Synthesis of Uniform Anatase TiO₂ Nanoparticles by Gel–Sol Method

1. Solution Chemistry of Ti(OH)_{4-n} Complexes

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The mole fractions of hydroxo complexes of titanium(IV) ion in an aqueous solution with 0.10 mol dm⁻³ NaClO₄ at 25 °C have been determined as a function of pH by a newly developed analytical procedure based on UV spectrophotometry, using a metastable homogeneously distributed Ti(OH)₄ solid, or the solubility of Ti(OH)₄ solid in an inhomogeneous system, has been obtained by ICP measurement for the solution phase. A combination of these data yielded the absolute concentration of each complex species in equilibrium with Ti(OH)₄ solid, or the solubility of Ti(OH)₄ solid in the gel–sol system.

Key Words: titania; anatase; nanoparticles; hydroxo complex; stability constants; titanium hydroxide; gel–sol method.

INTRODUCTION

Monodispersed anatase titania particles were prepared by the gel–sol method based on a phase transformation process from titanium hydroxide gel or hydrous TiO₂ (1, 2). In this study it was found that spindlelike uniform titania particles (length $\geq$0.3 μm; aspect ratio $\leq$8) were obtained in the presence of ammonia as a powerful shape controller and that much smaller nanoparticles of smaller aspect ratios were produced in a lower pH range in the absence of ammonia. For understanding the more detailed background of the gel–sol process, it seems necessary to study the complex chemistry and dynamic behavior of complexes in much simpler systems. Thus, as part 1 of this series, we would like to start with the study on the solution chemistry of titanium hydroxo complexes leading to the formation of anatase titania.

Ti(IV) ion is known to form complexes with a wide variety of anions and other complexing agents, such as hydroxide (3–12), fluoride (12–16), sulfate (3, 4, 17, 18), phosphate (11, 19, 20), chloride (4, 13, 21), carbonate (22), hydrogen peroxide (23, 24), oxalate (25–28), citrate (29–31), lactate (31), tartrate (29, 32, 33), malate (34, 35), ammonia (11, 12), amines (36), 8-hydroxyquinoline (9, 24, 29, 37, 38), thionylfluoracetone (9, 10), etc. Relevant textbooks (39), reviews (40, 41), and data books (42–44) are also available. The measurements are based on ion-exchange elution (3), batchwise ion exchange (4–7, 17, 21), ion-exchange chromatography (8, 13, 25), liquid–liquid extraction (9, 10, 29, 32, 34, 37), potentiometry (14, 20, 23), dialysis (8, 31), solubility measurement (5, 8, 9, 11, 29, 30, 32), spectrophotometry (37, 38), radiochemical paper electrophoresis (7), NMR (33), etc. For studying the solution chemistry of hydroxo complexes, the pH control has been performed by using inert acids and bases, such as perchloric acid and sodium hydroxide. However, to the best of our knowledge, spectrophotometric analysis on hydroxo complexes of Ti(IV) has never been reported.

The solubility of hydrous TiO₂ is known to be virtually constant above pH 4, but sharply decrease below pH 3 (5, 8, 9, 39). The constant solubility above pH 4 may suggest the dominance of the neutral complex, Ti(OH)₄, and it seems evident that the dominant species in HClO₄ solutions in the pH range, at least, from 1 down to 0 is Ti(OH)₂⁺ (or TiO³⁺) from the measurements based on cation-exchange methods (3–7). The pH-dependent solubility of hydrous TiO₂, nearly proportional to the second power of the acid concentration below pH 2, may support the predominance of Ti(OH)₂⁺ in this pH range.

However, the composition of the hydrous TiO₂ does not appear to have clearly been defined, and there seems to be no definite evidence that a single species, Ti(OH)₂⁺, is dominant below pH 2. In addition, although the presence of Ti(OH)₃ has been expected, its reliable data are unavailable as yet probably because of the difficulty in detection by conventional methods (39).

