

383. Chelates formed by Tin(II) with Citric and Tartaric Acids, and Their Interaction with Certain Transition-metal Ions

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pH-Titrations have shown that tin(II) forms stable chelates with citric and tartaric acids, and enable the stability constants to be calculated. The addition of iron(III) or copper(II) to a solution containing tin(II) citrate or tin(III) tartrate results in the formation of a 1 : 1 : 1 chelate of iron(III) or copper(II) with tin(II) and citrate or tartrate.

As part of a study of the oxidation of tin(II) by molecular oxygen in aqueous solutions of carboxylic acids, chelates formed by tin(II) with citric and tartaric acids have been investigated. Although various studies concerning the use of tin(II) in the presence of carboxylic acids as volumetric reagents have suggested that stable chelates are formed, it seems that the range of stability and stoichiometry of tin(II) chelates of citric and tartaric acid have not been studied. Lingane¹ noted the marked effect of pH on the anodic and cathodic half-wave potentials, and concluded that there is a fundamental difference in the composition of the tin(II) chelates in acid and alkaline solution. In a strongly alkaline medium, part of the co-ordinating tartrate is probably replaced, to form a hydroxo-tartrate chelate.

Titration curves for tin(II) in the presence of various amounts of citric acid are shown in Figure 1. When the ratio tin(II) : citric acid is 1 : 1, as in curve B, precipitation occurs at pH 5.6, as indicated by the arrow. When the ratio reaches 1 : 1.5, precipitation begins at pH 6.7; at higher ratios it begins at about pH 9.2. The data for the titration curves refer to a total volume of solution of 100 ml., and 0.1M with respect to sodium perchlorate. The formation curve for tin(II) citrate chelates was calculated from information contained in curves E and F, and is shown in Figure 1a. Values of \bar{n} rise to somewhat greater than unity; therefore, the highest chelate is at least $\text{Sn}(\text{HL})_2^{4-}$, where HL^{3-} is the trinegative ion of citric acid.² For simultaneous formation of two chelates:

$$\bar{n} = \frac{\beta_1[\text{HL}^{3-}] + 2\beta_2[\text{HL}^{3-}]^2}{1 + \beta_1[\text{HL}^{3-}] + \beta_2[\text{HL}^{3-}]^2}$$

By using the relationship:

$$\left(\frac{1 - \bar{n}}{\bar{n}}\right)[\text{HL}^{3-}]\beta_1 + \left(\frac{2 - \bar{n}}{\bar{n}}\right)[\text{HL}^{3-}]^2\beta_2 = 1,$$

β_1 and β_2 were evaluated from a plot of $\left(\frac{1 - \bar{n}}{\bar{n}}\right)[\text{HL}^{3-}]$ against $\left(\frac{2 - \bar{n}}{\bar{n}}\right)[\text{HL}^{3-}]^2$, substituting the values of \bar{n} from Figure 1a. The result is shown in Figure 1b, giving $\log \beta_1 = 7.37$, and $\log \beta_2 = 12.8$. The value of 7.37 for $\log K_{\text{MHL}}^{\text{M}}$ of the tin(II) citrate chelate is larger than that reported for the lead(II) chelate, as would be expected.³ In each case, the amount of hydrogen ion liberated is greater than can be accounted for from citric acid alone, so that hydrolysis of the chelates must take place. Stock solutions of tin(II), containing various amounts of citric acid, on standing for a few days, give rise to a precipitate even at pH values of about 2.0. The composition of the precipitate isolated from a solution containing a four-fold excess of citric acid approximates to a chelate containing tin(II) and citric acid in 1 : 1 proportion, with the possible composition $(\text{SnH}_2\text{L})_2\text{O}$ (Found: C, 22.75; H, 2.12; Sn, 35.5. Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_{15}\text{Sn}_2$: C, 22.65; H, 2.20; Sn, 37.28%).

¹ Lingane, *J. Amer. Chem. Soc.*, 1943, **65**, 866.

