Inorganica Chimica Acta, 20 (1976) 99–104

The Dissolution Process of Potassium-μ-Oxalato-Di[trisoxalatostannate(IV)] Tetrahydrate in Water

E. L. J. BREET and R. VAN ELDIK

Research Unit for Chemical Kinetics, Department of Chemistry, Potchefstroom University for C.H.E., Potchefstroom 2520, South Africa

Received April 1, 1976

The dissolution process of the complex $K_6Sn_2(C_2O_4)_7\cdot4H_2O$ in water has been studied. A theoretical treatment of the results obtained by combined spectrophotometric, column chromatographic and pH titration techniques, indicates that three oxalate groups are released on dissolution of each complex molecule. This result, together with experimental evidence that the release of approximately one hydrogen ion per complex molecule is facilitated by an acid–base equilibrium, leads to the proposition of two possible solution processes that fit all the experimental data.

Introduction

In a recent paper we described the synthesis and crystal structure of the complex $K_6Sn_2(C_2O_4)_7\cdot4H_2O$ [1]. Since we intend studying the photolysis process of the complex in aqueous solution, it is essential to determine the manner in which the complex exists under such conditions.

Dey and Bhattacharya [2–4] found conductometric and spectroscopic evidence for the complex species $Sn(C_2O_4)_2$ and $Sn(C_2O_4)_4^{4-}$ in aqueous mixtures of $SnCl_4$ and $H_2C_2O_4$ or $K_2C_2O_4$. Apparently these complex species only exist in solution since it was shown [1, 5] that the only product isolatable from mixtures with an oxalate to tin ratio varying from less than three to one to more than four to one, is the complex $K_6Sn_2(C_2O_4)_7\cdot4H_2O$. It is possible that this complex dissociates into these species on dissolution in water, although the evidence regarding their occurrence is considered not quite unequivocal [6].

Experimental

Various techniques including spectrophotometry, column chromatography and pH titrations were adopted for the present investigation. The spectrophotometric analyses of aqueous solutions of the complex were performed on a Unicam SP1800 spectrophotometer. It turned out to be convenient to control spectrophotometrically whether during the elution of a complex solution through a given column, the total amount of a given species was collected. A variety of columns, *viz.*, an anion exchanger (Amberlite IRA-400, Cl^- form), a cation exchanger (Dowex 50W-X4, H^+ form), a silica gel (Kieselgel, 0.2–0.5 mm) and a molecular sieve (Merck) were employed. The titration of aqueous solutions of the complex with standard alkali was followed with a Unicam 292 pH meter, while the determination of tin for several eluates was performed with a Varian Techtron AA6 atomic absorptiometer. The oxalate content of various eluates was determined by means of a permanganate titration [7].

Results and Discussion

The ultraviolet absorption spectra of aqueous solutions of the complex are given in Figure 1. The absorption maximum at 258 nm varies with molar concentration according to the Beer–Lambert relation ($\epsilon = 285\ M^{-1}\ cm^{-1}$). The spectra resemble those of aqueous solutions of the complex $K_2Ge(C_2O_4)_3\cdot H_2O$ after its preequilibration, for which it is known that oxalate is released in aqueous solution [8]. This led to the presumption that free oxalate becomes available on dissolving the complex in water. A further experimental indication that structural changes accompany the dissolution process, is the low pH of an aqueous solution. It is 2.92 if [complex] = $1.0 \times 10^{-3}\ M$, implying that approximately one hydrogen ion is released by each complex molecule. The statement of Willard and Toribara [5] that the complex $K_6Sn_2(C_2O_4)_7\cdot4H_2O$ exists in solution as $3K_2C_2O_4$, $2Sn(C_2O_4)_2$ and $4H_2O$, is contrary to their observation that it yields an acidic solution, and to our results obtained with the anion and cation exchanger that the final complex species is negatively charged.

