Synthesis and Characterization of Halogen-free, Transparent, Aqueous Colloidal Titanate Solutions from Titanium Alkoxide

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Transparent, aqueous colloidal titanate solutions were prepared by a reaction between titanium alkoxide and alkylamines or tetraalkylammonium hydroxides. The chemical species containing titanium atoms were found to be a colloidal particle (15 nm) with a layered structure. The formation reaction can be explained as an acid−base reaction between the amines and titanic acid derived from the alkoxide to yield ammonium titanates. Both the basicity of the amines and the sizes of the conjugate acid (ammonium cations) are crucial factors to determine whether the aqueous solutions can be prepared. Similarly, aqueous oxo metalate solutions of V, Nb, Ta, Al, Si, and Sn are easily prepared from corresponding alkoxides.

Introduction

In recent years "aqueous" solution chemistry has been attracting increasing interest as a way to synthesize compounds and/or materials without organic solvents in both inorganic[1] and organic[2] fields. Water is more economical, less toxic, and easier to handle compared with other solvents. Groups 4 and 5 metal ions play a significant role in ceramics,[3] electrodevices,[4] and catalysts.[5] However, it is very difficult for them to exist as aqueous complexes in water because they are strongly hydrolyzed to insoluble oxo species because of their high charge density. Therefore, a highly acidic condition or chelation to the metal[1,6−7] is required to keep the solution stable, so that few papers related to aqueous solutions free of halogen and chelating ligands are reported.[8] There are two patents that reported the preparation of colloidal solutions, using a reaction of hydrate metal oxide or metal alkoxides with quaternary ammonium hydroxides or amines as peptizers.[9,10] The chemical species were written as a colloidal hydrous metal oxide (e.g., hydrous stannic oxide). These patents, however, did not report on the colloidal solutions containing titanium with amines as peptizers because these inventions were focused on tin.

We recently showed that concentrated, halogen-free aqueous titanate solutions were obtained by direct reaction of titanium isopropoxide (TIP) with some alkylamines or tetraalkylammonium hydroxides.[11] The features of these aqueous solutions are (1) easy preparation, (2) free of halogens, alkaline metals, and chelating ligands, and (3) stability over a long period of time, more than 1 year. These solutions are found to be very useful as water-soluble precursors for functional ceramics such as TiO_2 and potassium titanyl phosphate (KTP: $KTiOPO_4$).

In this paper, the factors to control the formation of aqueous solutions and the structure of chemical species in the solution are discussed. Furthermore, preparation of aqueous solutions derived from metal alkoxides (V, Nb, Ta, Al, Si, and Sn) is similarly examined.

Experimental Section

Chemical Reagents. Commercial extrapure reagents, aqueous solutions of ammonia (28%, NH_3), methylamine (40%, $MeNH_2$), ethylamine (70%, $EtNH_2$), dimethylamine (50%, Me_2NH), trimethylamine (30%, Me_3N), and tetramethylammonium hydroxide (15%, TMAOH) were used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. *tert*-Butylamine (*t*-$BuNH_2$), diethylamine (Et_2NH), triethylamine (Et_3N), pyridine (C_5H_5N), tetrapropylammonium bromide (TPABr), and NaOH were also used as received from Wako Pure Chemical Industries, Ltd., Osaka, Japan. Titanium tetraisopropoxide ($Ti(OPr^i)_4$: TIP, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used after distillation under reduced pressure. Aluminum isopropoxide ($Al(OPr^i)_3$), tetraethyl orthosilicate ($Si(OEt)_4$, Wako Pure Chemical Industries, Ltd., Osaka, Japan), zirconium tetra-*n*-butoxide in *n*-butanol ($Zr(OBu^n)_4$, Mitsuwa Pure Chemical Co., Osaka, Japan), vanadium(V) triethoxideoxide ($VO(OEt)_3$, 5 N), niobium pentaethoxide ($Nb(OEt)_5$, 3 N), tantalum pentaethoxide ($Ta(OEt)_5$,

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5 N, High Purity Chemical Co., Saitama, Japan) were used as received. Stannic acid, which was obtained by a reaction of $SnCl_4$ with aqueous NH_3, was used as a tin source. A layered titanate, $H_2Ti_4O_9$, was prepared through an ion-exchange reaction of $K_2Ti_4O_9$ (Otsuka Chemical Co. Ltd., Osaka, Japan) by HCl.

Characterizations. The chemical species in the solutions or precipitates were examined by elemental analysis (CHN CORDER MT-6, Yanako Analytical Instruments Co., Kyoto, Japan) and thermogravimetric and differential thermal analysis (TG-DTA, Models DTA 50 and TGA 50, Shimadzu, Kyoto, Japan) at a heating rate of 5 °C/min from room temperature to 800 °C under flowing dry air.

Aqueous titanate solutions were examined also by electrical conductivity (Twin Cond B-173, Horiba Ltd., Kyoto, Japan), pH, dynamic light scattering (DLS-700, Otsuka Electronics Co. Ltd., Osaka, Japan), and Raman spectroscopy (NR-1800, JASCO Co., Tokyo, Japan).

For the thin films prepared from the titanate solutions at room temperature, XRD patterns (Model Geigerflex, Rigaku Co., Tokyo, Japan) were recorded using graphite monochromated Cu Kα radiation with a scanning speed of 2°/min over the 2θ range of 2°−70°.

