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The effect of tin(II) chloride adsorption on the electrochemical oxidation of tin(II) and other reactions at gold and platinum electrodes ^a

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Abstract

During a study of the electrooxidation of tin(II) chloride at gold and platinum electrodes by cyclic voltammetry, a remarkable hysteresis was associated with the oxidation of tin(II) chloride that is attributed to the adsorption of tin(II) chloride on the gold electrode. The adsorbed tin(II) chloride inhibits the oxidation of the bulk tin(II) chloride and therefore shifts the potential for oxidation to more positive values. However, once the adsorbed tin(II) chloride is oxidized, the dissolved tin(II) chloride is oxidizable at less positive potentials. This inhibition by adsorbed tin(II) chloride also affects other inner-sphere electrode reactions (e.g., oxidation of I^-), but not outer-sphere reactions. This inhibition is explained in terms of the need of a bridging ligand to facilitate electron transfer in inner sphere reactions. This inhibition is even more pronounced on Pt electrodes, where no oxidation wave for tin(II) chloride is observed. However, adsorption of chloride ions, 2-mercaptoethanol, or iodide causes desorption of the tin(II) chloride and the appearance of an irreversible wave for oxidation of the tin(II) in solution.

INTRODUCTION

This paper deals with the unusual behavior of tin(II) during oxidation at gold ultramicroelectrodes (UME), (see Fig. 1), and the role played by chloride ions in the observed voltammetric curves. The electrochemistry of the tin(II)/tin(IV) system on solid electrodes, and in particular the oxidation of tin(II), has been the subject of only a few studies. Polarography at mercury electrodes has been the electrochemical technique most frequently applied [1] to examine the reduction of tin(IV) and tin(II). Both species need the presence of either strong complexing agents, such as EDTA [2,3] or pyrogallol [4], or highly acidic media [5,6] to prevent the formation of hydroxy-species and insoluble compounds. The tin(II)/tin(IV) chloride system is

^a Dedicated to the memory of Professor Amatzya Y. Meyer, a unique person, teacher and chemist.

highly irreversible, although in the presence of high concentrations of halides the polarographic waves are sufficiently developed for electroanalytical purposes [7]. Esin and Loshkarev [8], Vetter [9], and Monien [10] studied the electroreduction of tin(IV) at Hg in hydrochloric acid. From these studies it was concluded that the reaction was irreversible and also that chloride ions play an important role in the reaction mechanism. The oxidation of tin(II) could not be studied in this medium on an Hg electrode, because it occurs at more positive potentials than oxidation of the Hg electrode itself.

There are only a few electrochemical studies of tin species at solid electrodes. Olson and Adams [11] studied the electroreduction of tin(II) on a carbon paste electrode, while Bard [12] found that proton reduction was inhibited following the electroreduction of tin(IV) on a Pt electrode. Lerner and Austin [13] investigated the tin(II)/tin(IV) couple at pyrolytic carbon electrodes and concluded that the mechanism consisted of two consecutive one electron transfers, as suggested by Vetter [9]. The electrochemical oxidation of tin(II) using a rotating gold ring-disk electrode was carried out by Vincente and Bruckenstein [14] in 4.0 M HCl. Their main conclusions were that tin(II) was adsorbed on gold at potentials more negative than +0.2 V vs. SCE and that underpotential deposition of tin(0) occurred at $-0.6 < E < 0$ V vs. SCE.

However, none of these studies described the behavior of the tin(II)/tin(IV) system, and its dependence on the chloride concentration, as discussed in this paper. The aim of this paper is to discuss the strong effect of the nature of the electrode surface on the oxidation of tin(II) at gold and platinum electrodes. Our major findings are that tin(II) chloride is strongly adsorbed at Au and Pt, in agreement with previous studies. This adsorption of tin(II) chloride affects the oxidation strongly of the dissolved tin(II) chloride and other inner-sphere electron transfer processes while it does not affect outer-sphere electron transfer mechanisms. Chloride ions affect the overall process as well, because they compete with tin(II) chloride for adsorption sites on the electrode.

EXPERIMENTAL

Cyclic voltammetry experiments were performed either with a PAR model 173 potentiostat equipped with a model 175 programmer (Princeton Applied Research, Princeton, NJ) or with a BAS 100A electrochemical analyzer (Bioanalytical Systems, West Lafayette, IN). A one compartment electrochemical cell, with a Pt counter electrode and a silver/silver chloride reference electrode, was used in all the experiments.