The objectives of the present study are to specify the composition of the hydrous TiO₂, to re-evaluate the contribution of each complex species to the solubility of the hydrous TiO₂, and to...
identify the precursor species for the formation of anatase TiO₂ nanoparticles from the hydrous TiO₂, as essential bases for the mechanistic studies on the formation of anatase TiO₂ nanoparticles in the gel–sol system. For these purposes, a new analytical method, based on the UV spectrophotometry for a metastable homogeneous system of titanium hydroxo complexes, has been introduced.

EXPERIMENTAL

Materials

Reagent-grade titanium (IV) isopropoxide, sodium hydroxide, and perchloric acid have been used as received.

Preparation of Titanium Hydrous Oxide

Titanium hydrous oxide precipitate was prepared by mixing titanium isopropoxide (TIPO: Ti(OCH(CH₃)₂)₄) with deionized water at a varying pH containing HClO₄ or NaOH and NaClO₄ to adjust the pH value of 0.10 mol dm⁻³ HClO₄. Then the pH value of 0.10 mol dm⁻³ HClO₄ (100 cm³) after mixing with a known amount of titanium hydroxide precipitate was compared to the calibration curve to determine the mole number of the released OH⁻ ion, leading to the composition of the dominant hydroxo complex. The exact amount of Ti(IV) in this solution was determined by ICP measurement after the pH measurement. For this experiment, the titanium hydroxide precipitate was prepared, purified, and used without freeze-drying. The approximate molarity of Ti(IV) in the stock suspension of titanium hydroxide precipitate was predetermined by dissolving a part of the homogenized stock suspension in 1.0 mol dm⁻³ HClO₄, followed by ICP measurement.

To check if or not a single species is dominant at pH ≥ 1, the behavior of the UV spectrum was observed with the change of pH around this pH.

Solubility of Titanium Hydrous Oxide as a Function of pH

After preparation and purification of titanium hydroxide precipitate, 10⁻¹⁻¹ mol of the titanium hydroxide oxide precipitate was directly suspended in 20 cm³ of water of different pH values, ranging from 1 to 12, with an ionic strength of 0.1, adjusted with NaClO₄, and aged at 25°C for 72 h, which was sufficient for establishing the equilibrium between the complexes in the solution phase and the hydroxide oxide precipitate, as confirmed by ICP measurement as a function of time for the supernatant solution. After the measurement of the final pH of each aged sample, they were centrifuged at 18,000 rpm for 30 min, and the supernatant Ti(IV) concentrations were measured by ICP.

Formation Rate of Anatase TiO₂ Dependent on pH

Forty cubic centimeters of 0.25 mol dm⁻³ titanium hydroxide oxide gel, instantly formed upon mixing titanium(IV) isopropoxide with water at a varying pH containing HClO₄ or NaOH and NaClO₄ to adjust the final ionic strength to 0.10, was aged for 2 h at room temperature to stabilize the pH and then for 30 min in an oil bath preheated at 100°C. The initial pH of each sample at the start of aging at 100°C ranged from 0.7 to 11.6. The yield of anatase titania particles from titanium hydroxide oxide in each sample was determined by dissolving the remaining titanium hydroxide oxide in a solution of 2.0 mol dm⁻³ HNO₃ and ICP analysis on the supernatant Ti(IV) after centrifugal separation of anatase TiO₂ settled intact in the 2.0 mol dm⁻³ HNO₃. This method is based on the nature of hydrous TiO₂ ready dissolved in 2.0 mol dm⁻³ HNO₃, and of crystalline anatase TiO₂, virtually undissolved in 2.0 mol dm⁻³ HNO₃.

