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Redox processes in the solution of Ni(II) complex with *salen* type ligand and in the polymer films

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Abstract

The investigations of oxidation processes of (\pm)-*trans*-*N,N'*-bis(3,5-di-methylsalicylidene)-1,2-cyclohexanediaminenickel(II) [Ni(salcn(2Me))] and ligands with Me substituents attached in *o*- (H₂salcn(Me)) or *o*- and *p*- positions (H₂salcn(2Me)) in CH₂Cl₂ were performed by CV, exhaustive electrolysis, UV VIS NIR and IR methods. H₂salcn(Me) and H₂salcn(2Me) are irreversibly oxidized to phenoxyl radicals and bis-phenoxyl radicals. The hydrogen bonds stabilize both forms of the oxidized ligands. [Ni(salcn(2Me))] is oxidized in three steps. The overall process involves ligand and partially nickel ion. In the I step, [Ni(salcn(2Me))] is oxidized to phenoxyl radical complex, which is well stabilized by the nickel ion. In the II step the oxidation is realized by forming bis-phenoxyl radicals and phenoxonium cations complexes. The films derived from *salen* complexes deposited on the Pt electrode surface (*poly*[Ni(salcn)], *poly*[Ni(salcn(Me))], *poly*[Ni(salcn(Bu))]) were obtained as a result of anodic electropolymerization processes. On the basis of FTIR ATR spectroscopy and CV experiments, the relationship of the polymer films structures, charge transport and the potential range of the applied electrosynthesis was shown.

Keywords: Schiff base, phenoxyl radical, electropolymerization, nickel, conducting polymer

1. Introduction

Complexes of *d*-block elements with donor ligands containing O and / or N atoms are widely studied for their use in analysis, catalysis and electrocatalysis [1]. Our interests are focused on complexes with N₂O₂ ligands. Many of them, in the form of a polymer, are used in heterogeneous electrocatalysis [2]. Hence, it is important to analyze the electrode processes occurring on the polymer / electrode interface and many works are devoted to this problem [3-8]. Such polymers are usually formed by anodic electropolymerization. Audebert *et al.* and Timonov *et al.* demonstrated a mechanism based on central ion oxidation [3, 4], Freire *et al.* proposed mechanism based on ligand oxidation [5-7], while Dahm *et al.* [8] proposed a complex

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