Ultrapure hydrochloric acid was purchased from Alfa Products (Danvers, MA) and high purity (99.9995%) tin beads from Aldrich (Milwaukee, WI). Milli-Q reagent water was used for all solutions. All other chemicals were reagent grade, obtained either from Fisher Scientific (Fair Lawn, NJ) or from J.T. Baker Inc. (Phillipsburg, NJ), and were used as received. Gold ultramicroelectrodes (UME) (12.7 μm diameter, Alfa Products) were fabricated as previously described [15].

Larger gold disk electrodes were made by sealing 0.25 mm diameter gold wire in glass tubing with Torr-Seal (Varian Associates, Inc., Lexington, MA). After the Torr-Seal was completely cured the electrode was polished first with abrasive paper (240 and 600 grit) and then with alumina (1, 0.3, and 0.05 μm). The electrode was repolished before each experiment. The platinum electrode was made from Pt wire (0.25 or 0.5 mm diameter) sealed in soft (borosilicate or uranium) glass and polished with abrasive paper followed by diamond paste (6, 3, 1, and 0.25 μm).

Stock solutions of tin(II) chloride (0.25 M and 2 mM) were prepared by dissolving either SnCl_2 or tin metal (with heating) in concentrated HCl under a N_2 atmosphere and diluting it with water to yield 1 M HCl. Tin(IV) chloride solutions were obtained by dissolving $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ in concentrated HCl in the same way. Before each experiment the gold and the platinum electrodes were repolished and cycled in 1 M H_2SO_4 ; 1.2 V to -0.8 V (Au), or 1.15 V to -0.7 V (Pt) vs. SMSE (a saturated K_2SO_4 mercurous sulfate electrode) for 20 min. They were then washed quickly with 1 M HCl before immersing them into a deaerated solution of tin(II) chloride.

RESULTS

Voltammetry of tin(II) on gold electrodes

The cyclic voltammogram of a 2 mM SnCl_2 + 1 M HCl solution at a 12.7 μm gold electrode at a scan rate (v) of 50 mV/s is shown in Fig. 1. Note the hysteresis of the anodic wave. A second scan taken immediately after the first exactly overlapped the first cycle. The current at the UME on the forward scan rose rather slowly to the steady state value (i_{ss}) with a potential at $i_{\text{ss}}/2$ of 0.48 V. On scan reversal at +0.60 V, the current remained at i_{ss} until about 0.4 V, with $i_{\text{ss}}/2$ on the reverse scan at +0.33 V. No cathodic current is observed in the potential region +0.60 to 0 V. Clearly the oxidation of tin(II) chloride is more facile after it has once been initiated, i.e., on the reverse scan. The i_{ss} at the gold UME was linear with the

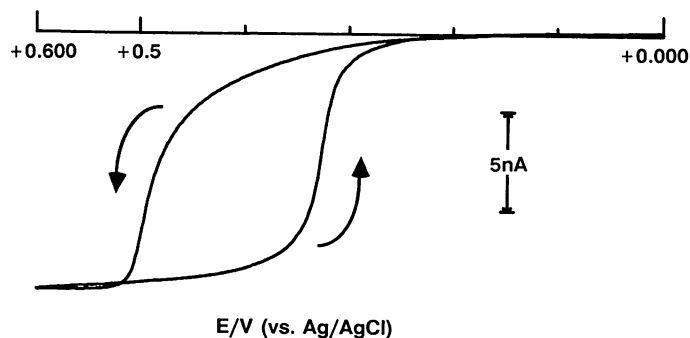


Fig. 1. Cyclic voltammogram of a 2 mM SnCl_2 + 1 M HCl solution taken with a 12.7 μm diameter gold electrode and a scan rate of 50 mV s^{-1} .

concentration of Sn(II) as expected [16] and the diffusion coefficient of the electroactive tin(II) species, estimated from the i_{ss} -values, was $1.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is somewhat larger than that previously reported ($7.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [13]). Varying the scan rate between 10 and 500 mV/s affected neither the i_{ss} nor the degree of the hysteresis. Moreover, the hysteresis was still seen when the initial potential was made more positive, up to the foot of the anodic wave. Once the potential exceeded ca. 0.4 V vs. Ag/AgCl the kinetics of the oxidation process became more facile and