Reaction of TIP with Alkylamines or Alkylammonium Hydroxides and Examination of the Chemical Species Separated from the Solutions. The reaction of TIP with amines in the presence of H_2O was conducted at room temperature in air. The molar ratio of the amine or ammonium hydroxide to titanium in the reaction mixtures was denoted as R. The detailed experimental procedure and the results of elemental analysis are described as follows. All the products used for elemental analysis were highly hygroscopic.

Reaction of TIP with $MeNH_2$. When 3.0 mL of TIP (10 mmol) was mixed with 0.8 g of 40% aqueous solution of $MeNH_2$ (10 mmol), exothermic reaction instantly occurred to give a white precipitate. They were separated by centrifugal separation and then washed by deionized water. This separation−washing process was repeated three times and the mixture finally dried in vacuo at room temperature. The elemental analysis of the powder gave the following results: H 2.89, C 3.16, N 3.30, Ti 44.4%, suggesting the composition $[CH_3NH_3][HTi_4O_9]\cdot 3H_2O$ (H 3.10, C 2.84, N 3.31, Ti 45.3%). The yield of the dried powder was 0.8 g (76%).

NH_3 and $EtNH_2$ were found to behave similarly to $MeNH_2$ and gave the following results: For the NH_3 system, H 2.69, C 0.00, N 2.82, Ti 44.7%, suggesting the composition $[NH_4][HTi_5O_{11}]\cdot 5H_2O$ (H 2.88, C 0.00, N 2.67, Ti 45.6%). For the $EtNH_2$ system, H 3.57, C 5.99, N 3.27, Ti 44.4%, corresponding to the composition $[C_2H_5NH_3][HTi_4O_9]\cdot 3H_2O$ (H 3.46, C 5.50, N 3.21, Ti 43.9%).

Reaction of TIP with Et_2NH. When 3.0 mL of TIP (10 mmol) was mixed with 1.0 mL of Et_2NH (10 mmol), followed by the addition of pure water, exothermic reaction instantly occurred to give a solid mass. However, the solid product was gradually dissolved under stirring and yellow clear solution with the concentration of 0.5 M was obtained within 1 day. The solution was very stable for more than 1 year. The yellow powder was obtained by evaporation of the solvent and unreacted amine in vacuo at room temperature. The powder was not dissolved in water but redissolved by the addition of the amine. The elemental analysis of the powder gave the following results: H 3.46, C 10.4, N 2.83, Ti 40.9%, suggesting the composition $[(C_2H_5)_2NH_2][HTi_4O_9]\cdot 3H_2O$ (H 4.12, C 10.3, N 3.01, Ti 41.2%). The yield of dried powder was 1.4 g (86%).

t-$BuNH_2$ and Et_3N showed the same reaction tendency as Et_2NH. The colors of the solutions from *t*-$BuNH_2$ and Et_3N were colorless and yellow, respectively. For the Et_2NH system, H 3.51, C 10.6, N 2.77, Ti 41.4%, suggesting the composition $[(CH_3)_3CNH_3][HTi_4O_9]\cdot 3H_2O$ (H 4.12, C 10.3, N 3.01, Ti 41.2%). For the Et_3N system, H 3.45, C 9.31, N 1.84, Ti 43.9%, suggesting the composition $[(C_2H_5)_3NH][HTi_7O_{15}]\cdot 4H_2O$ (H 3.54, C 9.38, N 1.82, Ti 43.6%).

Reaction of TIP with TMAOH. TIP (3.0 mL, 10 mmol) was directly added into 2.4 g of aqueous solution of 15% tetramethylammonium hydroxide (TMAOH, 4 mmol), almost exothermically affording an opaque colloidal solution under stirring. Then the degree of transparency of the solution increased with time, and finally a clear solution (1 M) was obtained within a few hours. A precipitate was obtained by the addition of an excess amount of 2-propanol to the solution, separated by filtration, washed several times with 2-propanol to remove unreacted ammonium species, and finally dried in vacuo. The elemental analysis of the powder gave the following results: H 5.60, C 11.4, N 3.30, Ti 34.8%, suggesting the composition $[(CH_3)_4N][HTi_3O_7]\cdot 5H_2O$ (H 5.51, C 11.4, N 3.33, Ti 34.1%). The white powder was readily dissolved in water, and the total yield of dried powder was 1.3 g (99%).

Synthesis of Water-Soluble Titanium Alkylammonium Oxalate from Aqueous Titanate Solutions. Oxalic acid dihydrate ($H_2C_2O_4\cdot 2H_2O$, 2.5 g, 20 mmol) was added to the 20 mL of 0.5 M aqueous solution of TIP−TMAOH ($R = 2$). The acid was quickly and completely dissolved with some heat evolution, yielding colorless clear solution. After the solution was stirred for 24 h, the addition of a large quantity of 2-propanol to the solution caused a precipitate. The precipitate was separated by filtration, washed with 2-propanol, and finally dried under vacuum at room temperature. The elemental analysis of the powder gave the following results: H 7.19, C 33.7, N 6.57, Ti 11.2%, which are consistent with the calculated data (H 6.84, C 32.6, N 6.33, Ti 10.8%) for tetramethylammonium dioxalato oxotitanate(IV) trihydrate $[(CH_3)_4N]_2[TiO(C_2O_4)_2]\cdot 3H_2O$. The white powder was readily redissolved in water, and the yield was 4.0 g (90%).

