

are either hydrophilic or hydrophobic. Finally, the colloidal dispersion is polymerized again.

Compared to the one-step method based on emulsions or microemulsions, the two-step method can employ a smaller amount of surfactant. As a result, composites with

better mechanical properties are expected to be obtained.

**Registry No.** Poly(styrenesulfonic acid) sodium salt, 62744-35-8; polystyrene, 9003-53-6; (acrylamide)(*N,N*-methylenebisacrylamide) (copolymer), 25034-58-6; (divinylbenzene)(styrene) (copolymer), 9003-70-7.

## Surface-Modified Electrodes Based on Nickel(II) and Copper(II) Bis(salicylaldimine) Complexes

Lisa A. Hoferkamp and Kenneth A. Goldsby\*

Department of Chemistry, The Florida State University, Tallahassee, Florida 32306-3006

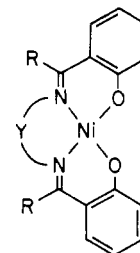
Received August 22, 1988

Surface-modified electrodes have been prepared by the oxidative polymerization of nickel(II) *N,N'*-ethylenebis(salicylaldimine) {[Ni(H-sal<sub>2</sub>en)]}, copper(II) *N,N'*-ethylenebis(salicylaldimine) {[Cu(H-sal<sub>2</sub>en)]}, and substituted nickel(II) and copper(II) bis(salicylaldimine) complexes. The modified electrodes were prepared in weak-donor solvents by repetitively cycling the potential in the oxidative region or by constant-potential electrolysis. For [Ni(H-sal<sub>2</sub>en)], the surface coverage increased linearly for the first several voltammetric scans, and the initial rate of film growth increased linearly with the concentration of [Ni(H-sal<sub>2</sub>en)]. For [Cu(H-sal<sub>2</sub>en)], the rate of film growth decreased steadily from the initial scan. The resulting modified electrodes exhibited single reversible redox waves of modest stability in fresh electrolyte solution. Scan rate dependence of the current and peak potential separations are consistent with slow electron transfer for surface-immobilized redox couples. Electrodes prepared in various weak-donor solvents (acetonitrile, acetone, methylene chloride) showed essentially identical electrochemical behavior in fresh acetonitrile electrolyte, although scanning electron microscopy revealed a difference in surface morphology. The properties of this new family of surface-modified electrodes are discussed in terms of the proposed mechanism for polymer film formation and electron transfer.

### Introduction

The study of polymer-modified electrodes continues to be an area of great interest and intense activity.<sup>1-3</sup> Much of the work in this area has been stimulated by the potential application of these new materials as electrocatalysts, chemical sensors, electrochromic displays, and microelectronic devices.<sup>2b</sup> An important theme in the design and development of chemically modified electrodes has involved extending the known redox reactivity of discrete homogeneous species to the electrode surface, and the rich redox chemistry of transition-metal complexes has played a prominent role in this area. The development of heterogeneous electrocatalysts based on known homogeneous transition-metal catalysts is one important example of this approach.<sup>4</sup>

We recently reported a solvent dependent mechanism for the oxidation of nickel(II) bis(salicylaldimine) complexes (I).<sup>5,6</sup> The nickel(II) complexes are reversibly oxidized in strong-donor solvents which stabilize the nickel(III) oxidation state. In weak-donor solvents, however,



I [Ni(R-sal<sub>2</sub>Y)]

the complexes are oxidatively polymerized at the electrode surface. Electropolymerization is a particularly attractive method for preparing modified electrodes given the good stability and high density of redox sites often observed for the resulting polymer films.<sup>14,9</sup> Therefore, the oxidative polymerization of bis(salicylaldimine) complexes may offer a potentially useful route to surface-modified electrodes based on these complexes.

In this paper we report the preparation and properties of surface-modified electrodes obtained by the oxidative polymerization of nickel(II) and copper(II) bis(salicylaldimine) complexes. Bis(salicylaldimine) complexes of a number of transition metals (including nickel<sup>7</sup> and copper<sup>8</sup>) have shown catalytic activity for the oxidation of organic molecules<sup>7-10</sup> and the reduction of CO<sub>2</sub>.<sup>11</sup> Given

(1) (a) Murray, R. W. *Ann. Rev. Mater. Sci.* **1984**, *14*, 145. (b) Murray, R. W. *Electroanal. Chem.* **1984**, *13*, 141. (c) Chidsey, C. E. D.; Murray, R. W. *Science* **1986**, *231*, 25. (d) Murray, R. W. *Acc. Chem. Res.* **1980**, *13*, 135.