The mean size of the anatase TiO₂ particles after aging for 24 h at 100°C as a function of pH was measured by transmission electron microscopy.
DATA ANALYSIS

If the hydroxo complexes of titanium(IV) in water are assumed to be generally written as Ti(OH)_{n}^{(4-n)+} (n = 2, 3, 4) the UV absorbance of their homogeneous solution, \( A_i \), in a quartz cell of light path length of 1 cm at a wavelength \( \lambda_i \) may be given as

\[
A_i = \varepsilon'_a c_a + \varepsilon'_b c_b + \varepsilon'_c c_c, \tag{1}
\]

where \( \varepsilon'_a \), \( \varepsilon'_b \), and \( \varepsilon'_c \) are absorption coefficients (mol\(^{-1}\) dm\(^3\) cm\(^{-1}\)); \( c_a \), \( c_b \), and \( c_c \) are the concentrations of Ti(OH\(_2^+\)), Ti(OH\(_3^+\)), and Ti(OH\(_4^-\)), respectively. The stability constants of Ti(OH\(_2^+\)), \( K_b \), and of Ti(OH\(_3^+\)), \( K_c \), may be defined as

\[
K_b = \frac{c_b}{c_a[OH^-]} \tag{2}
\]

and

\[
K_c = \frac{c_c}{c_b[OH^-]} \tag{3}
\]

If the total concentration of these complexes is denoted by \( c_0 \), it holds that

\[
c_a + c_b + c_c = c_0. \tag{4}
\]

A combination of Eqs. [1]–[4] yields

\[
A_i = \frac{c_0(\varepsilon'_a + \varepsilon'_b K_b[OH^-] + \varepsilon'_c K_b K_c[OH^-]^2)}{1 + K_b[OH^-] + K_b K_c[OH^-]^2}. \tag{5}
\]

If the pH is sufficiently low, the contribution of Ti(OH\(_4^-\)) may be ignored and thus Eq. [5] may be approximated by

\[
A_i = \frac{c_0(\varepsilon'_a + \varepsilon'_b K_b[OH^-])}{1 + K_b[OH^-]}. \tag{6}
\]

or

\[
A_i = -\frac{1}{K_b} A_i - \varepsilon'_b c_0 + \varepsilon'_b c_0. \tag{7}
\]

If \( \varepsilon'_b \) is known, one may plot \( A_i \) against \( (A_i - \varepsilon'_b c_0)/[OH^-] \) (≡ \( X_i \)) based on Eq. [7], yielding \( K_b \) from the slope of the straight line and \( \varepsilon'_b \) from the intercept of the \( A_i \) axis at \( X_i = 0 \). Here, \( [OH^-] \) is defined by \( 10^{-14 + \text{pH}} \).

If the contribution of the third component, Ti(OH\(_4^-\)), becomes significant with increasing pH, one must use the following formula transformed from Eq. [5] without approximation:

\[
A_i = \frac{1}{K_c} \left[ A_i - \varepsilon'_c c_0 \right] + \varepsilon'_c c_0. \tag{8}
\]

Since \( K_b \) and \( \varepsilon'_b c_0 \) are now known from the plot of Eq. [7], one can plot \( A_i \) against \( (A_i - \varepsilon'_c c_0)/[OH^-]^2 + (A_i - \varepsilon'_b c_0)/[OH^-] \) (≡ \( Y_i \)), yielding \( K_c \) from the slope and \( \varepsilon'_c \) from the intercept at \( Y_i = 0 \).

From Eqs. [2] and [3], \( \log c_a \) and \( \log c_b \) are given as a function of pH,

\[
\log c_a = -2\text{pH} + \log c_c - \log K_b K_w - \log K_c K_w \tag{9}
\]

and

\[
\log c_b = -\text{pH} + \log c_c - \log K_c K_w. \tag{10}
\]

where \( K_w = [H^+][OH^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \). Here, it is noteworthy that \( c_c \), or [Ti(OH\(_4^-\)), is constant, regardless of pH, in the presence of Ti(OH\(_4^-\)) precipitate, as may be detected as a plateau of the solubility curve of titanium hydroxide precipitate in the higher pH range. Once \( c_c \) is determined from the measurement of the solubility of the hydroxide precipitate, \( \log c_a \) and \( \log c_b \) are given as fixed straight lines with slopes -2 and -1, against pH, and the relative positions of these two lines and \( \log c_c \) may be illustrated as in Fig. 1.

