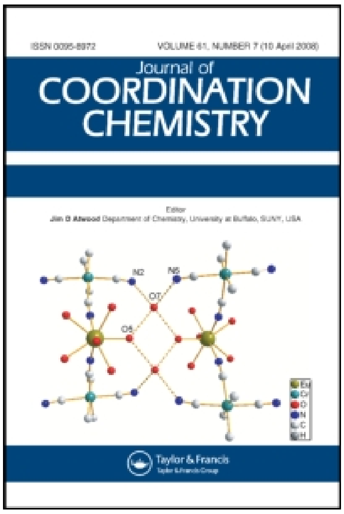

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Nickel(II) complexes with tetraaza macrocycles in the electrocatalytic oxidation of sulfite

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The electrocatalytic oxidation of sulfite (SO_3^{2-}) in basic medium (pH = 10.2) at [Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annuleneH]$^{++}$/glassy carbon (mono-[Ni(II)tmdnTAA]$^{++}$/GC), and poly-[Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza [14]annuleneH]$^{++}$/glassy carbon(poly-[Ni(II)tmdnTAA]$^{++}$/GC) modified electrodes was investigated. Both modified electrodes were characterized by cyclic voltammetry. These modified electrodes show an important catalytic effect for sulfite oxidation mediated by the Ni(III)/Ni(II) redox couple. The potential shifted about 570 mV in cathodic direction with respect to bare Glassy carbon. The amperometric response (I_{pa}) for sulfite oxidation at pH = 10.2 in phosphate buffer or a carbonate buffer with both modified electrodes gives a linear correlation between 0.92–1.8 mM for mono-[Ni(II)tmdnTAA]$^{++}$/GC, and 0.25–1.50 mM for poly-[Ni(II)tmdnTAA]$^{++}$/GC respectively.

Keywords: [Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annuleneH]$^{++}$; Sulfite oxidation; Electrocatalysis; Glassy carbon modified electrodes

1. Introduction

The transformation of sulfur oxoanions ($S_2O_3^{2-}$, $S_4O_6^{2-}$, HSO_3^-, SO_3^{2-}) is a matter of great interest in chemistry and biology [1–7]. The presence of metals in the catalytic transformation of sulfur (IV) oxides plays an important role in environmental atmospheric chemistry (acid rain), as well as in biochemistry. Toxic effects associated with sulfite include asthma, mutagenic or comutagenic effects, and its ability to act as a cocarcinogen [6, 7]. Therefore, the oxidation of SO_3^{2-} is an important reaction in fluegas desulfurization, pollution, and health problems. A different process for absorbing and converting sulfur dioxide must be promoted. Several oxidation studies of sulfite using

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different catalysts, electrocatalysts or photocatalysts have been investigated [8–18]. There is much research related to sulfur oxoanions oxidations using metal porphyrin or metal phthalocyanine complexes as effective catalysts [8–12, 15, 17–19]. In recent years there has been a tremendous demand for low cost, sensitive, selective, and reliable devices that are readily portable for determination of sulfite and SO_2. Chemically modified electrodes (CMEs), have great potential in this respect. Recently, a number of CMEs have been demonstrated for determination of sulfite [20–25], but the development of low cost, sensitive and reliable devices for sulfite determination is a permanent challenge. We have reported the synthesis, spectroscopic, electrochemical, and photochemical behaviour of [M(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annuleneH]$^{++}$ macrocycle complex (M(II) = Ni(II), Cu(II)) [26–28]. These complexes catalyze photoreduction of CO_2 to CO, and also presented very interesting species in the ground and excited states.

This work describes the electrocatalytic oxidation of sulfite by adsorption of monomeric species of [Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14] annuleneH]$^{++}$ (see figure 1) on glassy carbon electrode(mono-[Ni(II)tmdnTAA]$^{++}$/GC), and by electropolymerization of this complex on a glassy carbon electrode(poly-[Ni(II)tmdnTAA]$^{++}$/GC). Both modified electrodes can be used for the determination of sulfite in aqueous solutions at basic pH (10.0–10.2).

2. Experimental

2.1. *Chemicals and electrochemical instrumentation*

All chemicals were of analytical grade and used as provided. Aqueous solutions were prepared from doubly-distilled water, and were deoxygenated for 30 min with pre-purified nitrogen. Buffer solutions for pH = 7.2 to 12.0 were prepared with $H_2PO_4^-/HPO_4^=$ or $HCO_3^-/CO_3^=$, and pH = 13.0 from 0.1 M NaOH aqueous solution. For each experiment fresh solutions were used. pH values were measured with a Cole Palmer model Digi-Sense digital pH meter.