(2) (a) Wrighten, M. S. In *Catalysis and Electrocatalysis*; Miller, J. S., Ed.; ACS Symposium Series 192; American Chemical Society: Washington, DC, 1982; p 99. (b) Wrighten, M. S. *Science* **1986**, *231*, 32.

(3) Faulkner, L. R. *Chem. Eng. News* **1984**, *62*, 28.

(4) (a) Simon, R. A.; Mallouk, T. E.; Daube, K. A.; Wrighton, M. S. *Inorg. Chem.* **1985**, *24*, 3119. (b) Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710. (c) Issahary, D. A.; Ginzburg, G.; Polak, M.; Meyerstein, B. *J. Chem. Soc., Chem. Commun.* **1982**, 441. (d) Samuels, G. J.; Meyer, T. *J. Am. Chem. Soc.* **1981**, *103*, 307.

(5) Goldsby, K. A.; Blaho, J. K.; Hoferkamp, L. A. *Polyhedron* **1989**, *8*, 113.

(6) The abbreviated names, [M(R-sal<sub>2</sub>Y)] (M = Ni, Cu) are derived from structure I where Y is en (ethylenediamine, CH<sub>2</sub>CH<sub>2</sub>) or phen (*o*-phenylenediamine, *o*-C<sub>6</sub>H<sub>4</sub>).

(7) Yoon, H.; Burrows, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 4087.

(8) Kitajima, N.; Whang, K.; Moro-oka, Y.; Uchida, A.; Sasada, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1504.

(9) (a) Siddall, T. L.; Miyaura, N.; Huffman, J. C.; Kochi, J. K. *J. Am. Chem. Soc., Chem. Commun.* **1983**, 1185. (b) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.

(10) (a) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580, and references therein. (b) Nishinaga, A.; Iwasaki, H.; Shimizu, T.; Toyoda, Y.; Matsuura, T. *J. Org. Chem.* **1986**, *51*, 2257, and references therein.

the rich redox chemistry of transition-metal bis(salicylaldehyde) complexes and the relative ease with which these complexes can be prepared,<sup>12</sup> the opportunity to translate this reactivity to the electrode surface may be of great importance.

### Experimental Section

**Materials.** Reagent grade solvents and chemicals were used in the syntheses of the nickel(II) and copper(II) complexes. Electrochemical solvents were distilled from the appropriate drying agents<sup>13</sup> and stored over 4-Å molecular sieves. Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was synthesized by a literature procedure,<sup>14</sup> recrystallized two times from aqueous ethanol, and dried in a vacuum oven. The bis(salicylaldehyde) complexes were prepared by standard literature procedures<sup>12</sup> and recrystallized prior to electrochemical investigations.

**Measurements.** Electrochemical measurements were obtained on a Princeton Applied Research Model 173 potentiostat equipped with a Model 175 linear programmer. Cyclic voltammograms were recorded on a Houston Instrument Model 200 X-Y recorder. The working electrode was a platinum disk electrode (Bioanalytical Systems), unless specified otherwise. The area of the platinum disk was determined to be 0.019 cm<sup>2</sup> by a literature technique.<sup>15</sup> The working electrode was polished routinely with 0.05-μm alumina micropolish. A platinum wire sealed in a glass tube served as the auxiliary electrode. The half-wave potential ( $E_{1/2}$ ) is defined as  $(E_{pa} + E_{pc})/2$ . Potentials were measured vs a saturated sodium calomel electrode (SSCE). No *iR* compensation was employed, unless otherwise stated. Electronic spectra were obtained by polymerizing thin films onto indium tin oxide (ITO) coated glass electrodes (Delta Technologies, Limited). The polymerized ITO electrodes were placed in 1-cm optical cells filled with acetonitrile, and the electronic spectra were measured on a Milton Roy 1201 spectrophotometer. Scanning electron micrographs were obtained with a JOEL CX-100 scanning electron microscope at an accelerating voltage of 20 keV. The samples for scanning electron microscopy were prepared by polymerizing [Ni(H-sal<sub>2</sub>en)] onto thin sheets of platinum foil, and the resulting polymer films were critical point dried<sup>16</sup> and sputter coated with gold/palladium.