Efforts were made in vain to separate the complex species in solution from any possible free oxalate by

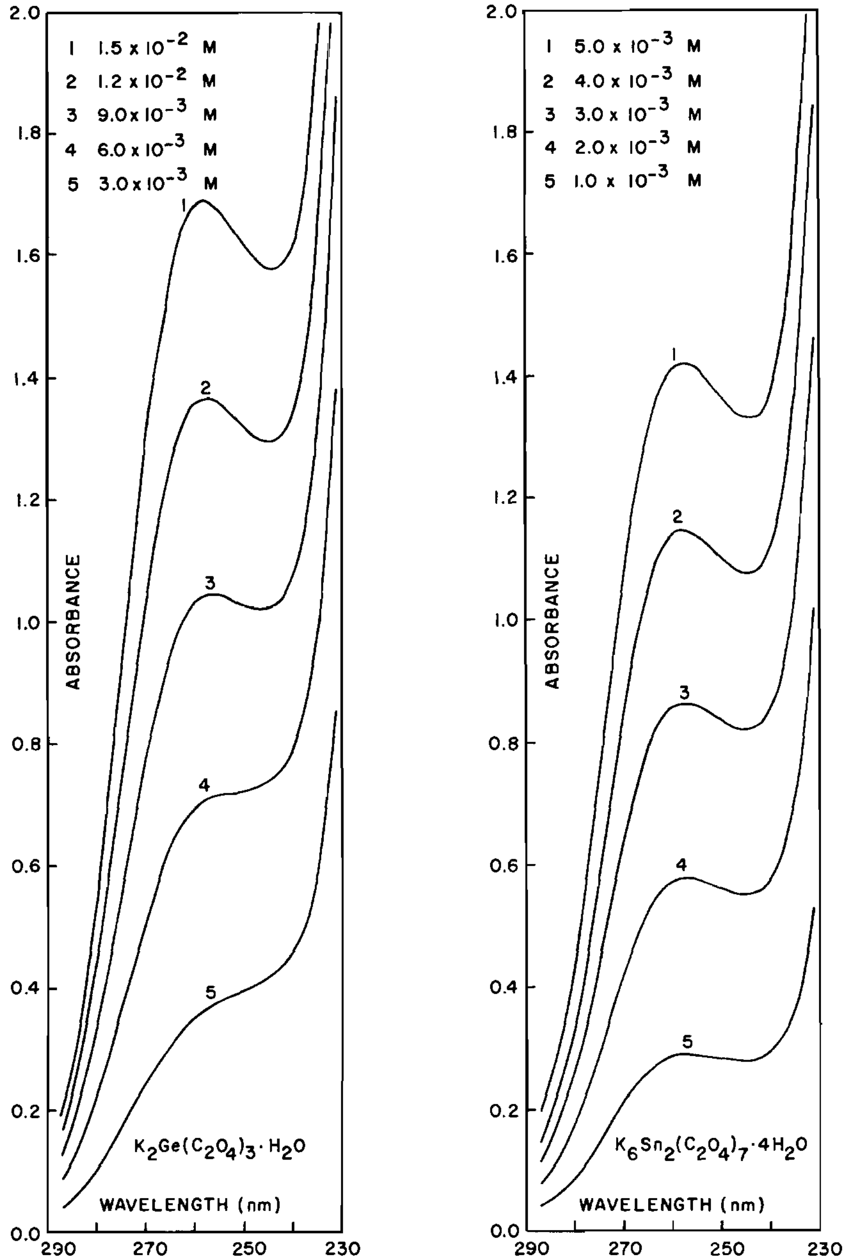

Fig. 1. Ultraviolet absorption spectra of aqueous solutions of $K_2Ge(C_2O_4)_3 \cdot H_2O$ and $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$.

employing column chromatographic techniques based on an assumed difference in retention rates for bonded and free oxalate. It was found that the various fractions collected from the anion exchanger, silica gel and molecular sieve columns, contained approximately 100% of the total oxalate, while the tin apparently hydrolysed or complexated on the column material. The oxalate groups of the complex species are obviously not tightly bonded.

