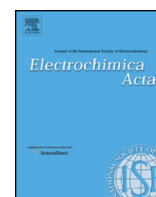


Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electactaELECTROCHEMICAL BEHAVIOR OF PILLAR[5]ARENE ON GLASSY CARBON ELECTRODE AND ITS INTERACTION WITH Cu^{2+} AND Ag^+ IONSV.A. Smolko^a, D.N. Shurpik^b, R.V. Shamagsumova^a, A.V. Porfireva^a, V.G. Evtugyn^c, L.S. Yakimova^b, I.I. Stoikov^b, G.A. Evtugyn^{a,*}^a Analytical Chemistry Department of Kazan Federal University, Kremlevskaya, 18, 420008 Kazan, Russian Federation^b Organic Chemistry Department of Kazan Federal University, Kremlevskaya, 18, 420008 Kazan, Russian Federation^c Interdisciplinary Center for Analytical Microscopy of Kazan Federal University, Kremlevskaya, 18, 420008 Kazan, Russian Federation

ARTICLE INFO

Article history:

Received 25 August 2014

Received in revised form 1 October 2014

Accepted 2 October 2014

Available online 8 October 2014

Keywords:

electrochemical sensor
pillar[5]arene
mediated electron transfer
cyclic voltammetry
self-aggregation

ABSTRACT

The electrochemical behavior of pillar[5]arene (P[5]A) and of its reaction products with Ag^+ and Cu^{2+} ions has been investigated using cyclic voltammetry, optical methods and transmission electron microscopy (TEM). Stepwise oxidation of hydroquinone units of P[5]A molecule is guided by self-assembling and acid–base interactions. From one to three hydroquinone units per P[5]A molecule are oxidized depending on the measurement conditions. The deposition of P[5]A on glassy carbon electrode (GCE) partially blocks the electron transduction. Interfering influence of dissolved oxygen can be partially eliminated by the use of carbon black as immobilization matrix. The reaction of P[5]A with silver ions results in formation of most stable form with three benzoquinone and two hydroquinone units stabilized by quinhydrone-like structure. The Ag nanoparticles formed in the reaction retain electron transduction with the electrode due to involvement of shielding P[5]A molecules. Similar reaction with Cu^{2+} ions does not lead to stable products because of the formation of Cu_2O particles detected by UV spectroscopy and TEM. Possible analytical applications of the materials obtained were proved by electrocatalytic reduction of hydrogen peroxide and mediated oxidation of thiocholine as model systems. In both cases, high sensitivity and wide range of the concentration determined were shown.

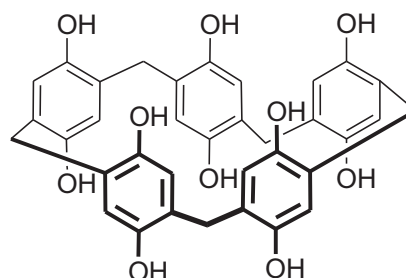
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1. Introduction

Phenolic compounds are widely used in electroanalytical chemistry as mediators of electron transfer and matrices for immobilization of other redox active species and biomolecules [1,2]. Although some substituted phenols tend to oxidation followed by electrode fouling [3], they can be involved in electron transduction by adsorption on solid electrodes [4–6], substitution of polymeric modifier [7], and involvement in the self-organized layers [8] or carbon paste [9]. The interest to the electrochemistry of phenolic compounds is also related to the model investigations of complex electrode reactions complicated with the H^+ transfer and competitive chemical steps of oxidation/dimerization [10–12]. Substituted phenols are used as industrial reagents in the production of rubber, dyes, plastics, pharmaceuticals, and cosmetics [13]. Some of them like dopamine or l-DOPA are known as metabolites and neurotransmitters which play significant role in biochemical reactions of living beings [14]. Thus the use of electrochemical methods directed

to the application and investigations of novel multifunctional phenolic compounds is important in terms of their usability in electrochemical sensors and biosensors [15,16] and monitoring of industrial wastes in pharmacy and clinical chemistry [17–19] and of the surface waters [20].

P[5]A (1), a representative of [1n]paracyclophanes, was synthesized in 2008 by T. Ogoshi et al. from permethylated derivative obtained in one step from commercially available chemicals [21].



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