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The Effects of Organic Adsorbates on the Underpotential Deposition of Silver on Pt(111) Electrodes

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ABSTRACT

Studies have been undertaken to determine the effects of competing organic adsorbates on the underpotential deposition of silver on Pt(111). The adsorbates studied are known to bind to Pt primarily through the hetero-atom (either nitrogen or sulfur) and include pyrazine, 2,2'-bipyridyl, 4,4'-bipyridyl, 4-phenylpyridine, 1,2-Bis(4-pyridyl)ethane, 2-mercaptopyridine and 4-mercaptopyridine. The effects of the adsorbate layer on silver deposition are strongly dependent on the nature and structure of the co-adsorbed species. Adsorbates that bind primarily through a ring nitrogen atom were found to inhibit the deposition of the second, but not the first, silver monolayer. This may be explained by the formation of a Pt(111)/Ag/adsorbate structure in which the silver deposits underneath the adsorbate layer. These adsorbates also displayed a significant pH dependence likely due to protonation of the binding atom. In contrast, the sulfur-containing adsorbates inhibited all deposition processes at the electrode surface except that of bulk silver deposition. In this case there was a significant overpotential to bulk deposition. Moreover, a monolayer of electrodeposited silver could be displaced from the Pt surface upon exposure of the electrode to a solution of 2-mercaptopyridine. This behavior would indicate a higher bond strength between the sulfur atom and the Pt surface than that between the ring nitrogens and the Pt surface. These results are consistent with the expected strengths of adsorption.

INTRODUCTION

The process of underpotential deposition (UPD) of metals on foreign metal substrates has been studied extensively through the use of electrochemical and surface spectroscopic techniques [1,2]. The use of electrochemical techniques such as cyclic voltammetry provides a means of probing the energetics of the system and also allows for an indirect characterization of the processes taking place. Features in the voltammetry are generally sensitive to the mechanism of deposition and as a result can provide information regarding structural transitions as well as interactions between the surface and the UPD layer. The underpotential deposition of silver on polycrystalline Pt and single crystal Pt surfaces is one system that has received considerable attention [3-11].

The presence of co-adsorbed species would be anticipated to have a pronounced effect on the voltammetric features of an underpotential deposition system. This should reflect the interactions present between the co-adsorbed species, the electrode surface and the metal overlayer. There have been studies performed on the Ag/Pt system involving co-adsorbates, but these have mainly been restricted to the adsorption of iodine adlattices on the Pt surface [12-15]. However, numerous organic species have also been shown to form adlayers on Pt(111) electrodes [16-20]. It is anticipated that these species would influence the deposition of silver due to the relatively strong interaction between the adlayer and the substrate surface. Such interactions may alter the kinetics and mechanism of electrodeposition, and thus the interest in carrying out electrochemical and surface studies on the effects of co-adsorbates on the UPD process.

We present studies of silver UPD on Pt(111) electrodes in the presence of co-adsorbed species. The adsorbates, chosen to study substrate/adsorbate interactions based on the size and structure of the molecule and on the nature of the adsorbing group, were 2,2'-bipyridyl, 4,4'-bipyridyl, 4-phenylpyridine, 1,2-Bis(4-pyridyl)ethane, pyrazine, 2-mercaptopyridine, and 4-mercaptopyridine. These materials represent systematic variations in both the adsorbing atom and the structure of the adsorbate. The results indicate a strong dependence of the voltammetry on the nature of the adsorbate that are consistent with the strength of adsorption with the platinum surface.

EXPERIMENTAL

The working electrode was a 1 cm diameter Pt single crystal disk prepared at the Materials Preparation Facility at Cornell University. The crystal was grown from the melt, oriented by Laue photography, and cut in the (111) direction. Chemical and metallographic polishing were performed until a finished mirror surface was obtained on both faces. The crystal was supported by two 0.020-in Pt wires spot-welded to the sides in such a way so as to allow only one face of the crystal to come in contact with the solution. Thus, the response obtained is characteristic of a single Pt(111) face. Prior to experiments, the crystal was immersed in hot (~80°C) nitric acid for 10 minutes.

The electrode pretreatment consisted of heating the crystal to approximately 1000°C in a gas/oxygen flame for three minutes and then allowing it to cool for 60 s in the vapor of deaerated supporting electrolyte before quenching in the same solution. The waiting time was necessary to avoid strains induced by rapid quenching. Surface cleanliness was determined by cyclic voltammetry in 0.1 M H_2SO_4, which produced the characteristic "butterfly" shape first described by Clavilier [21]. The annealed crystal was held at open circuit for three minutes in contact with a solution of the adsorbate in either water or 0.1 M H_2SO_4 and was then rinsed with deaerated pure supporting electrolyte before bringing it into contact with the 1.0 mM silver solution. The potential was then scanned in the negative direction at 2.0 mV/s from a starting potential of +0.870 V. All solutions were 1 mM in the adsorbate of interest. This concentration is at the limiting plateau in adsorption isotherms derived for each molecule [17-20]. In addition, no appreciable differences were noted when longer contact times were used.

All solutions were prepared using water purified with a Millipore Milli-Q system. Aqueous 0.10 M sulfuric acid (ULTREX, J.T. Baker) was used as the supporting electrolyte. 1 mM silver solutions were prepared by dissolving silver sulfate (Aldrich, 99.999%) in the base electrolyte. Pyrazine (99+%), 2,2'-bipyridyl (99+%), 4,4'-bipyridyl (98%), 4-phenylpyridine (99%), 1,2-Bis(4-pyridyl)ethane (99%) and 2-mercaptopyridine (99%) were used as received from Aldrich Chemical Co. 4-mercaptopyridine (Aldrich, tech.) was recrystallized 3 times from absolute ethanol prior to use.

Cyclic voltammetry was performed using a BAS CV-27 potentiostat. Data were recorded using a Soltec X-Y recorder. All potentials are referenced to a Ag/AgCl (sat'd NaCl) electrode without regard to the liquid junction potential. Typical uncertainties are ±2 mV. A large area Pt foil was used as the auxiliary electrode.

Charges for silver deposition and stripping were determined after correction for the background charge measured under identical conditions except in the absence of silver ions in solution. Conditions and assumptions for these calculations have been previously addressed [11].

RESULTS

As a point of reference for the following studies, the voltammetry for the deposition of silver from a 1 mM solution onto a clean and well-ordered bare Pt(111) surface is displayed in **Figure 1**. Silver deposition under these conditions has been shown to take place over four distinct regions [10,11]: 1) the deposition of 1.2 monolayers from +0.870 to +0.700 V, 2) the deposition of 0.1 monolayers between +0.700 and +0.500 V, 3) the deposition of 0.7 monolayers from +0.425 to +0.375 V, and the deposition of bulk silver at potentials more negative than +0.375 V. The coulometric charge for the three peaks in the underpotential region correspond to the deposition of approximately two full monolayers of silver. It has previously been shown that the mechanism of silver electrodeposition at this concentration involves adsorption in a well-defined manner, yielding an ordered and commensurate overlayer [11].

When the potential sweep is reversed prior to bulk deposition, it is seen that the removal of the deposited silver takes place over two regions, denoted 4 and 5 in Figure 1. A sharp peak at a potential of +0.462 V represents the removal of the second silver layer. A more positive peak in the potential range of +0.725 to +0.930 V corresponds to the dissolution of the silver deposited in the first two underpotential regions (regions 1,2; vide supra). It is believed that the shoulder at +0.800 V represents the stripping of the silver deposited over the second peak, while the main peak at +0.840 V is attributed to the stripping of the silver deposited over the first deposition region.

In experiments involving silver deposition onto an electrode pretreated with an adsorbate, it is expected that the voltammetry would differ from that on a bare Pt surface in a way that reflects a competition between the interaction of the adsorbate with the electrode and with the silver. For the results discussed below, the peaks present in each voltammogram are assigned to the deposition and stripping of a silver overlayer and directly compared with those seen when no adsorbate layer is present. A scan of the pretreated electrode in pure supporting electrolyte is shown in each case so as to note that the peaks observed when the electrode is placed in a silver solution are due to silver deposition and not to other processes involving the adsorbate layer on the Pt electrode. The peak positions for the deposition and stripping of silver from a Pt(111) electrode in the presence and absence of an adsorbate layer are summarized in Table 1, whereas the charges associated with the deposition and stripping of silver are presented in Table 2. We consider below the voltammetric response in the presence of the various adsorbates.