Reaction of Aqueous Titanate Solutions with Aqueous KCl Solution. 0.5 M TIP−Et_2NH ($R = 2$) (8 mL, 4 mmol) solution was mixed with 12 mL of 1.0 M KCl aqueous solution (12 mmol), yielding a white precipitate. The precipitate was separated by centrifugal separation and then washed with deionized water. This separation−washing process was repeated five times and the mixture finally dried at 110 °C in air. The resultant powder was found to be amorphous by XRD and did not contain both carbon and nitrogen components from elemental analysis. XRD and Raman spectra of the powder heat-treated at 800 °C were the same as those of an authentic sample of $K_2Ti_6O_{13}$ (TISMO−N, Otsuka Chemical Co., Ltd., Osaka, Japan). The amorphous powder before heat treatment can be formulated as $K_2Ti_6O_{13}\cdot 4H_2O$ from TG-DTA and elemental analysis. The yield of the powder was 0.42 g (98%). The $K_2Ti_6O_{13}$ powder was similarly prepared from the aqueous solutions of TIP−Et_3N ($R = 1$) and TIP−TMAOH ($R = 0.4$).

Results

Factors Controlling the Formation of Aqueous Metalate Solutions. TIP was mixed with neat Et_2NH, affording a homogeneous solution without heat evolution. When water was added to the resultant solution at room temperature, exothermic reaction occurred and at the same time white solid was formed. However, the solid slowly dissolved, finally giving a yellow clear solution within 1 day. Similarly, pale yellow clear solutions were obtained from Me_2NH, Me_3N, and Et_3N, while colorless clear solutions were more rapidly obtained from quaternary ammonium hydroxides (TMAOH and TBAOH) within a few hours. In place of TIP, titanic acid, which was obtained by hydrolysis of TIP, can be used to yield similar clear solutions. Regardless of the molar ratios of amines or ammonium hydroxides to TIP, if they were larger than 0.5−1.0, similar solutions could be obtained, and the larger the ratios, the more quickly formed the solutions. The representative titanate solution is shown in Figure 1, along with distilled water and crystalline TiO_2 (anatase) suspension (STS-01, Ishihara Sangyo Kaisha, Ltd., Osaka, Japan) for comparison. The titanate solution was not suspension because it had a transparency comparable to water. When a He−Ne laser

Table 1. Influence of the Basicity of the Amines on the Formation of Aqueous Solutions Derived from TIP

amine	pK_a[a]	state	estimated chemical composition[b]
C_5H_5N	5.2	white precipitates	$TiO_2 \cdot 0.75H_2O$
(NH_3)	9.24	white precipitates	$[NH_4][HTi_5O_{11}] \cdot 5H_2O$
$MeNH_2$	10.64	white precipitates	$[CH_3NH_3][HTi_4O_9] \cdot 3H_2O$
$EtNH_2$	10.63	white precipitates	$[C_2H_5NH_3][HTi_4O_9] \cdot 3H_2O$
t-$BuNH_2$	10.69	colorless clear solution	$[t\text{-}C_4H_9NH_3][HTi_4O_9] \cdot 3H_2O$
Me_2NH	10.77	pale yellow clear solution	
Et_2NH	10.93	yellow clear solution	$[(C_2H_5)_2NH_2][HTi_4O_9] \cdot 3H_2O$
Me_3N	9.8	pale yellow clear solution	
Et_3N	10.72	yellow clear solution	$[(C_2H_5)_3NH][HTi_7O_{15}] \cdot 4H_2O$
(TMAOH)		colorless clear solution	$[(CH_3)_4N][HTi_3O_7] \cdot 5H_2O$
(TBAOH)	strong base	colorless clear solution	
(NaOH)		white precipitates	

[a] Conjugate acid of corresponding amines. [b] Based on elemental analysis. [c] Tetrabutylammonium hydroxide.

Figure 1. Photograph of the solutions of (a) distilled water, (a) 1 M TIP−TMAOH (R = 0.4) and (c) 0.5 M crystalline anatase suspension (STS-01).

light was illuminated to them, the trace of the light passage through the titanate solution was clearly recognized, indicative of the colloidal nature of the solutions.

The addition of a large amount of 2-propanol to these clear solutions caused precipitates, which redissolved in water, indicating that the solutions contain ionic species or colloids. As described in the Experimental Section, the elemental analysis showed that all of the powders obtained from the clear solutions could be formulated as $[R_nH_{4-n}N^+][HTi_mO_{2m+1}^-]$ (R: alkyl group; n, m: integer, $n = 1-4$, $m = 4-7$). Namely, the powders are not a simple colloidal mixture (e.g., TiO_2) but the compounds with some stoichiometry. The molar ratio of nitrogen to titanium (N/Ti) in the compounds changed a little bit with the basicity or the size of ammonium ions and is almost independent of the ratios amine/TIP in the starting mixtures.

On the other hand, the reaction of TIP with aqueous solutions of primary amines $MeNH_2$ and $EtNH_2$ exothermically occurred to give white precipitates, but it had never been dissolved even in the presence of an excess amount of the amines or when refluxed for more than a week. However, *t*-$BuNH_2$ was interestingly effective for preparing similar clear solutions. In the case of pyridine and ammonia only precipitates were obtained. It is very interesting to note that, except for pyridine, all precipitates formed contained corresponding amines in some stoichiometric amounts and could be formulated again as $[R_nH_{4-n}N^+][HTi_mO_{2m+1}^-]$ (n = 0 or 1, m = 4 or 5), while pyridine afforded simple titanic acid or hydrous titanic oxide ($TiO_2 \cdot nH_2O$).