The [Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14]annuleneH]$^{++}$ cation complex (see figure 1) was prepared and characterized as described previously [26]. The molar conductivities in methanol, DMF or CH_3CN solutions indicated 1 : 2 electrolyte where chloride is the anion accompanying the Ni^{2+} complex.

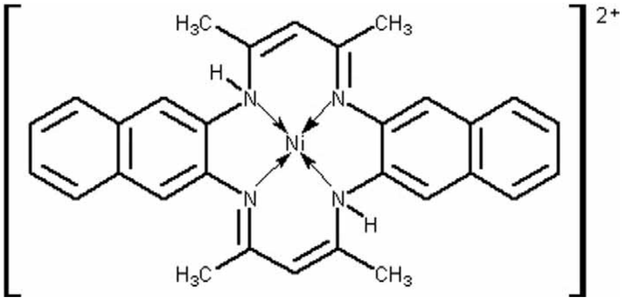

Figure 1. Molecular structure for [Ni(II)-5,7,12,14-tetramethyldinaphtho[b,i]-1,4,8,11-tetraaza[14] annuleneH]$^{++}$ cation complex [Ni(II)tmdnTAA]$^{++}$.

The electrochemical measurements were performed with a Princeton Applied Research Potentiostat/Galvanostat PAR-173, a digital Coulometer PAR-179, coupled to a Universal Programmer PAR-175, and a Graphtec X-Y recorder WX4301.

Cyclic voltammetry experiments were performed using a three-electrode system. A glassy carbon-[Ni(II)dinaphtho tetraaza[14]annulene]$^{++}$ modified electrode was used as working electrode and the auxiliary electrode was a platinum wire. All potentials were measured *versus* a Ag/AgCl/KCl(3M) reference electrode.

Bulk electrolysis experiments were performed for 8 h in an electrolysis cell described in previous work [29]. Analytical test for SO_4^{2-} was performed after each electrolysis experiment [30].

2.2. *Preparation of modified electrodes*

2.2.1. Monomer species of [Ni(II)tmdnTAA]$^{++}$ adsorbed on glassy carbon. The working electrode was glassy carbon with a polytetrafluoroethylene coating, which exposed a disk surface of geometrical area (A) of 0.46 cm^2. The glassy carbon electrode was polished before each experiment with 0.05 µm alumina followed by ultrasonic treatment in distilled water for 2 min. The adsorption of Ni(II) macrocycle complex were achieved by placing one drop of 1 mM solution of the complex in CH_3CN on the electrode surface; and then it was dried at room temperature. The modified electrode was rinsed with doubly-distilled water; and then placed in 0.1 M NaOH aqueous solution and cycled between −0.2 and +0.6 V *versus* Ag/AgCl as shown in figure 2. The Epa for Ni(II) to Ni(III) oxidation in macrocycle complexes is a function of the pH, as reported by Bedioui *et al.* [31]. For instance, in our case the Epa at pH = 13 is 0.55 V, and at pH = 10.2 is 0.83 V *versus* Ag/AgCl.

The surface concentration of catalyst (Γ) was calculated from the electrical charge of this peak in figure 2 assuming $n = 1$ using $\Gamma = Q(n\mathrm{FA})^{-1}$ and gave a value of 1.05×10^{-7} mol cm^{-2}. This indicates that the modified film has several molecular

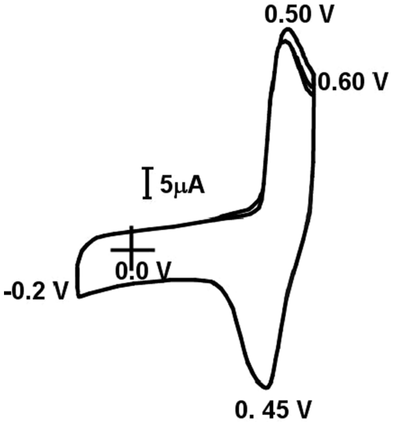

Figure 2. Cyclic voltammogram for [Ni(II)tmdnTAA]$^{++}$ – GC modified electrode in 0.1 M NaOH aqueous solution, until steady state response.