RESULTS AND DISCUSSION

Composition of Titanium Hydrous Oxide

Figure 2 shows the TG and DTA curves of the titanium hydrous oxide powder, prepared by mixing Ti(IV) isopropoxide with distilled water, purified by centrifugal rinsing with pure water, and freeze-dried. The stepwise weight loss with the endothermic transition at 70° C, the exothermal transition at 325° C, and the exothermal transition at 540° C may correspond to the evaporation of adsorbed water, the transition from
titanium hydrous oxide to TiO(OH)$_2$, and the transition from TiO(OH)$_2$ to TiO$_2$, respectively. If we assume that the actual weight loss of the titanium hydrous oxide started from 70°C, by which 4% of the original weight had already been lost, the total weight loss of the titanium hydrous oxide may be calculated as (0.34–0.04) × 100/(1.00–0.04) = 31.2%. This value is very close to the theoretical weight loss of 31.1% with the transition from Ti(OH)$_4$ to TiO$_2$. Hence, one may conclude that the titanium hydrous oxide assumes a composition of titanium hydroxide, Ti(OH)$_4$.

Characteristics of the UV Spectra in the Ti(IV) Complex System

Figure 3 shows UV spectra of the metastable complex system of 1.25 × 10$^{-4}$ mol dm$^{-3}$ in total Ti(IV) concentration at different pH values at 25°C. Here, the weak absorption of ClO$_4^-$ below 220 nm was subtracted. One of the most salient characteristics of these spectra may be that they are virtually fixed below pH 1.07 within the tested pH range, suggesting that a single complex species, whose absorption peak seems to be located at a wavelength much lower than 200 nm, is dominant. Another characteristic is that the absorption spectrum at pH 9.31 basically differs from those below pH 3.69, as is obvious from the absorbance at pH 9.31 significantly lower than those at pH 3.30 and 3.69 in the wavelength range between 240 and 340 nm. This may imply that the dominant species in the alkaline range is different from those below pH 3.69.

As is already expected from the spectra at pH 3.30, 3.69, and 9.31 with their relatively high backgrounds in the wavelength range above 340 nm, the solution was more or less unstable as showing some sign of the precipitation of Ti(OH)$_4$ gel in the pH range above pH 3. This fact may suggest the increasing contribution of the neutral complex, Ti(OH)$_4$, in this pH range.

Composition of the Complex at a pH ≤ 1

Figure 4 shows the calibration curve of [H$^+$] vs pH below pH 2. When 0.0131 mol dm$^{-3}$ Ti(OH)$_4$ was dissolved in 0.100 mol dm$^{-3}$ HClO$_4$, the resulting pH was found to be 1.21, corresponding to [H$^+$] = 0.075 mol dm$^{-3}$. Thus, 0.025 mol dm$^{-3}$ (=0.100–0.075) of hydroxide ion, OH$^-$, must have been released from the 0.0131 mol dm$^{-3}$ Ti(OH)$_4$. In other words, the average $n$ value for Ti(OH)$_{4-n}^+$ complexes at pH 1.21 is calculated as 2.09 (=4.00–0.025/0.0131). This means that the complex species at pH 1.21 is mostly Ti(OH)$_2^{2+}$, probably with a small content of a complex of high $n$, such as Ti(OH)$_3^+$. If we consider the presence of a single complex species below pH 1.07, as suggested from the UV spectra in Fig. 3, the single species must be Ti(OH)$_2^{2+}$. This conclusion is congruent with most data reported before for the overall composition of the complexes.
in this pH range (39). As has been confirmed that the complex species below pH 1 is a single species, Ti(OH)\(^{2+}\), it seems reasonable to consider that the increase in absorbance above pH 1 in Fig. 3 is due to the increasing contribution of Ti(OH)\(^{3+}\), followed by the increasing weight of the neutral complex, Ti(OH)\(_4\), above pH 3.