An alternative way of indicating the presence of free oxalate in solution was to compare the absorption spectrum of an aqueous solution of the complex with those of aqueous monovariant $SnCl_4$–$K_2C_2O_4$ mixtures ($SnCl_4$:$K_2C_2O_4$ = 1:0.5; 1:1, 1:1.5; 1:2; 1:2.5; 1:3; 1:3.5; 1:4) to determine whether the complex exists in solution as the species $Sn(C_2O_4)_2$ and/or $Sn(C_2O_4)_4^{4-}$ as suggested by various authors [4, 5]. The ultraviolet absorption spectra A, B, C in Fig. 2 are of the same $SnCl_4$–$K_2C_2O_4$ mixtures, but A was recorded immediately after, B 5 hours after and C 24 hours after mixing. The mixtures for which $SnCl_4$:$K_2C_2O_4$ = 1:0.5 and 1:1 were initially turbid. They eventually became clear but, as in the case of the mixtures for which $SnCl_4$:$K_2C_2O_4$ = 1:1.5;

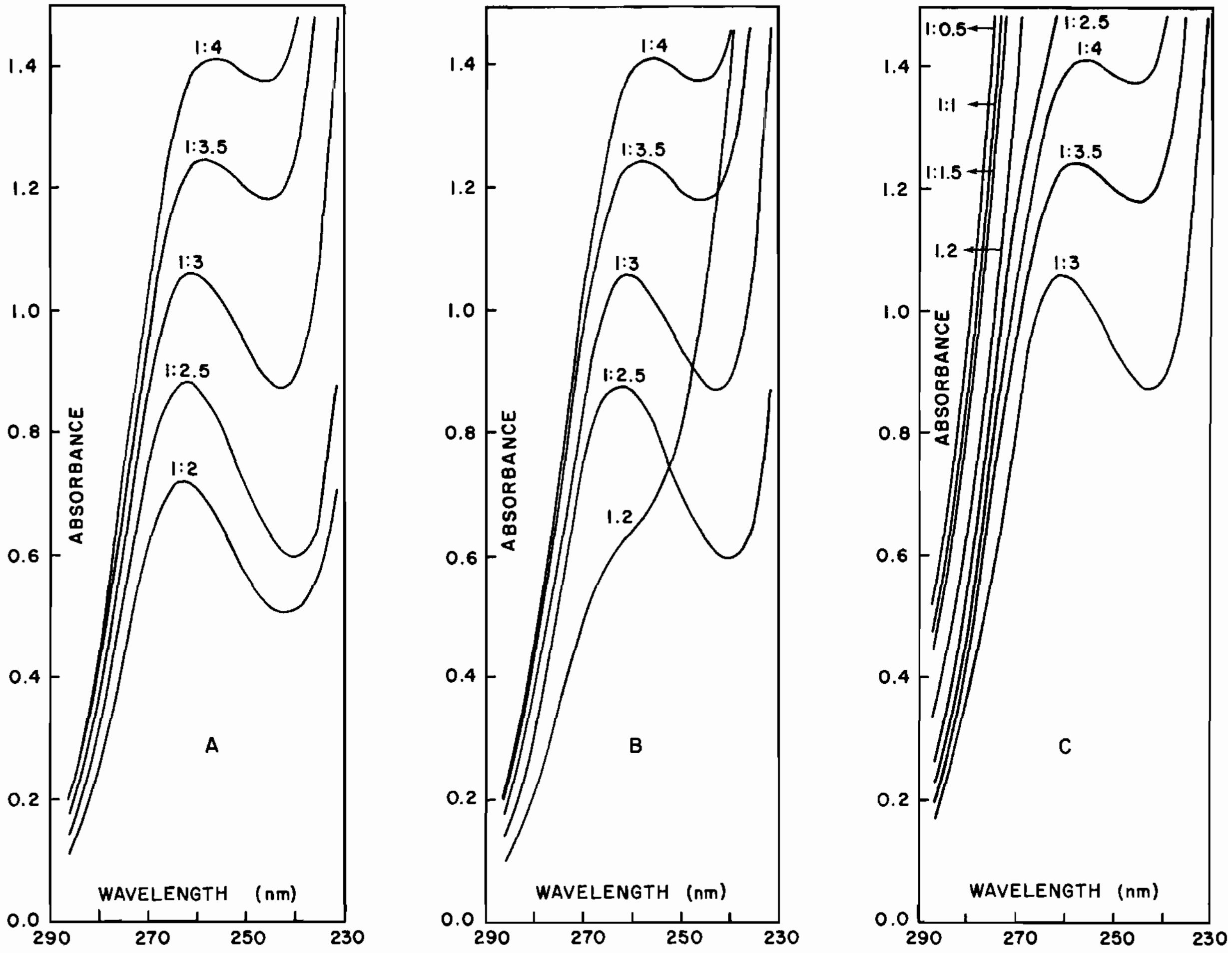

Fig. 2. Ultraviolet absorption spectra of $SnCl_4$-$K_2C_2O_4$ mixtures.

1:2 and 1:2.5, yielded structureless absorptions after 24 hours (spectra C). A complex species is formed as soon as $SnCl_4$:$K_2C_2O_4$ $\geqslant$ 1:2 (spectra A). However, this species is not neutral, since it was shown spectrophotometrically that it is sorbed on the anion exchanger and let through by the cation exchanger. The species is thus negatively charged. The change of the spectrum into a structureless absorption (spectra B and C) indicates that the species is unstable in aqueous solution due to the hydrolysis of tin that even occurs in strongly acidic solutions [9].

The complex species formed in the mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:2, is obviously also formed in the mixtures for which $SnCl_4$:$K_2C_2O_4$ = 1:2.5; 1:3; 1:3.5 and 1:4, but it is increasingly stabilised by the higher free oxalate concentrations in solution. The mixtures for which $SnCl_4$:$K_2C_2O_4$ = 1:3, 1:3.5 and 1:4 remain stable indefinitely. The only crystalline product isolatable from these mixtures is $K_6Sn_2(C_2O_4)_7{\cdot}4H_2O$. The spectrum of the mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:3.5 coincides with that of an aqueous