Polarography of Tin(IV)-Pyrogallol Complexes.

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Polarography of Tin(IV)-Pyrogallol Complexes

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▶Tin(IV) produces a reversible, two-step reduction wave in a pyrogallol medium. This reduction was investigated at various pyrogallol and hydrogen ion concentrations, and a 0.1*M* $HClO_4$, 1*M* $NaClO_4$, 0.1*M* pyrogallol, 0.002% Triton X-100 solution appeared best suited for analytical applications. In this solution tin(IV) forms a complex containing two molecules of pyrogallol and two hydroxyl groups per atom of tin, while tin(II) is uncomplexed. The diffusion current of both waves is proportional to concentration of stannic tin up to 1 m*M*. The polarographic reduction wave was characterized by a minimum; the current decreased sharply after attaining a flat diffusion current plateau. This minimum was investigated in solutions with and without Triton X-100, and a mechanism for this effect is proposed.

THE POLAROGRAPHIC REDUCTION of tin(IV) is generally characterized by irreversible and ill-defined waves (*5*). Even in the supporting electrolyte recommended (*10*) (4*M* ammonium chloride–1*M* hydrochloric acid) the diffusion current for the reduction of tin(IV) is not fully developed before the second stage of the reduction [tin(II) to the metal] begins. Phillips and Morgan (*16*) recently found a pyrogallol medium to be convenient for the polarographic determination of tin(IV) and indium (III) mixtures, but did not investigate the reversibility or properties of the tin(IV) reduction in this medium. Stannic tin produces a reversible, two-step, reduction wave in an acidic pyrogallol (1,2,3-trihydroxybenzene) medium. This reduction was investigated at various pyrogallol and hydrogen ion concentrations to determine the optimum conditions for analytical applications and to elucidate the composition of the tin(IV)-pyrogallol complex.

EXPERIMENTAL

Apparatus. Polarograms were taken with a Sargent Model XXI Polarograph. For exact measurement of diffusion currents and half-wave potentials the procedure of Meites (*13*) was employed, using a Moseley X-Y recorder, calibrated to an accuracy of 0.1% and requiring 0.5 second for full scale pen travel, to measure the instantaneous current. Potentials were measured with a Leeds & Northrup Model 8687 potentiometer. Current-time curves were recorded on a DuMont Model 401-A oscilloscope using a DuMont Type 353 camera. pH was determined with a Leeds & Northrup Model 7664 pH meter.

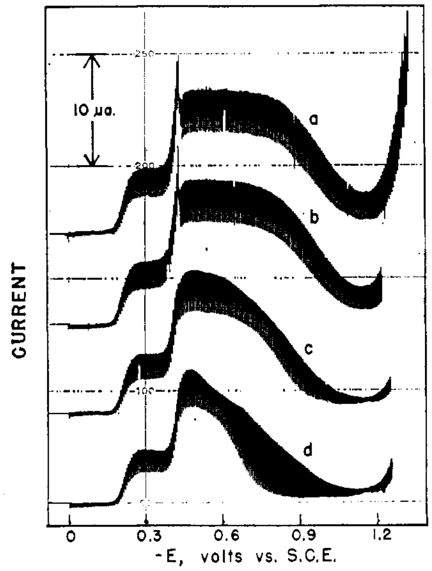


Figure 1. Effect of Triton X-100 concentration on polarographic reduction of tin(IV)-pyrogallol complex

Solution contained 0.1*M* $HClO_4$, 0.50*M* pyrogallol, and 0.98m*M* tin(IV)
a. Triton X-100 concentration, 0
b. 0.0006%
c. 0.0016%
d. 0.0026%

The cell was an H-cell, containing a potassium nitrate-agar plug. An external saturated calomel electrode (S.C.E.) with a potassium chloride-agar salt bridge was immersed in one side of the cell (containing only supporting electrolyte) and the dropping mercury electrode (D.M.E.) was immersed in the other side containing the test solution. This arrangement prevented both the diffusion of chloride ion into the test solution and the contamination of the reference electrode with pyrogallol. The total resistance between the D.M.E. and the S.C.E. was about 400 ohms and potentials were corrected for *IR* drop through the cell. The D.M.E. capillary had a value of $m^{2/3}t^{1/6}$ of 2.086 at −0.28 volt *vs.* S.C.E. in a 0.1*M* $HClO_4$, 0.1*M* $NaClO_4$, 0.1*M* pyrogallol solution. All measurements were made at a temperature of 25.00° ± 0.05° C.