2,2'-bipyridyl

The voltammetry for silver deposition on a Pt(111) electrode pretreated with a 1 mM solution of 2,2'-bipyridyl is shown in Figure 2. Figure 2A represents the case where adsorption was from a water solution, and it is quite evident that the UPD process has been altered considerably. Deposition of the first monolayer is seen to take place in a broad peak over the range of +0.850 to +0.500 V, while deposition of the second monolayer is completely inhibited. The appearance of a well-defined stripping peak at +0.845 V indicates that although the deposition process is poorly defined, the formation of a silver adlayer does occur. This is similar to the effect observed by White and Abruña for the UPD of copper onto a Pt(111) electrode pretreated with 2,2'-bipyridyl [22].

The shape of the voltammetric wave for silver deposition suggests kinetic limitations in the formation of the metal adlayer. Studies by Hubbard et al. suggest that 2,2'-bipyridyl adsorbs onto Pt(111) from a potential of 0.00 V in a twisted conformation with one ring bonded through the nitrogen atom and the second bonded through the π structure of the ring [18]. Assuming the molecule adopts this conformation when it is adsorbed at open circuit, this adlayer would block numerous sites for silver deposition due to the large effective cross-sectional area (molecular footprint) of the twisted structure. As a result, the process of silver deposition would become hindered. The broadness of the peak may also indicate that the deposition process takes place in a more disordered fashion than that seen for UPD on a clean and well-ordered bare Pt(111) electrode. Moreover, it could also imply that deposition takes place on a number of energetically distinct sites.

In contrast, when the electrode is pretreated with a solution of 2,2'-bipyridyl in 0.1 M H_2SO_4 (Figure 2B), the voltammetry is essentially identical to that obtained on a clean and well-ordered bare Pt(111) surface. Since 2,2'-bipyridyl has a pK_a value of 4.44, it would be expected that in 0.1 M H_2SO_4 the ring nitrogens would be protonated.

The blocking of these sites would then preclude the adsorption of the molecule onto the surface, resulting in the observed voltammetric response.

Pyrazine

The voltammetry for silver deposition onto a Pt(111) surface pretreated with 1 mM pyrazine in water is shown in Figure 3A. Here it is seen that silver deposition takes place in a well-defined peak at a potential of +0.712 V with a broad shoulder that extends from +0.625 to +0.520 V. As with the previous example, the formation of a second monolayer of silver is suppressed in the presence of the pyrazine adlayer. Assuming an adsorption orientation in which pyrazine is bonded to the surface vertically through one of the ring nitrogens but with a slight tilt angle relative to the surface normal [17], the footprint of the molecule on the Pt surface would be considerably smaller than that of 2,2'-bipyridyl. This may allow for deposition to take place in a relatively unhindered and more ordered fashion, as suggested by the shape of the deposition peak. The rather large shift of ~60 mV in the deposition potential suggests a significant strength of interaction between the nitrogen of the pyrazine ring and the Pt surface that must be overcome in order for silver deposition to take place.

As shown in Table 2, the charge associated with the stripping of the silver overlayer in the presence of adsorbed pyrazine is significantly higher than that for the corresponding silver deposition process. A similar charge imbalance has been observed for silver deposition on a bare Pt(111) electrode, where it has been suggested that the potential region between +0.725 V and +0.930 V in the anodic sweep could represent both the stripping of the silver adlayer as well as the onset of platinum oxide formation [23]. Although it is known that on a clean and well-ordered Pt(111) surface, the formation of a platinum oxide layer occurs at more positive potentials than for a polycrystalline Pt electrode [24,25], it is believed that the removal of silver adatoms causes some disorder on the Pt(111) surface which may facilitate the onset of oxide formation.**

The deposition behavior for an electrode pretreated with 1 mM pyrazine in 0.1 M H_2SO_4 (Figure 3B) is virtually identical to that described above. Since pyrazine has a pK_a value of +0.68, it would be expected that in 0.1 M H_2SO_4 it would remain largely unprotonated. This would leave both nitrogen sites available for adsorption to the electrode surface, and its adsorption behavior would then be minimally, if at all, altered. The voltammetry obtained is fully consistent with this.

4,4'-bipyridyl

When a Pt(111) electrode is pretreated with a 1 mM solution of 4,4'-bipyridyl in water, the voltammetric behavior for the underpotential deposition of silver is that shown in Figure 4A. Silver deposition takes place over a broad range from +0.800 V to +0.400 V with a well-defined peak occurring at +0.710 V. As with the previous examples, the deposition of a second silver layer is suppressed in the presence of the adsorbate layer. The shift in the deposition potential of ~60 mV is similar to that observed for pyrazine, which may indicate a similar strength of interaction of this adsorbate with the electrode surface. In comparison to the voltammetric scans observed with 2,2'-bipyridyl, the deposition peak is better defined, possibly indicating that the adsorbate lattice is more ordered in this case. As indicated in Table 2, the charge associated with silver deposition in the presence of 4,4'-bipyridyl (168±5 $\mu C/cm^2$) is

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** Consistent with this are voltammetric results which show that on consecutive (first vs. subsequent) scans of the underpotential deposition of silver on a clean and well-ordered bare Pt(111) surface there are significant differences in the coulometric charges for deposition and stripping. In particular, while the charge associated for silver deposition in regions 1 and 3 (see Figure 1) diminishes, there is a significant increase in the charge over region 2. It is within this potential region that the reduction of a platinum oxide layer would be expected to occur. The disruption of the surface by the onset of oxide formation should yield a decrease in the deposition charge as fewer bare Pt sites are available.

somewhat less than that observed for pyrazine (180±6 $\mu C/cm^2$), possibly due to the slightly larger molecular footprint of the molecule. 4,4'-bipyridyl adsorbed on a Pt(111) has been shown to bind through one of the ring nitrogens with a tilt angle of 81° relative to the surface normal [18]. This is similar to the orientation previously described for pyrazine. However, 4,4'-bipyridyl has a second pendant ring with a certain degree of rotational freedom that, in addition to extensive ring interaction within the adsorbed layer, may create kinetic limitations in the deposition process.

A more significant difference for 4,4'-bipyridyl in relation to the adsorbates previously discussed is seen in the stripping behavior. The removal of silver with adsorbed 4,4'-bipyridyl takes place over a broad region from +0.685 V to +0.950 V with a charge approximately equal to that of deposition, unlike the voltammetry observed for pyrazine and 2,2'-bipyridyl. These differences may be the result of structural characteristics of the adsorbate layer which yield kinetic limitations in the deposition of silver. When 4,4'-bipyridyl binds to the platinum surface, an unbound nitrogen remains on the pendant ring. It is possible that this free nitrogen atom is able to coordinate to silver ions in solution [26], thus hindering the diffusion of silver to the electrode surface. In addition, the adsorbate layer in this case would be twice the thickness and would contain extensive ring interactions, both of which may create a barrier to silver ions reaching the Pt surface. In contrast, the smaller structure of the pyrazine molecule may allow less hindered access of the surface by silver ions. In the case of 2,2'-bipyridyl, once bound by one of the nitrogens, the remaining pyridine ring would be unable to coordinate to silver due to steric constraints.

It has been mentioned for the case of pyrazine adsorption that the stripping region may also involve the formation of platinum oxides on the electrode surface. In the presence of an adsorbed 4,4'-bipyridyl layer, it is possible that the thickness of this overlayer relative to that of pyrazine (two pyridine rings vs. one) may act to prevent the transfer of oxygen at the electrode surface. This would suppress the formation of platinum oxides, resulting in a smaller charge imbalance between deposition and stripping regions. This assertion may also apply to the adsorbates to be discussed below.

The deposition of silver on an electrode pretreated with adsorbed 4,4'-bipyridyl displays an unusual pH dependence. The voltammetry for the deposition of silver onto a Pt(111) electrode pretreated with 4,4'-bipyridyl in 0.1 M H_2SO_4 is shown in Figure 4B. In this case, the deposition potential has been shifted to +0.770 V (a value virtually identical to that in the absence of any co-adsorbate) and the charge associated with silver deposition (251±8 $\mu C/cm^2$) is significantly higher than for adsorption from water (168±5 $\mu C/cm^2$), as described above. With a pK_a value of 4.87 it would be anticipated that the ring nitrogens would be protonated in this medium. however, it is possible that due to the extensive conjugation present, the second nitrogen site is more difficult to protonate and remains available for bonding. The shift in UPD potential and increased deposition charge might be explained by considering that each adsorbed 4,4'-bipyridyl molecule possesses a net positive charge which will result in a repulsion from the positively charged electrode as well as create electrostatic repulsive interactions within the adsorbed layer itself. These repulsive effects should result in the formation of a less densely packed 4,4'-bipyridyl layer relative to that when adsorption takes place from water, yielding a diminution in the interactions between rings. This should help to facilitate silver deposition at the electrode surface.