solution of the complex of corresponding molar concentration and has the same form as that of the mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:2 if it is borne in mind that the difference in absorbance and the slight shift of the absorption maximum are only attributable to tailing of the increased oxalate absorbance in this wavelength region, measured spectrophotometrically with respect to water as the reference.

These results led to the presumption that the complex species in solution exists as a negatively charged 1:2 complex stabilised by three oxalate groups per complex molecule. Efforts were made to confirm this experimentally by recording the absorption spectrum of the complex with reference to an aqueous $K_2C_2O_4$ solution with molar concentration three times that of the complex solution. However, the obtained spectrum did not exactly coincide with that of a corresponding concentration of an aqueous mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:2 and hence no final conclusions could be made. Efforts were also made to isolate the complex species formed in the mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:2. The addition of a tenfold volume of ethanol brought about the precipitation of a powder which, after subjected to chemical analysis, turned out to be a mixture of the reactants.

The observations that the complex species in the mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:2 is negatively charged and that the absorption spectrum of the complex, isolated from a mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:4, coincides with that of a mixture for which $SnCl_4$:$K_2C_2O_4$ = 1:3.5, throw doubt on the claimed existence of the complex species $Sn(C_2O_4)_2$ and $Sn(C_2O_4)_4^{4-}$ [4]. The author concerned, made his conclusions from breaks at 2 and 4 oxalate groups per tin atom from his graphical representation of mixture composition versus required thickness of solution for producing absorption up to 2618 Å. However, the graph exhibits many other breaks that make the interpretation rather doubtful.

