Hydrolysis of Titanium(IV) in Aqueous (Na,H)Cl Solution

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Hydrolysis of titanium(IV) has been studied in 2.0 mol dm^{-3} aqueous (Na,H)Cl solution at 25 °C by means of e.m.f. measurements of a cell containing 0.019 3—0.048 2 mol dm^{-3} titanium(IV). Titanium(IV), which is present in the form of titanyl ion, $[TiO]^{2+}$, is partially hydrolyzed to form a polynuclear cationic complex, $[(TiO)_8(OH)_{12}]^{4+}$ ($\log \beta_{8,12} = -1.6_8 \pm 0.1_0$).

It is well known [1] that titanium(IV) forms a hydroxide precipitate even in highly acidic solution. In such a case the presence of cationic or anionic hydrolyzed species, other than the slightly soluble neutral species $TiO(OH)_2$ or $Ti(OH)_4$, should be anticipated. Few studies have, however, hitherto been made on the formation and presence of such ionic complex species, although some data have been reported for the mononuclear hydrolyzed species $[Ti(OH)]^{3+}$, $[TiO(OH)]^+$ {or $[Ti(OH)_3]^+$}, *etc.*[2-7]

The present study has been carried out to elucidate hydrolytic equilibria of titanium(IV) in aqueous solution and to reveal the formation and presence of polynuclear cationic hydrolyzed species for titanium(IV) in 2.0 mol dm^{-3} aqueous (Na,H)Cl solution at 25 °C. Potentiometry with a constant ionic medium [8] was adopted in principle for the present study, but the ' batch ' system [9] was used instead of the ' titration ' system because of very slow attainment of equilibrium.

EXPERIMENTAL

Reagents.—Titanium(IV) stock solution was prepared either by diluting titanium(IV) tetrachloride directly in aqueous hydrochloric acid or by precipitating once as a hydroxide followed by dissolving the precipitate in the aqueous hydrochloric acid. The absence of such catonic impurities as silicon(IV), iron(III), zirconium(IV), and tin(IV) which may also cause the hydrolysis, was ascertained by the conventional spectrophotometric analytical methods,[10] *i.e.* silicon(IV) as silicomolybdate, iron(III) as bipyridyl complex after its reduction with hydroxylamine hydrochloride, zirconium(IV) as the alizarin sulphonate complex, and tin(IV) as the 8-hydroxyquinoline complex, respectively. The stock solution was standardized for titanium(IV) concentration by the conventional gravimetric method, for the free hydrogen-ion concentration by potentiometric titration with the method of Gran's plot,[11] and for chloride-ion concentration by the conventional precipitation-titrimetric method, respectively, to be 0.937 mol dm^{-3} titanium(IV) in 3.968 mol cm^{-3} aqueous hydrochloric acid solution.

Sodium chloride solution was prepared from the recrystallized salt. Its concentration was determined by evaporating an aliquot portion to dryness at *ca.* 120 °C and weighing the residue. Hydrochloric acid was standardized after the appropriate dilution with sodium carbonate as the primary standard according to the conventional procedure. Sodium hydroxide solution was prepared and standardized as reported earlier.[9]

Chemicals used were of analytical reagent grade as supplied by Wako Pure Chemicals Ind., Ltd., Japan, unless otherwise stated. The same precautions for co-existing impurities as in the previous study [9] were taken for the present study.

Apparatus.—The apparatus used in the previous study [9] was also applied in the present case.

Procedure.—Potentiometric measurements were carried out on several series of solutions, which constituted part

$$\mathrm{Hg,Hg_2Cl_2|3.33\ mol\ dm^{-3}\ KCl||2.0\ mol\ dm^{-3}\ KCl||2.0\ mol\ dm^{-3}\ NaCl||test\ solution|glass\ electrode}$$

of the cell shown above. The test solution had the following composition: B mol dm^{-3} $[TiO]^{2+}$, H mol dm^{-3} H^+, $(2.0 - H - 2B)$ mol dm^{-3} Na^+, and 2.0 mol dm^{-3} Cl^-. The e.m.f of the cell containing the test solution was measured after standing for 7 h at 25°C, which was sufficient to attain equilibrium (variations in e.m.f. were less than ±0.2 mV).

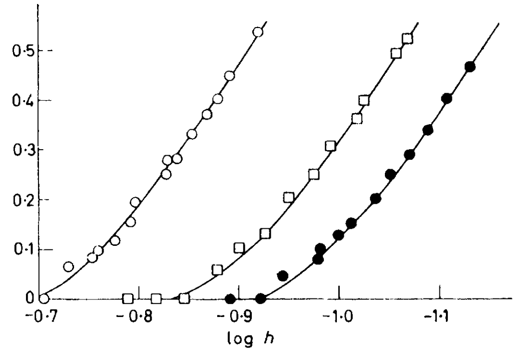

Figure 1 Relation between Z and $\log h$ for specified values of B. $-\log B = 1.317$ (○), 1.578 (□), and 1.714 (●). The full lines are theoretical curves drawn by using the value of $\log \beta_{8,12} = -1.6_8$

The equilibrium hydrogen-ion concentration ($[H^+] = h$) was calculated from the measured e.m.f. according to

$$E/\mathrm{mV} = E^{\ominus} + 59.15 \log h + E_j(h) \qquad (1)$$

equation (1), where $E^{\ominus}$ is the standard electrode potential and $E_j(h)$ the liquid junction potential of the cell respectively, the latter of which could be approximated by the relation $E_j(h) = E_j{\cdot}h$.

