

## THE OXALATO COMPLEXES OF TITANIUM(IV)—I

### MONONUCLEAR $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$ IN SOLUTION

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**Abstract**—Molecular weight, electro dialysis and anion exchange measurements between pH 1 and 4 showed that the titanyl oxalate anion is present in solution as mononuclear  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  units. pH studies of solutions of  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$  in 0.5 M  $\text{NaClO}_4$  medium and computer evaluation and simulation by LETAGROP and HALTAFALL showed that the behaviour of such solutions can be simulated by applying stability constants of  $\log \beta_1 = 7.90 \pm 0.02$  and  $\log \beta_2 = 13.24 \pm 0.07$ , when using hydrolysis constants given by Nazarenko *et al.*

In an attempt to determine the stability constant  $\beta_2$  spectrophotometrically using an exchange method with pyrocatechol, a mixed ligand complex was found with a Ti:pyrocatechol:oxalate ratio of 1:1:1.

#### INTRODUCTION

As was found by crystal structure determination of ammonium titanyl oxalate monohydrate [1] the anion in the solid state consists of cyclic tetranuclear di- $\mu$ -oxo-dioxalato units. Brintzinger and Eckardt [2] concluded from a dialysis study of several metal oxalate complexes in ammonium oxalate solutions that the titanyl oxalate anion in water had to be defined as  $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$ . Pecsok [3] determined the amount of protons involved in the reduction of  $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$  to  $\text{Ti}(\text{C}_2\text{O}_4)_2^-$  by measuring the effect of pH on the halfwave potential of titanyl oxalate. As this numbered 2 it confirmed the formula to be either  $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$  or  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$ . Several investigators [4-7] determined stability constants for the 1:2 and in some cases also for the 1:1 complex. The published results show a very large spread:  $\log \beta_2$  from 9.9 to 14.8 and  $\log \beta_1$  from 6.6 to 9.7 (see also Table 4).

The purpose of the study reported here was to obtain more precise information about the behaviour of titanyl oxalate solutions and the stability constants of the complexes. In particular it was tried:

—to confirm the mononuclear state and the charge of the 1:2 anion;

—to establish whether there is any tendency for polymerization in the pH range 1 to 3;

—to distinguish between  $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$  and  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$ .

It was also hoped to confirm the results by spectrophotometric measurements using an exchange method with pyrocatechol.

#### EXPERIMENTAL

**Chemicals and methods of analysis.** Ammonium titanyl oxalate monohydrate,  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$  was synthesized using the method described earlier [1], except that ethanol was added via a capillary ending under the surface of the solution, in order to avoid contamination by hydrolysis products and inclusion of oxalic acid in the crystals. Titanium was determined by the method of EDTA/ $\text{H}_2\text{O}_2$  addition and back-titration with a standard lead nitrate solution [8]. In the electro dialysis experiments titanium was determined spectrophotometrically using  $\text{H}_2\text{O}_2$  as reagent [9]. Oxalate was determined by permanganate titration.

In the anion-exchange experiments DOWEX 1-X8 anion

exchanger in the chloride form was used. Exchanged amounts of chloride were determined gravimetrically by precipitation with  $\text{AgNO}_3$  at low pH. For freezing point depression measurements recrystallized acetamide (Merck, reinst) was used as the solvent.

Solutions of  $\text{HClO}_4$ , made up to ionic strength 0.5 by  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (Baker Anal.) were standardized with recrystallized THAM, tris-(hydroxymethyl)-aminomethane (Merck, p.a.).

**Apparatus.** Freezing point depression measurements were performed in a simple large test-tube arrangement with a loop agitator in a carefully heated beaker water-bath, using a verified Anschütz thermometer for temperature measurements. Further apparent molecular weight determinations were done with a Knauer vapour pressure osmometer, a Knauer temperature measuring instrument and a Kipp BD10 recorder in a thermostatted room. The osmometer was of the differential temperature measuring type with two thermistor heads. Electro dialysis studies were performed in a three compartment dialysis cell, also in a thermostatted room. The cell was constructed according to Nabivanets [10], with platinum electrodes and two Cuprophane-20 membranes.

For polarography experiments with ammonium titanyl oxalate solutions a Beckmann Electroscan TM30P was used. Potentiometric data were obtained with a Metrohm compensator E368, with Metrohm glass electrode EA109UX and calomel electrode Ingold 303 NS. The calomel electrode had a 1.0 M  $\text{NaNO}_3$  bridge. Spectrophotometric measurements were carried out on a Cary 17I double beam spectrophotometer with 10 mm cells.