Chemicals. Standard tin(IV) solutions were prepared by dissolving granulated tin in a hydrochloric-nitric acid mixture and boiling to remove oxides of nitrogen. The final stock solution was 0.05*M* in stannic tin and approximately 1*M* in hydrochloric acid, so that test solutions containing 1m*M* tin(IV) contained about 0.02*M* chloride ion. Pyrogallol was generally added as a solid to deaerated solutions immediately before use to prevent possible air oxidation.

RESULTS AND DISCUSSION

Effect of Pyrogallol Concentration and pH on $E_{1/2}$. A typical polarogram for the reduction of tin(IV) in a pyrogallol medium is shown in Figure 1,*a*. The first wave is due to the reduction of tin(IV) to tin(II), and the second the reduction of tin(II) to tin amalgam. The maxima on the second reduction waves were suppressed by 0.002% Triton X-100. The current decrease following the second wave is caused by an adsorption effect which will be discussed later. The log $\frac{i_d - i}{i}$ *vs.* *E* plots of waves in a 0.1*M* $HClO_4$, 0.1*M* pyrogallol solution are linear with slopes of 0.0344 and 0.0301 for the first and second waves, respectively. The slope of the first wave differs slightly from the theoretical slope for a reversible, two-electron reduction, but we assume that the reduction is sufficiently reversible so that valid thermodynamic conclusions may be drawn from half-wave potential data.

To determine the composition of the tin-pyrogallol complexes, the variation of $E_{1/2}$ with pyrogallol concentration was measured in solutions of various hydrogen ion concentrations (Table I). In 0.1*M* $HClO_4$ measurements were made to the nearest 0.1 mv. The solutions of tin(IV) at pH's of 1.75 and 3.00 appeared somewhat cloudy, indicating some hydrolysis of stannic ion. The rate of hydrolysis of the tin(IV) complex was sufficiently slow that measurements could be made at these pH's. In these solutions the first diffusion current was often not fully developed before the start of the second wave, and the $E_{1/2}$ values are more approximate.

The number of pyrogallol molecules per tin atom in the complex was determined from plots of $E_{1/2}$ *vs.* log pyrogallol concentration (Figure 2). In 0.1*M*

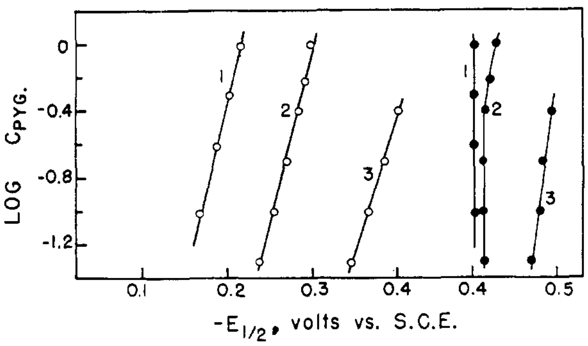


Figure 2. Half-wave potential of tin(IV)-pyrogallol complex as function of pyrogallol concentration

1. 0.1*M* $HClO_4$, 1*M* $NaClO_4$, 0.002% Triton X-100
2. pH = 1.75
3. pH = 3.0

○ First wave
● Second wave

$HClO_4$, the slope is -0.0523, corresponding to 1.77 pyrogallol molecules per tin atom. Since the $E_{1/2}$'s were determined to the nearest 0.1 mv., the deviation from 2.00 is outside experimental error. We think this deviation is caused either by some tin(IV) in the form of a complex containing only one pyrogallol molecule per tin atom, or to a slight amount of irreversibility in the reduction.

