dibasic behavior in the propylamine solution must be attributed to the intermediate monolayer formation and following coagulation. In fact, the formation of the colloid solution was not observed in other *n*-alkylamines.

Conclusion

(1) Stoichiometric $H_2Ti_5O_{11}$ (H-TiO_2(A)) intercalated *n*-alkylamines 1.0 mol per 1.0 mol of $H_2Ti_5O_{11}$ suggested the monobasic acid–base reaction with H^+ and gave well-defined X-ray diffraction patterns of the bilayer structure of *n*-alkylamine. Non-stoichiometric $H_{0.7}Ti_{1.825}O_4$ (H-TiO_2(B)) intercalated *n*-alkylamines 0.20–0.35 mol per 1 mol of $H_{0.7}Ti_{1.825}O_4$ were due to the incomplete acid–base reaction. Most of the

products were amorphous in the X-ray diffraction pattern.

(2) The sample for $n_c = 3$ in H-TiO$_2$(A) was rather amorphous, presumably due to the formation of an exfoliated monolayer or nano-sheet.

(3) The bilayer formation of *n*-alkylamine molecules in the intercalation compound of H-TiO$_2$(A) was found to have a solvent effect similar to that in γ-titanium(IV) and γ-zirconium(IV) phosphates. The interlayer distance of *n*-alkylamine intercalated H-TiO$_2$(A) increased regularly with increasing the number of carbon atoms in the *n*-alkyl chain. The slope of the *n*-alkyl chain in the bilayer form was estimated to be about 66° against the basal plane of the host layered lamellae.

(4) The dynamic light scattering study on the intercalation compound of H-TiO$_2$(A) with propylamine prepared in a benzene solution as well as in aqueous propylamine and tetrabutylammonium hydroxide solutions suggested the intermediate formation of an exfoliated monolayer and following coagulation to form a fluffy suspended colloid.

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