490. *The Chelates formed by Tin*(II) *with Certain Amino-polycarboxylic Acids.*

By T. D. Smith.

pH titration and polarographic work with tin(II) chloride and EDTA, confirmed by use of 1,2-cyclohexylenediaminetetra-acetic acid, indicates formation of a range of chelate compounds. Polarography of tin(II)-EDTA may provide a method of analysis for the metal. The results are briefly discussed in relation to those for other metals.

In order to assess the factors involved in the formation of stable chelates of cations with small negative partial molal entropies the behaviour of tin(II) with a number of amino-carboxylic acids has been studied. Few investigations of the stability constants have been carried out [1] but studies of the tin(II) chelates involved in analytical work indicate that tin(II) complexes may be formed with a wide range of organic ligands.

Titration curves for the tin(II)-ethylenediamine-*NNN'N'*-tetra-acetic acid (EDTA) system are shown by Fig. 1. An inflexion occurs in curve C when *a*, the number of equivalents of alkali added per g.-atom of metal ion, is two. This corresponds to the formation of a 1 : 1 chelate: $Sn^{2+} + H_2Y^{2-} \rightleftharpoons SnY^{2-} + 2H^+$ where Y^{4-} is the tetra-negative anion of the amino-carboxylic acid. Above pH ~7 the curve rises less steeply and is presumably due to the liberation of further quantities of hydrogen ion: $SnY^{2-} + H_2O \rightleftharpoons [SnY\cdot OH]^{3-} + H^+$, though this equilibrium does not account quantitatively for the deviation from ideal behaviour. Curve D illustrates that a second ligand is not added. When the molar ratio of tin(II) to EDTA disodium salt was 1 : 0·5 no precipitation occurred on titration. The chelate formed must be Sn_2Y, the reaction, $Sn^{2+} + \frac{1}{2}H_2Y^{2-} = \frac{1}{2}Sn_2Y + H^+$, leading to an inflexion at $a = 1$. It is assumed therefore that the chelate is readily hydrolysed.

The ultraviolet absorption spectra of the tin(II) chelate of EDTA depends markedly on the pH of the solution (see Fig. 2). The absorbance increases steadily up to pH ~2·80; then a large increase occurs; the absorbance is unchanged from pH 4·0 to pH ~7·0, whereafter it again increases; finally, at pH 10·3 it decreases. The effect of pH on the ultraviolet spectrum of EDTA is also shown. The changes in absorption of the tin(II) chelate solution cannot be explained in terms of the variation of absorption of the reagent itself, and indeed at pH 2·80 the absorption of the chelate solution is greater than that of the reagent. The changes in absorbance of the chelate above pH 7·0 are paralleled by changes in the pH titration curves which have been ascribed to hydrolysis.

A similar series of changes takes place in the case of the tin(II) chelate of 1,2-cyclohexylenediaminetetra-acetic acid. The variation in the absorption of the reagent itself with pH is similar to that shown by Fig. 2.

Further evidence of the range of existence and stability of the tin(II) chelates may be obtained from polarographic data. Typical polarograms for solutions of tin(II) and EDTA at various pH's are shown in Fig. 3. At pH 2·80 a wave is obtained at about —0·80 v. At pH's above 2·80 the wave at —0·80 v disappears, leaving one at —0·20 v which has substantially the same height over the pH range of 1·8—7·5. At pH ~9·0 the wave at —0·2 v decreases in height and a new wave appears at —0·08 v.

A study of the polarographic behaviour in the presence of the other reagents mentioned substantiates these observations. For example, the tin(II) chelate of 1,2-cyclohexylenediaminetetra-acetic acid gives waves at —0·14 v and —1·03 v, and at pH >9·50 the height of the wave at —0·14 v decreases.

Solutions of tin(IV) in the presence of EDTA and 1,2-cyclohexylenediaminetetra-acetic acid over the pH range 1·50—9·50 gave no polarographic response. The wave

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[1] " Stability Constants," Part I and Part II (L. E. Sutton), *Chem. Soc. Special Publ. No.* 7, 1957.

obtained at —0·20 and —0·14 v for tin(II) may thus result from the oxidation of the tin(II) to the tin(IV), though the invariance of $E_{\frac{1}{2}}$ and wave-height over the range of pH remains unexplained. The oxidation of tin(II) at about —0·2 v in the presence of the amino-carboxylic acids is similar to that obtained in acetate and tartrate media.[2]

FIG. 1. pH *Titration of the tin*(II)–EDTA *system.* Ratio tin(II) : H_2Y^{2-}; A, 0 : 1; B, 1 : 0·5; C, 1 : 1; D, 1 : 2.