The $E_{1/2}$ of the second wave is independent of pyrogallol concentration and is -0.4024 ± 0.0007 volt *vs.* S.C.E. This value agrees well with -0.410 volt reported for the polarographic reduction of tin(II) in perchloric acid (*17*) and -0.382 volt calculated for the reduction of uncomplexed stannous tin from thermal data (*8*). We conclude that in a 0.1*M* $HClO_4$ medium, tin(IV) is predominantly in the form of a complex containing two pyrogallol molecules, and tin(II) is uncomplexed.

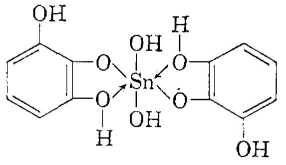
Table I. Half-wave Potentials for First [$E_{1/2}(1)$] and Second [$E_{1/2}(2)$] Waves for Polarographic Reduction of Tin(IV) in Various Solutions

Pyrogallol Concentration (moles/liter)	Volt *vs.* S.C.E. $-E_{1/2}(1)$	Volt *vs.* S.C.E. $-E_{1/2}(2)$
1*M* $HClO_4$		
0.10	0.1846	0.409
1.0	0.2293	0.404
0.1*M* $HClO_4$, 1*M* $NaClO_4$		
0.098	0.1670	0.4027
0.245	0.1881	0.4034
0.490	0.2036	0.4014
0.980	0.2162	0.4021
pH = 1.75		
0.050	0.238	0.415
0.100	0.256	0.413
0.200	0.270	0.413
0.400	0.284	0.416
0.600	0.291	0.420
1.00	0.298	0.426
pH = 3.00		
0.050	0.346	0.470
0.100	0.367	0.480
0.200	0.386	0.483
0.400	0.40	0.495

The predominant tin(IV) and tin(II) species are the same in 1*M* $HClO_4$ and at a pH of 1.75. At a pH of 3.0, formation of a tin(IV) complex containing three pyrogallol molecules, and a tin(II) complex with one pyrogallol molecule is indicated. At higher pH's the solution clears, but at a pH of 6, no reduction wave appears before the reduction of the supporting electrolyte (-1.8 volts *vs.* S.C.E.).

The number of hydrogen ions involved in the electrode reaction was determined from the variation of $E_{1/2}$ with pH. The slope of the $E_{1/2}$ *vs.* pH curve from 0.1*M* $HClO_4$ (pH = 0.94) to pH = 3.0 is -0.12; yielding four hydrogen ions consumed per atom of tin.

Structure of Tin(IV)-Pyrogallol Complex. The tin(IV)-pyrogallol complex in 0.1*M* $HClO_4$ is probably



and the electrode reactions [writing $C_6H_3(OH)_2O^-$ as X^-] are:

$$\text{Wave I:}\quad SnX_2(OH)_2 + 4H^+ + 2e = Sn^{+2} + 2HX + 2H_2O \quad (1)$$

$$\text{Wave II:}\quad Sn^{+2} + Hg + 2e = Sn(Hg) \quad (2)$$

Further evidence for this uncharged complex is that the polarogram of the complex is obtained even after passage of the test solution through a strongly basic anion exchange resin (Dowex 2-X4) and through a strongly acidic cation exchange resin (Dowex 50W-X8). Although structures with bonding of all three —OH groups of pyrogallol have been proposed (*20, 21*), steric considerations make this behavior unlikely, and bonding with separate hydroxyl groups is more probable.

An approximate value for the formation constant of the tin(IV)-pyrogallol complex may be calculated as follows. For Reaction 1 we derive by the usual methods (*5*):

$$E_{1/2} = E^\circ_s - 0.059 \log [HX] - 0.1182\ \text{pH} - 0.0296 \log K \quad (3)$$

at 25° C., where E°_s is the standard potential for the reaction: $Sn^{+4} + 2e = Sn^{+2}$, and is taken as -0.09 volt *vs.* S.C.E. (*8*), and K is the apparent equilibrium constant (including activity coefficients) for the reaction:

$$Sn^{+4} + 2HX + 2H_2O = SnX_2(OH)_2 + 4H^+. \quad (4)$$

From the data taken in 0.1*M* $HClO_4$ (pH = 0.94) we calculate $K = 3.5$. For the reaction:

$$Sn^{+4} + 2X^- + 2H_2O = SnX_2(OH)_2 + 2H^+ \quad (5)$$

we calculate, using a value of the first ionization constant of pyrogallol of 1×10^{-9} (*1, 19*), that

$$K_f = \frac{[SnX_2(OH)_2]\ [H^+]^2}{[Sn^{+4}]\ [X^-]^2} \cong 4 \times 10^{18} \quad (6)$$

The magnitude derived for K_f must be considered very approximate, since it involves uncertainties not only in $E_{1/2}$'s, but also in the literature value of E°_s, which include contributions from hydrolysis of tin(IV), complexation with chloride ion, etc.