**Stability Constants and Mole Fractions of the Complexes**

For the analysis of the spectrophotometric data, the UV spectra at different pH values in Fig. 3 were modified into the absorbance as a function of pH for each wavelength, as shown in Fig. 5. Here, each curve in Fig. 5 was obtained as a sixth-degree polynomial by least squares for the data points.

Figure 6 shows the plot of \(A_i\) vs \(X_i\) in Eq. [6] for wavelengths 260, 270, 280, 290, and 300 nm, using the data of \(A_i\) as a function of pH in Fig. 5. Here, each \(\epsilon_i^a\) used in this plot was obtained from the UV spectra at a pH \(\leq 1.07\) in Fig. 3, as listed in Table 1. We could obtain a linear relationship for \(A_i\) vs \(X_i\) in the pH range from ca. 1.5 to 2.3, and \(A_i\) gradually deviated downward from the straight line with the decreasing \(X_i\) or increasing pH, suggesting the increasing contribution of another complex, Ti(OH)\(_4\), of a lower absorption coefficient in the higher pH range. From the average slope of the linear range and the individual intercepts for different wavelengths, we obtained \(\log K_b = 11.9\) and each \(\epsilon_i^b\) as listed in Table 1.

Incidentally, if the increasing absorbance with increasing pH from 1 to 2.5 in Fig. 3 is assumed to be due to the increasing contribution of Ti(OH)\(_4\) instead of Ti(OH)\(^{3+}\), there must be a linear relationship in the plot of \(A_i\) vs \((A_i - \epsilon_i^c c_0)/[OH^-]^2\)

and downward deviation in the higher pH range. However, since this plotting resulted in only a curve going up with increasing curvature above pH 1.5, there is no doubt that the increasing absorbance with pH from 1 to 2.5 is not due to the increasing contribution of Ti(OH)\(_4\).

Figure 7 shows the plot of \(A_i\) vs \(Y_i\) corresponding to Eq. [8] for a higher pH range above 2 in Fig. 5. From the average slope and the individual intercepts for different wavelengths, we obtained \(\log K_c = 10.3\) and each \(\epsilon_i^c\) as listed in Table 1.

Figure 8 shows the changes of the mole fractions of the three complex species with pH, as calculated from the stability constants, \(K_b\) and \(K_c\). In particular, it is noteworthy that the presence of the Ti(OH)\(^{3+}\) complex and its significant contribution have clearly been revealed.

**Solubility of Ti(OH)\(_4\) Precipitate as a Function of pH**

The solubility data of the Ti(OH)\(_4\) precipitate, obtained from the ICP measurement of the supernatant solutions, are shown as a function of pH in Fig. 9 by closed circles. The straight

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**TABLE 1**

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>(\epsilon_i^a)</th>
<th>(\epsilon_i^b)</th>
<th>(\epsilon_i^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260</td>
<td>(6.40 \times 10^3)</td>
<td>(7.27 \times 10^3)</td>
<td>(6.18 \times 10^3)</td>
</tr>
<tr>
<td>270</td>
<td>(5.60 \times 10^3)</td>
<td>(6.59 \times 10^3)</td>
<td>(5.42 \times 10^3)</td>
</tr>
<tr>
<td>280</td>
<td>(4.00 \times 10^3)</td>
<td>(5.36 \times 10^3)</td>
<td>(4.58 \times 10^3)</td>
</tr>
<tr>
<td>290</td>
<td>(3.20 \times 10^3)</td>
<td>(4.22 \times 10^3)</td>
<td>(3.29 \times 10^3)</td>
</tr>
<tr>
<td>300</td>
<td>(2.48 \times 10^3)</td>
<td>(2.97 \times 10^3)</td>
<td>(2.32 \times 10^3)</td>
</tr>
</tbody>
</table>

Stability constants

\[\log K_b = 11.9\]

\[\log K_c = 10.3\]
lines of log $c_a$ and log $c_b$ as a function of pH were obtained from the experimental data of log $c_i (= -5.5)$, represented by the horizontal line, and the data of $K_b$ and $K_c$. The dashed curve represents the calculated solubility as the total of $c_a$, $c_b$, and $c_c$. Obviously, there is good agreement between the solubilities obtained directly from the ICP measurement and those calculated from $c_c$, $K_b$, and $K_c$ on the basis of UV spectrophotometry.