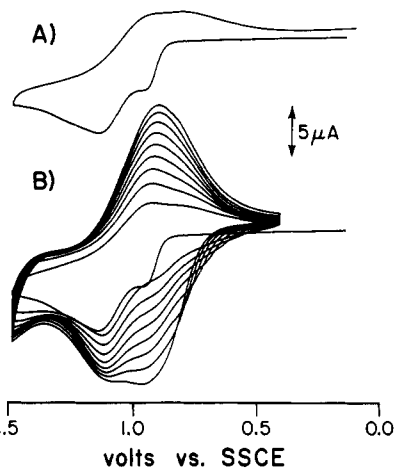
**Calculation of Apparent Surface Coverage.** Apparent surface coverage (ASC) was determined by a variation of the method used by Meyer and Murray.<sup>17</sup> Calculations are based on the eq 1, where  $Q$  is the charge required to oxidize (or reduce)

$$ASC = Q/nFA \quad (1)$$

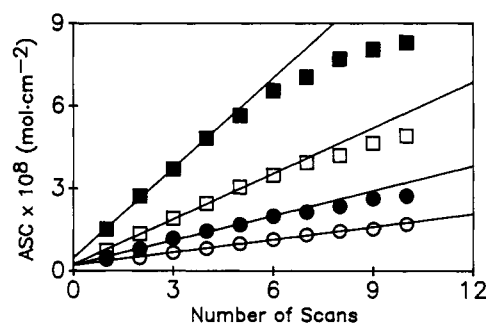
the surface wave,  $n$  is the number of electrons passed per monomeric subunit of the polymer film,  $F$  is Faraday's constant, and  $A$  is the area of the electrode. In our treatment,  $Q$  was estimated by taking one-half the area (i.e., charge) enclosed in the voltammetric trace. Although this treatment gives at best a rough estimate for the actual surface coverage, it is adequate for monitoring the rate of polymer film growth at the electrode surface.

### Results

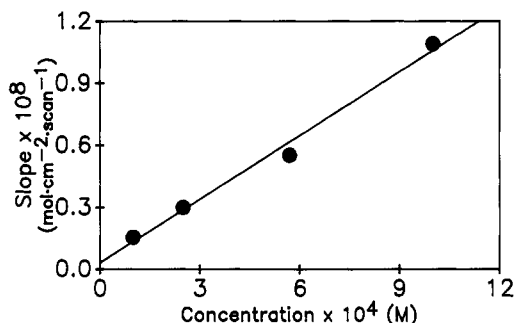
We have previously reported that [Ni(H-sal<sub>2</sub>en)], [Ni(Me-sal<sub>2</sub>en)], and [Ni(H-sal<sub>2</sub>phen)] are oxidatively polymerized at electrode surfaces in a variety of weak-donor solvents.<sup>5</sup> In this paper, we will focus on the preparation and properties of modified electrodes based on the parent [Ni(H-sal<sub>2</sub>en)] complex. Modified electrodes prepared from the substituted nickel(II) bis(salicylaldehyde) com-



**Figure 1.** Initial (A) and repetitive scan (B) cyclic voltammograms showing the oxidative polymerization of [Cu(H-sal<sub>2</sub>en)] in 0.1 M TBAH/CH<sub>3</sub>CN at a platinum disk electrode. The scan rate is 100 mV·s<sup>-1</sup>.



**Figure 2.** Graph of the apparent surface coverage (ASC) vs the scan number for the oxidative polymerization of [Ni(H-sal<sub>2</sub>en)] in 0.1 M TBAH/CH<sub>3</sub>CN. The concentrations of [Ni(H-sal<sub>2</sub>en)] are 1.0 × 10<sup>-4</sup> M (○), 2.5 × 10<sup>-4</sup> M (●), 5.7 × 10<sup>-4</sup> M (□), and 1.0 × 10<sup>-3</sup> M (■). The scan rate is 100 mV·s<sup>-1</sup>.



**Figure 3.** Graph of the initial slope (obtained from the data in Figure 2) vs concentration for the oxidative polymerization of [Ni(H-sal<sub>2</sub>en)].

plexes yielded results analogous to those described for [Ni(H-sal<sub>2</sub>en)], and specific reference to these electrodes will be limited to discussions of substituent effects. Likewise, we have succeeded in preparing modified electrodes for a variety of copper(II) bis(salicylaldehyde) complexes; however, only the [Cu(H-sal<sub>2</sub>en)]-modified electrodes will be discussed here.

**Electrode Modification and Film Growth.** Cyclic voltammograms illustrating the general scanning procedure used in preparing the modified electrodes are shown in Figure 1 for [Cu(H-sal<sub>2</sub>en)]. The increase in current with repetitive scanning is due to film growth on the electrode surface. The rate of film growth on the electrode can be represented by plotting the apparent surface coverage (see Experimental Section) vs the scan number. For [Ni(H-

(11) Pearce, D. J.; Pletcher, D. J. *Electroanal. Chem.* 1986, 197, 317.