4-phenylpyridine

Some insight into the behavior of 4,4'-bipyridyl at low pH values is obtained when the electrode surface is pretreated with 4-phenylpyridine. The voltammetry for the deposition of silver onto a Pt(111) electrode pretreated with a 1 mM solution of 4-phenylpyridine in water is shown in Figure 5A. Silver deposition takes place over a broad potential range from +0.825 V to +0.500V with a pronounced peak occurring at

+0.755 V. Again, it is seen that the formation of a second silver monolayer is completely inhibited in the presence of this co-adsorbate layer. The voltammetric scans observed for 4-phenylpyridine adsorbed from water are similar to those obtained when the electrode was pretreated with 4,4'-bipyridyl in 0.1 M H_2SO_4. The resemblance in shape between the voltammetry for silver deposition and stripping in the presence of the aforementioned molecules would seem to indicate that similar structural properties exist in the formation of each of the adsorbate layers. This may provide support to our assertion that 4,4'-bipyridyl is protonated at one nitrogen site in acid medium. The analogous situation exists when 4-phenylpyridine is adsorbed to the Pt surface. In both instances, the adsorbed molecule is capable of binding to the electrode surface through only one nitrogen site. The coulometric charge associated with silver deposition in the case of 4-phenylpyridine is significantly smaller (154±5 $\mu C/cm^2$) than with 4,4'-bipyridyl in 0.1 M H_2SO_4 (251±8 $\mu C/cm^2$). However, the absence of a net charge on the 4-phenylpyridine molecule should allow for a more densely packed adsorbate layer, resulting in a smaller deposition charge relative to 4,4'-bipyridyl.

The voltammetry of silver deposition onto an electrode pretreated with 4-phenylpyridine in 0.1 M H_2SO_4, shown in Figure 5B, displays the same behavior as that seen on a clean and well-ordered bare Pt(111) surface. This may indicate that at this pH, the ring nitrogen has been protonated and is unable to bind to the Pt surface thus precluding adsorption.

1,2-Bis(4-pyridyl)ethane

The voltammetry for the underpotential deposition of silver onto a Pt(111) electrode pretreated with 1 mM 1,2-Bis(4-pyridyl)ethane in water is shown in Figure 6A. Silver deposition occurs from +0.800 V to +0.475 V with a defined peak appearing at a potential of +0.719 V. As indicated in Table 2, the charges associated with the deposition and stripping of silver from the Pt surface are essentially equal (178±6

$\mu C/cm^2$). This is similar to the behavior observed with 4,4'-bipyridyl adsorbed from water. The structure of the 1,2-Bis(4-pyridyl)ethane molecule is somewhat analogous to that of 4,4'-bipyridyl in that they both possess two pyridine rings with a coordinating nitrogen site available at the 4-position on each ring. As such, this may help to support the premise of a situation in which the structure of the adsorbed molecule hinders the deposition of silver on the electrode surface. Assuming that this adsorbate binds to the electrode surface through one of the ring nitrogens, the adsorbed layer then has a structure that is slightly more than two rings thick, possibly yielding extensive ring interaction in the adsorbed layer as discussed previously. This species would also possess a certain degree of rotational freedom from the pendant pyridine ring which may enhance the kinetic limitations posed by the structure of the adsorbed molecule. As discussed previously, there is the additional possibility of the formation of a silver complex with the unbound nitrogen which may prevent the diffusion of silver to the surface. These circumstances should result in a smaller amount of silver being deposited on the Pt surface.

The voltammetry for the deposition of silver onto a Pt(111) surface pretreated with 1,2-Bis(4-pyridyl)ethane in 0.1 M H_2SO_4 is shown is Figure 6B. Again it can be seen that the deposition behavior represents that seen on a bare Pt(111) electrode. In this case, it is possible that the lack of conjugation between the two rings results in the protonation of both nitrogens at this pH. This would prevent the adsorption of this molecule to the surface.

2-mercaptopyridine

The voltammetric scan for the deposition of silver onto a Pt(111) electrode pretreated with 2-mercaptopyridine in water is shown in Figure 7A. It is immediately apparent that the response obtained with this adsorbate differs considerably from the previous examples. In the presence of the 2-mercaptopyridine adlayer, the Pt surface is completely inhibited to the underpotential deposition of silver. The only process seen to occur is that of bulk deposition at a potential of +0.300 V, representing an overpotential of ~70 mV relative to deposition at a bare Pt(111) surface. The complete passivation of the surface and the shift in the onset of bulk deposition are indicative of a very strong bond between the sulfur-containing species and the Pt electrode. If it is assumed that 2-mercaptopyridine binds to the surface primarily through the sulfur atom [20], this would imply that 2-mercaptopyridine has a higher affinity for the Pt surface than the previously mentioned nitrogen containing adsorbates. However, the sulfur and nitrogen atoms are positioned in a manner that may allow both to bind to the electrode surface, resulting in a chelate structure for the adsorbed 2-mercaptopyridine. Upon reversing the direction of the potential sweep, a pronounced hysteresis is observed. This may be a result of the overpotential required to remove the adsorbate layer. Once the adlayer is removed from the surface, the potential is well past that required for bulk deposition, resulting in the aforementioned hysteresis. It should be noted that even after bulk deposition, no stripping of UPD silver is observed. This suggests that the strength of interaction between the sulfur atom and the Pt surface is greater than that between the deposited silver and the surface. In this situation, 2-mercaptopyridine would displace all silver from the electrode surface upon stripping of bulk silver. Support for this behavior is shown in the inset of Figure 7, where a solution of 2-mercaptopyridine was introduced after the deposition of the first UPD silver monolayer. It is clearly evident that no stripping of the silver adlayer is observed upon reversal of the potential sweep, strongly suggesting that the monolayer has been displaced by adsorbed 2-mercaptopyridine.

When the electrode is pretreated with a 1 mM solution of 2-mercaptopyridine in 0.1 M H_2SO_4 (Figure 7B), the response is identical to that obtained for a solution in water. As described above, no silver deposition is seen to occur prior to that of bulk deposition. Since at this pH the pyridine nitrogen is likely protonated, this would imply that the strength of interaction is dominated by the -SH group, as would be anticipated.

4-mercaptopyridine

From studies involving the adsorption of mercaptopyridines on Ag(111) surfaces, it has been proposed that the adsorption of 4-mercaptopyridine is potential dependent, with the adsorbed molecule forming a dimer at higher potentials [20]. However, the adsorbate continues to bind to the electrode surface through the sulfur atom in a vertical orientation, which should result in behavior similar to that observed for 2-mercaptopyridine. Figure 8A displays the silver deposition voltammetry obtained when a Pt(111) electrode is pretreated with a 1 mM solution of 4-mercaptopyridine in water. Again, the surface is passivated to all processes except that of bulk silver deposition which occurs at ~+0.320 V, suggesting a higher strength of adsorption to the Pt surface for adsorbates which bind primarily through a sulfur atom. This potential for bulk deposition, however, represents a shift to more positive values by ~20 mV relative to that observed with adsorbed 2-mercaptopyridine. In addition, it can be noted that the shape of the voltammetric wave corresponding to bulk deposition is sharper and better defined in the case of adsorbed 4-mercaptopyridine. This observation and the shift in bulk deposition potential might suggest slight differences in the strength of adsorption and in the structure of the adsorbate layers. In particular, it has been suggested that 2-mercaptopyridine is capable of binding to the Pt surface through interaction of both the nitrogen and sulfur atoms. This enhanced interaction of the adsorbate with the electrode surface might make it more difficult for silver atoms to displace the adsorbate layer, as reflected in the peak shape and shift in deposition potential. In contrast, the structure of 4-mercaptopyridine precludes the formation of a similar chelate with the Pt surface, and the bonding of this molecule to the surface is thought to be solely through the sulfur atom. This may result in a diminution of the interaction of the adsorbed layer with the electrode yielding the observed positive shift in the bulk deposition potential and the sharper definition of the voltammetric response.