Although our data for the solubility in the alkaline range, determined by the equilibrium concentration of Ti(OH)$_4$ complex, agree with most of the preceding data in the literature (39), those below pH 2 are somewhat higher than the preceding data. This may probably be due to the nature of the hydroxide gel. For example, we used freshly prepared Ti(OH)$_3$ precipitate without drying, and its solubility was likely to be lowered even with freeze-drying or with aging for a long time or at a relatively high temperature. In fact, we observed a dramatic reduction of the solubility of Ti(OH)$_4$ gel during the first aging period at 100°C in a gel–sol system for the synthesis of uniform anatase TiO$_2$ particles in the presence of triethanolamine and with the elevation of temperature to 140°C for the following second aging period (1, 2). These effects of aging time and temperature may be explained in terms of transition to a more rigid gel structure with the progress of hydrogen bonding. If the Ti(OH)$_4$ solids used in the foregoing studies were subjected to some of such effects, the somewhat lower solubility below pH 2 in the literature may readily be understood. If it is the case, the actual equilibrium concentration of Ti(OH)$_4$ complex in the literature may possibly be somewhat lower than reported.

In the solubility curve of Fig. 9, one may find a pH range from 3 to 8 where the experimental data are a little higher than the average solubility level. The slightly higher solubilities were not affected by variation of the rotation rate for the centrifugal separation of the Ti(OH)$_4$ precipitate up to 50,000 rpm for 30 min. In view of the virtually pH-independent deviation from the average solubility level, this may not be due to the contribution of dehydrated, dimerized, or trimerized clusters of a charged complex, such as Ti(OH)$_3^{2+}$, since their concentrations must be proportional to the first, second, or third power of the concentration of the coexisting charged single complex, respectively. On the other hand, the measured solubilities above pH 10 appear to be lower than the average level. Hence, the most likely is the variation of the concentration of Ti(OH)$_4$ complex in equilibrium with the Ti(OH)$_4$ gel whose rigidity, or degree of hydrogen bonding, may depend on pH to some extent.
The contribution of complexes of higher coordination of \( \text{OH}^- \), such as \( \text{Ti(OH)}_{6}^{2+} \), leading to the increase in solubility in the high pH range, was not observed in the tested range.