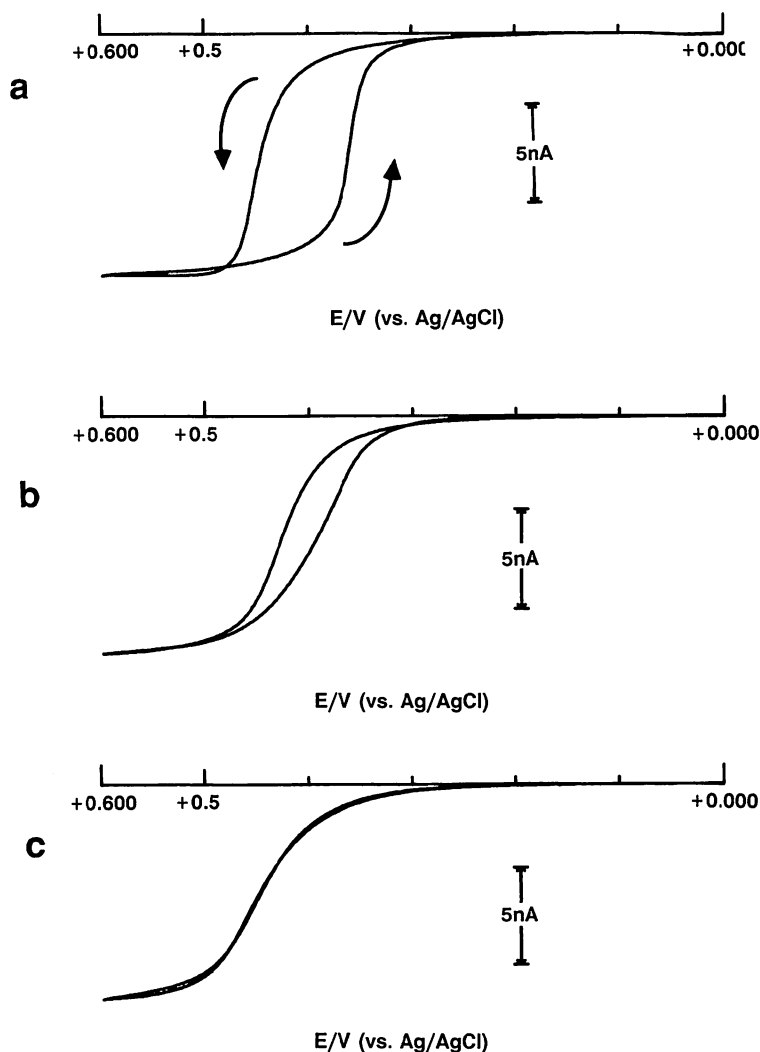


Fig. 2. Cyclic voltammogram of a 2 mM SnCl_2 + 1 M HCl solution taken with a 12.7 μm diameter gold electrode and a scan rate of 50 mV s^{-1} with addition of KCl: (a) 1 M, (b) 2 M, (c) 3 M.