**Methods.** The e.m.f. measurements were carried out in a nitrogen atmosphere as a series of potentiometric titrations with  $\text{HClO}_4$  in 0.5 M  $\text{NaClO}_4$  medium. The temperature of the titration cell was maintained at  $25 \pm 0.05^\circ\text{C}$  using a Lauda ND8/17 circulating bath. Standard  $\text{HClO}_4/\text{NaClO}_4$  solutions of ionic strength 0.5 were used for standardizing the electrode system and determining the liquid junction e.m.f.  $j_{ac}$  in the expression  $E = E^0 + 59.157 \log [\text{H}^+] + j_{ac}[\text{H}^+]$ . The mathematical analysis of e.m.f. data was performed with a FORTRAN edition of the least squares program LETAGROP, version ETITR [11, 12]. The standard deviations were defined and calculated according to Sillén [13, 14]. For simulating the equilibrium concentrations of the systems for given sets of stability constants use was made of the program HALTAFALL [15]. Computation was performed on a DEC 10-70 computer.

#### RESULTS AND DISCUSSION

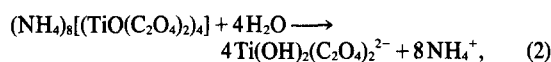
##### *Molecular weight*

Several materials were tried as the solvent for freezing point depression determinations. It was found that

acetamide, melting point around 79.5°C, was the most suitable in our case. The molal freezing-point depression constant  $k_f$  in the simplified formula (1) was determined with  $\text{NH}_4\text{I}$ , after which the dissociation number  $n$  of different solutes could be determined:

$$n = \frac{M \times \Delta T \times w_{\text{solv}}}{k_f \times w_s \times 1000} \quad (1)$$

where  $M$  is molecular weight of solute;  $\Delta T$  = freezing point depression;  $w_{\text{solv}}$  and  $w_s$  are weights of solvent and solute. The experiments were carried out with different solvent/solute ratios (acetamide 1–4 g, compound 20–100 mg) and for comparison measurements were also performed on some other complexes containing different amounts of crystal water. The average dissociation numbers have been collected in the upper part of Table 1. Other complexes such as  $\text{K}_3\text{Cr}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cu}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$  did not dissolve in acetamide. If monomer anions  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  are present in solution this would correspond with the following way of dissociation:



giving a dissociation number  $n = 12$ . As can be seen the dissociation numbers reported in Table 1 are sometimes lower and sometimes higher than expected. As for the vanadyl complex, it is not certain that the ligand  $\text{H}_2\text{O}$  group [16] is really kept within the anion during dissolution.

The way in which the ammonium and potassium titanyl oxalate dissociate, compared to the other compounds with crystal water, could very well be an illustration of mechanism (2), in which crystal water is used. Neither dissociation into a tetramer and 4 molecules of water (leading to dissociation number 13), nor dissociation into another than a 1:2 chelate are definitely ruled out by these results.

Molecular weight determination by means of a Knauer vapour pressure osmometer with water as solvent resulted in an average dissociation number of 12.23 (lower part of Table 1), obtained on the basis of molality calibration with glucose. The molality of glucose solutions were in the range of  $2 \times 10^{-3}$  to  $0.1 \text{ mole kg}^{-1}$ , of the ammonium titanyl oxalate solutions  $1 \times 10^{-3}$  to  $4 \times 10^{-3} \text{ mole kg}^{-1}$  calculated as tetramer. Lower and higher molalities led to discrepancies due to the instrument and to deviation from ideality. The apparent molecular weight found for the titanyl oxalate complex was 96.2. Upon division of the molecular weight of the tetramer (1176.1)

Table 1. Dissociation number of different compounds in acetamide and water, respectively

Freezing point depression of acetamide	$n$
$\text{NH}_4\text{I}$	(2.00) (calibration)
$(\text{NH}_4)_8[\text{TiO}(\text{C}_2\text{O}_4)_2)_4] \cdot 4\text{H}_2\text{O}$	$11.3 \pm 0.4$
$\text{K}_8[\text{TiO}(\text{C}_2\text{O}_4)_2)_4] \cdot 8\text{H}_2\text{O}$	$17.3 \pm 0.3$
$(\text{NH}_4)_2[\text{VO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}] \cdot \text{H}_2\text{O}$	$4.12 \pm 0.04$
$\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	$6.3 \pm 0.2$
Vapour pressure lowering of water	
$\text{C}_6\text{H}_{12}\text{O}_6$ , glucose	(1.0) (calibration)
$(\text{NH}_4)_8[\text{TiO}(\text{C}_2\text{O}_4)_2)_4] \cdot 4\text{H}_2\text{O}$	$12.23 \pm 0.13$

by this number the above-mentioned value of 12.23 was obtained. This also resulted when the molecular weight of the anhydrous compound (1104.1) was divided by 90.3 (obtained by correction for crystal water content). Release of crystal water or the participation of water in mechanism (2) cannot be measured in the large amount of solvent water, so the result of 12.23 is in conformity with theory (12.0) and definitely rules out dissociation into ammonium ions and tetrameric or dimeric anions.

#### Electrodialysis

To investigate the influence of pH on possible polymerization or dissociation of the complex ions an electro dialysis method according to Nabivanets [10] and Somova *et al.* [17] was used. At constant ionic strength, constant quantity  $E \times t$  ( $E$  voltage,  $t$  duration in minutes), constant analytical concentration of the metal at the beginning and constant pH during electro dialysis the equivalent concentration of cations or anions in the anolyte and catholyte compartments is proportional to their mobility.