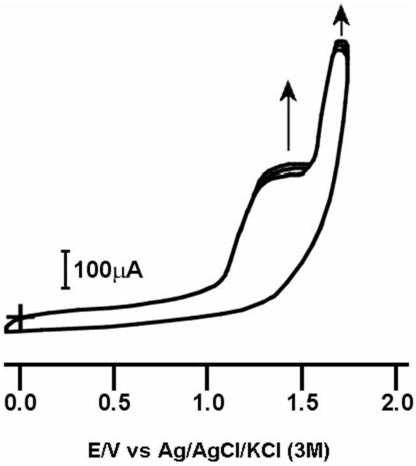

Figure 3. Cyclic voltammogram for electropolymerization of [Ni(II)-tmdnTAA]$^{++}$ onto glassy carbon (GC) between −0.10–1.82 V *vs.* Ag/AgCl/KCl (3 M).

monolayers of the adsorbed complex on the glassy carbon electrode. This modified electrode is stable for one week in air at room temperature.

2.2.2. Oxidative electropolymerization of [Ni(II)tmdnTAA]$^{++}$ over glassy carbon electrode. The poly-[Ni(II)tmdnTAA]$^{++}$ films were obtained by oxidative electropolymerization onto a glassy carbon working electrode from dry CH_3CN solutions containing 1 mM of Ni(II) cation complex and 0.1 M $(C_2H_5)_4NClO_4$ by cycling the glassy carbon working electrode potential repetitively between −0.10 and +1.82 V *versus* Ag/AgCl, as shown in figure 3. The increase of the intensity in each cycle for the two ligand center oxidation waves at 1.23 and 1.60 V *versus* Ag/AgCl arises because of growth of conducting polymer film. This behaviour is similar to that observed by Deronzier and Marques [32] for the oxidative electropolymerization of Ni(II) and Cu(II) dibenzo 14 annulene complexes. They reported two irreversible oxidation peaks at 0.56 and 1.14 V *versus* ECS corresponding to γ–γ and γ'–γ' coupling of the diiminate backbone of the oxidized species.

3. Results and discussion

Electro-oxidation of sulfite on the modified electrodes.

1. *General conditions*
   Figure 4 shows the multiple scan cyclic voltammogram for the poly-[Ni(II)tmdnTAA]$^{2+}$ modified electrode in the presence of sulfite. After 50 potential cycles the variation of I_{pa} is ±3%. Therefore, the CME did not change after several potential cycles in the electrocatalytic medium. After that, all experiments with modified electrodes were performed in fresh and stirred solutions. The pH value (10.0–10.2) is obtained in phosphate or a carbonate buffer. For the catalytic current

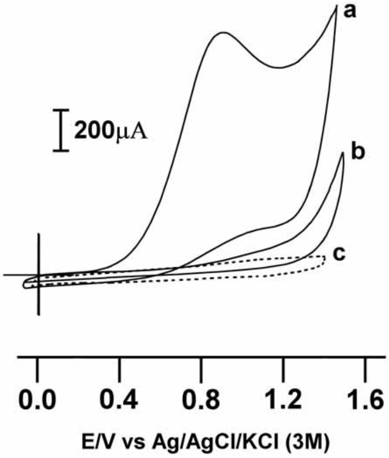

Figure 4. Cyclic voltammogram for sulfite oxidation obtained on (a) poly-[Ni(II)tmdnTAA]$^{++}$/GC modified electrode, (b) bare glassy carbon, and (c) CME without sulfite at pH = 10.2 carbonate buffer solution.

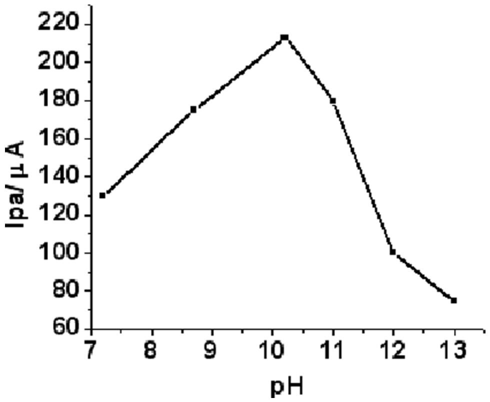

Figure 5. I_p *vs*. pH for monomeric [Ni(II)tmdnTAA]$^{++}$/GC(mono-[Ni(II)tmdnTAA]$^{++}$/GC) modified electrode.

peak determinations the background current from the modified electrode, in buffer solution, 0.1 M $(C_2H_5)_4NClO_4$ was subtracted.