Table 2. Relationship between pK_a Values of Metallic Acids and the Conjugate Acids of Alkylamines and Tetraalkylammonium Hydroxide on the Formation of the Aqueous Solutions of Metalate Ions (sol = Clear Solution, ppt = Precipitates)[a]

metallic acids	pK_a	$EtNH_2$ 10.63	Et_3N 10.72	Et_2NH 10.93	(TMAOH) strong base
H_3VO_4	3.78	sol	sol	sol	sol
H_2SnO_3	9.4	sol	sol	sol	sol
$Nb(OH)_5$		sol	sol	sol	sol
$Ta(OH)_5$	9.6	ppt	sol	sol	sol
H_2SiO_3	9.7	sol	sol	sol	sol
$TiO(OH)_2$		ppt	sol	sol	sol
H_3AlO_3	11.2	ppt	ppt	ppt	sol
$Zr(OH)_4$		ppt	ppt	ppt	ppt

[a] The addition of pyridine (pK_a = 5.2) and ammonia (pK_a = 9.24) to the metallic acids in this table resulted in precipitates.

All of the results found for the preparation of the solutions are summarized in Table 1. The composition of the isolated solution species or the precipitates, which were evaluated from the elemental analysis, was recited. The pK_a values of the conjugate acids of the corresponding amines are also included in this table.[12] This table indicates that amines that were relatively large in molecular size and strong bases with pK_a values more than 9 tended to yield clear titanate solutions. Tetraalkylammonium hydroxides are typical ones. However, it is interesting that alkaline hydroxides such as NaOH, which are strong bases but contain small cations, resulted in precipitates, indicating that both basicity and size of the bases played an important role in the formation of clear solutions.

The reactions of some metal alkoxides other than titanium with alkylamines and TMAOH were similarly investigated and the results are summarized in Table 2. Here, again, pK_a values of both metallic acids and conjugate acids of the amines are also shown in this table.[12] When the pK_a value of an amine was larger than that of a metallic acid, that is, the amine was more basic than the acid, clear metalate solutions can be prepared regardless of the size of the amines used. Vanadic acid, the most acidic in this study, easily gave clear solutions by reaction with amines, and the metallic acids with almost the same pK_a values such as $Ta(OH)_5$, H_2SiO_3, and H_2SnO_3 showed similar tendencies. Aluminic acid was soluble only in the presence of strongly basic

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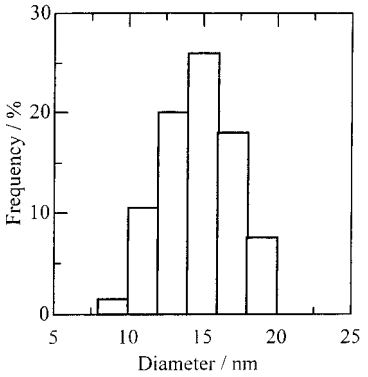

Figure 2. Size distribution of the particles in the aqueous colloidal solution of TIP−TMAOH (0.5 M, $R = 1$).

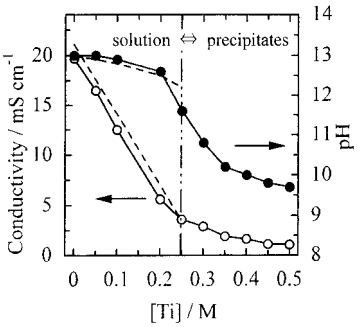

Figure 3. Electric conductivity and pH change of the TIP−TMAOH solution.

TMAOH because of its weak acidity (pK_a 11.2). Zirconic acid is thought to be much more basic than aluminic acid and was difficult to dissolve by reaction with amines.

Measurements of Electric Conductivity, pH Values, and Dynamic Light Scattering (DLS) of the TIP−TMAOH Solution. All of the titanate solutions prepared in this study were highly transparent and looked like common aqueous solutions. However, the colloidal nature was recognized as shown in Figure 1, and, hence, the size distribution of colloidal particles in the TIP−TMAOH (0.5 M, $R = 1$) solution was measured by DLS. The results are shown in Figure 2. The average size was estimated to be 15 nm.

The solution species is expected to contain a kind of ammonium titanates that may be dissociated to free ions, and hence the solution may be highly electrically conductive. If the equivalent ionic conductance were obtained, a rough measure of anion size and hence the structure would be evaluated. Figure 3 shows the electric conductivities and the pH values for various TIP−TMAOH solutions at 20 °C. The measurement was made under conditions that the titanium concentration was varied in the range of [Ti] = 0−0.5 M with keeping the TMA^+ concentration at [TMA^+] = 0.1 M. The clear solutions were obtained from [Ti] = 0−0.25, while colloidal suspension or precipitates were obtained at a concentration higher than 0.25 M, indicating that a N/Ti ratio of more than 0.4 is necessary to yield clear solutions. This ratio is roughly the same as the composition of the isolated solution species (N/Ti = 0.33) that was assumed from the elemental analysis. In Figure 3, as the [Ti] concentration was increased, both electric conductivity and pH decreased. These results will be discussed later.