The presence of free oxalate in solution had to be confirmed by another experimental method. The release of hydrogen ions during the dissolution process offered the possibility of titrating aqueous solutions of various molar concentrations with standard alkali. It became apparent from a number of preliminary titrations that the determination of the titration curves is time dependent, due to the occurrence of slow equilibria in solution during titration. Thus a constant time interval was allowed between successive additions of identical quantities of alkali and the solutions were magnetically stirred for a constant period after each addition before the pH was measured. The titration curves of 50.0 cm³ solutions for which [complex] = 1.0×10^{-3}; 5.0×10^{-3}; 1.0×10^{-2}; 1.5×10^{-2} *M* are given in Fig. 3.

The pH increases uniformly with the addition of alkali until a value of 4.5–5.0 is attained. From there the pH increases more gradually, resulting in a break in the titration curve. The solutions for which [complex] = 1.0×10^{-2} and 1.5×10^{-2} *M*, become turbid in the region of this break, probably due to precipitation of $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$. They become clear again after reaching the endpoint (pH ~ 8), probably because of the formation of $Sn(OH)_6^{2-}$ or SnO_3^{2-} in excess alkali [9].

The alkali consumed to reach the break is in all cases more than the theoretical quantity required to neutralise the free hydrogen ions that determine the initial pH. The additional quantity is used for neutralising titratable free oxalate in solution, for deprotonating water and/or oxalate groups or for

