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Characterization of nickel tetrahydroxy phthalocyanine complexes and the electrocatalytic oxidation of 4-chlorophenol: Correlation of theory with experiments

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ABSTRACT

This work reports on the use of nickel(II) tetrahydroxy ($NiPc(OH)_4$) and (*poly*-$Ni(OH)Pc(OH)_4$) phthalocyanine complexes as films on ordinary poly graphite electrode (OPGE) for the electrochemical oxidation of 4-chlorophenol (4-CP). The $NiPc(OH)_4$ film was electrotransformed to $Ni(OH)Pc(OH)_4$ film in aqueous 0.1 M NaOH solution to the ‘O–Ni–O oxo’ bridge form. The result showed that the $Ni(OH)Pc(OH)_4$ film on OPGE was more electroactive in terms of increase in current and less catalytic in terms of potential compared to the adsorbed $NiPc(OH)_4$ on OPGE. The reactivity of the two molecules was explained by theoretical calculations. The energies of the frontier orbitals of $NiPc(OH)_4$, $Ni(OH)Pc(OH)_4$ and 4-chlorophenol were calculated using density functional theory (DFT) method. The inter molecular hardness (η) and donor–acceptor hardness (η_{DA}) of $Ni(OH)Pc(OH)_4$, $NiPc(OH)_4$, $Ni(OH)Pc(OH)_4$/4-chlorophenol and $NiPc(OH)_4$/4-chlorophenol were estimated. The $Ni(OH)Pc(OH)_4$, showed stronger interaction with 4-chlorophenol than $NiPc(OH)_4$. DFT method was also used to model IR and Raman spectrum of $H_2Pc(OH)_4$ and $NiPc(OH)_4$.

1. Introduction

Over the years a huge number of different metallophthalocyanines (MPcs) have been produced and found their application in various fields such as, synthesis of carbon nanotubes [1–3], nonlinear optics [4] and solar cells [5]. Metallophthalocyanines are also well known electrocatalysts for the oxidation of a variety of analytes including chlorophenols [6–8]. The electronic structures of MPcs are known to have a strong effect on their electrocatalytic activity. Theoretical interpretation of MPcs electronic spectra has been a subject of great interest for a long time [9–11]. In the past calculations which made use of semi-empirical methods, with questionable accuracy, were used. More recently more accurate high level density functional theory (DFT) calculations are used [12–14]. Global and local reactivity of MPc complexes involved in electrocatalytic processes have been predicted by use of DFT methods [15–17]. In this work, DFT calculations were carried out in order to predict the effect of OH substituents on the infrared (IR) and Raman spectra of unmetalated tetrahydroxy phthalocyanine ($H_2Pc(OH)_4$) and nickel tetrahydroxy phthalocyanine ($NiPc(OH)_4$) complexes. The OH ligand was chosen for its simplicity and electron donating nature (making the molecule to be easy to oxidize, hence a potentially good electrocatalyst for oxidation of 4-chlorophenol). Density functional theory (DFT) calculations were carried out in order to describe the molecular structure, atomic charges, IR and Raman spectra of these complexes.

Chlorophenols constitutes a major class of organic pollutants that contaminate the ecosystem and accumulate in the food chain [18–20]. Unmodified electrodes such as glassy carbon, platinum (Pt) and gold have been used for electro-oxidation of chlorophenols but they showed instability towards electrode fouling [21–26].

Electrodes modified with Ni macrocycles such as Ni porphyrin and NiPc derivatives [8,27,28] have been shown to be successful in preventing fouling of the electrode. It has been observed that the nature of the ring substituents of the Ni macrocyclic complexes affects the stability of the modified electrodes [8]. Hence extending the range of Ni macrocyclic compounds for chlorophenol oxidation is important.

In this work we present the electro-oxidation of 4-chlorophenol (4-CP) on ordinary poly graphite electrode (OPGE) coated with films of adsorbed $NiPc(OH)_4$ which was polymerised (in 0.1 M NaOH) to form (*poly*-$Ni(OH)Pc(OH)_4$) containing Ni–O–Ni bridges. The concept of donor–acceptor hardness (η_{DA}) [16,17] is used to explain the reactivity of electrodeposited $NiPc(OH)_4$ and films of *poly*-$Ni(OH)Pc(OH)_4$ on OPGE electrode for catalysis of 4-cholorophenol, assuming that the distance is kept constant between the $NiPc(OH)_4$, $Ni(OH)Pc(OH)_4$ and the 4-chlorophenol.

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