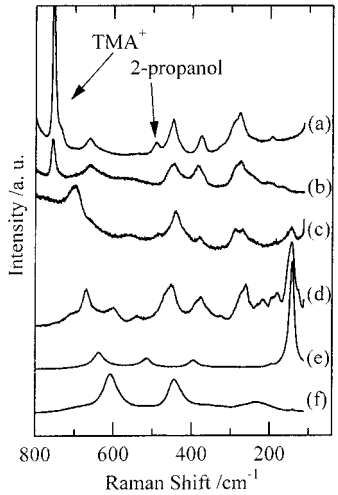

Figure 4. Raman spectra of various titanium compounds: (a) 1 M TIP−TMAOH ($R = 1$) solution, (b) powder obtained from 1 M TIP−TMAOH ($R = 0.4$) solution, (c) 0.5 M TIP−Et_2NH ($R = 1$) solution, (d) $H_2Ti_4O_9$, (e) anatase powder, and (f) rutile powder.

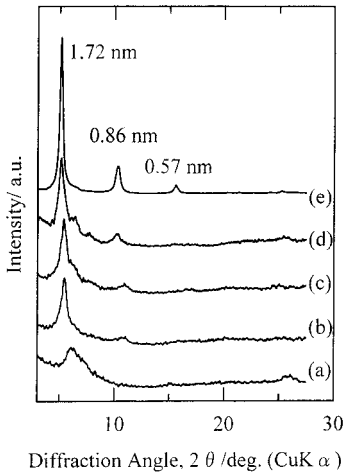

Figure 5. Reflux time dependence of XRD patterns of thin films prepared on a glass plate at room temperature from 0.5 M TIP−TMAOH ($R = 1$) solution: (a) as-prepared, (b) 1 h, (c) 2 h, (d) 3 h, and (e) 6 h.

Raman Spectra. Figure 4 shows the Raman spectra of the tetramethylammonium titanate solution and the powder isolated from the solution, along with those of TiO_2 (anatase and rutile). A layered titanate, tetratitanic acid ($H_2Ti_4O_9$), is also recorded for comparison. The tetramethylammonium titanate solution (Figure 4a) had four peaks at 279, 376, 449, and 662 cm^{-1} in addition to the peaks assignable to 2-propanol and TMA^+. No peak shifts were observed when Ti or TMAOH concentration was varied, and even after the solution was refluxed for 6 h. The powder obtained from the solution after evaporating water gave the fundamentally same spectrum as shown in Figure 4b. In the case of Et_2NH, no distinct spectra were observed. However, the same pattern as TMAOH was recognized after refluxing for a week as shown in Figure 4c. The spectra of the titanates powder (Figure 4a,b) were rather similar to that of the tetratitanic acid ($H_2Ti_4O_9$, Figure 4d), and completely different from those of anatase and rutile (Figures 4e,f), strongly suggesting that the titanate solution is not a simple colloidal

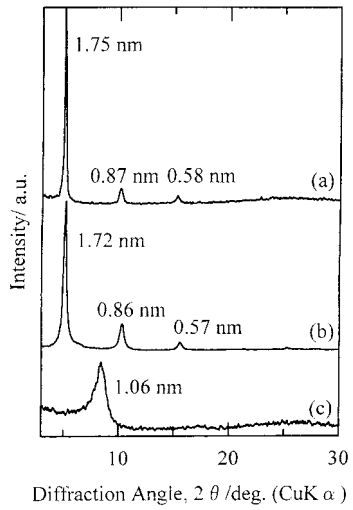

Figure 6. XRD patterns of thin films prepared from (a) 0.3 M TIP−TBAOH (R = 1) refluxed for 6 h, (b) 0.5 M TIP−TMAOH (R = 1) refluxed for 6 h, and (c) 0.5 M TIP−Et_2NH (R = 1) refluxed for 7 days.

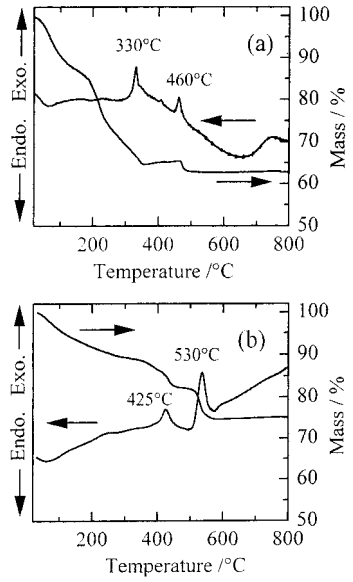

Figure 7. TG-DTA of the powder prepared from the solutions of (a) TIP−TMAOH (R = 0.4) and (b) TIP−Et_3N (R = 0.5).

dispersion of TiO_2 (anatase or rutile) but contains a layered structure.

XRD. Figure 5 shows XRD patterns of the films prepared from the TIP−TMAOH solution refluxed for a period within 6 h. The films were dip-coated on glass (Corning Inc., #7059) and dried in vacuo at room temperature.

From the as-prepared solutions, only a very broad peak was found at about 6° (2θ). However, as the solution was refluxed for a longer period of time, the peak became sharper with shifting slightly to a lower angle. After the solution refluxed for 6 h, three diffraction peaks with regular interplanar spacing were clearly observed, indicating that refluxing helped crystallization in a layered compound.[13] Similar tendencies were observed in the case of TBAOH and alkylamine systems as shown in Figure 6.