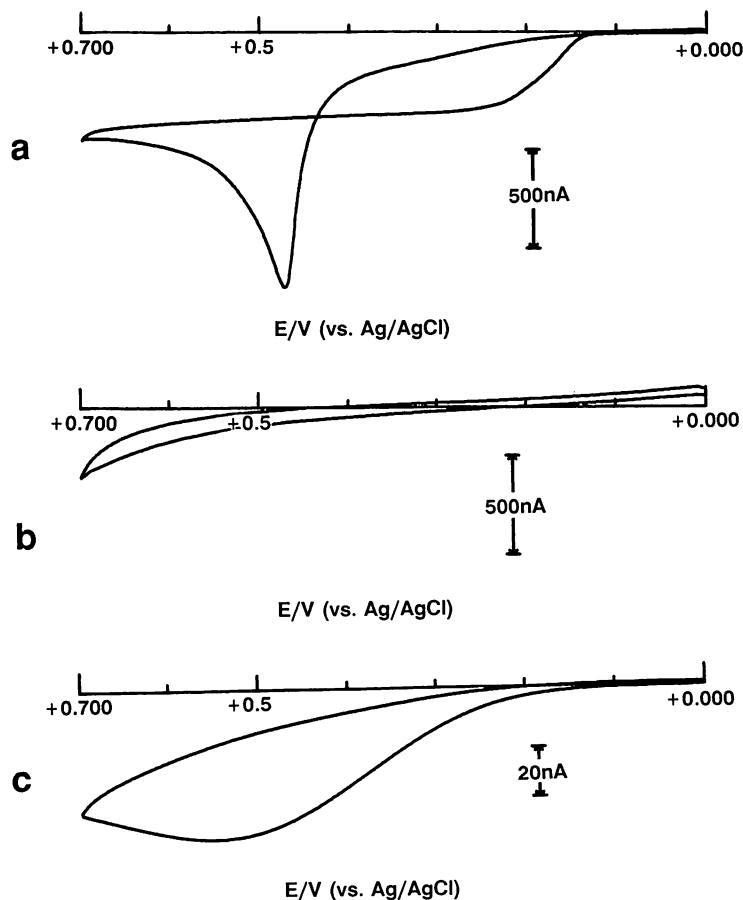


Fig. 3. Cyclic voltammogram of a 2 mM SnCl_2 + 1 M HCl solution taken with: (a) gold electrode, 0.25 mm diameter, (b) platinum electrode, 0.25 mm diameter, (c) glassy carbon electrode, 3 mm diameter, and a scan rate of 50 mV s^{-1} .

then the oxidation proceeded at less positive potentials on reversal. The addition of tin(IV) chloride (up to 0.01 M) did not affect this basic behavior. However, the addition of Cl^- (as KCl) did affect the CV response (Fig. 2). Clearly, upon addition of Cl^- the oxidation of SnCl_2 in the forward scan shifted to less positive potentials, until, at 3 M KCl, the forward scan merged with the reverse scan.

This unusual hysteresis was also seen with larger Au disk electrodes (Fig. 3a), i.e., a peaked anodic wave on the forward scan and anodic currents at less positive potentials in the reverse scan. Note however that SnCl_2 was not oxidized over this potential region at a Pt electrode (Fig. 3b). A glassy carbon electrode showed a broad irreversible wave with no hysteresis (Fig. 3c). For the peaked wave observed at the larger Au electrode, the peak anodic current (i_p) varied linearly with the square root of the scan rate ($i_p/v^{1/2} = 1.8 \times 10^{-6} \text{ A V}^{-1/2} \text{ s}^{1/2}$), indicating that i_p

is diffusion controlled. As mentioned earlier, increasing the concentration of Cl^- without changing the pH altered the shape and the peak potential of the wave until, in 4 M Cl^- , a normal irreversible wave was obtained.

The overall oxidation of tin(II) chloride is a two electron process (eqn. 1). However, although Vetter [9] and Lerner [13] claimed that the overall process consists of two consecutive one electron transfers, Sn(III) chloride has never been detected electrochemically in aqueous solutions, and a detailed analysis of the $i-E$ behavior has not been reported. In addition, the oxidation of tin(II) chloride probably proceeds via an inner sphere mechanism that also involves the addition of chloride to the tin species in the overall process.



For such an inner sphere process, the type of electrode, e.g., Au vs. Pt, and the nature of the inner layer, will play an important role in the electrochemical process. To verify that the observed hysteresis is not due to an electrochemical surface process involving the adsorption of chloride ion on the Au electrode, CV curves in the presence and absence of Cl^- were recorded. The adsorption of chloride on gold surfaces has been studied by electrochemical methods [17–19] and more recently by scanning tunneling microscopy [20]. These studies show that chloride ions adsorb on a gold surface, and this adsorption can lead to changes in the morphology of the surface, i.e., smoothing by dissolving atomic steps [20]. However an examination of the CV charging current at a gold electrode in 1 M H_2SO_4 ($-0.4 \text{ V} < E < 0.2 \text{ V}$ vs. SSCE) and in 1 M HCl ($0 \text{ V} < E < 0.6 \text{ V}$ vs. SCE) revealed that there are no faradaic processes on the surface (over these potential regions) and the cyclic voltammograms were very similar.

The possibility that the hysteresis was caused by adsorption of impurities either in the tin(II) chloride or in the hydrochloric acid was eliminated by repeating these experiments after dissolving high purity tin in ultrapure HCl; additionally, the results were very reproducible with different batches of SnCl_2 , HCl, and water. However, when the Au electrode was immersed in 1 M HCl for about 20 min after cycling in H_2SO_4 , and prior to immersing it in the tin(II) chloride/1 M HCl solution, the hysteresis in the CV curve decreased and did not reappear after repeated CV cycles or standing at open circuit or at 0 V vs. Ag/AgCl in this solution. Figure 4 shows the effect of the time the electrode was left in a stirred 1 M HCl solution on the cyclic voltammetry of tin(II) chloride. Conversely, when the electrode was immersed in a 2 mM SnCl_2 + 1 M HCl solution, immediately after cycling in 1 M H_2SO_4 and washing only briefly with 1 M HCl, the oxidation of tin(II) was accompanied by the hysteresis effect. The adsorption of tin(II) chloride and chloride, and their competitive adsorption on the same sites on the gold surface (with tin(II) chloride being adsorbed relatively more strongly than Cl^-) is probably responsible for the observed effects.