(12) Holm, R. H.; Everett, G. W.; Chakravorty, A. *Prog. Inorg. Chem.* 1966, 7, 83.

(13) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon Press: Oxford, 1980.

(14) Sawyer, D. T. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1976.

(15) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980.

(16) Bartlett, A. A.; Burstyn, H. P. In *SEM/1975 Proceedings of the 8th Annual SEM Symposium*; 1975; Part I, pp 305-316.

(17) Ellis, C. D.; Margerum, L. D.; Murray, R. W.; Meyer, T. J. *Inorg. Chem.* 1983, 22, 1283.

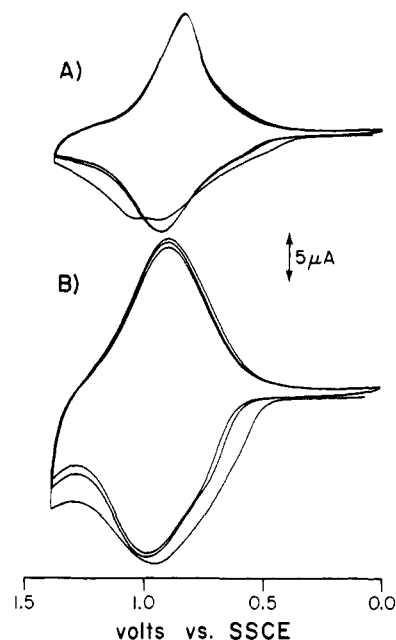
sal<sub>2</sub>en)], the apparent surface coverage increased linearly for the first several scans, followed by a gradual reduction in the rate of film growth (Figure 2). The initial rate of polymerization (obtained from the slope of the linear portion of these plots) increased linearly with the concentration of [Ni(H-sal<sub>2</sub>en)] used in the polymerization experiment (Figure 3). Continued scanning resulted in a further reduction in the rate of film growth until film growth virtually stopped by the 50–100th scan. A decrease in rate following initially linear film growth has been observed previously in other electropolymerization studies.<sup>17–19</sup> Further scanning resulted in a loss of redox activity of the surface wave, and eventually complete passivation of the electrode occurred (i.e., the electrode became totally redox inactive). Even after complete passivation, an orange film remained clearly visible on the electrode surface, suggesting that passivation may be due to formation of an insulating layer between the electrode and the polymer film.<sup>17</sup>

Initial scan voltammograms of [Cu(H-sal<sub>2</sub>en)] were considerably more complex than those of [Ni(H-sal<sub>2</sub>en)],<sup>5</sup> exhibiting three oxidations followed by two reductions (Figure 1A). Continued scanning resulted in a characteristic enhancement of the surface wave. The rate of film growth decreased steadily with increasing scan number, and total passivation of the electrode occurred much sooner than it did with [Ni(H-sal<sub>2</sub>en)]. The polymer film remained clearly visible on the electrode surface even after total passivation.

The effect of extending the anodic scan range to include the [Ni(H-sal<sub>2</sub>en)]<sup>0/-</sup> and [Cu(H-sal<sub>2</sub>en)]<sup>0/-</sup> couples was also investigated. The polymerization of [Ni(H-sal<sub>2</sub>en)] was carried out by repetitively scanning between +1.4 and -1.8 V in 0.1 M TBAH/CH<sub>3</sub>CN. In addition to observing the [Ni(H-sal<sub>2</sub>en)]<sup>0/-</sup> couple at -1.65 V, an oxidative prepeak appeared at roughly 0.3 V. The [Ni(H-sal<sub>2</sub>en)]<sup>0/-</sup> couple and the prepeak grew in with the anodic surface wave for the first several scans, but upon further cycling these features disappeared. Similar results were observed for the oxidative polymerization of [Cu(H-sal<sub>2</sub>en)]. Extending the scan range to include the [Cu(H-sal<sub>2</sub>en)]<sup>0/-</sup> couple at -1.23 V<sup>20</sup> also yielded an oxidative prepeak at roughly 0.3 V. Subsequent scans resulted in a decrease in the size of the [Cu(H-sal<sub>2</sub>en)]<sup>0/-</sup> wave and an increase in intensity and anodic shift for the oxidative prepeak. By the fourth scan, the prepeak was no longer visible, although it is not clear whether the prepeak disappeared (as it did for [Ni(H-sal<sub>2</sub>en)]) or simply merged with the [Cu(H-sal<sub>2</sub>en)]<sup>+0</sup> surface wave. The origin of the prepeak is presently unknown, although similar behavior has been observed in other electropolymerization studies.<sup>18,19,21,22</sup>