TG-DTA. Figure 7 shows TG-DTA curves of the powders prepared from the solutions of the TIP−TMAOH (R = 0.4, Figure 7a) and TIP−Et_3N (R = 0.5, Figure 7b). The Ti content (wt %) in the powder was calculated from the final mass loss in the TG curves, which was shown in the Experimental Section. As clearly seen, the final decomposition temperature for the TIP−TMAOH (460 °C) was much lower than that of the TIP−Et_3N (530 °C), suggesting that TMA^+ in the titanate powder is more easily removed than Et_3NH^+.

Discussion

Interaction between TIP and Alkylamines or Alkylammonium Hydroxides and Factors To Yield Clear Aqueous Titanate Solutions. The results of elemental analysis (Table 1) suggest that an acid−base reaction between amines and titanic acid derived from the hydrolysis of TIP occurred to yield the alkylammonium titanates. For example, the following reaction schemes can be written.

Hydrolysis reaction:

$$m\mathrm{Ti(OPr^{\mathit{i}})_4} + (2m+1)\mathrm{H_2O} \rightarrow \mathrm{H_2Ti_{\mathit{m}}O_{2\mathit{m}+1}} + 4m\mathrm{Pr^{\mathit{i}}OH} \quad \text{(I)}$$

Acid−base reaction:

For weak bases (alkylamines),

$$\mathrm{H_2Ti_{\mathit{m}}O_{2\mathit{m}+1}} + \mathrm{R_{\mathit{n}}H_{4-\mathit{n}}N^+OH^-} \rightarrow [\mathrm{R_{\mathit{n}}H_{4-\mathit{n}}N^+}][\mathrm{HTi_{\mathit{m}}O_{2\mathit{m}+1}^-}] + \mathrm{H_2O} \quad \text{(II)}$$

For strong bases (tetraalkylammonium hydroxides),

$$\mathrm{H_2Ti_{\mathit{m}}O_{2\mathit{m}+1}} + 2\mathrm{R_4N^+OH^-} \rightarrow [\mathrm{R_4N^+}]_2[\mathrm{Ti_{\mathit{m}}O_{2\mathit{m}+1}^{2-}}] + \mathrm{H_2O} \quad \text{(III)}$$

The first reaction is a simple hydrolysis reaction to afford polymeric titanic acid or hydrous titanium dioxide (I), and the others are the acid−base reactions of the titanic acid with the alkylamines or alkylammonium hydroxides, yielding alkylammonium hydrogen titanates (II) and alkylammonium titanates (III), respectively. The acid−base reactions take place when the alkylamines or alkylammonium hydroxides are more basic than titanate ion. Otherwise, only hydrolysis reaction may occur and pure hydrous oxides would be obtained. Pyridine is the very case, and neutral ammonium compounds such as bromide also have no interaction with titanic acid. The facts that the reaction time required to form the final clear solution depended on the basicity and the aqueous titanate solutions also could be prepared directly even from titanic acid strongly support the idea of acid−base interaction. On the other hand, in the case of the strong base-like TMAOH, it is possible to lead the second acid−base reaction, yielding neutral salts (III).

The pK_a (pK_1: primary dissociation exponent) value of titanic acid, which is not available in the literature, can be estimated to be around 9 because stoichiometric amounts of ammonium ion NH_4^+ was found in the precipitates derived from the reaction of TIP with ammonia (pK_a = 9.24). According to Pauling's rule on

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the acidity of oxo acids,[14] it can be assumed that the pK_2 value for the titanic acid is around 15, and thus second proton dissociation is impossible by the amines, but possible by the strong bases such as TMAOH. This can well account for the difference in the N/Ti ratios between the products obtained from the alkylamines and TMAOH. In the case of the alkylamines, only the first acid−base reaction may take place, to give acidic salts (II). The composition, namely, the number of *m* in the formula (II), varies in the range from 4 to 7 depending on the kind of amines. It is inferred that the variation is probably due to the formation of mixture containing tetratitanate, hexatitanate, and so on. At any rate, dissociable protons still remain in the titanates (II) derived from the alkylamines. As described later, the titanates are considered to have a layered structure, and the interaction between the titanate layers through a proton (including hydrogen bonding) would be enhanced because the charge density of the proton (H^+) is much higher than that of TMA^+ or alkylammonium cations ($R_nH_{4-n}N^+$). This may be the reason the decomposition temperature of the powder derived from TIP−Et_3N (type (II)) was higher than that of the powder from TIP−TMAOH (type (III)) shown in Figure 7.

It can be thought also that titanic acid is depolymerized in basic conditions to yield soluble oligomeric species. Actually, isopoly oxometalates are well-known to be depolymerized or decomposed to lower condensed species in basic conditions. Isopolymolybdate (VI), for example, undergoes the following reaction:[15]

$$[Mo_7O_{24}]^{6-} + 8OH^- \rightarrow 7MoO_4^{2-} + 4H_2O$$

Furthermore, the fact that water-soluble complexes such as $[(CH_3)_4N]_2[TiO(C_2O_4)_2]$ could be synthesized from the addition of oxalic acid to the basic titanate solution clearly indicates that the depolymerization of tetramethylammonium titanate by organic chelates readily occurs to transform a monomer-like structure. Accordingly, the chemical species in the titanate solutions seems to have a soft, flexible structure easily changeable by a reaction with bases or chelate ligands.