Tin(II) can form a variety of complexes with chloride ions. The equilibrium constants for the association reaction (eqn. 2, for $n = 1, 2, 3$) were determined by Vanderzee and Rhodes [21]. Their results and other studies [22] imply that the

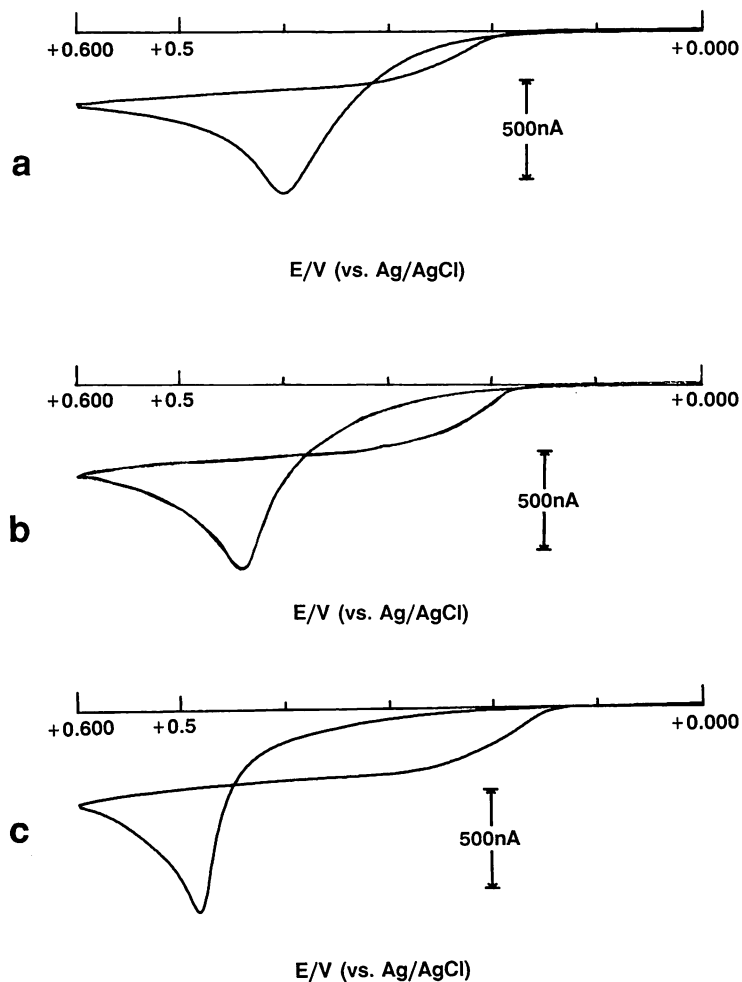


Fig. 4. Cyclic voltammogram of a 2 mM SnCl_2 + 1 M HCl solution taken with a 0.25 mm gold electrode and a scan rate of 100 mV s^{-1} , after leaving the electrode in a stirred 1 M HCl solution for (a) 20 min, (b) 10 min, (c) 2 min.

dominant species in 1 M HCl is SnCl_2 rather than SnCl_3^- . The existence of the doubly charged SnCl_4^{2-} was questioned in these studies.



Adsorption of tin(II) chloride

Previous reports [14,23–25] have shown that tin(II) chloride adsorbs on gold and on platinum surfaces. We found similar adsorption in a voltammetric experiment. A gold electrode (from 0.25 mm diameter wire whose area was measured by chro-