Electropolymerization of [Ni(H-sal<sub>2</sub>en)] and [Cu(H-sal<sub>2</sub>en)] was also achieved by constant-potential electrolysis at 1.4 V. The electrodes modified in this manner exhibited behavior in fresh 0.1 M TBAH/CH<sub>3</sub>CN essentially identical with that observed for the electrodes prepared by repetitive scanning through the oxidation waves.

The preparation of modified electrodes by oxidative polymerization of the free ligand, H<sub>2</sub>(H-sal<sub>2</sub>en), was also



**Figure 4.** Cyclic voltammograms of (A) [Ni(H-sal<sub>2</sub>en)]- and (B) [Cu(H-sal<sub>2</sub>en)]-modified electrodes in fresh 0.1 M TBAH/CH<sub>3</sub>CN showing the first three scans. The scan rate is 100 mV·s<sup>-1</sup>.

attempted. Initial-scan voltammograms of H<sub>2</sub>(H-sal<sub>2</sub>en) in 0.1 M TBAH/CH<sub>3</sub>CN showed two closely spaced irreversible oxidations at roughly 1.2 V. The electrode became totally passivated by the fifth scan. Rapid passivation of the electrode was observed for all of the H<sub>2</sub>(R-sal<sub>2</sub>Y) ligands investigated.

**Properties of Modified Electrodes.** The [Ni(H-sal<sub>2</sub>en)]-modified electrodes used in these studies were generally prepared by cycling a freshly cleaned electrode 10 times in the potential region 0.4–1.4 V; a scan range of 0.5–1.4 V was used for preparing the [Cu(H-sal<sub>2</sub>en)]-modified electrodes. The resulting modified electrodes were thoroughly rinsed with acetone and examined in fresh 0.1 M TBAH/CH<sub>3</sub>CN solution. Electrodes modified in this manner exhibited single reversible oxidative redox couples by the second or third scan; however, the initial anodic scans were often broad and misshapen (Figure 4), which we attribute to the oxidation of residual monomer and small unpolymerized oligomers remaining in the polymer film. At scan rates of 100 mV·s<sup>-1</sup>, the [Ni(H-sal<sub>2</sub>en)]- and [Cu(H-sal<sub>2</sub>en)]-modified electrodes typically exhibited broad reversible waves at half-wave potentials of roughly 0.87 and 0.96 V, respectively. For both electrodes,  $\Delta E_p$  decreased with decreasing scan rate; e.g., for a typical [Ni(H-sal<sub>2</sub>en)]-modified electrode,  $\Delta E_p$  decreased from 250 mV at 200 mV·s<sup>-1</sup> to 90 mV at 10 mV·s<sup>-1</sup>. Large peak potential separations and decreases in  $\Delta E_p$  with decreasing scan rate are indicative of slow electron transfer in the polymer film.<sup>23,24</sup> Plots of cathodic peak current ( $i_{p,c}$ ) vs scan rate were linear, which also suggests slow heterogeneous electron-transfer reactions for the surface couple.<sup>24</sup>

The electrode polymerization procedures described above were carried out in a variety of weak-donor solvents, including acetone, methylene chloride, and propylene carbonate, and the resulting electrodes were investigated in fresh acetonitrile electrolyte. Although the shapes of the voltammograms showing film growth differed some-

(18) Bailey, C. L.; Bereman, R. D.; Rillema, D. P.; Nowak, R. *Inorg. Chem.* 1986, 25, 933.

(19) Calvert, J. M.; Schmell, R. H.; Sullivan, B. P.; Facci, J. S.; Meyer, T. J.; Murray, R. W. *Inorg. Chem.* 1983, 22, 2151.

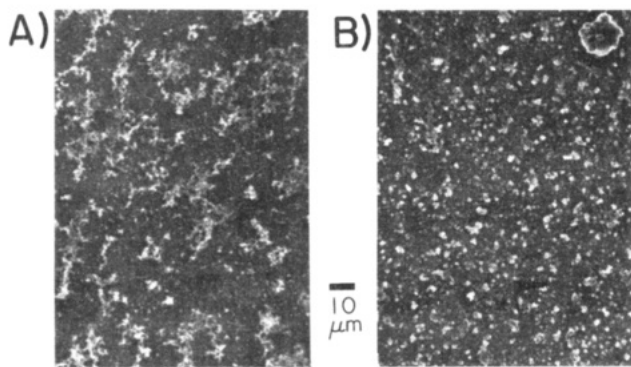
(20) The [Cu(H-sal<sub>2</sub>en)]<sup>0/-</sup> couple is not truly reversible. A Cu<sup>0</sup> desorption wave was observed after the first reductive scan at roughly -0.3 V, presumably due to the disproportionation of copper(I).

