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ELECTROCHEMICAL INVESTIGATION OF IMIDAZOL AZO CHROMOTROPIC ACID AND ITS Pd(II) COMPLEX

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Abstract

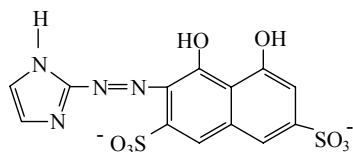
The electrochemical behaviour of 1,8-dihydroxy-2-(imidazol-2-ylazo)-naphthalene-3,6-disulphonic acid (IACA) and its complex with Pd(II) was investigated using cyclic voltammetry. Experiments were performed in the concentration range from $5 \times 10^{-6} \text{M}$ to $4.8 \times 10^{-4} \text{M}$ of IACA. Linear dependence of current intensity vs. IACA concentration was obtained in the investigated concentration range. According to the obtained results, process is controlled by diffusion.

Introduction

Azo compounds are among the most profoundly explored classes of organic compounds both from theoretical and practical viewpoints [1]. The power of cyclic voltammetry results from its ability to rapidly provide considerable information of redox processes, the kinetics of heterogeneous electron transfer reactions or adsorption processes [2]. The aim of this study was to investigate the electrochemical behaviour of IACA and its complex with Pd(II) using different electrochemical conditions. It is presented here the preliminary results obtained with glassy carbon (GCE) and carbon paste electrodes (CPE). Pd(II)-IACA complex was investigated beforehand by using of spectrophotometric methods [3].

Experimental

IACA (Scheme 1) was synthesized as described previously [4]. Cyclic voltammetry experiments were performed using a modular electrochemical system (BAS 100). A GCE was used as a working electrode; with an Ag/AgCl and a Pt coil as the reference and auxiliary electrodes, respectively. Before each electrochemical step, the solutions were deoxygenated by purging with pure nitrogen. GCE and blank electrode for the CPE



Scheme 1.

were supplied by BAS Inc. CPE was prepared by mixing of IACA and carbon powder with paraffin oil in an 80:20 (m/m) mass ratio until a homogeneous paste was obtained. The pastes were packed into the electrode and smoothed until a shiny, smooth surface was obtained. The blank CPE was prepared in the similar way without adding the modifier.

Results and Discussion

All experiments were carried out in quasi-isothermal conditions, at room temperature. Scan rates in the range from 25 to 200 mV/s were used. The potential range in which voltammograms were recorded was between 0 and -1.2 V. The supporting electrolyte was Britton–Robinson buffer (pH 4). Cyclic voltammograms, recorded for IACA concentrations in the range from 5×10^{-6} M to 4.8×10^{-4} M, with GCE as a working electrode at scan rate 100 mV/s are presented on Fig. 1.

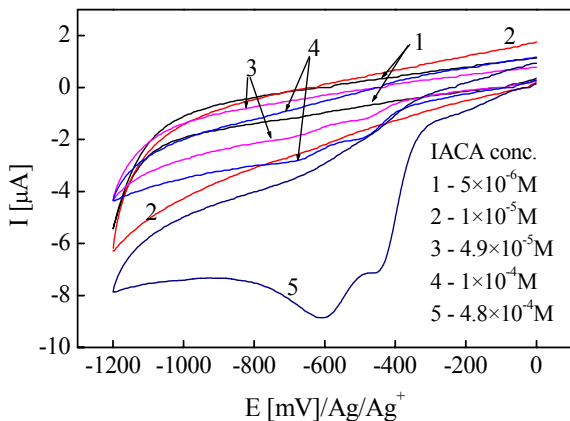
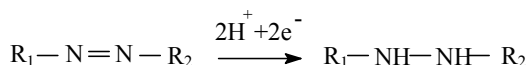


Figure 1. Cyclic voltammograms of IACA obtained at scan rate 100 mV/s on CPE.

As expected, the reduction curves confirmed the linear relationship between the current intensity and IACA concentrations. Two reduction peaks have been observed in this potential range at -600 and -450 mV for IACA concentration 4.8×10^{-4} M. According to Refs. [5,6] these peaks could be attributed to the following processes on the level of azo group:



and further, two electrons participate in the reduction to the corresponding amines.

Table 1. Electroanalytical data regarding the electrochemical behaviour of investigated substances (scan rate 50 mV/s)

Substance	E_{red}^1 [V/Ag/Ag ⁺]	I_{red}^1 [μA]	E_{red}^2 [V/Ag/Ag ⁺]	I_{red}^2 [μA]
IACA	-0.51	-0.86	-0.86	-3.85
Pd(II)	-1.10	-371.29	-0.85	-259.00
IACA : Pd	-1.05	-429.82	-0.90	-158.65

¹ glassy carbon electrode

² carbon paste electrode (unmodified)

The regression equation line for the IACA concentration range from 5×10^{-6} M to 4.8×10^{-4} M was $I = (0.01 \times C_{IACA} + 0.36)$ where I is in μA and C_{IACA} is in $\mu mol/dm^3$ ($r^2 = 0,99$) and allow the determination of IACA with good results. The reduction potentials for IACA, Pd and their complex are given in Table 1.

Cyclic voltammograms obtained for electrochemical system with GCE as working electrode for $4.9 \times 10^{-5} \text{M}$ Pd-IACA complex at different scan rates is presented on Fig. 2.

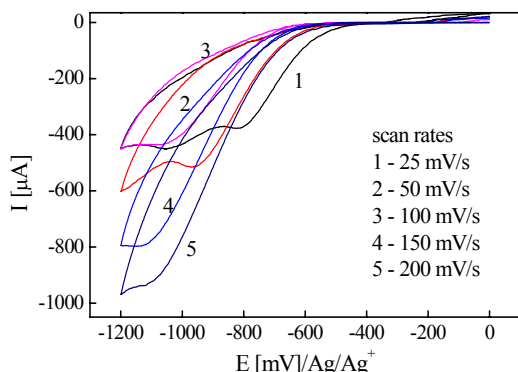


Figure 2. Cyclic voltammograms obtained for $4.9 \times 10^{-5} \text{M}$ Pd-IACA complex at different scan rates, on GCE.

As we see from Fig.2 the peak potentials shift toward negative values with increasing sweep rate, which indicates that at lower overvoltages the reduction is controlled by electron transfer process. Consequently, the second cathodic peak shifts out of range of potential axis at sweep rates higher than 150 mV/s. For the first cathodic peak, linear dependence of peak current on square root of sweep rate was evidenced, which indicates that at high overvoltages the reduction process becomes diffusion controlled.

Conclusion

IACA and its Pd(II) complex may be reduced on glassy carbon and carbon paste electrodes, respectively. The reduction is two-step quasireversible process. The peak current was found to depend linearly on concentration, for IACA/CPE, and on square root of sweep rate, for IACA-Pd(II)/GCE.

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