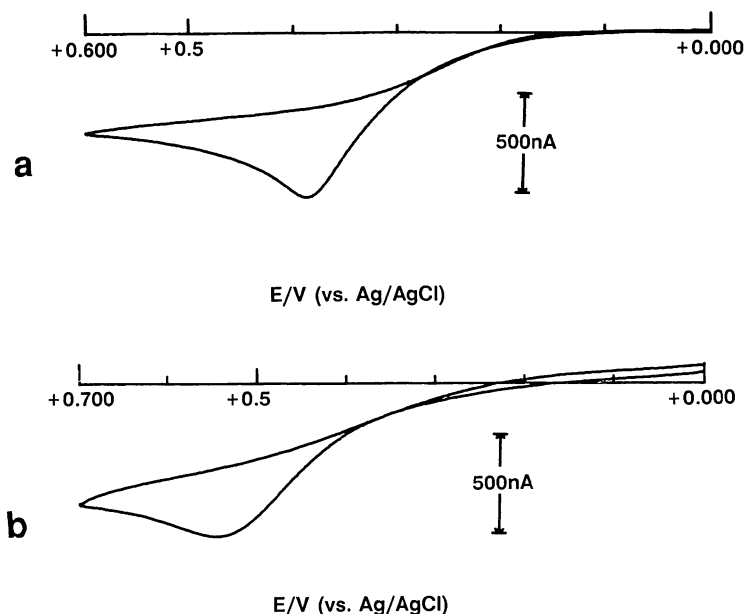


Fig. 5. Cyclic voltammogram of a 2 mM SnCl_2 + 1 M HCl solution, after soaking in 0.1 M 2-mercaptoethanol (a) a 0.25 mm gold electrode, (b) a 0.25 mm Pt electrode.

nocoulometry of $\text{Fe}(\text{CN})_6^{4-}$, after polishing and cycling, was soaked for a given time in a 2mM tin(II) or tin(IV) chloride + 1 M HCl solution and then washed quickly with 1 M HCl before transferring it to the 1 M HCl test solution. The surface excess of the adsorbed tin species (Γ) was calculated from the area (charge) under either the anodic ($\text{Sn}(\text{II}) \rightarrow \text{Sn}(\text{IV})$) or the cathodic ($\text{Sn}(\text{IV}) \rightarrow \text{Sn}(\text{II})$) cyclic voltammetric (CV) waves. Tin(II) chloride was strongly adsorbed on gold, forming a monolayer ($\Gamma = 6.8 \times 10^{-10} \text{ mol/cm}^2$); tin(IV) chloride was not adsorbed. Its surface coverage was at least 20–25 times smaller than that of tin(II) chloride. This is in accordance with the results of Vincente and Bruckenstein [14], who found that tin(II) chloride is strongly adsorbed ($\Gamma = 5.3 \times 10^{-10} \text{ mol/cm}^2$) and is not removed until the electrode potential reaches +0.17 V vs. SCE where the adsorbed Sn(II) is oxidized to soluble Sn(IV). Thus the observed hysteresis can be attributed to blocking of Sn(II) oxidation by a monolayer of adsorbed SnCl_2 . To confirm the role of adsorbed SnCl_2 in the observed hysteresis, the gold electrode was soaked in a 0.1 M 2-mercaptoethanol solution for 10 s and washed with water and 1M HCl before immersing it into the tin(II) chloride + 1 M HCl solution. Since thiols are very strongly adsorbed on gold surfaces [26], a monolayer of the short chain thiol might prevent the adsorption of tin(II) chloride and change the rate of electron transfer to electroactive Sn(II). Figure 5a shows the cyclic voltammogram of tin(II) chloride in 1 M HCl after this pretreatment. A normal irreversible wave at less positive potential is obtained. Hence we propose that adsorbed tin(II) chloride is responsible

for the hysteresis and must be oxidized before oxidation of the tin(II) chloride in the bulk can occur. The adsorbed SnCl_x^{2-x} is oxidized at a more positive potential than bulk Sn(II), which is consistent with a need to overcome the Gibbs energy of adsorption (although this is an irreversible wave) [27]. Once adsorbed SnCl_x^{2-x} is oxidized, the bulk tin(II) is oxidizable. The potential at this point is positive of the potential where bulk Sn(II) oxidizes in the absence of adsorbed Sn(II) and as a result the current increases sharply, almost as if a potential step had been applied to the electrode. On the reverse scan, the adsorbed Sn(II) is missing, and the wave occurs at less positive potentials.

These results indicate also that the role played by the chloride ions is the same as that of the thiol, i.e., desorption of the SnCl_x^{2-x} from the gold surface. However, we cannot distinguish between desorption caused by the adsorption of chloride, which is competitive only when the Cl concentration is increased, or desorption of the tin(II) caused by the predominance of another tin(II) chloride complex, i.e., SnCl_3^- , which may be only weakly adsorbed on gold. The pretreatment of the gold surface with chloride (Fig. 4) as probed by changes in the oxidation of tin(II) chloride is interesting itself. The time scale of these changes is much larger than expected for the specific adsorption of Cl^- , therefore suggesting that surface changes may accompany the adsorption of chloride.