(21) Ellis, C. D.; Murphy, W. R.; Meyer, T. J. *J. Am. Chem. Soc.* 1981, 103, 7480.

(22) Daire, F.; Bedioui, F.; Devynck, J.; Bied-Charreton, C. *J. Electroanal. Chem.* 1987, 224, 95.

(23) Even with *iR* compensation, substantial peak potential separations were observed; e.g.,  $\Delta E_p \approx 70$  mV at 100 mV·s<sup>-1</sup>.

(24) Pearce, P. J.; Bard, A. J. *J. Electroanal. Chem.* 1980, 114, 89.



**Figure 5.** Scanning electron micrographs of modified electrodes obtained by the oxidative polymerization of [Ni(H-sal<sub>2</sub>en)] in (A) 0.1 M TBAH/CH<sub>3</sub>CN and (B) 0.1 M TBAH/CH<sub>2</sub>Cl<sub>2</sub> (see the Experimental Section for details).

what with solvent, the resulting modified electrodes gave essentially identical behavior in fresh 0.1 M TBAH/CH<sub>3</sub>CN.

The redox stability of the polymer films was determined by measuring the area under the voltammetric trace as the modified electrode was scanned from 0.0 to 1.4 V at 100 mV·s<sup>-1</sup> in fresh 0.1 M TBAH/CH<sub>3</sub>CN. The ratio of the area under the 25th scan relative to the area under the third scan was taken as a measure of the film's redox stability. The third scan was used to avoid including the additional current due to oxidative polymerization of residual monomer and small oligomers in the film (note above). The [Ni(H-sal<sub>2</sub>en)]-modified electrodes exhibited a redox stability of roughly 70%. For comparison, the [Ni(H-sal<sub>2</sub>phen)]- and [Ni(Me-sal<sub>2</sub>en)]-modified electrodes were also prepared and evaluated with respect to their redox stability. In general, the [Ni(H-sal<sub>2</sub>phen)]-modified electrodes exhibited greater stability than the parent [Ni(H-sal<sub>2</sub>en)]-modified electrodes, while the [Ni(Me-sal<sub>2</sub>en)]-modified electrodes were somewhat less stable. The redox stability of the [Cu(H-sal<sub>2</sub>en)]-modified electrodes was considerably less than that of the analogous [Ni(H-sal<sub>2</sub>en)]-modified electrodes.

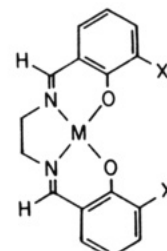
**Electronic Spectra.** Solution spectra of [Ni(H-sal<sub>2</sub>en)] and [Cu(H-sal<sub>2</sub>en)] in CN<sub>3</sub>CN exhibit charge-transfer manifolds with band maxima at 422 and 360 nm, respectively. Spectra of the [Ni(H-sal<sub>2</sub>en)] and [Cu(H-sal<sub>2</sub>en)] polymer films taken on indium tin oxide coated glass electrodes showed broad absorption bands at roughly 425 and 375 nm, respectively, consistent with the proposed polymers. An increase in broadness for the electronic spectra of polymerized transition-metal complexes relative to solution spectra of the parent monomeric complexes has been noted previously.<sup>16,17</sup>

**Solvent Effects and Scanning Electron Microscopy.** Scanning electron micrographs for films prepared in 0.1 M TBAH/CH<sub>3</sub>CN and 0.1 M TBAH/CH<sub>2</sub>Cl<sub>2</sub> are shown in Figure 5. The micrographs reveal that the surface structure consists of small, amorphous balls. Similar micrographs have been reported for other electropolymerized films.<sup>25</sup> Interestingly, a difference in surface morphology was observed for the films prepared in acetonitrile, acetone, and methylene chloride. Extensive aggregation was observed for the polymer films obtained in acetonitrile, while a more uniform surface was found for the films prepared in methylene chloride. Films prepared in acetone showed a level of aggregation between those prepared in acetonitrile and methylene chloride. In in-

terpreting these results, it should be noted that the solvent dependence of the film's morphology may be a consequence of the method used to dry the films and not the polymerization process itself. The drying technique used for these films involves "solvent" exchange between the solvent trapped within the polymer film during polymerization and critical point CO<sub>2</sub>.<sup>16</sup> Aggregation in the films polymerized from polar solvents like acetonitrile may be a result of the lower solubility of that solvent in liquid CO<sub>2</sub>. No long-term structural order was observed for any of the polymer films.

