



Interaction of amines with electrodes modified by polymeric complexes of Ni with salen-type ligands



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ABSTRACT

Chemically modified electrodes based on complexes of transition metals with N,N'-ethylenediamine (salicylimine) (salen) type ligands are reported to act as redox mediators due to axial coordination of exogenous ligands to metal atom in oxidized form of complex. Thus such electrodes can be used as amperometric and voltammetric detectors of various compounds. However, effects of ligand structure and ligand-analyte specific interactions on the electrochemical response of said complexes have not been studied yet for organic analytes. In this article we demonstrate that some aromatic amines can interact with salen-type ligands by several routes, depending on the ligand and amine structure. It leads to the ligand polarization, and thus to the unique shape of voltammetric curves of chemically modified electrodes, based on polymeric salen complexes, immersed in amines solutions. Such feature allows using the electrodes as sensors for molecular recognition. The same electrodes can act as electron transfer catalysts of the amines oxidation, and may be applicable to the quantitative analysis of amines with the detection limit about $10 \mu\text{mol l}^{-1}$.

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1. Introduction

Square-planar complexes of transition metals with N,N'-ethylenediamine (salicylimine) (salen) type ligands ([M(Schiff)]) are known as effective electron transfer catalysts and redox mediators due to possibility of exogenous ligands axial coordination to the metal center of the oxidized form of the salen complex [1–4]. This makes chemically modified electrodes based on [M(Schiff)] polymers and thin films promising systems for amperometric and voltammetric detection of various compounds, such as nitric oxide [5], pyridine [6], pyridoxine [7], cysteine [8,9], and dipyrone [10]. Previous studies have largely been focused on metal complexes with unsubstituted salen ligands. However, it is well known that oxidation of salen complexes is ligand-based, at least at the first oxidation step [2,11–13]. This provides for flexible fine-tuning of electronic properties of salen-based materials via introducing

various functionalities in the imine bridge and aldehyde moiety of the ligand. Electrochemical properties of modified electrodes based on polymerized [M(Schiff)] complexes strongly depend on the electronic density distribution in the ligand structure, so the oxidation potentials and the shape of cyclic voltammograms are different for complexes with different ligand structure [2,13–15]. Moreover, the shape of voltammograms depends on the ligand polarization caused by interaction of charged species, such as metal ions, with specific functionalities of the ligand [11]. It makes the polymeric salen complexes candidate materials for ion recognition; their application for detection of Ba^{2+} , Li^+ , K^+ , Mg^{2+} and other ions have been reported [11,16–18]. However, the effect of ligand polarization caused by interaction of the polymeric complex with neutral molecules has so far received little attention. To study this effect, we have chosen several salen-type complexes (Fig. 1) with different substituents in the imine bridge and aldehyde moiety electropolymerized on the surface of glassy carbon electrodes. As possible analytes we have selected a set of aromatic amines comprising aniline, benzylamine, and dimethylaniline. These amines are widely used in chemical industry;

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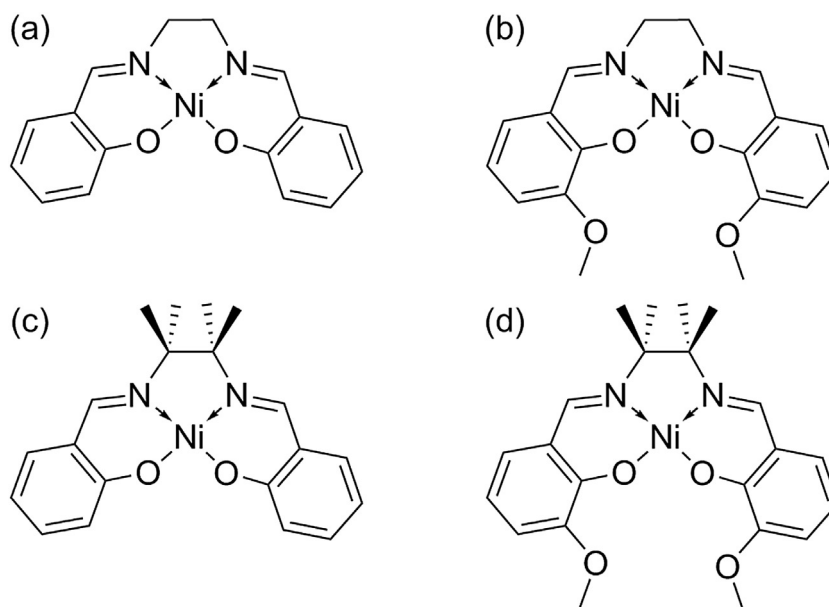


Fig. 1. Structures and abbreviations of [Ni(Schiff)] complexes. (a) [Ni(Salen)], (b) [Ni(CH₃OSalen)], (c) [Ni(Saltmen)], (d) [Ni(CH₃OSaltmen)].

despite the apparent similarity, they differ significantly in electronic structure and nitrogen atom environment.