The behavior of tin(II) chloride on Pt electrodes

Recall that no anodic wave representing the oxidation of tin(II) chloride was detected in 1 M HCl when the potential of the Pt electrode was cycled between +0.6 V and 0 V vs. SCE. This observation suggests that SnCl_x^{2-x} is adsorbed even more strongly on Pt than on Au, shifting the potential of the adsorbate oxidation, and as a result the potential of the electroactive species in solution, to more positive potentials. Since thiols adsorb on Pt very strongly as well, one would predict that a monolayer of thiol on Pt would prevent Sn(II) adsorption and allow the tin(II) chloride in the solution to be oxidized. Figure 5b shows that this is indeed the case. An irreversible anodic wave is observed, when tin(II) chloride is oxidized on a Pt electrode that had been precoated with a monolayer of thiol by immersion in a solution of 0.1 M 2-mercaptoethanol for a few seconds, then rinsed with water. Nevertheless, the rate of electron transfer was still lower than that at a similarly-treated gold electrode, as indicated by the more positive peak potential and the shape of the wave. Similarly, addition of Cl^- had the same effect on Pt, although much higher concentrations of Cl^- were needed to obtain a well-defined wave. At a concentration of 6 M Cl^- (1 M HCl and 5 M NaCl) the anodic wave no longer depended upon Cl^- concentration. This does not imply that the adsorption of tin(II) chloride on Pt is stronger than that on gold, since the relative strength of adsorption of Cl^- on Pt needs to be considered as well.

Effect of tin(II) chloride adsorption on other electrode reactions

Although our model fits the results of this and previous studies, it is not clear why and by what mechanism the adsorbed tin(II) chloride on the electrode surface

inhibits the oxidation of the dissolved tin(II) chloride. To test whether adsorbed Sn(II) would affect other electrode reactions, we examined the cyclic voltammetry of three other reversible compounds, $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, $\text{W}(\text{CN})_8^{3-/4-}$, and I_2/I^- in the presence of tin(II) chloride. We performed two sets of experiments. In the first set, the cyclic voltammetry of these redox couples was studied in 1 M HCl (without tin(II) chloride) at gold and platinum electrodes that were preadsorbed with tin(II) chloride. In the second set of experiments their electrochemical behavior was studied in a 2 mM SnCl_2 + 1 M HCl solution. We found that the presence of tin(II)