2. *Monomer [Ni(II)tmdnTAA]$^{++}$ complex adsorbed onto glassy carbon*

Figure 5 shows a plot of I_{pa} (μA) *versus* pH for the catalytic oxidation of 1 mM sulfite solution. A maximum peak current is obtained at phosphate buffer solution of pH 10.0–10.2. Therefore this range is the best for studying sulfite oxidation over this modified electrode.

Figure 6 shows the voltammetric response of the modified electrode with the monomer complex in the presence of 1×10^{-3} M sulfite at phosphate buffer solution (pH = 10.2) at different scan rates, which indicates that the E_{pa} shifts in a positive direction when the scan rate is increased indicating that the electron transfer process is slow compared to the rate of potential scan. The insert shows a plot of E_p *versus* $v^{1/2}$ (where v is the potential scan rate) the linear plot suggests a diffusional process

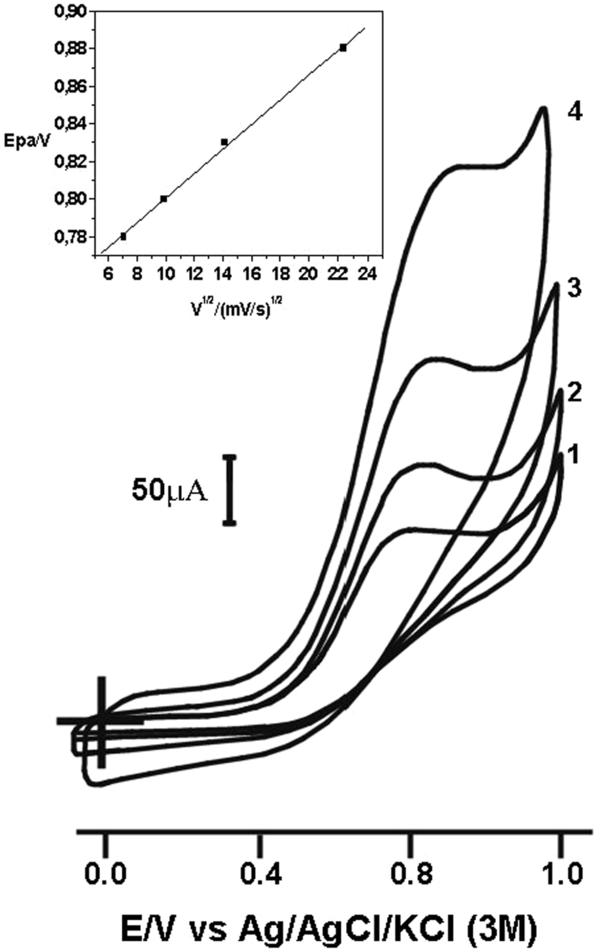

Figure 6. Cyclic voltammetry for sulfite oxidation over mono-[Ni(II)tmdnTAA]$^{++}$/GC modified electrode at pH = 10.2 at (1) $-50\,\mathrm{mV\,s^{-1}}$, (2) $-100\,\mathrm{mV\,s^{-1}}$, (3) $-200\,\mathrm{mV\,s^{-1}}$, (4) $-500\,\mathrm{mV\,s^{-1}}$ scan rates. The inset show the plot of the anodic peak potential (E_{pa}) *vs.* of the square root of scan rate ($v^{1/2}$).

of sulfite from bulk solution to CME surface. This electrode presents the catalytic oxidation peak (E_{pa}) at +0.83 V *versus* Ag/AgCl/KCl(3M) at $200\,\mathrm{mV\,s^{-1}}$, which corresponds to the Ni(III)/Ni(II) couple in the tetraazamacrocycle as shown in figure 6.

Figure 7 shows a plot of the anodic peak current, I_{pa}, *versus* sulfite concentration for cyclic voltammetry at the modified electrode, which is linear in the 0.9 to 1.5 mM concentration range. The detection limit (taken as the concentration that gives a signal equal to blank plus three times its standard deviation, calculated from calibration curve) was 0.74 mM.