If polymerization takes place the mobility is determined of that fraction which has such a low degree of polymerization that the particle size is still smaller than the pore dimensions of the membrane. The electro dialysis factor  $\gamma$ , for the situation when the metal forms ions of only one type is given by:

$$\gamma = \frac{a - n}{c' + c + n} \quad (3)$$

where  $a$  = metal concentration in anolyte after electro dialysis;  $n$  = metal concentration in anolyte or catholyte in experiments without the passage of electric current (after the same time interval used in the actual electro dialysis experiments);  $c'$  = metal concentration in central compartment after electro dialysis; and  $c$  = metal concentration in catholyte after electro dialysis.

Change of  $\gamma$  with changing pH of the starting solutions would be a relative measure for change in polymerization with pH. The central compartment was filled with ammonium titanyl oxalate solution of ionic strength 0.5 M ( $\text{H}$ ,  $\text{NaClO}_4$ ) and the end compartments with oxalic acid of the same concentration and pH. The voltage  $E$  was 5 V, the duration of each experiment 120 min, and the apparatus was situated in a thermostatted room of  $21 \pm 0.5^\circ\text{C}$ . During the experiments the pH in the catholyte and anolyte compartments were held constant by periodic addition of concentrated  $\text{HClO}_4$  and  $\text{NaOH}$  solutions, respectively. The results have been collected in Table 2.

The electro dialysis factor  $\gamma$  proves to be constant within the limits of experimental error in the pH-range 1–3 and does not significantly decrease with increasing pH. Polymerization of titanium(IV) complexes mostly occurs at higher pH (e.g. 5.5 for the Ti tartrato complexes [17]), but because of possible  $\text{Ti}(\text{OH})_4$  precipitation the pH-range

Table 2. Influence of pH on electro dialysis parameters (eqn (3)); concentrations in  $\text{mole l}^{-1}$ , starting concentration  $3.65 \times 10^{-3} \text{ mole l}^{-1} \text{ Ti(IV)}$

pH	$a \times 10^4$	$n \times 10^4$	$c' \times 10^3$	$c \times 10^4$	$\gamma \times 10^3$
2.9	2.60	2.35	3.14	2.15	6.96
2.4	2.78	2.53	3.08	2.19	7.04
1.9	3.13	2.88	3.02	2.51	7.02
1.0	2.95	2.70	2.94	2.15	7.30

above 3.0 could not be studied for the oxalate complexes.

The results in Table 2 only prove that if at pH 3.0 the 1:2 complex is a monomeric species, this is also the case at pH 1.0. Probable dissociation into a 1:1 complex and hydroxo complexes do not cause a fundamental change in mobilities. It cannot be excluded that the 1:1 complex which is formed largely at pH < 1.0 slowly polymerizes.

#### Charge

In order to confirm the charge 2- proposed for the  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  anion the method described by Nabivanets [18] was used. This is based on the relationship between the number of  $M_1^{z_1}$  ions displaced from an ion exchanger by the complex ions and the charge  $z$  of the absorbed  $M^z$  ions. Concentration changes for the ion under investigation ( $\Delta M^z$ ) and the displaced ions ( $\Delta M_1^{z_1}$ ) are determined after equilibration of the solution with an ion-exchanger originally in the  $M_1^{z_1}$  form. The charge is calculated from:

$$z = \frac{\Delta M_1^{z_1}}{\Delta M^z} \quad (4)$$

where  $\Delta M_1^{z_1}$  is expressed in equiv.  $\text{l}^{-1}$  and  $\Delta M^z$  in mole  $\text{l}^{-1}$ . Experiments with cation-exchanger resulted in hardly any exchange with titanyl oxalate solutions, so the amount of positive titanium hydroxo species or other positive titanium complexes is negligibly small.

Anion-exchange was accomplished with about 0.5 g ion-exchanger in 85.0 ml with total Ti(IV) concentrations of about  $2.0 \times 10^{-2}$  mole  $\text{l}^{-1}$ . Equilibration time was usually 16 hr. The exchange was found to be independent of ionic strength, so that  $\text{NaClO}_4$  could be omitted. Table 3 gives some of the results. In most cases extra oxalic acid and ammonium oxalate was added to the ammonium titanyl oxalate solutions. The concentration change  $\Delta \text{Cl}$  then had to be corrected for  $\text{Cl}^-$ -exchange with  $\text{C}_2\text{O}_4^{2-}$  or  $\text{HC}_2\text{O}_4^-$  ions by means of (5):

$$\begin{aligned} \Delta \text{Cl} &= [\text{Cl}]_t - \Delta \text{Cl}_{\text{corr}} \\ &= [\text{Cl}]_t - f\{[\text{C}_2\text{O}_4]_0 - [\text{C}_2\text{O}_4]_t + 2[\text{Ti}(\text{IV})]_t\} \end{aligned} \quad (5)$$

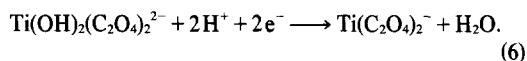
where  $[\text{C}_2\text{O}_4]_0$  means the concentration of added oxalate at the beginning of ion-exchange,  $f$  is the charge factor  $\text{Cl}/\text{C}_2\text{O}_4$ , and the subscripts  $0$  and  $t$  denote the beginning and end of ion-exchange. The charge factor  $f$  represents the amount of  $\text{Cl}^-$  ions exchanged for one oxalate group. It has to be determined separately at each pH studied, without titanium. It decreased with decreasing pH because of increasing concentrations of the  $\text{HC}_2\text{O}_4^-$  and  $\text{H}_2\text{C}_2\text{O}_4$ .

