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Effect of copper ions on voltammetric signals of aminopurines at a carbon electrode

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Abstract

Electrochemical oxidations of aminopurines (adenine–Ade, 2–aminopurine, 2AP, 2,6–diaminopurine, 2,6–DAP) and their complexes with Cu(I) on carbon electrodes (pencil–PeGE) were investigated by means of linear sweep voltammetry (LSV) and elimination voltammetry with linear scan (EVLS). We found that the Cu(I)–purine complex was formed not only by aminopurines but also by purine. On the other hand the complex is not formed in the case of imidazol or cytosine. The results showed that carbon electrodes in connection with EVLS can be an excellent prototype for cheap and fast working sensor for aminopurines in the presence of copper.

Keywords: Copper, voltammetry, aminopurines

Introduction

Anodic signal of Ade and guanine on the solid carbon electrode was studied and described in details by Dryhurst (Dryhurst 1977). The oxidation involves electrons exchange at carbon C2, C8 and N7 (peak Ox_{Ade}, potential about 1.2 V). Copper ions Cu(I) give an additional oxidation voltammetric peak (peak Ox_{com}) with simultaneous enhancement of peak Ox_{Ade} (Jelen et al. 2004; Shiraishi and Takahashi 1993). The former peak appeared at less positive potential (ca. 0.4 V) due to the re–oxidation of Ade–Cu(I) complex, which had been formed at electrode at sufficient starting potential and accumulation time. In this study, we use simple transfer technique for the electrochemical analysis of Ade and some purine derivatives in the presence of Cu(II) in connection with elimination voltammetry (Trnkova and Dracka 1996, Trnkova 2007).

Materials and Methods

Voltammetric measurements (LSV) were performed with an AUTOLAB analyzer (EcoChemie, The Netherlands) connected with a VA–Stand 663 (Metrohm, Zurich, Switzerland). A standard cell with three electrodes was used. The working electrode was a PeGE with the surface area of 1.67 mm^2 (Tombow 05 HB, Japan). The electrode Ag/AgCl/KCl (3 M) as a reference electrode and platinum wire as an auxiliary electrode were used. Three LSV curves were measured at the same experimental conditions for three scan rates and were taken into EVLS procedure.

Results and Discussion

Using LSV we studied selected aminopurines (Ade, 2-AP and 2,6-DAP) on PeGE . In the absence of Cu(II) ions Ade, 2-AP and 2,6-DAP yielded small oxidative signals. The essential difference at these substances was observed when monovalent copper was generated on the electrode. Aminopurines with Cu(I) form a complex which is responsible fora new oxidative signal (Ox_{Com}) and for enhanced signals of corresponding aminopurines. The Fig. 1a and Fig. 1b show LSV and EVLS results, respectively.

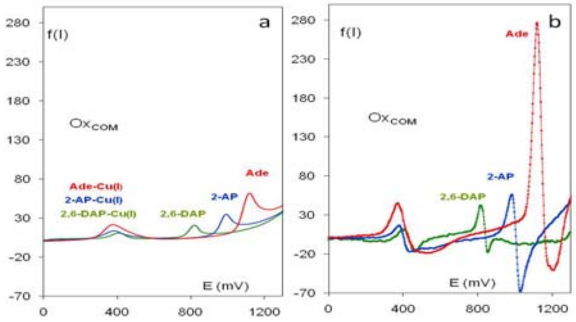

Figure 1: LSV (1a) and EVLS curves (1b) of Ade, 2-AP and 2,6-DAP (10 µM) with 20 µM Cu(II), reference scan rate 250 mV/s

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LSV in connection of EVLS revealed that in case of Ox_{com} peak, the mechanism of total electrode reaction can be described as an ECE mechanism where electrochemical steps reduction of Cu(II) to Cu(I) and oxidation of Cu(I) from purine–Cu(I) complex. Chemical process represents complexion between Cu(I) and purine with subsequent adsorption of complex on the electrode surface. The complex formation and its oxidation can be described by following scheme:

a) Cu(II) + e = Cu(I) (at deposition potential –0.15 V)
b) Cu(I) + purine = [purine– Cu(I)] (on PeGE surface)
c) [purine– Cu(I)= [purine– $Cu(I)]_{ads}$ (adsorption of the complex)
d) [purine– $Cu(I)]_{ads}$ = [purine– $Cu(II)]_{ads}$ +e (stripping, peak Ox_{Com})
e) [purine– $Cu(II)]_{ads}$ = $purine_{ox}$ + Cu(II) +e (stripping, peak Ox).

Conclusion

We found that the studied Cu(I)–Ade complex was formed not only by aminopurines (Ade, AP and DAP) but also by purine. On the other hand the complex is not formed in the case of imidazol and cytosine. According to presented and previous results it can be assumed that the complex formation involves not only nitrogen in the position 9, but also nitrogen atom of pyrimidine ring.

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