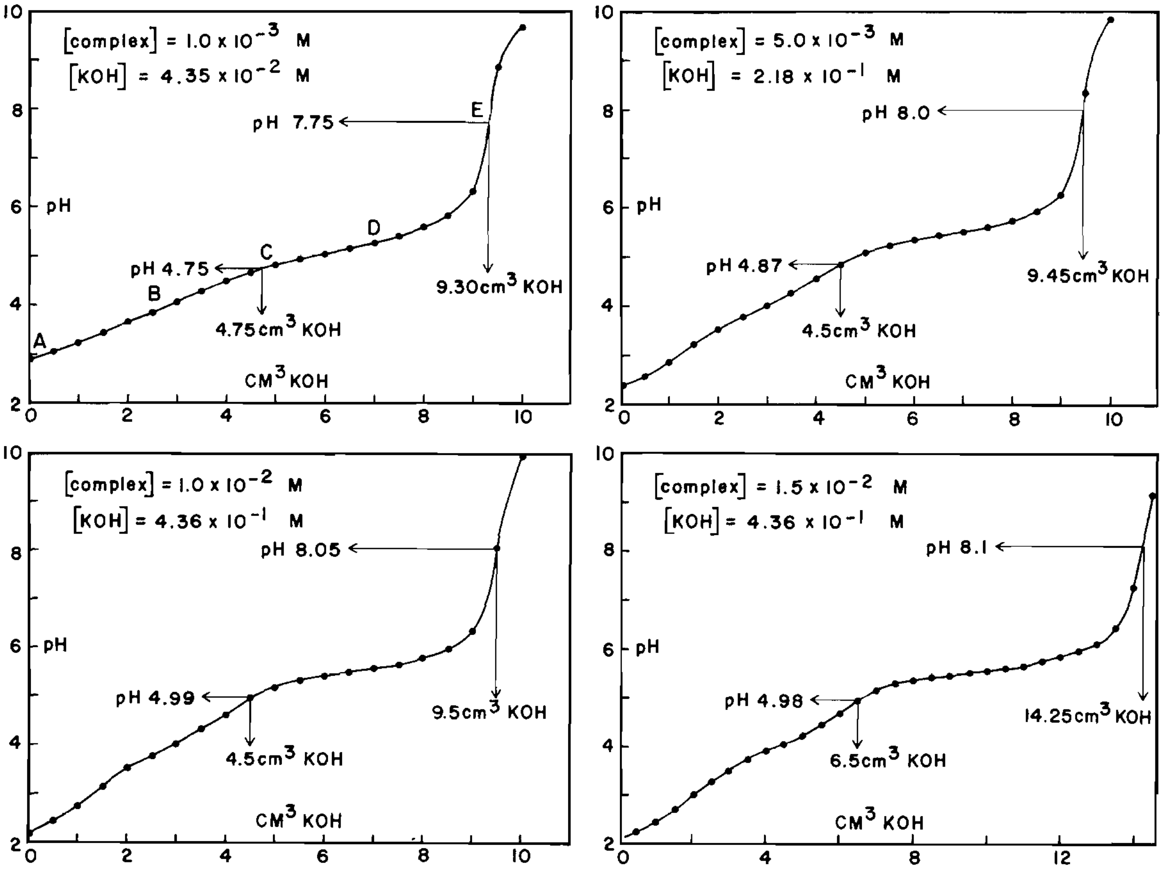

Fig. 3. pH titrations of aqueous solutions of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ with standard alkali at 25 °C.

converting blonded tin in to $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$. The latter possibility is rather improbable because the absorption spectrum of the complex solution does not change on the addition of sufficient alkali to reach the break. On further addition of alkali after reaching the break, the spectrum changes to a structureless absorption that indicates the formation of $Sn(OH)_4$ or SnO_2 xH_2O.

If it is assumed that only free hydrogen and titratable oxalate ions are neutralised till the break in the titration curve is reached, it is possible to calculate the concentration titratable oxalate and hence the total concentration free oxalate in solution as the hydrogen ion concentration is known from the initially measured pH. It is illustrated below for [complex] = 1.0×10^{-3} *M*, the results for all concentrations being summarised in Table I.

TABLE I. Calculated Values of [total oxalate] and [KOH]/[complex].

[complex] (mol liter^{-1})	0.001	0.005	0.010	0.015
[total oxalate] (mol liter^{-1})	0.00304	0.01496	0.03054	0.04497
[KOH]/[complex] at Break	4.1	3.9	3.9	3.8
[KOH]/[complex] at Endpoint	8.1	8.3	8.3	8.3

A quantity 4.75 cm^3 4.35×10^{-2} *M* KOH, *i.e.* 0.2066 millimol of KOH, is required to reach the break. Thus at the break [KOH]/[complex] = 4.1. The change in pH from 2.92 to 4.75 requires 0.0592 millimol of KOH. The titratable oxalate is thus 0.2066–0.0592 = 0.1474 millimol. The equation [total oxalate] = $\{1 + K_1/[H^+] + K_1K_2/[H^+]^2\}$ $[H_2C_2O_4]$ with $K_1 = 5.9 \times 10^{-2}$ and $K_2 = 6.4 \times 10^{-5}$ M[10] allows the fraction existing as $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ at pH 2.92 to be calculated as $f_{H_2C_2O_4} = 0.0190$; $f_{HC_2O_4^-} = 0.9314$; $f_{C_2O_4^{2-}} = 0.0496$. If $[H_2C_2O_4]$ = x millimol, then $[HC_2O_4^-]$ = 49.07x millimol and $[C_2O_4^{2-}]$ = 2.61x millimol. The titratable oxalate is thus 2x + 49.07x = 0.1474, from which it follows that x = 0.0028. Thus $[H_2C_2O_4]$ = 0.000057 *M*, $[HC_2O_4^-]$ = 0.002833 *M* and $[C_2O_4^{2-}]$ = 0.000151 *M* or [total oxalate] = 0.003041 *M*. A quantity 9.30 cm^3 4.35×10^{-2} *M* KOH, *i.e.* 0.4046 millimol of KOH, is required to reach the endpoint. The pH of the water changed from 5.25 to 7.75, requiring 0.0003 millimol of KOH. The complex consumed 0.4046–0.003 = 0.4043 millimol of KOH. Thus at the endpoint [KOH]/[complex] = 8.1.