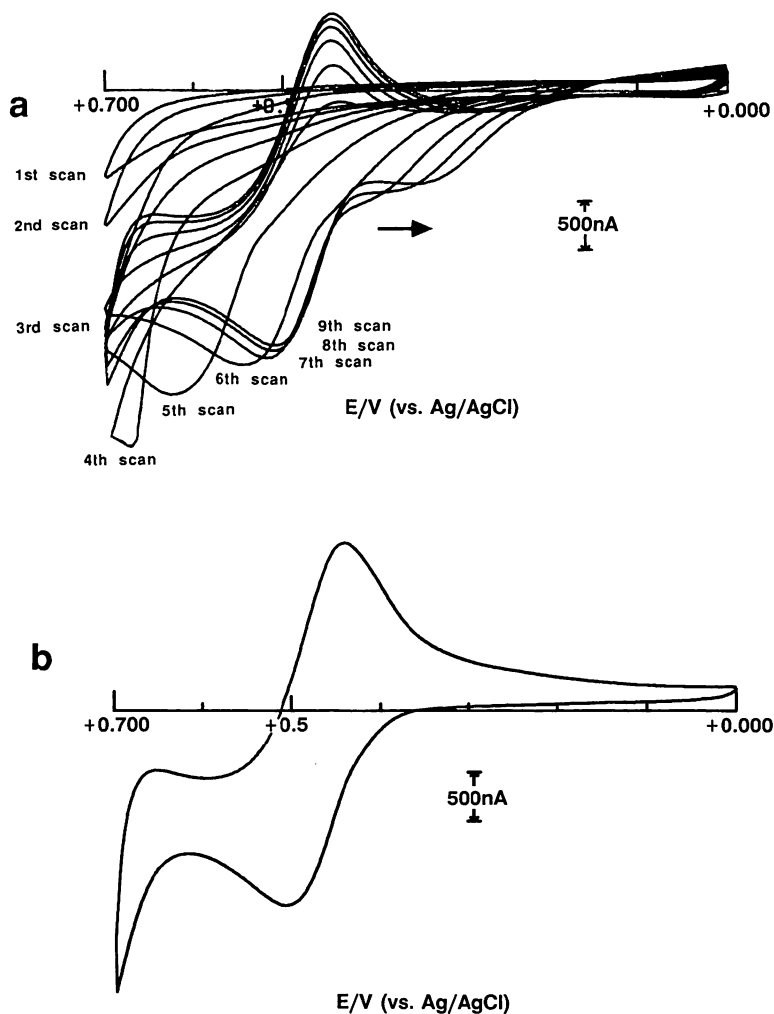


Fig. 6. Cyclic voltammogram of (a) 2.5 mM KI, 2.5 mM SnCl_2 + 1 M HCl, (b) 2.5 mM KI + 1 M HCl solutions taken with a 0.5 mm Pt electrode and a scan rate of 100 mV s^{-1} .

chloride in solution or adsorbed on the electrode had no effect on the reversibility or on the peak potentials of $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ and of $\text{W}(\text{CN})_8^{3-/4-}$. Conversely, the oxidation of iodide was strongly affected by adsorbed tin(II) chloride (Fig. 6). It should be noted that no influence on the cyclic voltammetry of I^-/I_2 was observed when SnCl_2 was added after iodide, but only when SnCl_2 was introduced first. This can be explained by the fact that iodide and iodine adsorb very strongly on Pt [28]. Clearly, once adsorbed SnCl_2 is oxidized, iodide replaces it and as a result a reversible oxidation–reduction wave of I^-/I_2 is seen in the succeeding scans. In addition, an anodic wave due to tin(II) chloride oxidation is then found at less positive potentials. This wave is a result of the absence of SnCl_2 on the electrode surface that no longer inhibits the oxidation of bulk SnCl_2 .

DISCUSSION

These results suggest that the adsorption of tin(II) chloride on gold or platinum electrodes affects only inner-sphere electron transfer processes whereas the kinetics of outer-sphere electron transfer systems, e.g., $\text{Ru}(\text{NH}_3)_6^{3+/2+}$, are not influenced by this adsorption. This is understandable if we invoke the model suggested by Weaver et al. for distinction between inner- and outer-sphere processes at solid electrodes [29]. Using adsorbed iodide on Pt or gold as a probe to inhibit the inner-sphere mechanism, they could distinguish between inner- and outer-sphere processes. The rate of reduction of various Co(II) complexes decreased significantly once I^- was adsorbed on the electrode. The iodide restricted the number of coordination sites available to the redox couples and this eliminated the possibility of ligand-bridging which is vital to achieve efficient inner-sphere electron transfer.

The tin(II) chloride performs the same function as the iodide in our system. Namely, adsorbed tin(II) chloride inhibits the efficient inner-sphere electron transfer between reactants such as iodide and bulk tin(II) chloride by preventing ligand bridging. On the other hand, outer-sphere processes which are adiabatic should not be affected by changes on the surface unless these changes are accompanied by changes in the electrostatic interactions between the redox couple and the electrode. Therefore, one would not anticipate that the adsorption of SnCl_2 would affect the kinetics of redox couples like $\text{Ru}(\text{NH}_3)_6^{3+/2+}$. Once tin(II) chloride is replaced by chloride, iodide, or even 2-mercaptoethanol, the rate of electron transfer of SnCl_2 oxidation is enhanced because of their superior properties as ligand bridges. It is interesting that 2-mercaptoethanol exhibits such properties and that a monolayer of this substance does not affect the kinetics of iodide oxidation as well. This is presumably due to appropriate ligation through the oxygen atom.

CONCLUSIONS

The electrochemical oxidation of tin(II) in the presence of chloride ions and in acidic media on gold and platinum electrodes was studied. The adsorption of a tin(II) chloride species affects the electrochemical oxidation of dissolved tin(II)

chloride strongly. The electroactive species in solution are oxidizable only after the adsorbed tin(II) chloride is oxidized to tin(IV) chloride, which is not strongly adsorbed and is thus removed from the electrode surface. Chloride and iodide, as well as thiols, cause the desorption of the adsorbed tin(II) chloride and, as a result, an oxidation wave for Sn(II) is observed on both gold and on platinum electrodes. The adsorption of tin(II) chloride also affects other inner-sphere electron transfer processes, while it does not affect outer-sphere reactions. We conclude that the adsorbed SnCl_2 inhibits ligand bridging between species oxidized by an inner-sphere mechanism and the electrode and thus reduces their rate of electron transfer.

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