2. Experimental

All reagents were purchased from Aldrich and used without further purification. Monomers [Ni(CH₃OSalen)], [Ni(Salen)], [Ni(CH₃OSaltmen)] and [Ni(Saltmen)] (Fig. 1) were synthesized by standard methods [19]. A 0.1 M solution of tetraethylammonium tetrafluoroborate N(Et)₄BF₄ in acetonitrile (CH₃CN) was used as supporting electrolyte. During the analysis amines (aniline, benzylamine, dimethylaniline) were added to electrolyte solution by mechanical pipette to achieve a predetermined concentration. Voltammetric measurements were performed in still solution; AUTOLAB RDE modulus (Eco Chemie, Netherlands) was used for amperometric analysis on rotating disc electrode. Autolab PGSTAT30 (Eco Chemie, Netherlands) was used for the synthesis of films and electrochemical measurements. The measurements were performed in a three-electrode cell consisting of a glassy carbon working electrode (0.07 cm²), platinum plate (1 cm²) as the auxiliary electrode, and MF-2062 (BASi, USA) reference electrode filled with 0.1 M AgNO₃ solution in acetonitrile. Potential of the latter electrode was 0.4 V relative to the saturated aqueous silver chloride electrode (Ag|AgCl|KCl sat.). All values of potentials in the present work are hereinafter reported vs (Ag|AgCl|KCl sat.) electrode.

Polymers were synthesized as thin films on electrode surface in a potentiodynamic cycling mode by scanning the potential between 0 V to 1.2 V in a solution containing 10⁻³ M [Ni(Schiff)] and N(Et)₄BF₄ in acetonitrile for 5 cycles with a scan rate of 50 mVs⁻¹. This method allows one to obtain polymeric films with reproducible electrochemical properties: the currents in the voltammograms of any two different samples of the same composition differ by less than 1%. Electrochemical properties of the modified electrode are quite stable if amine concentration does not exceed 100 μM. However, at higher concentrations of amines graduate decrease of voltammetric response from cycle to cycle was observed. Due to this reason, in order to obtain reliable data for each voltammetric measurement in the presence of a given amine a new polymer film was used, which was preliminarily cycled in

supporting electrolyte until stabilization of voltammetric curve (usually 5 cycles). First cycles of voltammograms, obtained after amine addition, were analyzed.

Installation for microgravimetric research consists of QCM200 Quartz Crystal Microbalance Analog Controller and QCM25 Crystal Oscillator (Stanford Research Systems, USA) with a sensitivity factor of 56.6 × 10⁶ Hz g⁻¹ cm² (i.e., 1 Hz corresponds to 17.7 ng cm⁻²). Quartz piezoelectric crystal sprayed with a layer of platinum on an area of 1.37 cm², used for microgravimetric measurements, was also connected to potentiostat as a working electrode, allowing polarization of the polymer film in the three-electrode cell.

Quantum chemical DFT calculations were carried out for complexes of [Ni(CH₃OSalen)]⁰ and [Ni(CH₃OSalen)]⁺ with two molecules of amines (aniline, benzylamine, and dimethylaniline). Charged and uncharged species were used to model oxidized and reduced forms of poly[Ni(CH₃OSalen)] films, respectively. Full geometry optimizations were carried out using B3LYP hybrid functional [20–22] followed by vibrational analysis and calculation of thermochemical parameters. For nickel atoms LANL2DZ effective core potential and basis set [23,24] were chosen, for all other atom types 6-31G(d,p) basis set was used. Medium effects were taken into account by employing the integral equation formalism for the polarizable continuum model (IEF-PCM) [25] with acetonitrile as solvent. All calculations were carried out using Gaussian 09 [26].

3. Results and discussion

3.1. Electrochemical measurements

Electrochemical oxidation of the amines was studied on bare glassy carbon electrode immersed in 10⁻³ M acetonitrile solution of each amine. Increase of the current in the anode region, corresponding to amine oxidation, was observed (Fig. 2). Dimethylaniline readily oxidizes on this electrode, demonstrating the highest peak current (46 μA) and the lowest oxidation potential (0.8 V). For aniline the oxidation current is slightly lower (40 μA), and the oxidation potential is more positive (1 V). Voltammetric curve of benzylamine oxidation contains no pronounced peaks in

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