² Rossotti and Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1961, ch. 5.

³ Smith, *J.*, 1961, 2554.

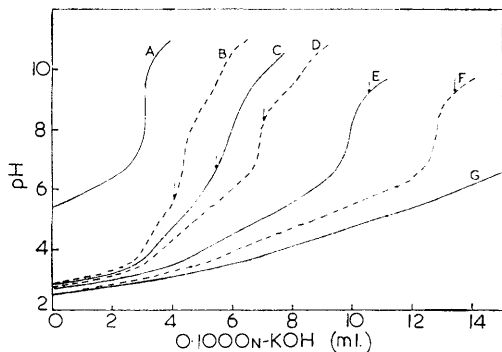


FIGURE 1

FIGURE 1. pH-Titration of the tin(II)-citric acid system. $[\text{Tin(II)}] = 1.0 \times 10^{-3}\text{M}$. Volume = 100 ml. Ratio tin(II): citric acid: A, 0:1; B, 1:1; C, 1:1.5; D, 1:2; E, 1:3; F, 1:4; G, 1:5

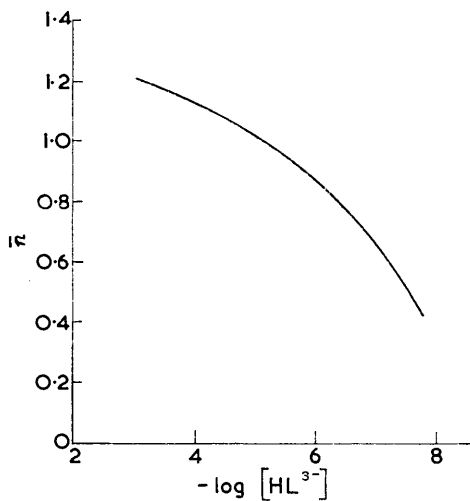


FIGURE 1a

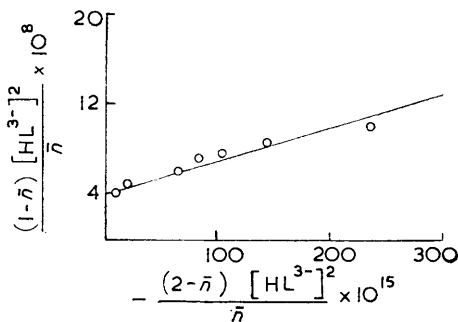


FIGURE 1b

FIGURE 1a. Formation curve for the tin(II)-citrate system

FIGURE 1b. Evaluation of β_1 and β_2

pH-Titration curves for the tin(II)-tartaric acid system are shown in Figure 2. When tartaric acid is present in 1:1 ratio, tin(II) is precipitated at low pH values, and evidently a chemically stable 1:1 chelate is not formed. Curve I depicts results for tin(II) and tartaric acid in 1:2 ratio, when a stable chelate is formed over a wide range of pH values. The formation curve for the tin(II)-tartrate system is shown in Figure 2a. By using the relationship:

$$\frac{\bar{n}}{(2-\bar{n})}[\text{H}_2\text{T}^{2-}]^2 \cdot \frac{1}{\beta_2} + \frac{(\bar{n}-1)}{(2-\bar{n})[\text{H}_2\text{T}^{2-}]} \cdot \frac{\beta_1}{\beta_2} = 1,$$

β_1 and β_2 were evaluated from a plot of $\frac{\bar{n}}{(2-\bar{n})}[\text{H}_2\text{T}^{2-}]^2$ against $\frac{(\bar{n}-1)}{(2-\bar{n})[\text{H}_2\text{T}^{2-}]}$, as shown in Figure 2b. From the intercept, $\log \beta_2 = 9.91$ and, from the slope, $\log \beta_1 = 5.2$. Again, the titration curves indicate that hydrolysis of the tin(II) tartrate chelate occurs.