As Table 3 shows the charge of the 1:2 chelate is clearly -2 and is unaffected by a change of pH. Calculated results for a model based on the dissociation of the tetramer into

monomeric 1:1 complex ions and free oxalic acid did not fit the experimental data.

#### Hydroxyl groups

It was felt to be necessary to repeat Pecsok's [3] and Viallet's [7] polarographic measurements to determine the amount of protons involved in the electrode reaction



When this reaction is correct, one expects that the half-wave potential  $E_{1/2}$  is a function of  $-0.059 \times n \times \text{pH}$  with  $n = 2.0$ . Pecsok found too low a value, probably because of  $\text{Cl}^-$  influence in his solutions of  $\text{TiCl}_4$  and oxalate. Viallet only studied the reaction below pH 1.7, but did find a value of 2. It was therefore decided to study solutions of 0.01 M ammonium titanyl oxalate in 0.5 M  $\text{NaClO}_4$  in the pH range of 1-3 (above pH 3 the wave becomes irreversible).

A linear relationship between  $-E_{1/2}$  and pH was observed with a slope of 0.113 V/pH-unit, which, when divided by 0.059 resulted in 1.91. This is in agreement with the predicted value of  $n = 2$  from reaction (6). As the identity of the yellow Ti(III) oxalate complex was established by Pecsok using Job's method [19] it is justified to propose  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  or  $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$ .

#### Stability constants

The combined results of molecular weight and polarographic measurements lead to the conclusion that mononuclear  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  is the major titanium oxalate species present in not too concentrated solutions.

To determine stability constants for  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  and  $\text{Ti}(\text{OH})_2\text{C}_2\text{O}_4$  the method of potentiometric (glass electrode) titrations of ammonium titanyl oxalate solutions with  $\text{HClO}_4$  was chosen, as the availability of pure crystals of  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$  meant a good starting point for preparing standard titanium(IV)/oxalate solutions. Titration with acid instead of base was chosen in order to prevent precipitation of hydroxide. Slight disadvantages of the method are the limited range of ligand-metal ratios and the low sensitivity at low pH (<1.0), because the pH is then mainly determined by added  $\text{HClO}_4$ . In the mathematical analysis we assumed  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  and  $\text{Ti}(\text{OH})_2\text{C}_2\text{O}_4$  as the titanium complexes present. The choice of the 1:1 chelate was based on different arguments.

Several authors [20-22] synthesized a 1:1 complex in different ways. This compound was formulated as  $\text{TiO}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$  with  $n \leq 2$ . In the solid state this might be polymeric or at least amorphous. Electrophoretic experiments in strong acid solutions by Babko and Dubovenko [4] supported the existence of the neutral complex  $\text{TiOC}_2\text{O}_4$ . Because of the results obtained for the

Table 3. Determination of charge  $z$  of  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$  by anion exchange with  $\text{Cl}^-$ . Analytical concentrations in mole  $\text{l}^{-1}$

pH	$[\text{Ti}(\text{IV})]_0$ $\times 10^2$	$[\text{Ti}(\text{IV})]_t$ $\times 10^2$	Extra $[\text{C}_2\text{O}_4]_0$ $\times 10^2$	$[\text{C}_2\text{O}_4]_t$ $\times 10^2$	$f$	$[\text{Cl}]_t$ $\times 10^2$	$z$
4.1	1.896	1.381				1.060	2.06
3.5	1.934	1.156	1.134	3.231	1.95	1.956	1.98
2.9	1.949	1.096	2.539	4.139	1.55	2.589	1.96
2.0	1.952	0.971	1.943	3.476	1.29	2.519	2.03

1:2 complex mentioned above and because units containing Ti=O are rarely found, we prefer the formulation of  $\text{Ti}(\text{OH})_2\text{C}_2\text{O}_4$  or rather  $\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_2\text{C}_2\text{O}_4$  to be present in solution. Protonated complexes such as  $\text{HTi}(\text{OH})_2(\text{C}_2\text{O}_4)_2^-$  and  $\text{H}_2\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2$  cannot definitely be excluded. According to Péchard[23] crystals of  $\text{H}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$  could be isolated. However, when his method of synthesis was repeated, starting from  $\text{BaTiO}(\text{C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O}$  and concentrated  $\text{H}_2\text{SO}_4$ , a product resulted which consisted of crystalline needles of  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and glass-like, X-ray amorphous, material  $\text{TiOC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . The exact nature of the latter compound was difficult to establish until now, because of the varying amounts of crystal water and the non-crystallinity of the product.