**Formation Rate of Anatase TiO\(_2\) as a Function of pH**

Figure 10a shows the yield of anatase TiO\(_2\) transformed from Ti(OH)\(_4\) gel (0.25 mol dm\(^{-3}\)) with [NaClO\(_4\)] = 0.10 mol dm\(^{-3}\) as a function of initial pH after aging for 30 min in an oil bath preheated at 100°C. The pH was measured after quenching to room temperature. The pH-dependent yield of TiO\(_2\) within a limited time, 30 min, may represent the formation rate of TiO\(_2\) from Ti(OH)\(_4\) gel as a function of pH. One may find that the formation rate of TiO\(_2\) significantly increases with the reduction of pH, especially in the acidic range. Figure 10b shows the final mean size of TiO\(_2\) as a function of initial pH after aging for 24 h at 100°C in the same system, where the yield of TiO\(_2\) after 24 h was virtually 100% below pH 7, but ca. 70% at pH 9.0 and ca. 0% at pH 11.6. Obviously, the final particle size is reduced with decreasing pH to ca. 2 but a slight increase below pH 2. From the comparison between Figs. 10a and 10b, one may conclude that the nucleation rate of TiO\(_2\) is greatly accelerated with the reduction of pH to ca. 2. If the nucleation rate of TiO\(_2\) were simply described only by the supersaturation for TiO\(_2\), there would be no pH dependence in its nucleation rate since the supersaturation for TiO\(_2\), represented by the concentration of Ti(OH)\(_4\) complex virtually in equilibrium with the Ti(OH)\(_4\) precipitate, is constant for all pH. In other words, the strong pH dependence in the nucleation rate of TiO\(_2\) reveals that some specific complex is responsible for the nucleation of TiO\(_2\) as a precursor intermediate. The sharp increase of the formation rate, or nucleation rate, with the reduction of pH from 6 to 2 in Fig. 10a may be closely related to the increase in the equilibrium concentration of Ti(OH)\(_3\)\(^+\) in Figs. 8 and 9. Moreover, the increase in the formation rate of TiO\(_2\) below pH 3 is rather small, as compared to the dramatic increase of the equilibrium concentration of Ti(OH)\(_2\)\(^+\) species in proportion to the square of [H\(^+\)]. Therefore, the Ti(OH)\(_3\)\(^+\) species is assigned to the precursor complex to anatase TiO\(_2\) in the gel–sol system.

On the other hand, if we take into account that the overall reaction for the transformation from Ti(OH)\(_4\) gel to TiO\(_2\) sol is Ti(OH)\(_4\) → TiO\(_2\) + 2H\(_2\)O, the precursor complex must only be a catalyst or an intermediate, and thus Ti(OH)\(_4\) complex, constantly furnished from the Ti(OH)\(_4\) gel with the progress of the reaction, may also contribute to the polycondensation reaction in the formation of TiO\(_2\) particles. Therefore, the following elementary processes may be involved in the overall reaction.

![Diagram](image_url)

The decrease in the formation rate of TiO\(_2\) below pH 2 in Fig. 10a may be due to the reduction of the concentration of Ti(OH)\(_4\) complex after the total dissolution of Ti(OH)\(_4\) gel in this pH range. This fact may support the above scheme in which Ti(OH)\(_3\)\(^+\) complex can play the role of the precursor to TiO\(_2\) in collaboration with Ti(OH)\(_4\) complex.

**CONCLUSIONS**

1. The composition of the freshly prepared hydroxide precipitate was found to be Ti(OH)\(_4\), as determined from the TG-DTA measurement.
(2) The predominant hydroxo complex of Ti(IV) in the pH range below 1 is Ti(OH)$_2^{2+}$, as confirmed by UV spectrophotometry and pH measurement of released OH$^-$ from Ti(OH)$_4$ gel.

(3) The concentrations of the Ti(OH)$_2^{2+}$ and Ti(OH)$_3^+$ complexes, $c_a$ and $c_b$, in equilibrium with the Ti(OH)$_4$ precipitate were determined as a function of pH from the stability constants of Ti(OH)$_2^{2+}$ and Ti(OH)$_3^+$ complexes, $K_b$ and $K_{ca}$, determined by UV spectrophotometry, and from the concentration of Ti(OH)$_4$ complex, $c_r$, in equilibrium with Ti(OH)$_4$ precipitate, determined by ICP measurement. In particular, the presence of Ti(OH)$_3^+$ complex was clearly manifested in the diagram for the mole fractions of the individual complexes as a function of pH. The total solubility as a function of pH, calculated from $c_a$, $c_b$, and $c_r$, was in good agreement with those directly measured by ICP.

(4) The precursor complex to anatase TiO$_2$ has been specified to be Ti(OH)$_4^3-$ in the gel–sol system.

(5) Elementary processes in the transformation of Ti(OH)$_4$ gel to TiO$_2$ sol, involving the neutral complex, Ti(OH)$_4^-$, as a counterpart of Ti(OH)$_3^+$, has been suggested.

REFERENCES