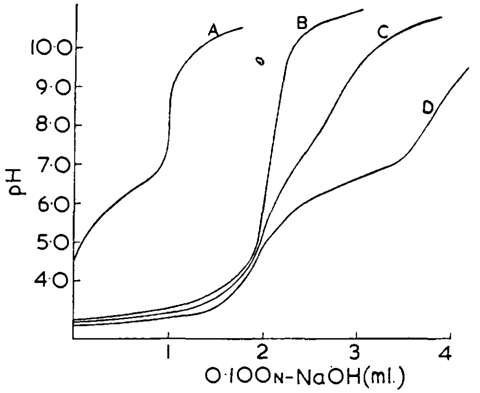


FIG. 3. *Polarographic responses of solutions containing* 10^{-3}M-*tin*(II), 10^{-2}M-EDTA, 0·1M-*sodium perchlorate, and* 0·005% *of gelatin.*

1, pH 2·80; 2, pH 4·15; 3, pH 9·25; 4, pH 10·20.

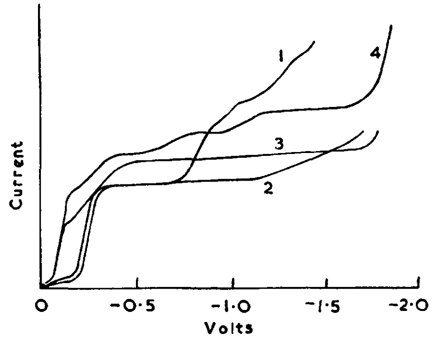


FIG. 2. *Spectra of solutions containing* 10^{-4}M-*tin*(II) *and* 10^{-4}M-EDTA.

1, pH 2·80; 2, pH 4·40; 3, pH 7·80; 4, pH 9·30; 5, pH 10·30.

Spectra of solutions containing 10^{-4}M-EDTA. A, pH 2·80; B, pH 7·90; C, pH 9·40; D, pH 10·30.

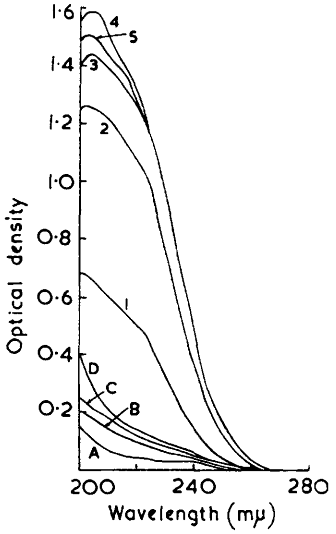
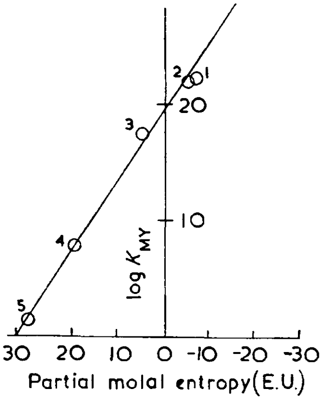


FIG. 4. *Correlation of stability constants with partial molal entropies of the cation.*

1, Sn(II); 2, Hg(II); 3, Pb(II); 4, Ag(I); 5, Tl(I).



The curve at —0·20 v for tin(II) in EDTA at pH 4·5 may be suitable for tin(II) analysis and, though this is dealt with in detail here, a study of the collected data [2] indicates that the wave may be suitable for the quantitative analysis of tin(II) in the presence of other metals. However, both polarographic and spectrophotometric observations indicate that between pH 3·6 and 6·0 the tin(II) chelate of EDTA has the composition SnY^{2-}.

[2] Lingane, " Electroanalytical Methods," Interscience Publ. Inc., New York, 1953.