The behavior of 4-mercaptopyridine is not strongly dependent on the pH of the solution, as indicated by the voltammetry of Figure 8B, which represents the deposition of silver onto a Pt(111) electrode pretreated with a 1 mM solution of 4-mercaptopyridine in 0.1 M H_2SO_4. As in the case of 2-mercaptopyridine, this suggests that the sulfur atom is largely responsible for bonding.

CONCLUSIONS

It is clear that the presence of co-adsorbates can have a pronounced effect on the underpotential deposition of silver on Pt(111). The differences observed are indicative of the relative strength of interaction between the metal surface and the adsorbate, as well as between the UPD layer and the adsorbate. As expected, the effects of the adsorbate layer on silver deposition are strongly dependent on the nature of the adsorbing group and the structure of the co-adsorbed species. In general, it is seen that those species which bind to the Pt surface primarily through the pyridine ring nitrogen inhibit the deposition of the second, but not the first, monolayer of silver. 2-mercaptopyridine and 4-mercaptopyridine, which presumably bind through the sulfur atom, form an adlayer on the Pt surface which passivates all processes except that of bulk deposition. This behavior would indicate a higher bond strength between the sulfur atom and the Pt surface than that between the ring nitrogens and the Pt surface. Such a trend is consistent with the anticipated bonding strengths of the adsorbates.

The inhibition of the deposition of the second silver layer onto a Pt(111) surface pretreated with the nitrogen containing adsorbates might be explained by the formation of an adsorbate/Ag/Pt structure in which the UPD silver deposits under the adsorbate layer. The adsorbate would then interact with the silver to preclude the deposition of another monolayer. If this were the case, then the stripping of the silver overlayer would take place from a bare Pt surface. As seen in Table 1, the potential for the removal of the first silver UPD layer is virtually the same for electrodes pretreated with an adsorbate layer and for the case of no adsorbate present. This is a strong indication that the silver being stripped is in direct contact with the Pt electrode. The relatively small variation in the observed stripping potentials may also suggest that the interaction between the adsorbate and the silver adlayer is relatively weak, yet still strong enough to inhibit the deposition of the second layer.

As seen in Table 2, the coulometric charges associated with the deposition of silver in the presence of an adsorbate are less than those observed for this process on a bare Pt(111) electrode. This observation and the shift in the deposition of the first silver layer to more negative potentials would indicate that the process is hindered when the surface contains an adsorbate layer. The magnitude of this shift may reflect the strength of interaction between the ring nitrogen and the Pt electrode that must be overcome prior to deposition. Due to this Pt-adsorbate interaction, it is possible that the adsorbed species may remain attached to the Pt surface in clustered areas during deposition forming a lattice containing islands of UPD silver and clusters of adsorbate. This may lead to a smaller quantity of silver being deposited on the surface than is seen for deposition on a clean Pt electrode as is observed. The lateral interactions between adsorbate and UPD silver would be small, as indicated by the stripping potentials. Experiments are being performed to determine the validity of this model.

It will be of interest to see if other adsorbates produce similar behavior to those studied above, as well as determining how the presence of these adsorbed species may affect the growth mechanism of the underpotential layer. In addition, LEED and Auger electron spectroscopy studies would be valuable for obtaining structural information about the metal overlayer and are currently being pursued on these and other systems.

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REFERENCES

1. D. Kolb in H. Gerisher and C. W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 11, Wiley, New York, 1978, p. 125.
2. R. R. Adzic in H. Gerisher and C. W. Tobias (Eds.), Advances in Electrochemistry and Electrochemical Engineering, Vol. 13, Wiley, New York, 1984, p. 159.
3. G. W. Tindall and S. Bruckenstein, Electrochim. Acta, 16, 245 (1971).
4. S. H. Cadle and S. Bruckenstein, Anal. Chem., 43, 1858 (1971).
5. S. Stucki, J. Electroanal. Chem., 80, 375 (1977).
6. J. S. Hammond and N. Winograd, J. Electroanal. Chem., 80, 123 (1977).
7. R. C. Salvarezza, D. Vázquez Moll, M. C. Giordano and A. J. Arvia, J. Electroanal. Chem., 213, 301 (1986).
8. B. I. Podlovchenko and E. A. Kolyadko, J. Electroanal. Chem., 224, 225 (1987).
9. D. Aberdam, C. Salem, R. Durand and R. Faure, Surf. Sci., 239, 71 (1990).
10. F. El Omar, R. Durand and R. Faure, J. Electroanal. Chem., 160, 385 (1984).
11. J. F. Rodríguez, D. L. Taylor and H. D. Abruña, Electrochim. Acta, 38, 235 (1993).
12. J. L. Stickney, S. D. Rosasco, D. Song, M. P. Soriaga and A. T. Hubbard, Surf. Sci., 130, 326 (1983)..
13. A. T. Hubbard, J. L. Stickney, S. D. Rosasco, M. P. Soriaga and D. Song, J. Electroanal. Chem., 150, 165 (1983).
14. A. Wieckowski, B. C. Schardt, S. D. Rosasco, J. L. Stickney and A. T. Hubbard, Surf. Sci., 146, 115 (1984).
15. N. C. Gibson, P. M. Seville and D. A. Harrington, J. Electroanal. Chem., 318, 271 (1991).
16. A. T. Hubbard and J. Y. Gui, J. Chim. Phys., 88, 1547 (1991).
17. S. A. Chaffins, J. Y. Gui, C.-H. Lin, F. Lu, G. N. Salaita, D. A. Stern and A. T. Hubbard, Langmuir, 6, 1273 (1990).
18. G. N. Salaita and A. T. Hubbard, Catal. Today, 12, 465 (1992).

19. S. A. Chaffins, J. Y. Gui, B. E. Kahn, C. -H. Lin, F. Lu, G. N. Salaita, D. A. Stern, D. C. Zapien and A. T. Hubbard, Langmuir, 6, 957 (1990).
20. J. Y. Gui, F. Lu, D. A. Stern and A. T. Hubbard, J. Electroanal. Chem., 292, 245 (1990).
21. J. Clavilier, J. Electroanal. Chem., 107, 211 (1980).
22. J. H. White and H. D. Abruña, J. Electroanal. Chem., 300, 521 (1991).
23. A. Wieckowski, personal communication.
24. J. Clavilier, D. Armand and B. L. Wu, J. Electroanal. Chem., 135, 159 (1982).
25. G. Jerkiewicz and B. E. Conway, J. Chim. Phys., 88, 1381 (1991).
26. W. J. Peard and R. T. Pflaum, J. Am. Chem. Soc., 80, 1593 (1958).

Table 1.

Peak Positions (V vs. Ag/AgCl, sat'd)

Deposition Region	**1**	**3**	**4**	**5**	**bulk**
1 mM Ag^+	0.775	0.395	0.462	0.840	0.375
2,2'-bipyridyl in water	0.755	---	---	0.845	0.365
2,2'-bipyridyl in 0.1 M H_2SO_4	0.770	0.397	0.458	0.840	0.375
Pyrazine in water	0.712	---	---	0.838	0.365
Pyrazine in 0.1 M H_2SO_4	0.710	---	---	0.838	0.370
4,4'-bipyridyl in water	0.710	---	---	0.825	0.350
4,4'-bipyridyl in 0.1 M H_2SO_4	0.770	---	---	0.838	0.365
4-phenylpyridine in water	0.755	---	---	0.842	0.364
4-phenylpyridine in 0.1 M H_2SO_4	0.775	0.399	0.461	0.842	0.370
1,2-bis(4-pyridyl)ethane in water	0.719	---	---	0.834	0.372
1,2-bis(4-pyridyl)ethane in 0.1 M H_2SO_4	0.773	0.399	0.461	0.844	0.375
2-mercaptopyridine in water	---	---	---	---	0.300
2-mercaptopyridine in 0.1 M H_2SO_4	---	---	---	---	0.300
4-mercaptopyridine in water	---	---	---	---	0.320
4-mercaptopyridine in 0.1 M H_2SO_4	---	---	---	---	0.315

Table 2.
Charges for Silver Deposition and Stripping (μC/cm^2)

Peak Number	**1**	**2**	**3**	**4**	**5**
1 mM Ag$^+$	290±9	28±1	166±5	183±6	360±12
2,2'-bipyridyl in water	144±5	---	---	---	205±7
2,2'-bipyridyl in 0.1 M H_2SO_4	271±9	28±1	149±5	180±6	367±12
Pyrazine in water	180±6	---	---	---	274±8
Pyrazine in 0.1 M H_2SO_4	193±6	---	---	---	292±10
4,4'-bipyridyl in water	168±5	---	---	---	178±6
4,4'-bipyridyl in 0.1 M H_2SO_4	251±8	---	---	---	280±9
4-phenylpyridine in water	154±5	---	---	---	209±7
4-phenylpyridine in 0.1 M H_2SO_4	242±8	23±1	126±4	138±5	373±12
1,2-Bis(4-pyridyl)ethane in water	178±6	---	---	---	178±6
1,2-Bis(4-pyridyl)ethane in 0.1 M H_2SO_4	245±8	30±1	127±4	134±5	375±12

FIGURE CAPTIONS

Figure 1: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 onto a Pt(111) electrode starting at +0.870 V. Numbers denote deposition regions previously specified. Scan Rate = 2.0 mV/s, Area = 0.78 cm^2

Figure 2: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1mM 2,2'-bipyridyl in (A) water, (B) 0.1 M H_2SO_4. Background, (- - -). Experimental parameters are the same as in Figure 1.