On addition of ferric ion to the solutions, less citric or tartaric acid was required to prevent precipitation of tin(II); this suggested that a chelate containing tin(II) and iron(III) was formed. Addition of tin(II) to a solution of ferric citrate caused an intensification of the yellow colour of ferric citrate. pH-Titration curves for the ferric citrate system are shown in Figure 3; curves M and O indicate that a 1:1 chelate is formed, hydrolysis

taking place beyond pH 5.0. Curve O provides no evidence for addition of a second ligand to ferric ion. The titration curve for a solution containing iron(III), tin(II), and citric acid in 1 : 1 : 1 ratio is shown by Q in Figure 4, and clearly indicates formation of a 1 : 1 : 1 chelate. For comparison, the pH-titration curve for tin(IV) citrate is shown by P in Figure 3, which from the quantity of alkali consumed, indicates that oxidation of tin(II) does not take place in the previous case discussed. Mattock⁴ found that, for tin(IV) in the presence of tartrate, the combining ratios were 1 : 1, 1 : 2, and possibly 1 : 4, although quantitative interpretation, particularly from electrometric measurements, was difficult. The presence of iron(III) in 1 : 1 ratio with tin(II) prevents precipitation of tin(II) citrate.

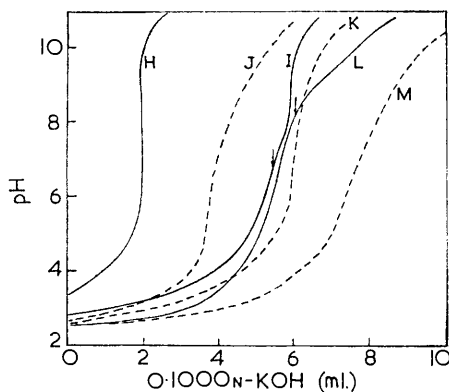


FIGURE 2. pH-Titration of the tin(II)-tartaric acid and tin(II)-iron(III)-tartaric acid systems. $[\text{Tin(II)}] = 1.0 \times 10^{-3}$ M. $[\text{Iron(III)}] = 1.0 \times 10^{-3}$ M. Volume = 100 ml. Ratio tin(II) : tartaric acid: H, 0 : 1; I, 1 : 2. Ratio iron(III) : tartaric acid: J, 1 : 1; K, 1 : 2. Ratio iron(III) : tin(II) : tartaric acid: L, 1 : 1; M, 1 : 1 : 2