By the way, it has been reported that water-soluble complexes of niobium and tantalum were formed with alkylamines.[16,17] Fairbrother et al. suggested that the amines coordinated to the central metals, forming amine-coordinated metal complexes through dative bonds. However, in our experiments, clear solutions of titanates, niobates, and tantalates were quickly and easily obtained from the corresponding alkoxides by reaction with basic 2,2,6,6-tetramethylpiperidine, which is hardly coordinated to metals because of steric hindrance of four methyl groups near the nitrogen atom. This fact suggests that the coordination to metals was not necessarily required to obtain clear metalate solutions.

The size of ammonium ion also seems to be a crucial factor for obtaining clear titanate solutions. According to the results of Raman spectra, XRD, and electrical conductivity, the chemical species in the solutions can be thought to contain layered titanate anions and the counterions alkylammonium ions. The latter may locate between the titanate sheets without dissociation as the conductivity measurements showed. In the case of larger ammonium ions, the sheets would be partially exfoliated to yield colloidal solutions containing particles around 15 nm in diameter (by DLS). However, when small amines were employed, the layered structure became too strongly tightened because of larger charge density to be exfoliated, leading to coagulation or precipitates. Actually, the influence of cation size on the formation of aqueous titanate solution was examined through observing the change that occurred upon the addition of several alkaline salts to the TIP−TMAOH solution. Here, chloride salts were used as a cation supplier. The addition of tetramethylammonium to the solution remained unchanged, while that of alkaline metal ions (Li^+, Na^+, K^+, Rb^+, and Cs^+) resulted in the formation of amorphous precipitates, which can be supposed to be alkaline metal titanates. Actually, irrespective of the type of the amines or ammonium hydroxides used, the precipitates derived from KCl were crystallized as potassium hexatitanate ($K_2Ti_6O_{13}$) when heated to 600 °C, even after washing of the K^+−titanate precipitates. In the case of the TIP−Et_2NH system, for instance, in Table 1, the amorphous powder from the solution had the composition corresponding to tetratitanate, and the Raman spectrum was almost the same as that of tetratitanic acid as shown in Figure 4. Nevertheless, hexatitanate ($K_2Ti_6O_{13}$) was obtained by ion exchange and subsequent heat treatment at 600 °C. These results seem to be somewhat contradictory, but can be understand by assuming that the structure in the solution is so flexible as to change the composition by the kind of the ion used or heat treatment and that crystalline $K_2Ti_6O_{13}$ is most stable in $K_2O-xTiO_2$ compounds.[18]

In the case of other metalates shown in Table 2, cation size is not as important as the basicity, indicating that the structure and nature of metalates may be different from that of titanates. The formation of clear titanate solution can be explained by a synergic effect between the acid−base reaction and the size of ammonium ion. At the same time, titanate polymers such as titanic acid would be depolymerized by the base and delaminated by the existence of large ammonium ion.[13,19−20] The chemical species in the solutions does not exist as simple colloidal dispersions but as a compound "layered alkylammonium titanate".

Electric Conductivities, pH Values of the TIP−TMAOH Solutions. As shown in Table 1, the clear solutions derived from the mixture of TIP and TMAOH may contain $[TMA^+][HTi_3O_7^-]$, which was formed through the following reactions.

Hydrolysis reaction:

$$3Ti(OPr^i)_4 + 7H_2O \rightarrow H_2Ti_3O_7 + 12Pr^iOH$$

Acid−base interaction:

$$H_2Ti_3O_7 + TMAOH \rightarrow TMA^+HTi_3O_7^- + H_2O$$

In the solution containing *x* M concentration of titanium

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(15) Pope, M. T. *Heteropoly and Isopoly Oxometallates*; Springer-Verlag: Berlin, 1983; p 15.
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(17) Fairbrother, F.; Robinson, D.; Taylor, J. B. *J. Chem. Soc.* **1958**, 2074.

[Ti] and 0.1 M of TMAOH, the following relationships hold true:

$$[\mathrm{Ti}] = x\ (\mathrm{M})\ (x = 0-0.25)$$

$$[\mathrm{TMAOH}] = [\mathrm{TMA^+}] = [\mathrm{OH^-}] = 0.1\ (\mathrm{M})$$
(complete dissociation)

If the resultant $[TMA^+][HTi_3O_7^-]$ is NOT dissociated to TMA^+ and $HTi_3O_7^-$ in the solution, the conductivity of $[TMA^+][HTi_3O_7^-]$ would become zero and the conductivity of the solution comes to depend only on that of unreacted, free TMA^+OH^-, that is,

$$[\mathrm{TMA^+}] = [\mathrm{OH^-}] = 0.1-x/3$$

Using the reported equivalent ionic conductivity of TMA^+ and OH^- ($\lambda^0(TMA^+OH^-) = 211$ ($S\cdot cm^2\cdot equiv^{-1}$), at 18 °C),[21] the dependence of the solution conductivity and pH value on Ti concentration x can be designated as follows:

$$\lambda = 211(0.1 - x/3)\ (\mathrm{mS\cdot cm^{-1}})$$

$$\mathrm{pH} = 14 + \log(0.1 - x/3)$$

Those curves derived from the equations are plotted in Figure 3 as dashed lines and agree approximately with the experimental results (solid lines) in the range of x from 0 to 0.3. The slight deviation might be attributed to that from the assumed composition and to the influence of the concentration of the solution species because the conductivity generally decreased with increasing concentration. On the other hand, in the range of x higher than 0.3, it is difficult to estimate the behaviors because of the precipitation. This result indicates that the tetramethylammonium titanate is not dissociated and the TMA^+ was trapped or constrained by the counteranions, namely, layered titanates.