Figure 3: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1mM pyrazine in (A) water, (B) 0.1 M H_2SO_4. Background, (- - -). Experimental parameters are the same as in Figure 1.

Figure 4: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1mM 4,4'-bipyridyl in (A) water, (B) 0.1 M H_2SO_4. Background, (- - -). Experimental parameters are the same as in Figure 1.

Figure 5: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1mM 4-phenylpyridine in (A) water, (B) 0.1 M H_2SO_4. Background, (- - -). Scan Rate = 2.0 mV/s, Area = 0.73 cm^2.

Figure 6: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1mM 1,2-bis(4-pyridyl)ethane in (A) water, (B) 0.1 M H_2SO_4. Background, (- - -). Experimental parameters are the same as in Figure 5.

Figure 7: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1 mM 2-mercaptopyridine in (A) water, (B) 0.1 M H_2SO_4. Experimental parameters are the same as in Figure 1.

Inset: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a bare Pt(111) electrode. The electrode was held at +0.715 V, then rinsed with clean supporting electrolyte before introducing a solution of 1 mM 2-mercaptopyridine in PDW for three minutes at open circuit. The electrode was then rinsed with supporting electrolyte and an anodic sweep was initiated.

Figure 8: Deposition of silver from a 1 mM solution in 0.1 M H_2SO_4 on to a Pt(111) electrode pretreated with 1 mM 4-mercaptopyridine in (A) water, (B) 0.1 M H_2SO_4. Experimental parameters are the same as in Figure 1.

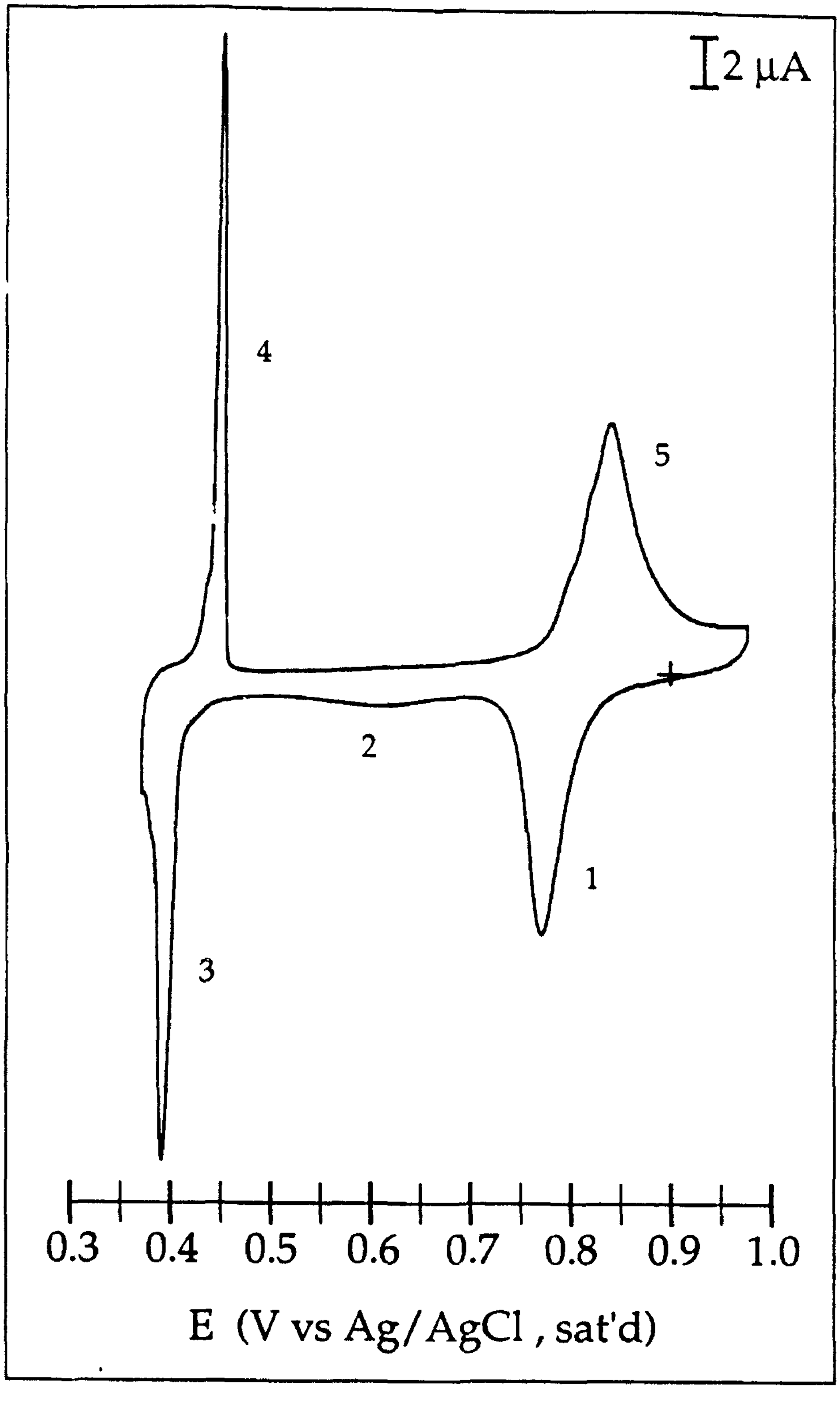

Figure 1.