In 1*M* $HClO_4$ the $E_{1/2}$ is more negative than in 0.1*M* $HClO_4$ probably because (in addition to possible changes in liquid junction potential) the complex in this solution contains H_2O rather than OH^- groups, and perhaps because a greater fraction of the complex contains only one pyrogallol molecule per tin atom.

Diffusion Current. The variation of the diffusion current (measured at the maximum of the instantaneous current), i_d, with tin(IV) concentration, C, in a 0.1*M* $HClO_4$, 1.0*M* $NaClO_4$, 0.1*M* pyrogallol solution, and 0.002% Triton X-100 is given in Table II. The diffusion currents for both the first, $i_{d(1)}$ and second, $i_{d(2)}$, waves were obtained manually by measuring the current at three points on the plateaus, subtracting the previously measured residual current, and averaging the results. The ratio i_d/C is constant for both waves for tin concentrations up to about 1m*M*; above this the ratio decreases. The ratio $i_{d(1)}/i_{d(2)}$ has a value slightly larger than one up to a 1m*M* tin concentration, and then decreases sharply.

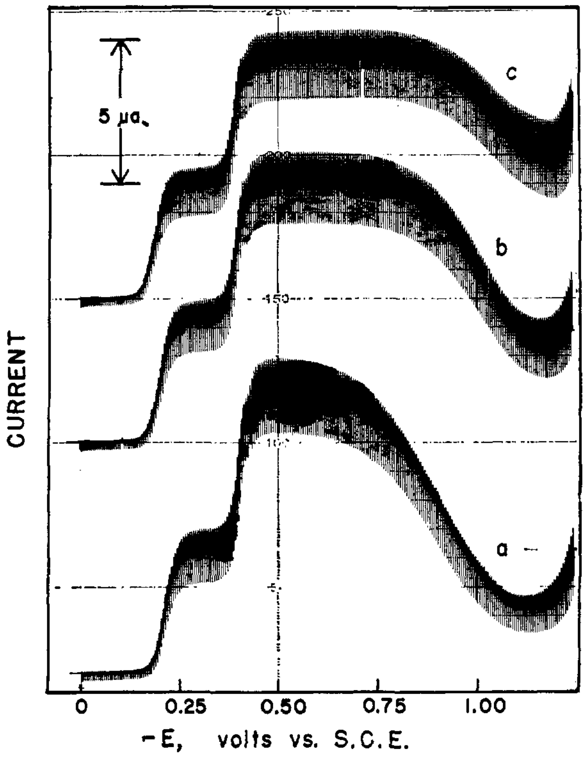


Figure 3. Effect of addition of NaClO$_4$ on polarographic reduction of tin(IV)-pyrogallol complex

Solution contained 0.1*M* HClO$_4$, 0.5*M* pyrogallol, 1m*M* tin(IV), and 0.002% Triton X-100

a. NaClO$_4$ concentration, 0
b. 0.8*M*
c. 1.6*M*

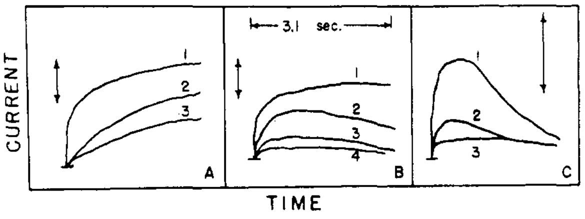


Figure 4. Current-time curves during polarographic reduction of tin(IV)-pyrogallol complex

Solution contained 0.1*M* HClO$_4$, 0.5*M* pyrogallol, and 0.98m*M* tin(IV)