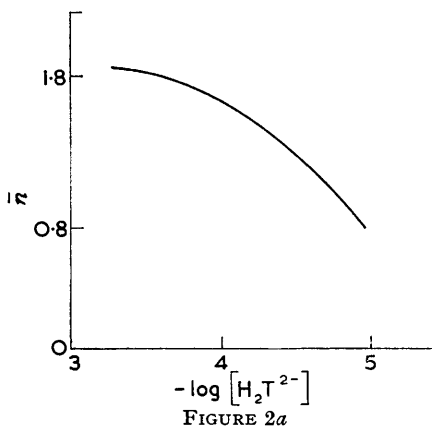


FIGURE 2a. Formation curve for the tin(II)-tartrate system

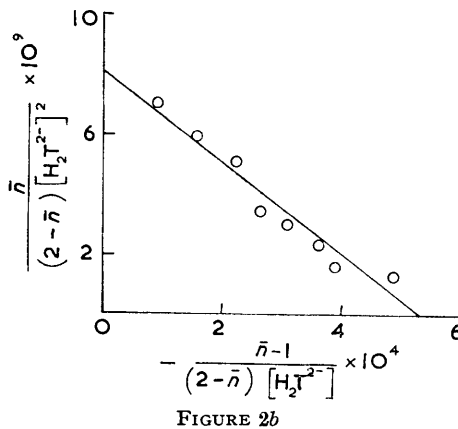


FIGURE 2b. Evaluation of β_1 and β_2

Formation of a 1 : 1 ferric tartrate chelate is represented by curve J (Figure 2) there is no evidence for the formation of a 1 : 2 chelate. It is remarkable that, although tartaric acid does not form a stable chelate when present in 1 : 1 ratio with tin(II), the pH-titration of a solution containing iron(III), tin(II), and tartaric acid, in 1 : 1 : 1 ratio, indicates the formation of a stable chelate over a wide range of pH values. Evidently, tartaric acid behaves as tetradentate ligand, as in the case of iron(III) alaine and tin(II) hydrolyses. For higher ratios of tartaric acid, the titration curves suggest that a 1 : 1 : 2 chelate may be formed with suppression of hydrolysis of the resulting chelate.

In principle, the polarographic behaviour of tin(II)-tartaric acid solutions containing

⁴ Mattock, J., 1954, 989.

iron(III) provides a further means of characterising the chelate containing both iron(III) and tin(II). In the absence of iron(III), tin(II)-tartaric acid gives rise to an anodic wave corresponding to oxidation to the stannic state, and a cathodic wave corresponding to reduction of tin(II) tartrate.¹ Both waves are of equal height, with half-wave potentials ($E_{\frac{1}{2}}$) versus the saturated calomel electrode varying with the pH of the solution. Thus, at pH 2.3, the anodic $E_{\frac{1}{2}}$ occurs at -0.14 v, and the cathodic $E_{\frac{1}{2}}$ at -0.49 v. Iron(III), in the presence of tartrate at pH 2.0, gives a well-defined reversible wave at $+0.12$ v, which moves to -0.19 v at pH 6.0.⁵ The polarographic behaviour of tin(II) and iron(III), contained separately in tartrate media, was studied over a range of pH values, and confirmed the findings reported in the literature. A solution containing a 1 : 1 ratio of tin(II) and iron(III) in excess of tartrate, over the same pH range, gave the same waves as were

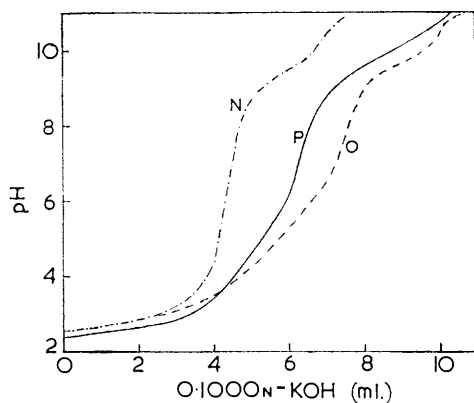


FIGURE 3

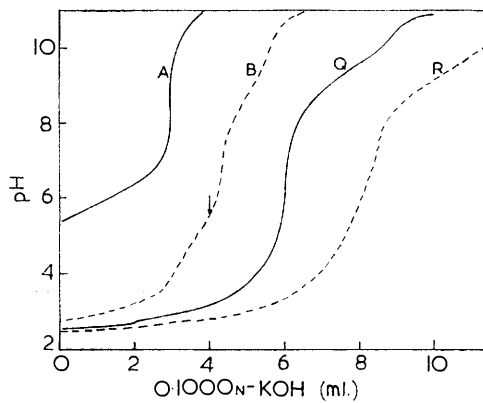


FIGURE 4

FIGURE 3. pH-Titration of the iron(III)-citric acid and tin(IV)-citric acid systems. [Iron(III)] : 1.0×10^{-3} M. [Tin(IV)] = 1.0×10^{-3} M. Volume = 100 ml. Ratio iron (III) : citric acid: N, 1 : 1; O, 1 : 2. Ratio tin(IV) = citric acid: P, 1 : 1

FIGURE 4. pH-Titration of the iron(III)-tin(II)-citric acid system. [Tin(II)] = 1.0×10^{-3} M. Total volume = 100 ml. Ratio iron(III) : tin(II)-citric acid: Q, 1 : 1 : 1; R, 1 : 1 : 2

obtained from the iron(III) and tin(II) separately, and the polarographic behaviour of the tin(II) was in no way altered by the presence of iron(III). The same behaviour was observed when citric acid was used. This may be due to the fact that excess of ligand had to be used in each case in order to obtain comparable results, or that the electrodeposition potential of the tin(II) is little altered by the presence of iron(III) in the chelate.