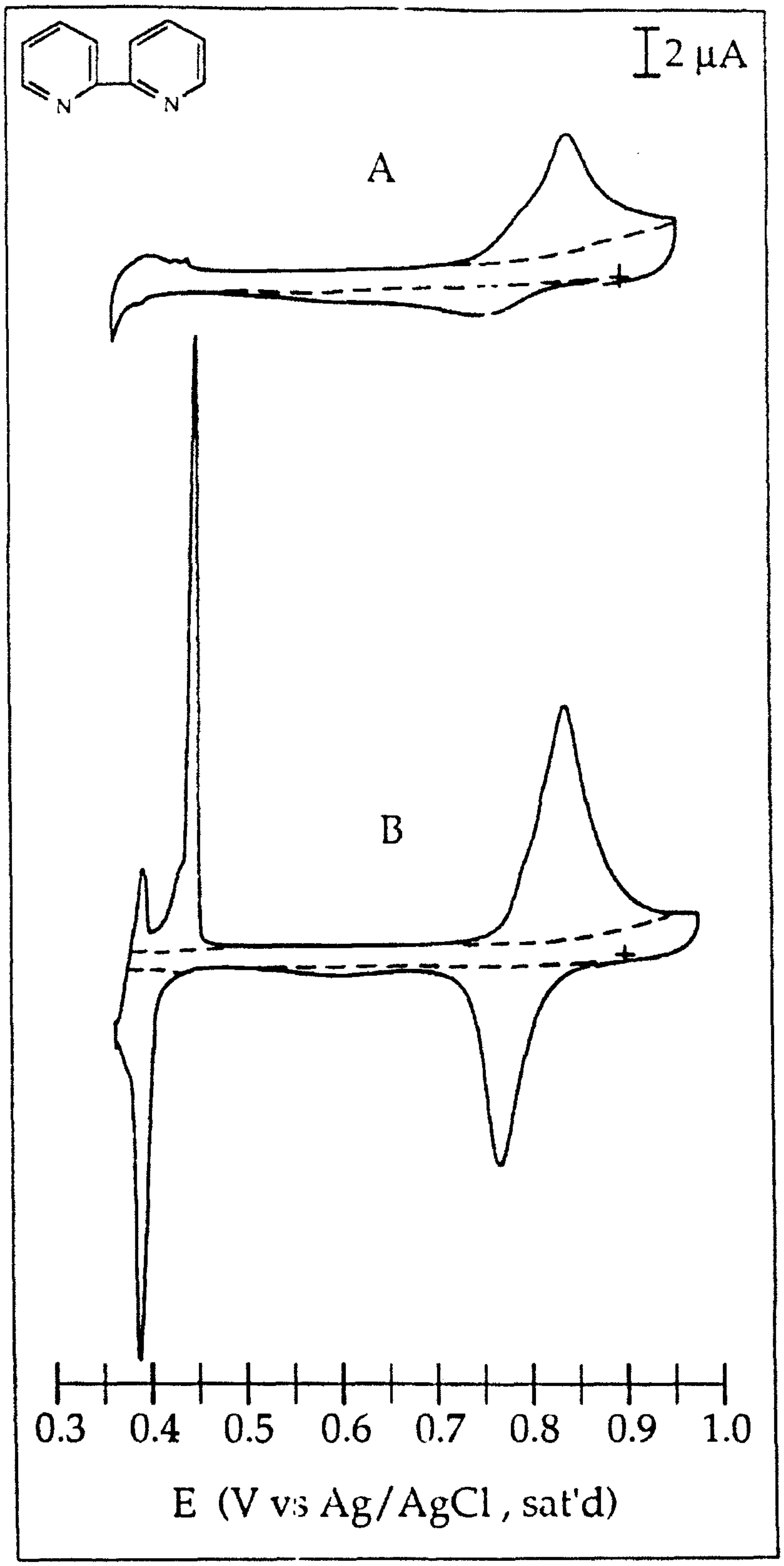

Figure 2.

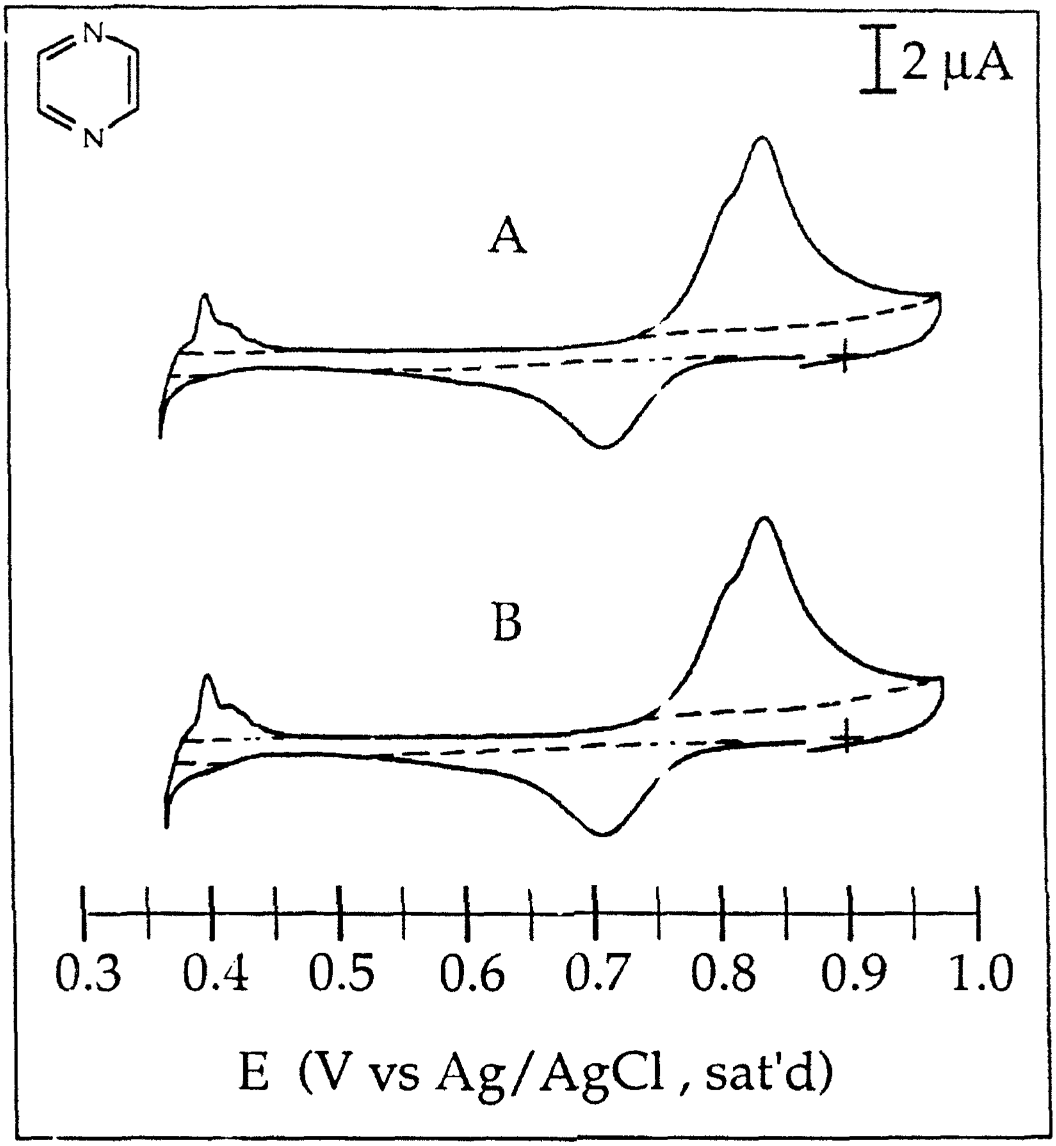

Figure 3.