## Discussion

The results of these studies clearly show that oxidative polymerization is a convenient route to surface-modified electrodes based on nickel(II) and copper(II) bis(salicylaldehyde) complexes. The electropolymerizations were carried out by conventional procedures, and the resulting polymer-modified electrodes exhibited electrochemical behavior characteristic of surface-immobilized redox couples. It is noteworthy that the modified electrodes described here were prepared by *direct* polymerization of the bis(salicylaldehyde) complexes. Generally, the preparation of polymer-modified electrodes based on transition-metal complexes requires the synthesis of substituted complexes containing pendant polymerizable groups (e.g., vinyl or pyrrole groups). Given the relative ease with which substituted bis(salicylaldehyde) ligands and their nickel(II) and copper(II) complexes can be synthesized,<sup>12</sup> a wide variety of modified surfaces can be readily prepared. Accordingly, it should be possible to optimize the properties of modified electrodes based on these complexes by varying the substituents on the bis(salicylaldehyde) ligand. For example, while the redox stability of the [Ni(R-sal<sub>2</sub>Y)]-modified electrodes varied little with changes in R and Y, the substituted bis(salicylaldehyde) complexes illustrated in structure II exhibit significantly enhanced redox stabilities.<sup>26</sup>



II: M = Ni, Cu  
X = CH<sub>3</sub>, OCH<sub>3</sub>

Although oxidative polymerization of the nickel(II) and copper(II) bis(salicylaldehyde) complexes is ultimately the result of ligand-localized redox chemistry, the metal redox couple plays an important role in the overall mechanism. The complexes [Co(H-sal<sub>2</sub>en)] and [VO(H-sal<sub>2</sub>en)] are reversibly oxidized in acetonitrile at 0.20 V<sup>27</sup> and 0.47 V<sup>28</sup> vs SSCE, respectively, and show no signs of oxidative polymerization. For these complexes, the metal oxidations occur at much lower potentials than the ligand oxidations, and no evidence for ligand redox chemistry is observed. Oxidation of the nickel(II) and copper(II) bis(salicylaldehyde) complexes occurs at much higher potentials, providing the opportunity for ligand oxidation and subsequent redox chemistry.

(26) Blaho, J. K.; Lewis, J. A.; Goldsby, K. A., unpublished results.

(27) Kapturkiewicz, A.; Behr, B. *Inorg. Chem. Acta* 1983, 69, 247.

(28) Bonadies, J. A.; Butler, W. M.; Pecoraro, V. L.; Carrano, C. J. *Inorg. Chem.* 1987, 26, 1218.

(25) Calvert, J. M.; Peebles, D. L.; Nowak, R. J. *Inorg. Chem.* 1985, 24, 3111.

The oxidative polymerization of phenol and substituted phenols is known to occur by a radical coupling mechanism,<sup>29,30</sup> and we have proposed a related ligand-radical coupling mechanism for the oxidative polymerization of nickel(II) bis(salicylaldehyde) complexes involving the phenolic portion of the salicylaldehyde chelate.<sup>5</sup> Nickel(II) bis(salicylaldehyde) complexes are reversibly oxidized in strong-donor solvents such as *N,N*-dimethylformamide and pyridine, consistent with stabilization of the high-valent nickel(III) oxidation state in these solvents.<sup>5,27</sup> In weak-donor solvents, however, metal oxidation is no longer stabilized relative to ligand oxidation. Electrodes modified in various weak-donor solvents exhibited essentially identical behavior in fresh acetonitrile electrolyte, consistent with the indirect role of the solvent in the polymerization scheme. Oxidation of [Ni(H-sal<sub>2</sub>en)] in acetonitrile is thought to involve initially metal-localized oxidation, followed by internal electron transfer to give the reactive ligand-radical species.<sup>31</sup> It is assumed the oxidative polymerization of the copper(II) bis(salicylaldehyde) complexes occurs by an analogous mechanism, although one cannot rule out the possibility of direct ligand oxidation.