The polarographic response of tin(II) solutions in the presence of EDTA provides a convenient method for measuring the concentration of tin(II). The addition of thorium ion in the presence of an acetate buffer, in amount equivalent to that of tin(II) chelate, at pH 4·00 resulted in the partial displacement of tin(II). It was established that, under the solution conditions, the wave-height at —0·47 v was proportional to the concentration of tin(II). The tin(II) concentration of a number of solutions containing stannous ion, EDTA, 0·02M-acetate, and 0·10M-sodium perchlorate at pH 4·00 was measured by noting the height of the wave at —0·47 v due to free tin(II), and the stability constant for the tin(II) chelate was computed by using the known value for the thorium chelate.[3] The exchange reaction may be represented: $SnY^{2-} + Th^{4+} \rightleftharpoons Sn^{2+} + ThY$. The stability constant K_{SnY} for the tin(II) chelate is given by the expression

$$\log K_{SnY} = \log K_{ThY} \cdot \frac{[SnY^{2-}][Th^{4+}]}{[Sn^{2+}][ThY]}$$

The equilibrium concentrations are shown in the Table.

Total concns. (10^{-3}M) of Sn(II) & Th(IV)	1·00	2·00	1·50	0·50
$[Sn^{2+}]$ (10^{-3}M)	0·78	1·48	1·20	0·39
$[SnY^{2-}]$ (10^{-3}M)	0·21	0·51	0·30	0·11
log *K*	22·09	22·28	21·98	22·09

In contrast to earlier considerations [4,5] which dealt with large stability constants arising from metal ions of large negative partial molal entropies the stability constant for the tin(II) chelate is large, though the partial molal entropy for tin(II) is considerably more positive. As shown in Fig. 4, correlation of partial molal entropies of the metal ions with the log *K* of their chelates with EDTA indicates that the ions of thallium(I), silver(I), lead(II), tin(II), and mercury(II) comprise a separate group; this correlation is a quantitative expression of the general similarity in chemical properties of these ions. Unfortunately no further quantitative data on the behaviour of tin(II) with other organic ligands are available.

However, for combination of the metal ions of this group with olefins a further refinement is obtained in that, whilst silver and mercury form complexes with olefins, tin(II), lead(II), and thallium(I) do not.

The stereochemistry of the ligand is important in determining the relative positions of the ions in this group. A study [1] of the chelating agents of the general formula $R{\cdot}N(CH_2{\cdot}CO_2H)_2$ indicates that the log *K* for the mercury(II) chelates is much smaller than those of lead(II). On the other hand in a study of ligands of the type $(HO_2C)_2N{\cdot}[CH_2]_n{\cdot}N(CO_2H)_2$ the log *K*'s for mercury(II) are found to be larger than those for the corresponding lead(II) chelate, which is little affected by change in *n* and consequently in ring size.

It is possible that, for the log *K* of the mercury(II) chelate to exceed that for lead(II), as in the case of EDTA, the stereochemistry must be suitable for the formation of *sp*-linear bonds, whilst lead(II) and tin(II) are able to form p^3d hybridised bonds with a greater variety of stereochemistry of the ligand.

EXPERIMENTAL

pH *Titrations*.—The technique was essentially that described previously.[4]

A 0·0100M-solution of tin(II) was prepared by dissolving "AnalaR" stannous chloride in 1·00 ml. of approximately 9N-hydrochloric acid contained in a stoppered flask. The flask was gently heated to effect dissolution, then cooled; after dilution the contents were transferred to a 1-l. flask and made up to volume. To determine the acidity of the stock solution due to

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[3] Schwarzenbach, Gut, and Anderegg, *Helv. Chim. Acta*, 1954, **37**, 937.

[4] Foreman and Smith, *J.*, 1752, 1957.

[5] Smith, *J. Inorg. Nuclear Chem.*, 1959, **11**, 314.

the hydrochloric acid the procedure was repeated, but stannous chloride was omitted: an aliquot part of this solution was titrated with base.

In the pH titration of tin(II)–EDTA solutions the acidity due to the hydrochloric acid was subtracted from the total figure to obtain that generated by chelate formation. Fresh stock solutions of tin(II) were prepared for each experiment.

The polarographic measurements were made with a Tinsley polarograph and an H-type cell, one arm consisting of a saturated calomel electrode in a thermostat at 20° ± 0·1°. Calibration waves were derived for the tin(II) ion by variation of concentration. In all cases the tin(II) solutions containing the chelating agents were set aside for 12 hr. at a given pH for equilibration. The absorption spectra of solutions of tin(II) chelates were recorded with a Unicam S.P. 500 spectrophotometer.

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[*Received, December 12th,* 1960.]