A. No Triton X-100, potentials vs. S.C.E.
  1. −0.6 volt
  2. −1.0 volt
  3. −1.1 volts
B. 0.0016% Triton X-100, potentials vs. S.C.E.
  1. −0.45 volt
  2. −0.85 volt
  3. −1.0 volt
  4. −1.15 volts
C. 0.0026% Triton X-100, potentials vs. S.C.E.
  1. − 0.77 volt
  2. −1.0 volt
  3. − 1.15 volts

That both diffusion currents are indeed diffusion controlled was shown by the variation of i_d with the square root of the head of mercury, $h^{1/2}$, (corrected for back pressure). The variation of the mercury head from 90 to 55 cm. in a 0.9825m*M* tin(IV) solution gave values of $i_d/h^{1/2}$ of 0.779 ± 0.006 and 0.741 ± 0.012 (average deviations) for the first and second waves, respectively. These values, at the corrected mercury height in Table II, correspond to values of i_d/C of 6.87 and 6.53, in excellent agreement with results at varying tin concentrations. With increasing pyrogallol concentration the diffusion currents of both waves decrease, probably because of the increasing viscosity of the solution, but the ratio $i_{d(1)}/i_{d(2)}$ remains constant.

Table II. Diffusion Currents for Reduction of the Tin(IV)-Pyrogallol Complex

Maximum value of instantaneous diffusion current measured at −0.30 and −0.50 volt *vs.* S.C.E., where the drop times were 3.21 and 3.39 seconds, respectively.

m = 2.251 mg./second $h_{\text{corrected}}$ = 75.0 cm.

Concentration Tin(IV) (m*M*)	$\frac{i_{d(1)}}{(\mu a.)}$	$\frac{i_{d(1)}}{C}$	$\frac{i_{d(2)}}{(\mu a.)}$	$\frac{i_{d(2)}}{C}$	$\frac{i_{d(1)}}{i_{d(2)}}$
0.125	0.842	6.74	0.784	6.26	1.07
0.249	1.710	6.86	1.599	6.41	1.07
0.496	3.421	6.90	3.207	6.46	1.07
0.740	5.087	6.87	4.765	6.43	1.07
0.982	6.727	6.85	6.424	6.53	1.05
1.93	11.96	6.20	13.4	6.97	0.90
2.84	16.02	5.65	21.0	7.43	0.76
4.55	24.0	5.27	35.0	7.69	0.69

$i_{d(1)}/C = 6.87 \pm 0.02^a$ $I_{d(1)} = 2.82^b$
$i_{d(2)}/C = 6.46 \pm 0.04^a$ $I_{d(2)} = 2.61^b$

$D = 5.44 \times 10^{-6}$ cm.^{2}/sec.[c]

[a] Average of results for concentrations of 0.249 to 0.982m*M*.
[b] $I_d = i_d/cm^{2/3}t^{1/6}$, corrected to average diffusion current, $i_{\bar{d}}$.
[c] Calculated from unmodified Ilkovič equation.

Table III. Magnitude of Current Decrease in Various Solutions

Pyrogallol Concentration (moles/liter)	% Decrease[a] in 0.1*M* HClO$_4$	% Decrease[a] in 0.1*M* HClO$_4$, 1*M* NaClO$_4$		pH, 1.75	pH, 3.00
0.05				20	41
0.10	10	4.5	(6[b])	33	63
0.20				47	60
0.25			(34[b])		
0.40	37			58	
0.50		14	(60[b])		
0.60				53	
1.0			(66[b])	60	

[a] Defined in text.
[b] Also containing 0.002% Triton X-100.

Adsorption Effects. The polarographic reduction wave in this case is characterized by a minimum; the current decreases sharply after attaining a flat diffusion current plateau (Figure 1). This current decrease is present in solutions with and without Triton X-100, and depends upon both the pyrogallol concentration and pH (Table III). The percentage decrease of the diffusion current, taken as $\frac{i_{d(2)} - i_{\text{at minimum}}}{i_{d(2)}} \times 100$, is independent of tin(IV) concentration and increases with increasing Triton X-100 concentration.