RESULTS

Figure 1 shows experimental data for the relation between Z, the average number of hydrogen ions released from each hydrolyzed titanium(IV) ion, and $\log h$, the logarithm of the free hydrogen-ion concentration at equilibrium, for the specified value of B, the total concentration of titanium(IV). It is evident from Figure 1 that polynuclear hydrolyzed complex species of titanium(IV) are formed and are present in the solution of *ca.* 0.1 mol dm^{-3} free acid concentration. If polynuclear species are expressed by the general formula $[(TiO)_q(OH)_p]^{(2q-p)+}$, then the hydrolysis of titanium(IV) is represented in equation (2), where p is the number of hydroxide groups and q the

$$q[\mathrm{TiO}]^{2+} \xrightleftharpoons{\beta_{qp}} [(\mathrm{TiO})_q(\mathrm{OH})_p]^{(2q-p)+} + p\mathrm{H}^+$$

$$\beta_{qp} = [(\mathrm{TiO})_q(\mathrm{OH})_p{}^{(2q-p)+}]h^p/[\mathrm{TiO}^{2+}]^q \qquad (2)$$

number of titanium(IV) atoms present in the hydrolysed species. Water of hydration in all the species has been omitted for simplicity. The terms Z and B are given by equations (3) and (4). From these equations, the total

$$Z = \frac{\sum_1^p \sum_1^q p\beta_{qp}[\mathrm{TiO}^{2+}]^{q-1}h^{-p}}{1 + \sum_1^p \sum_1^q q\beta_{qp}[\mathrm{TiO}^{2+}]^{q-1}h^{-p}} \qquad (3)$$

$$B = [\mathrm{TiO}^{2+}]\left(1 + \sum_1^p \sum_1^q q\beta_{qp}[\mathrm{TiO}^{2+}]^{q-1}h^{-p}\right) \qquad (4)$$

concentration of hydrogen ion released by the hydrolysis, BZ, can then be given by equation (5).

$$BZ = \sum_1^p \sum_1^q p\beta_{qp}[\mathrm{TiO}^{2+}]^q h^{-p} \qquad (5)$$

It is very difficult to deduce compositions and stability constants of the hydrolyzed species from these general expressions, so a further assumption was made that a unique hydrolyzed species is predominantly present in the solution. General mathematical treatments for polynuclear complexes have already been given by Sillen [12] and compiled in the monograph [13] by Rossotti and Rossotti; a somewhat different and simple treatment was applied for the present study.

In the case of a unique hydrolyzed species, the expressions (3)—(5) can be rearranged to equations (6) and (7).

$$Z^{-1} - (q/p) = (p\beta_{qp}[\mathrm{TiO}^{2+}]^{q-1}h^{-p})^{-1} \qquad (6)$$

$$BZ = p\beta_{qp}[\mathrm{TiO}^{2+}]^q h^{-p} \qquad (7)$$

$$(BZ)^{(q-1)/q}[Z^{-1} - (q/p)] = (p\beta_{qp})^{-1/q}h^{p/q} \qquad (8)$$

By combining these equations through the term $[\mathrm{TiO}^{2+}]$, equation (8) is obtained which can be rewritten as (9).

$$(q - 1)/q \log B + (q - 1)/q \log Z + \log [Z^{-1} - (q/p)] = (p/q) \log h - q^{-1} \log p\beta_{qp} \qquad (9)$$

Equation (9) implies that there should be (*i*) a linear relation between the terms log B and log h if Z is constant, with a slope of $(\partial \log B/\partial \log h)_Z = p/(q - 1)$, and (*ii*) a linear relation between the terms $-\log h + [(q - 1)/p] \log Z$ and $-(q/p) \log [Z^{-1} - (q/p)]$ if B is constant, with a unit slope. If the values of p and q are estimated from these relations the stability constant β_{qp} can hence be easily calculated from equation (10).