Layered Titanates. As shown in Figures 5 and 6, the reaction of TIP with tetraalkylammonium hydroxides was more likely to form the layered titanates than that with alkylamines. And the diffraction patterns showed regularly *d* spacings and are in good agreement with those of the layered titanates previously reported by several researchers.[19,20] Raman spectra (Figure 4) also support the presence of layered titanates comparable to layered $H_2Ti_4O_9$.

Generally, colloidal layered titanates have been synthesized by a multistep process, that is, solid-phase reaction, ion exchange, and delamination. As a typical example, first, $Cs_xTi_{(2-x/4)}\square_{x/4}O_4$ (□: vacancy) was synthesized by the solid-phase reaction of TiO_2 with $CsCO_3$. Second, an ion-exchange reaction of Cs^+ with H^+ for a few days gave $H_xTi_{(2-x/4)}\square_{x/4}O_4$, which was finally exfoliated by quaternary ammonium ion. This process requires high temperature and a large amount of ammonium ions and, moreover, takes a long time. On the other hand, our process consists of simple reactions at room temperature and is advantageous for saving time and materials. In addition, our solutions are completely free of halogen and alkaline ions, being most suitable as the starting materials for other titanium compounds. Using these solutions, not only layered titanates but also TiO_2 thin films can be prepared at low temperatures.[22] Our process and the chemical species formed by each step in this study can be illustrated as in Figure 8. Alkylammonium titanates can be prepared by the acid−base reaction of TIP with water and alkylamines or tetraalkylammonium hydroxides. Transparent titanate solutions are prepared when basic and bulky amines or ammonium hydroxides are used. Otherwise, amorphous precipitates are obtained. When one starts from the titanate solution, many kinds of compounds or precursor of ceramics can be prepared in an aqueous medium. Titanium chelate compounds are synthesized through depolymerization. Potassium hexatitanate ($K_2Ti_6O_{13}$) is prepared by ion exchange, followed by heat treatment at 600 °C. Potassium titanyl phosphate (KTP, $KTiOPO_4$) is easily prepared by mixing with potassium dihydrogen phosphate (KH_2PO_4) and then being heated at 600 °C.[11] The layered titanate film is dip-coated on glass, and anatase film can be obtained as low as 350 °C. The details of the preparation and characterization have been reported elsewhere.[22] The formation of these compounds described above demon-

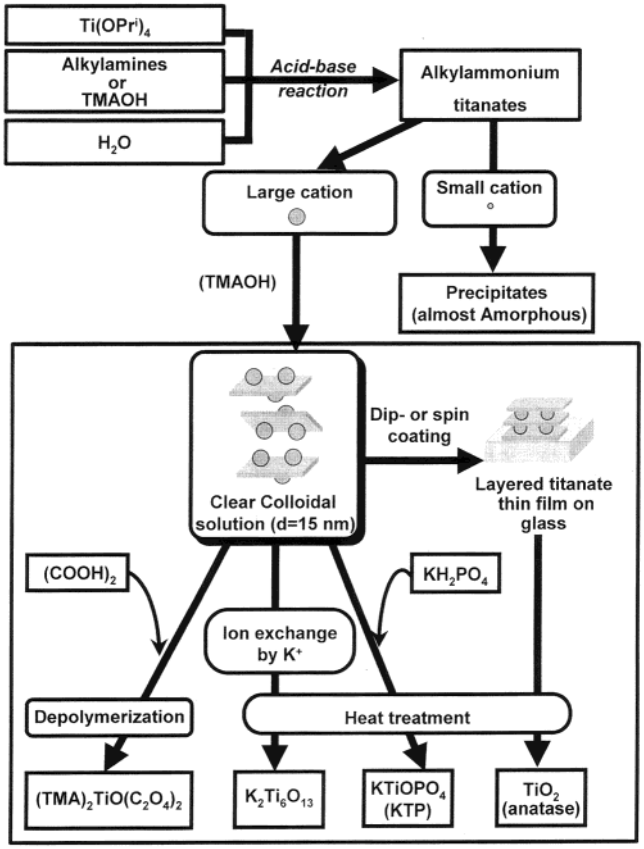

Figure 8. Schematic illustration for the reaction investigated in this study and for the usefulness of the aqueous titanate solution as a starting material.

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strates the availability, and at the same time, the properties of our titanate solutions.

Conclusions

It is concluded that very stable, clear titanate colloidal solutions were obtained by the reactions of metal alkoxides with bulky amines or quaternary ammonium hydroxides and that the reaction can be generalized as the acid−base reactions between metallic acids and amines based on pK_a values. The chemical species in the solutions exist not as simple colloidal dispersions of TiO_2 (anatase or rutile) but as the compounds "layered alkylammonium titanates". To our knowledge, this paper is the first report on the preparation of layered alkylammonium titanates by the solution method.

These aqueous metalate solutions are completely free of halogens, alkaline metal ions and chelates, and can be used as a source material for preparing various titanium compounds including use of the sol−gel technique and will realize a novel, environmentally friendly synthetic process of ceramic films, which can be applied to photocatalysts, zeolites, and optical and electronic devices.

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