Formation of a complex containing tin(II) and another metal ion has been observed in various systems. The orange-red solution resulting from reaction of tin(II) with platinum(II) contains complexes with tin : platinum ratios of 1 : 4. Reaction of 5 mol. of tin(II) with 1 mol. of platinum(II) results in 1 mol. of tin(II) being oxidised, whilst precipitation tests with strong alkali, phenylarsonic acid, and silver nitrate, as well as spectrophotometric evidence, reveal the formation of cationic complex $\text{PtSn}_4\text{Cl}_4^{4+}$ with platinum in the zero oxidation state.⁶ Similar results have been obtained for palladium and rhodium chlorides.⁷ More recently, a complex containing ruthenium and tin(II) has been studied.⁸ The isolation of polynuclear complexes of rhodium(III) and tin(II) with tertiary arsines has been studied, and a structure involving chloro-bridges has been suggested.⁹

⁵ Lingane, *J. Amer. Chem. Soc.*, 1946, **68**, 2448.

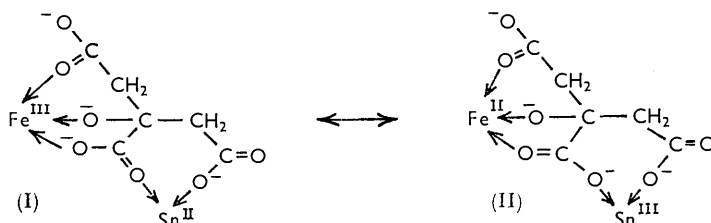
⁶ Ayres, *Analyt. Chem.*, 1953, **25**, 1626.

⁷ Meyer and Ayres, *J. Amer. Chem. Soc.*, 1955, **77**, 2671.

⁸ Okuno, Yamatera, and Ishimori, Proc. 7th Internat. Conf. Co-ordination Chemistry, Stockholm, 1962, p. 200.

⁹ Dwyer and Nyholm, *J. Proc. Roy. Soc. New South Wales*, 1952, **76**, 129.

A complex, $\text{Fe}(\text{CO})_4\text{Cl}_2\text{SnCl}_2$, has been reported by Miller.¹⁰ Spectrophotometric evidence has been adduced for the presence, in low concentration, of a 1 : 1 association complex between tin(II) and uranium(IV) in solutions of these species in hydrochloric acid.¹¹ From rate studies of the reduction of vanadium(V) by tin(II), Drye *et al.*¹² suggest that the initial product of an encounter between tin(II) and vanadium(V) may be an association complex which persists long enough to contribute to the reduction. There appears to have been no previous observation of a chelate containing both tin(II) and iron(III), although occurrence of a chelate containing uranium(IV), thallium(III), and tartrate, in 1 : 1 : 1 ratio, has been suggested to account for the catalytic effect of tartrate in the oxidation of uranium(IV) by thallium(III).¹³ pH-Titration results indicate that, although tin(II) forms a stable chelate with ferric citrate or tartrate, it undergoes hydrolysis. According to the heterometric determinations of Bobtelsky and Goldschmidt,¹⁴ in apparent confirmation of the conductometric, potentiometric, and thermometric studies of previous workers, the chelates existing in a solution of ferric citrate have the composition $2\text{Fe}(\text{III})-3\text{Cit}^{3-}$, where the hydroxyl group takes part in chelate formation, but is not ionised. Contrary to these observations, both Lanford and Quinan¹⁵ and Warner and Weber¹⁶ found the ratio of iron(III) to citrate to be 1 : 1. The pH-titration curves obtained for the ferric citrate system confirm the earlier conclusion of Warner and Weber that a 1 : 1 chelate is formed in which the ligand behaves as a tetranegative base, hydrolysis taking place beyond pH 5.0. Hamm *et al.*¹⁷ suggested that FeHCit^+ is the species present in acid solution, and that FeCit , $\text{Fe}(\text{OH})\text{Cit}^-$, and $\text{Fe}(\text{OH})_2\text{Cit}^{2-}$ are the forms of chelate ion in successively more basic solution. Bobtelsky and Goldschmidt have pointed out that, in the formation of a 1 : 1 ferric citrate complex, participation of all three carboxyl groups in complex-formation is virtually impossible. Since the citrate anion is able to chelate both iron(III) and tin(II) to form a 1 : 1 : 1 chelate, it seems reasonable to assume that citrate exerts its maximum co-ordinating ability to form a tetradentate structure, shown in (I).