For the equilibrium constants (formulated here as stability constants) of  $\text{HC}_2\text{O}_4^-$  and  $\text{H}_2\text{C}_2\text{O}_4$  at an ionic strength of 0.5 M ( $\text{NaClO}_4$ ) the values  $4.63 \times 10^3$  and  $7.41 \times 10^4$  respectively were taken from Bauer and Smith[24].

Table 4 gives some literature values of stability constants of titanium(IV) hydroxo and titanyl oxalate complexes. The hydrolysis constants have been reformulated for practical reasons (HALTAFALL[15] treatment) as given in the table. To make a start with estimation values of the stability constants for the input of HALTAFALL  $\beta_1$  of Babko and Dubovenko and  $\beta_2$  of Viallet were used, together with the hydrolysis constants of Nazarenko *et al.* In the input the ion  $\text{Ti}(\text{OH})_2^{2+}$  was used as the metal ion and reactions of the type  $\text{Ti}(\text{OH})_2^{2+} + 2\text{OH}^- = \text{Ti}(\text{OH})_4$  were written as  $\text{Ti}(\text{OH})_2^{2+} (+ 2\text{H}_2\text{O}) - 2\text{H}^+ = \text{Ti}(\text{OH})_4$ . The calculated pH was compared with the pH determined from e.m.f. data (some of which are given in Table 5). The computer simulation had the fortunate property that the pH calculated at the beginning of the titrations responded differently to input values of  $\beta_1$  and  $\beta_2$  from the pH calculated in the further part. When  $\beta_1$  was lowered all pH values decreased, but when  $\beta_2$  was lowered pH at the beginning decreased, but in the rest of the titration increased. In this way after several trial and error cycles  $\beta_2$  was found to be about  $2 \times 10^{13}$  and  $\beta_1$  about  $10^5$ .

Regarding the choice of values for the hydrolysis constants an estimation can be performed by the evaluation of mass and charge balances of ammonium

Table 4. Some literature values of equilibrium constants of titanium(IV) hydroxo- and oxalato-complexes. Stability constants defined as  $\text{Kh}_n = [\text{Ti}(\text{OH})_n]/[\text{H}^+]^n [\text{Ti}(\text{OH})_2]$ ,  $\beta_n = [\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_n]/[\text{Ti}(\text{OH})_2][\text{C}_2\text{O}_4]_n$ , solubility product as  $\text{K}_{\text{sp}} = [\text{Ti}(\text{OH})_2][\text{H}]^{-2}$

	$\text{Kh}_1$	$\text{Kh}_2$	$\text{Kh}_3$	$\text{Kh}_4$
Beukenkamp†	—	—	0.5	—
Liberti†	—	63.1	$3.98 \times 10^{-3}$	$3.2 \times 10^{-5}$
Nabivanets†	$6.7 \times 10^{-8}$	$6.1 \times 10^{-4}$	$3.2 \times 10^{-3}$	$3.23 \times 10^{-5}$
Lobanov†	5.57	3.85	0.12	0.011
Nazarenko[28]†	0.38	0.94	0.57	0.16
Liégeois[26]	633	588	$1.7 \times 10^{-7}$	—

	$\text{K}_{\text{sp}}$	$\beta_1$	$\beta_2$	
Babko†	$10^{-1}$	Babko[4]	$4.0 \times 10^6$	$8.0 \times 10^9$
Golub†	$3.8 \times 10^{-3}$	Grinberg[5]	$5.1 \times 10^9$	$6.6 \times 10^{14}$
Grinberg[5]	$10^{-2}$	Mazurenko[6]	$3.2 \times 10^6$	$9.5 \times 10^{11}$
Sillén[27]	$10^{-1}$	Viallet[7]	—	$9.8 \times 10^{12}$

†Values taken from Vasil'ev *et al.*[25].

Table 5. Change of pH from e.m.f. data. Titrations of 100.0 ml  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot \text{H}_2\text{O}$  solutions with 0.5176 M  $\text{HClO}_4$ , ionic strength 0.5 M ( $\text{H}$ ,  $\text{NaClO}_4$ ).  $\text{H}$  = total hydrogen concentration ( $\text{mole l}^{-1}$ )

ml	$\text{H} \times 10^{-3}$	0.005 M		0.01 M		0.02 M	
		$\text{pH}_{\text{exp}}$	$\text{pH}_{\text{calc}}$	$\text{pH}_{\text{exp}}$	$\text{pH}_{\text{calc}}$	$\text{pH}_{\text{exp}}$	$\text{pH}_{\text{calc}}$
0.0	0.0	3.347	3.347	3.294	3.299	3.259	3.259
0.1	0.517	3.125	3.123	3.105	3.107	3.093	3.095
0.2	1.033	2.944	2.945	2.942	2.946	2.952	2.952
0.5	2.575	2.611	2.612	2.628	2.627	2.652	2.648
1.0	5.125	2.322	2.324	2.341	2.342	2.365	2.368
2.0	10.15	2.026	2.028	2.045	2.046	2.063	2.071
5.0	24.65	1.639	1.639	1.651	1.654	1.669	1.676
10.0	42.74	1.353	1.354	1.367	1.367	1.385	1.387
20.0	86.27	1.085	1.085	1.095	1.097	1.117	1.115