3. *Electropolymerization of [Ni(II)tmdnTAA]$^{++}$ onto glassy carbon*

The voltammetric response of the electrode modified with poly-[Ni(II)tmdnTAA]$^{++}$ in the presence of 0.86 mM sulfite with a carbonate buffer solution (pH = 10.2) in comparison to voltammetric response for GC-CME without sulfite, and bare

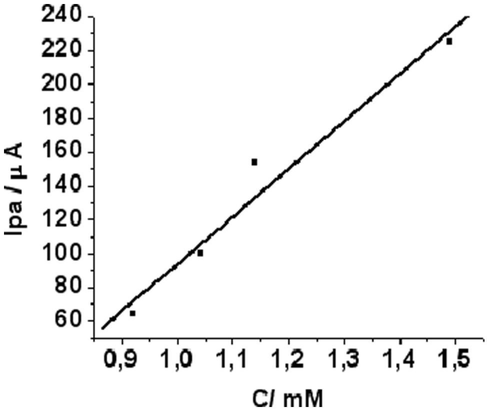

Figure 7. Plot I_p *vs.* sulfite concentration for mono-[Ni(II)tmdnTAA]$^{++}$/GC modified electrode at pH = 10.2 phosphate buffer solution.

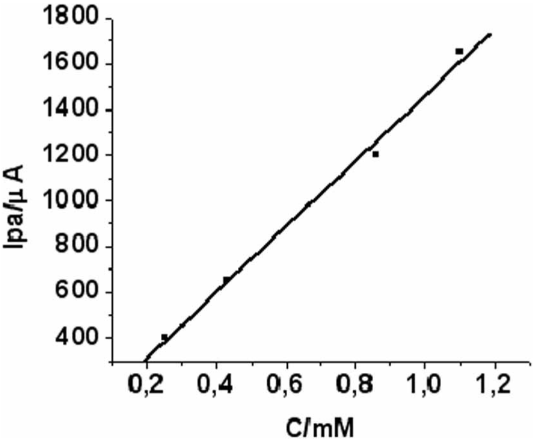

Figure 8. Calibration curve of I_p *vs.* sulfite concentration for poly-[Ni(II)tmdnTAA]$^{++}$/GC modified electrode at pH = 10.2 carbonate buffer solution.

GC in presence of sulfite is shown in figure 4. The catalytic effect of CME (0.83 V *versus* Ag/AgCl) shifted the sulfite oxidation potential 570 mV to the cathodic region with respect to bare GC (1.4 V *versus* Ag/AgCl) (see figure 4a, b). For equal sulfite solution concentration the modified electrode by electropolymerization shows about sixteen times higher current (I_{pa}) compared to that corresponding to the modified electrode with monolayers of the complex. The much higher response of the modified electrode with the polymerized complex seems to indicate that the polymeric film is porous, exposing a much higher area than monomeric film.

Figure 8 shows the calibration curve I_p (µA) *versus* sulfite concentration for the electropolymerized [Ni(II)-tmdnTAA]$^{++}$ onto glassy carbon at pH = 10.2, which is linear between 0.2 to 1.2 mM. From the calibration curve slope a higher amperometric sensitivity is observed, compared with non-electropolymerized modified electrode.

4. Conclusions

The $[Ni(II)tmdnTAA]^{++}$-glassy carbon modified electrodes — stable for several weeks in air and at room temperature (ca 15°C) — catalyze the oxidation of sulfite via adsorbed or electropolymerized layers mediated by the Ni(III)/Ni(II) couple and exhibit high catalytic activity for the electrochemical oxidation of sulfite compared with the unmodified glassy carbon electrode. They shifted the sulfite oxidation potential 540 mV with respect to unmodified GC electrode.

The anodic peak current Ipa for voltammetric behavior of mono- $[Ni(II)tmdnTAA]^{++}$/GC, and poly-$[Ni(II)tmdnTAA]^{++}$/GC modified electrodes changes linearly with sulfite concentration in the 0.9–1.5 and 0.2–1.2 mM range studied. The MCE studied has a very good response for sulfite oxidation in the pH range 9–11 but is small for real sample analysis. These modified electrodes can have applications in the analysis of sulfite in basic media when incorporated into an amperometric detector in a flow or stirred system. Further studies for improving the pH range, the detection limit, and selectivity in sulfite analysis using poly-$[Ni(II)tmdnTAA]^{++}$-glassy carbon modified electrode as an amperometric detector, are currently in progress.

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