It is not obvious why ferric citrate should be so much more effective in chelating tin(II) compared with the citrate anion itself. A possible explanation is that stability could be endowed by resonance between structures (I) and (II), a completely conjugated route being provided by the carboxyl group common to the chelate rings involving iron(III) and tin(II). A similar 1 : 1 : 1 chelate is formed by tartrate. That the hydroxyl group is necessary for the formation of such chelates, was shown by the fact that a series of carboxylic acids which do not have hydroxyl groups would not form chelates containing both iron(III) and tin(II) ions. It was found that tin(II) did not form stable complexes with the citrate or tartrate chelates of nickel(II), cobalt(II), aluminium(III), thorium(IV) uranium(VI), manganese(II), or iron(II). Further, there was no evidence of a chelate containing tin(IV) and iron(III) in citric acid. It was found that copper(II) citrate exhibits

¹⁰ Miller, U.S.P. 2,434,578/1948.

¹¹ Moore, *J. Amer. Chem. Soc.*, 1955, **77**, 1504.

¹² Drye, Higginson, and Knowles, *J.*, 1962, 1137.

¹³ Brubaker, Love, and Quinn, Proc. 7th Internat. Conf. Co-ordination Chemistry, Stockholm, 1962, p. 282.

¹⁴ Bobtelsky and Goldschmidt, *Bull. Res. Council Israel*, 1958, **7A**, 121.

¹⁵ Lanford and Quinan, *J. Amer. Chem. Soc.*, 1948, **70**, 2900.

¹⁶ Warner and Weber, *J. Amer. Chem. Soc.*, 1953, **75**, 5086.

¹⁷ Hamm, Shull, and Grant, *J. Amer. Chem. Soc.*, 1954, **76**, 2111.

a similar behaviour to iron(III) citrate in forming a chelate with tin(II). A readily available reduced valency state seems to be essential for the formation of the chelates of this type. The 1 : 1 : 1 chelate of tin(II) and iron(III) in citric and in tartaric acid may be regarded as the stable intermediate of an electron-transfer process, and, in fact, there is a rapid photochemical reduction of iron(III) by tin(II) in tartrate media.

EXPERIMENTAL

pH-Titrations.—The technique was essentially that described previously.¹⁸ The source of tin(II) was freshly recrystallised AnalaR stannous chloride. Stock solutions were prepared by dissolution of this material in AnalaR citric or tartaric acid, and dilution under nitrogen as required. Iron(III) was derived from AnalaR ferric ammonium sulphate. In the investigation of the precipitate obtained by allowing a tin(II) citrate solution to stand, filtration was carried out under nitrogen, the residue dried under nitrogen, and the tin(II) content determined by titration with a standard iodine solution.

Polarographic measurements were made with a Tinsley polarograph. The cell used was a modification of the conventional low-resistance H-type, having a saturated calomel electrode as reference in one limb, in a thermostat at $20^{\circ} \pm 0.1^{\circ}$. The absorption spectra of solutions of tin(II) and iron(III) chelates were recorded with a Unicam S.P. 500 spectrophotometer.

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¹⁸ Foreman and Smith, *J.*, 1957, 1752.