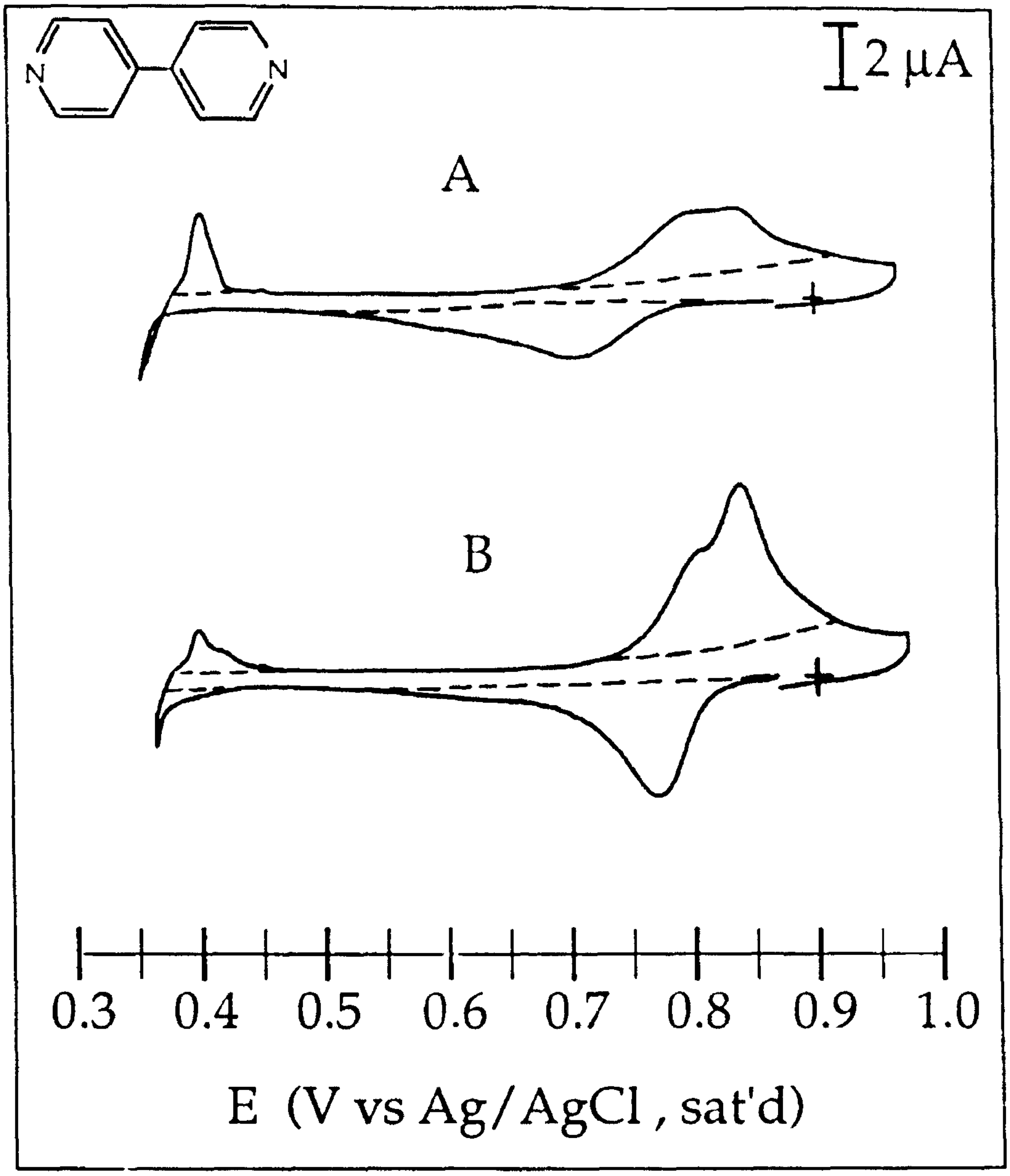

Figure 4.

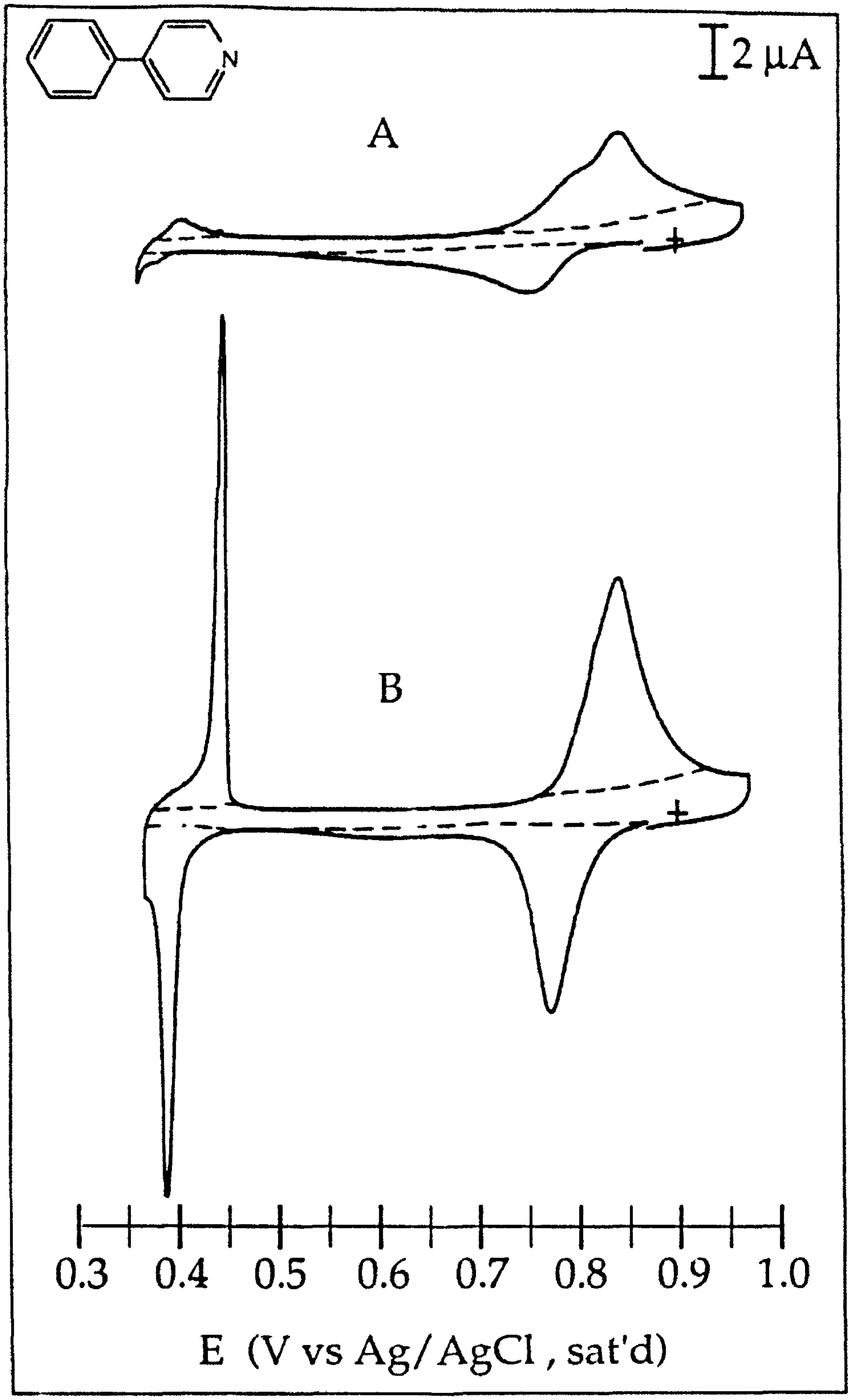

Figure 5.

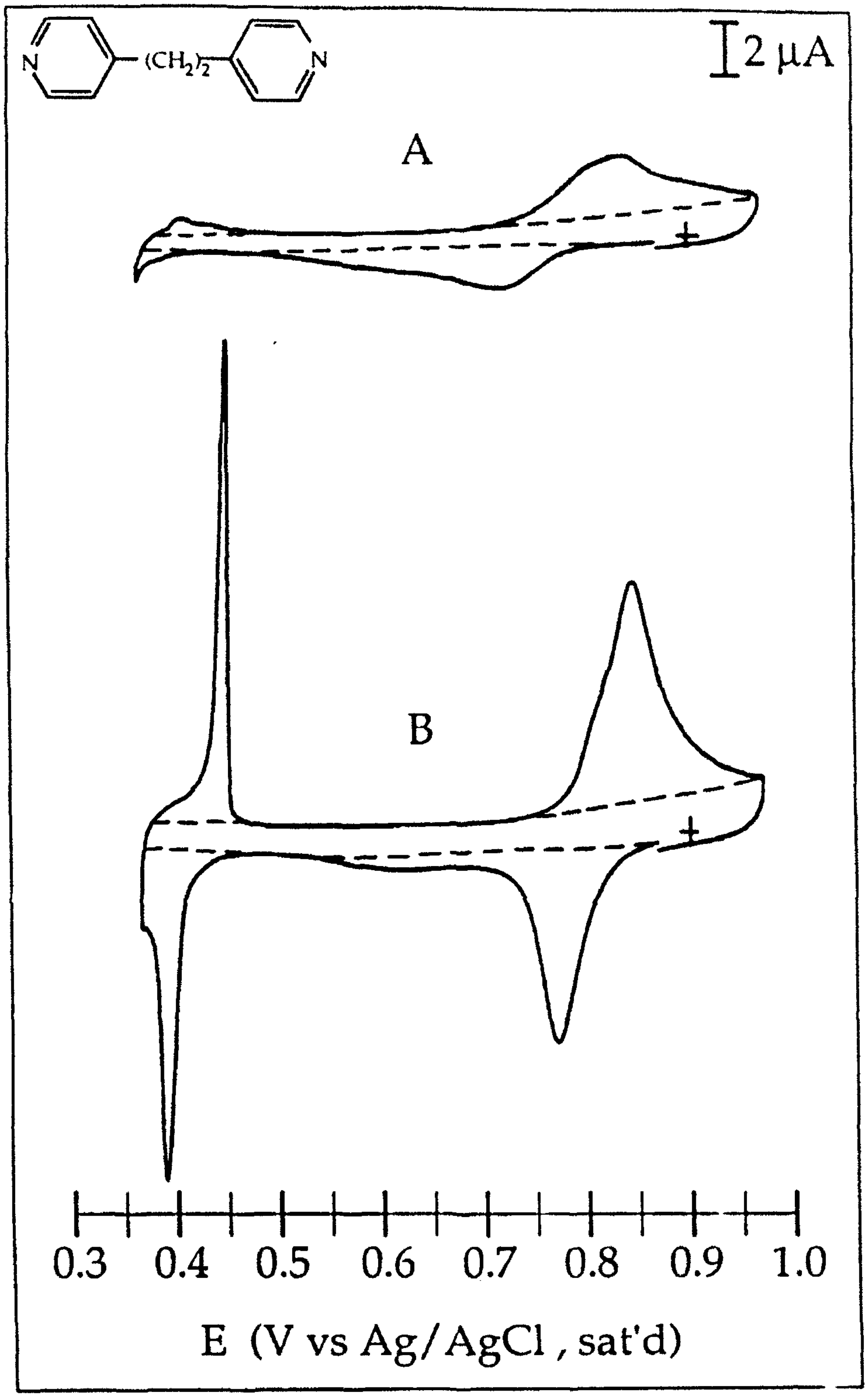

Figure 6.