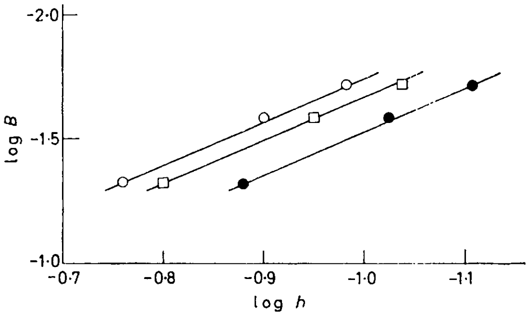

FIGURE 2 Relation between log B and log h for specified values of Z. $Z = 0.10$ (○), 0.20 (□), and 0.40 (●). The full lines have the same value of $p/(q - 1) = 1.71$

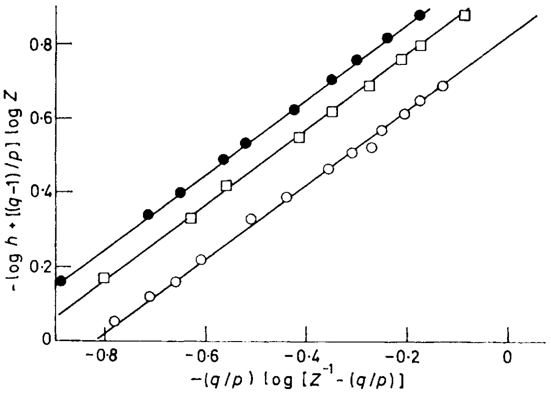

FIGURE 3 Relation between the terms $-\log h + [(q - 1)/p]$ log Z and $-(q/p) \log [Z^{-1} - (q/p)]$ for specified values of B. $-\log B = 1.317$ (○), 1.578 (□), and 1.714 (●). The full lines are theoretical curves drawn by using the value of log $\beta_{8,12} = -1.6_8$

$$-\log \beta_{qp} = \log p + p\{[(q - 1)/p \log B] - \log h + [(q - 1)/p \log Z] + (q/p) \log [Z^{-1} - (q/p)]\} \qquad (10)$$

The quotient $p/(q - 1)$ was found to be 1.71 ± 0.05 from Figure 2 for relation (*i*) and the individual values of p and q were estimated, both from relation (*ii*) (Figure 3) and from the best fit for the calculated value of log β_{qp} to the experimental data, to be $p = 12$ and $q = 8$ with a value of $-\log \beta_{8,12} = 1.6_8 \pm 0.1_0$. The best fit of the calculated value to the experimental data for log β_{qp} with only a specified value of p and q suggests that, besides $[\mathrm{TiO}]^{2+}$, there should be present a unique polycationic species of formula $[(\mathrm{TiO})_8(\mathrm{OH})_{12}]^{4+}$ under the conditions studied.

Hence the hydrolytic equilibrium of titanium(IV) in aqueous 2.0 mol dm^{-3} (Na,H)Cl solution at 25 °C is expressed as in (11) where $\log \beta_{8,12} = -1.6_8 \pm 0.1_0$.

$$8[\mathrm{TiO}]^{2+} \xrightleftharpoons{\beta_{8,12}} [(\mathrm{TiO})_8(\mathrm{OH})_{12}]^{4+} + 12\,\mathrm{H}^+ \qquad (11)$$

DISCUSSION

For the analysis of potentiometric data on the hydrolysis of titanium(IV) it is necessary to determine the nature of the chemical species of titanium(IV) present in the stock solution. Recent kinetic studies by Ellis *et al.*[4] clearly demonstrated that titanium(IV) is present in the form of $[\mathrm{TiO}]^{2+}$ and not $[\mathrm{Ti(OH)_2}]^{2+}$ in aqueous perchloric acid solution ($[\mathrm{H}^+] > 0.1$ mol dm^{-3}). This should also hold for the present case, *i.e.* for the stock solution, since chloride is unlikely to co-ordinate to titanium(IV) under the conditions adopted in this study. Our preliminary experiment on potentiometric titration by the method of Gran's plot [11] revealed that $\mathrm{TiCl_4}$ is partially hydrolyzed even in the stock solution ($[\mathrm{H}^+]$ = 0.5—4 mol dm^{-3}) to release 2 equivalents of HCl and to form $\mathrm{TiOCl_2}$ [or $\mathrm{Ti(OH)_2Cl_2}$], which is consistent with the result by Ellis *et al.*[4] Hence $[\mathrm{TiO}]^{2+}$ was preferred in this study to $[\mathrm{Ti(OH)_2}]^{2+}$.

In the present study, besides a mononuclear cationic species of $[TiO]^{2+}$, a unique polynuclear cationic species $[(TiO)_8(OH)_{12}]^{4+}$ was deduced to be present. (Analysis carried out under the assumption of the presence of two or more species was unsuccessful on the present experimental data.)

According to Liberty *et al.*,[2] Ellis and co-workers,[3,4] Nabivanets,[5] and Baes and Mesmer,[6] there are some mononuclear cationic species, such as $[Ti(OH)]^{3+}$, $[TiO]^{2+}$, and $[TiO(OH)]^{+}$ {or $[Ti(OH)_3]^{+}$}, in 0.1—2 mol dm^{-3} aqueous sodium perchlorate or chloride solution. These species were mainly identified by such methods as solvent extraction, ion exchange, and solubility measurements. On closer literature survey it can be found that in most cases the data analyses were carried out on the simple assumption of the formation of monomeric species. This, presumably, must be the principal cause of the discrepancy between the previous and the present studies. As far as the hydrolytic behaviour of titanium(IV) is concerned, the formation and presence in part of polynuclear cationic species should not be neglected together with a mononuclear cationic species even in highly acidic aqueous solution.

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