titanyl oxalate solutions. If the following abbreviations are used:

$$\begin{aligned} \text{Ti}_t &= \text{total titanium concentration,} \\ h &= [\text{H}^+], \\ \text{ox} &= [\text{C}_2\text{O}_4^{2-}], \\ \text{L} \times \text{ox} &= \text{ox} + [\text{HC}_2\text{O}_4^-] + [\text{H}_2\text{C}_2\text{O}_4] \\ &= (1 + 4630h + 74100h^2)\text{ox}, \\ z\text{TiO} &= [\text{Ti}(\text{OH})_2^{2+}] + [\text{Ti}(\text{OH})_3^+] + [\text{Ti}(\text{OH})_4] \\ &= (1 + \text{Kh}_3/h + \text{Kh}_4/h^2)[\text{Ti}(\text{OH})_2^{2+}], \end{aligned}$$

we have the following equations:

$$z\text{TiO} = [\text{TiOox}_2] + \text{L} \times \text{ox} - \text{ox}_t + \text{Ti}_t \quad (7)$$

(from Ti and oxalate mass balances),

$$[\text{TiOox}_2] = \frac{1}{2}h + \frac{1}{2}[\text{NH}_4^+] - \frac{1}{2}[\text{HC}_2\text{O}_4^-] - \text{ox} \quad (8)$$

(charge balance, with neglect of  $\text{Ti}(\text{OH})_2^{2+}$ ,  $\text{Ti}(\text{OH})_3^+$ ).

From these equations it follows that  $z\text{TiO}$  and  $[\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}]$  are functions of  $\text{ox}$  only. If, for the present,  $[\text{Ti}(\text{OH})_2\text{C}_2\text{O}_4]$  is related to  $[\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}]$  as:

$$[\text{TiOox}] = [\text{TiOox}_2]/2 \times 10^5 \times \text{ox},$$

then from the total Ti concentration a value for  $z\text{TiO}$  results. For example, for 0.01 M  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2$  ( $\mu = 0.5$  M  $\text{NaClO}_4$ ), with experimentally determined  $\text{pH} = 3.295$ ,  $z\text{TiO} = 9.5 \times 10^{-4}$ . This means that if  $\beta_2$  is given a value, then  $[\text{Ti}(\text{OH})_2^{2+}]$  can be calculated from  $[\text{TiOox}_2]$  and  $\text{ox}$ . From this the hydrolysis constant  $\text{Kh}_4$  is determined, if  $\text{Kh}_3$  is given (The other hydrolysis constants only play a minor part at this pH). Thus, if, e.g.  $\beta_2 = 1.75 \times 10^{13}$  and  $\text{Kh}_3 = 0.57$ , then  $\text{Kh}_4 = 0.16$  (fits with values of Nazarenko, Table 4) and  $\text{K}_{\text{sp}} > 5.8 \times 10^{-3}$ . For  $\beta_2 = 1.2 \times 10^{12}$  and  $\text{Kh}_3 = 0.12$ ,  $\text{Kh}_4 = 0.011$  (Lobanov) and  $\text{K}_{\text{sp}} > 8.5 \times 10^{-2}$ . For  $\beta_2 = 5.2 \times 10^9$  and  $\text{Kh}_3 = 3.2 \times 10^{-3}$ ,  $\text{Kh}_4 = 3.2 \times 10^{-5}$  (fits with values of Nabivanets) and  $\text{K}_{\text{sp}} > 19.7$ .

As the solubility product at an ionic strength of 0.5–1.0 M is given to be about  $10^{-2}$  in the literature ( $10^{-30}$  in normal definition), we do not accept the values of Nabivanets *et al.* notwithstanding that Vasil'ev *et al.*[25] preferred these constants for the calculation of standard free enthalpies. As the hydrolysis constants of Nazarenko *et al.*[28] are preferred slightly to those of Lobanov *et al.* ([25], *loc. cit.*) these were used for refinements with LETAGROP [11, 12, 14] and HALTAFALL[15] computations. Their values, given in Table 4, were determined at an ionic strength of 0.5 M ( $\text{KNO}_3$ ). In the least squares

program LETAGROP the parameter  $U = \sum (\text{Hcalc} - \text{H})^2$  was minimized using six titration groups (about 120 titration points) with different starting concentrations of ammonium titanil oxalate. The addition of the protonated complex  $\text{HTi}(\text{OH})_2(\text{C}_2\text{O}_4)_2^-$  to the computer input of species did not result in a lower  $U$ .

The following values of  $\log \beta_1$ ,  $\log \beta_2$  were obtained:

$$(\log \beta_1) \pm 3\sigma = 7.90 \pm 0.02$$

$$(\log \beta_2) \pm 3\sigma = 13.24 \pm 0.07$$

where  $\sigma$  is the standard deviation. These values were used for a final calculation of equilibrium concentrations with HALTAFALL. Figure 1 represents a distribution diagram of titanium complexes for 0.01 M  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2$  as a function of  $\log [\text{H}^+]$ .