The result that [KOH]/[complex] ~ 4 where the precipitation of $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ commences and [KOH]/[complex] ~ 8 where all the tin has been precipitated, is in agreement with the results obtained by Willard and Toribara [5], the somewhat high values at the endpoint being attributed to the partial conversion of $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ into $Sn(OH)_6^{2-}$ or SnO_3^{2-}.

In all the cases it can be concluded that three oxalate groups are released by each dissolved complex molecule if it is assumed that only free hydrogen and titratable oxalate ions are neutralised till reaching the break. The calculations and conclusions would be incorrect if any $Sn(OH)_4$ or SnO_2 xH_2O would form prior to reaching the break. This was checked by separating any possibly-formed neutral $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ from the negatively-charged complex species and free oxalate by means of the anion exchanger and determining the tin content of the eluate. The calculations could thus be modified and exact conclusions be made regarding the availability of free oxalate in solution.

The required amount of 4.35×10^{-2} *M* KOH were added to five 50.0 cm^3 aqueous solutions of the complex for which [complex] = 1.0×10^{-3} *M* with the purpose of obtaining the stages A, B, C, D and E indicated on the corresponding neutralisation curve in Figure 3. The solutions were then let through the anion exchanger, any possibly-formed $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ being eluted with water and diluted to a fixed volume. The adsorbed complex species and free oxalate were eluted with 5 *M* KOH and also diluted to a fixed volume. The tin content of the water fractions and the oxalate content of the alkali fractions, were determined. The results are presented in Table II.

TABLE II. Analysis of Anion Exchanger Eluate.

Stage	cm^3 4.35×10^{-2} *M* KOH Added	Resulting pH	%Sn in Eluate	%C_2O_4 in Eluate
A	0.00	2.92	0.0	100.0
B	2.75	4.00	0.0	99.8
C	5.50	4.90	5.0	100.0
D	7.50	5.40	52.1	100.0
E	9.50	7.50	83.2	100.0

The tin present as $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ at the endpoint is less than 100% (83.2%) because some tin remained in the anion exchanger as $Sn(OH)_6^{2-}$ or SnO_3^{2-}. The remaining tin could not be estimated accurately since the alkali used to elute the exchanger had to be of too high molar concentration. The rapid addition of alkali necessitated more than the required quantity of KOH to reach the break. The reason is that $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ formed prior to the complete neutralisation of the titratable oxalate, as can be inferred from the presence of 5% of the bonded tin in the water eluate. The calculations above had, therefore, to be modified with respect to the alkali required for the conversion and for the neutralisation of the remaining titratable oxalate at the resulting pH (4.90).

A quantity 5.5 cm^3 4.35 X 10^{-2} *M* KOH, *i.e.* 0.2393 millimol, was added. The change in pH from 2.92 to 4.90 requires 0.0595 millimol of KOH. The conversion of 5% of the bonded Sn(IV) to $Sn(OH)_4$ or SnO_2 xH_2O requires 0.01 millimol of KOH. The titratable oxalate is thus 0.2393–0.0695 = 0.1698 millimol. The fraction existing as $H_2C_2O_4$, $HC_2O_4^-$ and $C_2O_4^{2-}$ is $f_{H_2C_2O_4} = 0.0190$, $f_{HC_2O_4^-} = 0.9314$ and $f_{C_2O_4^{2-}} = 0.0496$ at pH 2.92 and $f_{H_2C_2O_4} = 0.00004$, $f_{HC_2O_4^-} = 0.1644$ and $f_{C_2O_4^{2-}} = 0.8356$ at pH 4.90. Thus [total oxalate] = 0.003502–0.000576 = 0.002926 *M* since the remaining titratable oxalate at pH 4.90 amounts 16.44% of the total oxalate concentration. This result confirms the conclusion that three oxalate groups are released by each complex molecule during the dissolution process.