Although it is difficult to resolve the precise nature of the surface redox couple (i.e., metal-localized vs ligand-localized), the voltammetric behavior does provide some information about the relative rates of electron transfer. As seen in Figure 3 for [Ni(H-sal<sub>2</sub>en)], the rate of film growth increases linearly with the concentration of complex, which suggests that the rate-determining step for polymerization at the electrode is not the radical coupling reaction. Instead, electron transfer may be the rate-determining process, which is supported by the linear relationship between cathodic peak current and scan rate. The large peak potential separations and scan rate dependence of  $\Delta E_p$  observed for the surface waves in fresh 0.1 M TBAH/CH<sub>3</sub>CN also suggests slow electron transfer in the [Ni(H-sal<sub>2</sub>en)]-modified electrodes. Unfortunately the [Cu(H-sal<sub>2</sub>en)]-modified electrodes were not sufficiently redox stable to obtain meaningful peak potential separations after the first several scans.

Our interest in the design of modified electrodes based on transition-metal bis(salicylaldehyde) complexes was motivated in part by the rich redox chemistry of these complexes. For example, [Co(H-sal<sub>2</sub>en)] is known to catalyze the insertion of oxygen into organic molecules<sup>10</sup> and the reduction of CO.<sup>11</sup> Furthermore, cobalt(II) bis(salicylaldehyde) complexes reversibly bind dioxygen, both

in solution<sup>32</sup> and in the solid state,<sup>33</sup> suggesting that [Co(R-sal<sub>2</sub>Y)]-modified electrodes might have potential applications for the reduction of dioxygen.<sup>2b</sup> Ironically, the low Co<sup>III/II</sup> couple and reversible redox chemistry that make cobalt(II) bis(salicylaldehyde) complexes attractive as potential redox catalysts prohibit the direct oxidative polymerization of these complexes as a route to surface-modified electrodes. Furthermore, oxidative polymerization of the bis(salicylaldehyde) ligand followed by insertion of cobalt(II) is not a viable approach. The oxidative electropolymerization of nonhindered phenols results in the formation of thin insulating poly(phenyl ether) films on the electrode surface and complete loss of redox activity.<sup>30</sup> Oxidative polymerization of the H<sub>2</sub>(R-sal<sub>2</sub>Y) ligands yielded similar results, presumably due to the formation of analogous poly(phenyl ether) films on the electrode surface. Attempts to insert nickel(II) or copper(II) into these films failed, which is not unexpected given the poor ligating ability of ether oxygens and the probable structural distortion for the chelate backbone upon polymerization. Therefore, unlike ligand systems containing pendant polymerizable groups where the ligand may be first polymerized and then metallated to give the desired modified electrode, the modified electrodes described here must be prepared from the preformed metal bis(salicylaldehyde) complexes. We are currently investigating the demetallation of [Cu(H-sal<sub>2</sub>en)]-modified electrodes as a route to new transition-metal bis(salicylaldehyde) electrodes.

**Summary.** Oxidative polymerization offers a convenient route to modified electrodes based on nickel(II) and copper(II) bis(salicylaldehyde) complexes. The modified electrodes exhibited single reversible redox waves of modest stability in fresh electrolyte solution. The scan rate dependence of  $i_p$  and  $\Delta E_p$ , as well as the linear relationship between concentration and the rate of film growth, suggest slow electron transfer for the surface-bound redox couples. Ongoing studies are aimed at improving the redox stability of the surface waves and extending the preparative methodology to include additional transition-metal ions.

**Acknowledgment.** We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Florida State University Foundation for partial support of this research. We thank Mike Davidson for assistance with the critical point drying and scanning electron micrographs. We also thank Professor Mark Deakin for helpful discussions.

(29) Musso, H. In *Oxidative Coupling of Phenols*; Taylor, W. I., Battersby, A. R., Eds.; Marcel Dekker: New York, 1967; Chapter 1.

(30) (a) Mengoli, G. *Adv. Polym. Sci.* **1979**, *33*, 1. (b) Subramanian, R. V. *Adv. Polym. Sci.* **1979**, *33*, 33.

(31) Goldsby, K. A. *J. Coord. Chem.* **1988**, *19*, 83.

(32) Vogt, L. H., Jr.; Faigenbaum, H. M.; Wiberler, S. E. *Chem. Rev.* **1963**, *63*, 269.

(33) (a) Drago, R. S.; Balkus, K. J., Jr. *Inorg. Chem.* **1986**, *25*, 716. (b) Tsuchida, E.; Nishide, H.; Ohyanagi, M.; Kawakami, H. *Macromolecules* **1987**, *20*, 1907.