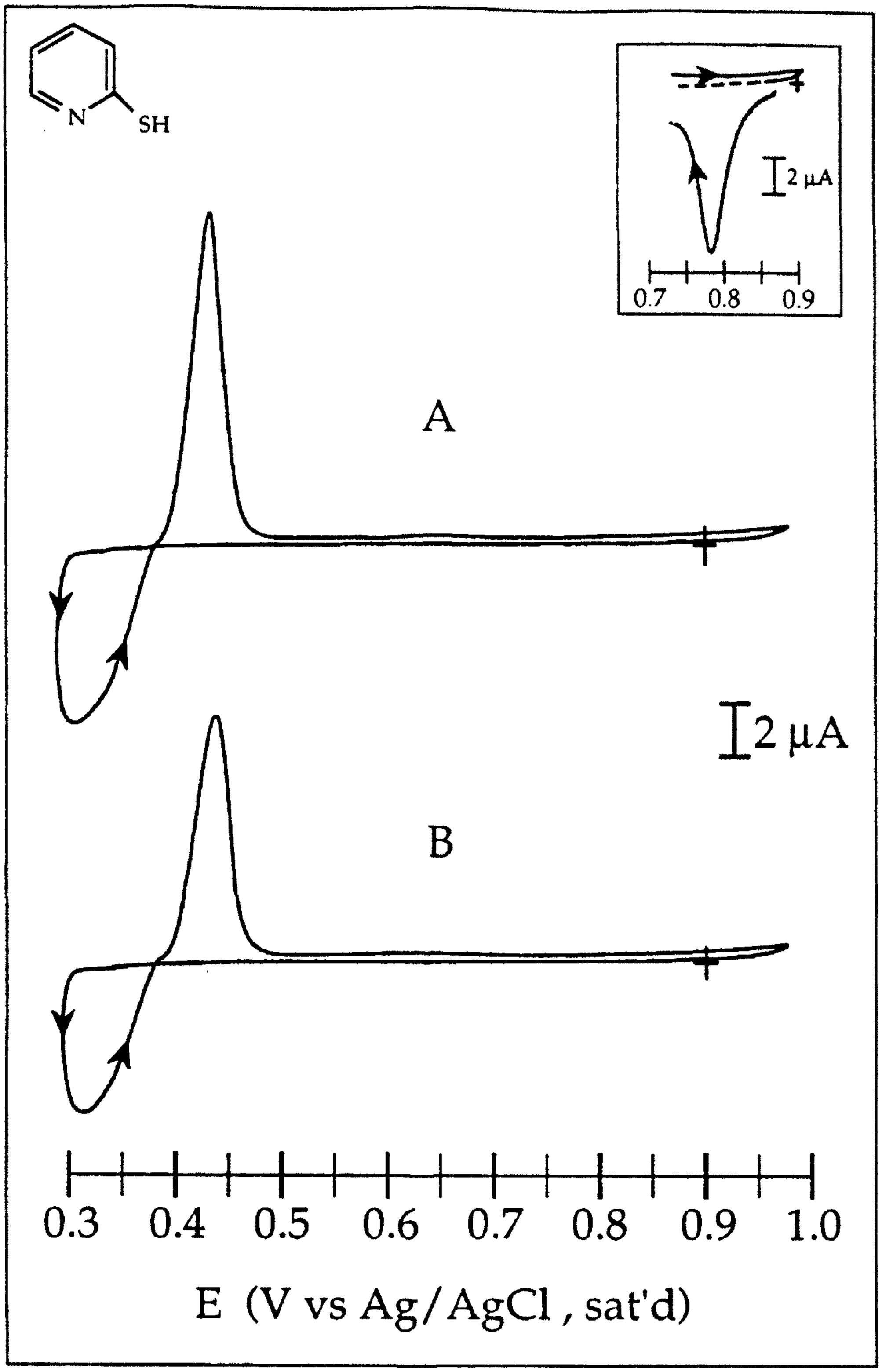

Figure 7.

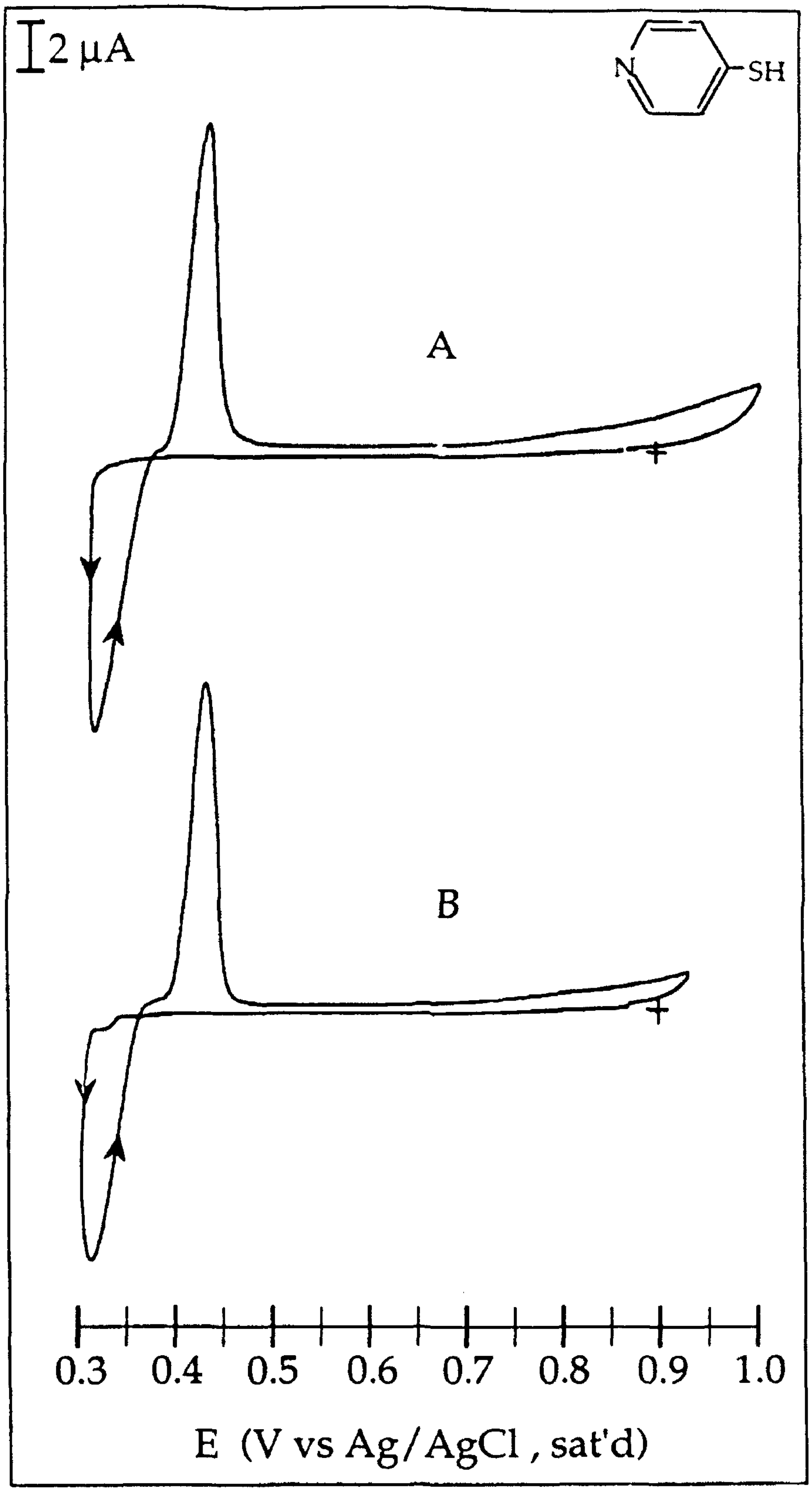

Figure 8.