There are experimental evidences that the release of the hydrogen ions is facilitated by an acid–base equilibrium, *viz.*:

i. The measured pH is not linearly related to the complex concentration as illustrated by the values in Table III;

ii. The pH values 3.0–3.5 cannot be attained by the addition of the theoretically-required quantity of standard alkali, whereas the pH values 1.5–2.0 are exactly obtainable with the required amounts of standard acid or alkali despite the low pH of the solution.

TABLE III. Relation between [complex] and [H$^+$]

10^2 [complex] (mol liter^{-1})	pH	10^3 [H$^+$] (mol liter^{-1})
0.10	2.92	1.20
0 50	2.40	3.98
1.00	2.21	6.17
1.50	2.14	7.24

The structural changes comprising the release of oxalate and hydrogen ions can be represented by two possible dissolution processes that fit all the experimental data, *viz.*

$$K_6Sn_2(C_2O_4)_7 + 6H_2O \rightarrow 2Sn(C_2O_4)(OC_2O_3H)(H_2O)(OH)_2^- + H^+ + HC_2O_4^- + 2C_2O_4^{2-} + 6K^+$$

$$2Sn(C_2O_4)(OC_2O_3H)(H_2O)(OH)_2^- \rightleftharpoons 2Sn(C_2O_4)(OC_2O_3)(H_2O)(OH)_2^{2-} + 2H^+$$

or

$$K_6Sn_2(C_2O_4)_7 + 4H_2O \rightarrow 2Sn(C_2O_4)_2(H_2O)(OH)^- + H^+ + HC_2O_4^- + 2C_2O_4^{2-} + 6K^+$$

$$2Sn(C_2O_4)_2(H_2O)(OH)^- \rightleftharpoons 2Sn(C_2O_4)_2(OH)_2^{2-} + 2H^+$$

In both cases 3H$^+$, $HC_2O_4^-$ and $2C_2O_4^{2-}$ are released, existing as H$^+$ and $3HC_2O_4^-$ at the pH values under consideration (Table III). Both the resulting dioxalato complex species contain two hydroxyl groups and exist as such till reaching the break in the titration curves (Figure 3) where [KOH]/[complex] = 4. It is completely converted into $Sn(OH)_4$ or $SnO_2 \cdot xH_2O$ at the endpoint where [KOH]/[complex] = 8. Both the suggested processes comprise a dissolution reaction followed by an acid–base equilibrium. A principal feature of the dissolution step is the formation of a six-coordinated dioxalato complex. The occurrence of a ring-opened species in the first suggested process may reasonably result from the presence of an oxalate-bridging group in the crystal state [1]. A study of the photochemical behaviour of aqueous solutions of the complex may be an approach to determine which process is to be favoured.

Acknowledgement

The authors gratefully acknowledge financial support from the South African Council for Scientific and Industrial Research.

References

1 G. J. Kruger, E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta, 19,* 151 (1976).
2 A. K. Dey and A. K. Bhattacharya, *J. Indian Chem. Soc., 25,* 571 (1948).
3 A. K. Dey and A. K. Bhattacharya, *Proc. Natl. Acad. Sci. India, A18,* 121 (1949).
4 A. K. Dey, *Proc. Natl. Acad. Sci. India, A26,* 126 (1957).
5 H. H. Willard and T. Y. Toribara, *J. Am. Chem. Soc., 64,* 1759 (1942).
6 K. V. Krishnamurty and G. M. Harris, *Chem. Rev., 61,* 215 (1961).
7 A. I. Vogel, "Quantitative Inorganic Analysis", 3rd edition, Longmans, 284 (1962).
8 E. L. J. Breet and R. van Eldik, *Inorg. Chim. Acta, 9,* 177 (1974).
9 M. J. Sienko and R. A. Plane, "Chemistry: Principles and Properties", McGraw–Hill, 491 (1966).
10 R. C. Weast, "Handbook of Chemistry and Physics", 49th edition, The Chemical Rubber Co., D90 (1968).