This type of behavior has been found with a number of systems, and has been ascribed to electrostatic repulsion at negative potentials of an anion undergoing reduction (*3*, *6*), to reaction with mercury (*4*), and to blocking of the electrode surface by adsorbed substances, such as camphor and quinoline (*2*, *7*). In this case the two former explanations cannot be invoked, since the electroactive species has no charge and oxidation of mercury is clearly not involved. A possible explanation of the current decrease may be based on the desorption of the tin-pyrogallol complex, assuming adsorption of the complex is necessary for its reduction and the rate of adsorption is large compared to the rate of diffusion of the species to the electrode surface. At negative potentials, the complex is desorbed, probably being replaced by pyrogallol or water molecules, and the current decreases.

In the presence of Triton X-100 at concentrations higher than 0.001%, the current decrease is more pronounced and begins at more positive potentials (Figure 1). The extent of decrease becomes smaller with increasing concentration of sodium perchlorate (Figure 3). For the reduction of an uncharged molecule Frumkin gives the equation (*3*):

$$i = kC_b \exp\left[-\alpha(\phi - \psi_1)F/RT\right]$$

(where k is a constant, C_b is the bulk concentration of the electroactive species, ϕ is the potential difference between the electrode itself and the solution, and ψ_1 is the potential of the inner Helmholtz layer). Adsorption of cations makes ψ_1 more positive, making the exponential term more positive and increasing the current at a given potential (ϕ). The increase of current at the minimum with increasing $NaClO_4$ concentrations may be this effect, and implies that the adsorbed film of Triton X-100 interferes with the electron-transfer step in the reaction rather than with the penetration-step of the complex through the adsorbed film [as was found by Loshkarev and Kryukova for the reduction of neutral species (*12*)].

Current-time curves during a single mercury drop are useful in examining adsorption effects (*2*, *18*). Current-time curves in this case indicate the difference of inhibition behavior in the absence and the presence of Triton X-100 (Figure 4). In the absence of maxima suppressor (Figure 4,*A*) curves are characteristic of processes where surface coverage is controlled by the adsorption equilibrium, in this case the desorption of the complex [compare with (*18*) Figure 4]. In the presence of Triton X-100 (Figure 4,*B* and *C*), the current-time curves go through a maximum, indicative of surface coverage controlled by the rate of diffusion of the inhibiting species [compare (*18*), Figure 2]. In this case the concentration of the adsorbing species (Triton X-100) is low, and the relative rate of coverage to rate of growth of the drop increases during the drop life.

The mechanism for the current decrease in the absence of maxima suppressor (desorption of the electroactive species) may be the same for the decreases found for molybdenum(VI) in tartrate media (*14*), and for vanadium (V) in oxalate (*11*) and EDTA (*15*) media. The current decrease in the presence of maxima supressor is similar to that found for tin(IV) in a chloride medium upon addition of camphor (*7*).

The decrease of i_d/C at tin concentrations greater than 1mM may be caused by the inability of an equilibrium amount of complex to be adsorbed during the drop life. A similar decrease of i_d/C was observed during the reduction of cadmium(II) in an alkaline tartrate medium (*9*). Since this wave was affected by addition of gelatin, an adsorption effect for the decrease seems likely.

Interference by other metals depends upon their polarography in a pyrogallol medium, a study of which is currently being made in this laboratory. In practical analysis, use may be made of the passage of the electroactive complex through both anion and cation exchange resins, and the nonreduction of the complex at pH's greater than 5 or 6.

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Polarographic Behavior of Indium in Presence of Chloride

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► **A study of indium reduction at the dropping electrode in noncomplexing perchlorate supporting electrolytes and in the presence of varying concentrations of chloride yielded results which cast considerable doubt on previously reported, polarographically obtained dissociation constants for the chloride complexes of In(III).**

Though chemically similar to gallium in many respects, indium differs from that element curiously in its pronounced ease of reduction in the presence of, e.g., chloride or thiocyanate (*3*, *7*, *10*, *11*). The reduction of indium at the dropping mercury electrode (d.m.e.), unlike that of gallium, exhibits a minimum on the diffusion current plateau in the presence of polarizable supporting electrolytes.

This paper discusses several aspects of indium polarography in the light of

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