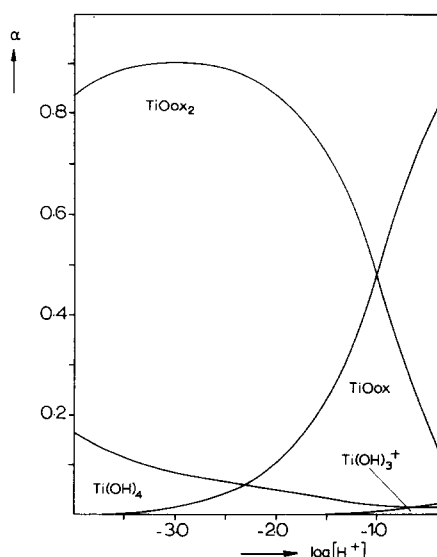
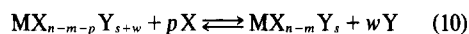
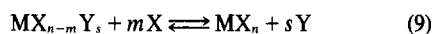


Fig. 1. The distribution of Ti(IV) species in 0.01 M  $(\text{NH}_4)_2\text{TiO}(\text{C}_2\text{O}_4)_2$  solution at an ionic strength of 0.5 M ( $\text{H}$ ,  $\text{NaClO}_4$ ), as a function of  $\log [\text{H}^+]$ .  $\text{TiOox}_2 = \text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$ ,  $\text{TiOox} = \text{Ti}(\text{OH})_2(\text{H}_2\text{O})_2\text{C}_2\text{O}_4$ .

#### Ligand exchange with pyrocatechol

It was tried to use the exchange method of Newman and Hume[29, 30] for spectrophotometric determination of the stability constant  $\beta_2$ . The following equilibria were considered:

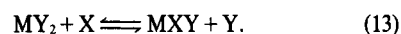
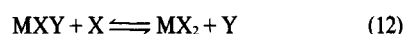


with equilibrium constants  $K_n$ ,  $K_{n-m}$ , respectively. Pyrocatechol was chosen as X, the absorbing ligand; Y was the oxalate (or hydrogen oxalate) ion. Titanium(IV) solutions were prepared by dissolving freshly precipitated  $\text{Ti}(\text{OH})_4$  (washed free of chloride) in dilute  $\text{HNO}_3$  and made up to ionic strength 0.5 M with  $\text{NaClO}_4$ . Absorbances were measured in the pH range 2.0 to 4.0, at a wavelength of 410 nm. Titanium concentrations usually were about  $10^{-4}$  M, of pyrocatechol about  $10^{-2}$  M and the oxalate concentration varied between  $5 \times 10^{-4}$ – $5 \times 10^{-3}$  M. In this pH range and at a high excess of pyrocatechol  $n$  in  $\text{MX}_n$  is always 2[31, 32]. At constant [X] and  $[\text{X}] \gg [\text{Y}] \gg [\text{M}]$  it is allowed to use equation (A13) of Newman and Hume[29]:

$$\log (E_o - E)/E = -\log \frac{X_t^m}{Y_t^s} - \log K_n \quad (11)$$

where  $E_o = \epsilon_n M_t$  is the absorbance of metal pyrocatecholate solution without oxalate at the measured pH;  $\epsilon_n$  is the extinction coefficient of  $\text{MX}_n$ ;  $M_t$  is the total metal concentration;  $X_t$  and  $Y_t$  are total concentrations of X and Y.

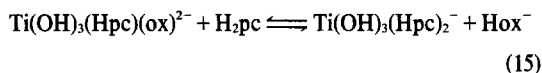
From this, by plotting  $\log (E_o - E)/E$  against  $\log Y_t$ , a value of  $S = 1.0$  resulted which remained constant with pH. This can only be explained if a mixed 1:1 complex, also absorbing at 410 nm, exists:



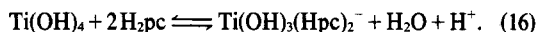
The equilibrium constant  $K_n$  for expression (12) was determined using the following formula ((A12), *loc. cit.*), valid for two absorbing complexes  $\text{MX}_2$  and  $\text{MXY}$ :

$$E = K_n (E_o - E) \frac{X_t}{Y_t} + \epsilon_{n-m} M_t \quad (14)$$

The results were that  $K_n$  slightly increased with pH, from 0.023 to 0.105, with a value of  $(3.7 \pm 1.0) \times 10^{-2}$  at pH 3.0. Equilibrium (12) can probably be written as:



where  $\text{Hpc}^-$  means singly protonated pyrocatechol ( $= \text{H}_2\text{pc}$ ). The composition of  $\text{Ti}(\text{OH})_3(\text{Hpc})_2^-$  is based on the results found by Zholnin[32], from which it is very probable that the main complexing reaction between Ti(IV) and pyrocatechol (added in large excess and pH about 4) is:



The stability constant for this system was about 28.0, based on the formulation of eqn (16). Analogous values can be obtained using values of other authors, e.g. 32.0 from Shnaiderman and Kalinichenko[33], and 16.0 from Sommer[31] (both at pH 3.2). This reformulation of the equilibrium constants is based on the assumption that  $\text{Ti}(\text{OH})_4$  instead of  $\text{TiO}^{2+}$  or  $\text{Ti}(\text{OH})_2^{2+}$  is the main Ti(IV) species and makes use of  $K_1 = 10^{13.0}$  and  $K_2 = 10^{9.3}$  for the formation of  $\text{Hpc}^-$  and  $\text{H}_2\text{pc}$  from  $\text{pc}^{2-}$  and  $\text{Hpc}^-$ , respectively [34].

Although the formation of the mixed complex instead of a complete oxalate/pyrocatechol exchange made it difficult to establish a value for  $\beta_2$ , it was nevertheless tried to determine this via the constant  $K_{n-m}$  of eqn (13). According to Newman and Hume (from equation (A10), *loc. cit.*),  $K_{n-m}$  can be determined from

$$K_n (E_o - E) \frac{X_t}{Y_t} - E = \frac{1}{K_{n-m}} E \frac{Y_t}{X_t} - \epsilon_{n-m} M_t \quad (17)$$

valid for three complexes of which two ( $\text{MX}_2$  and  $\text{MXY}$ ) absorb. At pH 3.0 a value of 0.38 was obtained for  $K_{n-m}$ . However, apparently the conditions for using eqn (17) were not fulfilled, because from the product  $K_n K_{n-m} = 0.014$  and Zholnin's equilibrium constant (defined for (16)) a value of  $2.0 \times 10^3$  is obtained for the quotient  $[\text{Ti}(\text{OH})_2\text{ox}_2^{2-}]/[\text{Ti}(\text{OH})_4][\text{Hox}^-]^2$ . When recalculated as

$[\text{Ti}(\text{OH})_2\text{ox}_2^{2-}]/[\text{Ti}(\text{OH})_2^{2+}][\text{ox}^{2-}]^2$ ,  $\beta_2 = 6.9 \times 10^9$  is obtained, which is much too low compared to the results reported above.

### CONCLUSION

The results obtained in this study warrant the conclusion that at concentrations less than 0.02 M and in the pH range 1–4 the main titanium(IV) species in ammonium titanyl oxalate solutions is  $\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2^{2-}$ . The combination of molecular weight and polarographic measurements confirm the original result found by Brintzinger and Eckardt[2] that the anion is a monomeric 1:2 chelate with charge 2–, but it was shown that the formulation  $\text{TiO}(\text{C}_2\text{O}_4)_2^{2-}$  is not correct.

From electro dialysis studies it followed that the degree of polymerization, if any, remains constant between pH 1 and 4. No fundamental change in mobilities occurred when the pH was lowered to 1.0.

On the basis of reports of synthesis and Job's method studies at low pH by Babko and Dubovenko[4] a 1:1 complex also exists and probably has to be formulated as  $\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_2(\text{C}_2\text{O}_4)$ . The existence of  $\text{H}_2\text{Ti}(\text{OH})_2(\text{C}_2\text{O}_4)_2$  or  $\text{HTi}(\text{OH})_2(\text{C}_2\text{O}_4)_2^-$  in solid and dissolved state was shown to be improbable. No attempt was made to study polymerization tendencies at higher concentrations, nor long-term effects of titanium(IV) hydrolysis, precipitation and polymerization (ageing) of hydroxo species.

It was shown that the calculated values of the stability constants  $\beta_1$  and  $\beta_2$  are influenced by the values chosen for the hydrolysis constants of titanium(IV) hydroxo complexes. Lower values of the latter will lead to lower values of the stability constants. Therefore, definite values of  $\beta_1$  and  $\beta_2$  cannot be established as long as the hydrolysis constants are not certain. Potentiometric titration results satisfy a calculation model with  $\log \beta_1 = 7.90$  and  $\log \beta_2 = 13.24$  together with the hydrolysis constants of Nazarenko *et al.*[28]. The constants of Lobanov *et al.* ([25] *loc. cit.*) lead to values of 6.47 and 11.97, respectively. Much lower hydrolysis constants such as reported by Nabivanets and Lukachina ([25] *loc. cit.*) do not comply with the pH of titanyl oxalate solutions, with earlier reported values of  $\beta_2$  and with the solubility product  $K_{sp}$  of  $\text{Ti}(\text{OH})_4(\text{s})$ .

Spectrophotometric confirmation of the stability constant  $\beta_2$  via the titanium(IV) bispyrocatechol complex did not lead to good results, probably because of predominating formation of a mixed 1:1:1 Ti(IV) pyrocatecholate–oxalate complex. The (apparent) formation constant of the mixed complex from Ti(IV) bispyrocatecholate and oxalate was found to have a value of  $27 \pm 5$  at pH 3.0 which slightly decreased with increasing pH.

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