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Investigation of poly(3,4-ethylenedioxythiophene) deposition method influence on properties of ion-selective electrodes based on bis(benzo-15-crown-5) derivatives

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ABSTRACT

Glassy carbon electrodes modified by conductive polymers and membrane with derivatives of bis(benzo-15-crown-5) were tested as solid contact ion selective electrodes for K^+ ions concentration determination. PEDOT with PSS, Cl^- and ClO_4^- counter ions was electrochemically deposited onto glassy carbon substrates using four different electrochemical approaches (potentiostatic, galvanostatic, potentiodynamic and potentiostatic pulses). Scanning electron microscopy was applied to investigate influence of electrodeposition method on morphology of polymer films and drop-casted pseudo liquid membrane with an ionophore. The presence of the polymer film and method of deposition affect morphology of tested electrodes and sensing properties as well. The best sensing properties were obtained for the electrodes with biscrown I as ionophore with polymer which have a developed surface prepared via potentiostatic pulses ($\log K_{K/Na} = -5.6$ using separate solution method (SSM 1M)). Galvanostatic method of electrodeposition which resulted in relatively smooth layer of the PEDOT exhibited the poorest sensing properties for sensor with biscrown I as ionophore ($\log K_{K/Na} = -4.3$ for SSM 1M). All prepared sensors exhibited very favorable values of selectivity coefficients $K_{K/Na}$ ($\log K_{K/Na} = -5.6$ - -4.0). Detection limit equals to 10^{-7} M was achieved. The influence of pH for sensing properties were investigated for the selected electrodes.

1. Introduction

The ability of precise determination of potassium ions activity is one of the most important part of a diagnostics of many diseases as well as in routine health screening which is conducted in large number of laboratories for medical analysis. The atomic absorption spectrometry (AAS), flame emission spectrometry and ion selective electrodes (ISEs) are currently leading methods of a determination of K^+ concentration in human blood. Since the AAS is relatively expensive method and its usage is limited by sophisticated apparatus, the potentiometric method with the use of the ISEs is the cheapest and fastest technique.

The most popular cationic ionophores are based on neutral, naturally occurring ion carriers. Among them, the most studied ionophore is valinomycin, which is selective for potassium cations and is most commonly used, *e.g.* in clinical applications [1]. Also popular group of synthetic ionophores used in ion-selective electrodes are biscrown ethers. For the first time, this type of compounds was tested by Kimura et al. in construction of classic ion-selective electrodes [2]. They have tested 9 compounds and concluded that an appropriate design regarding ring size, variety of heteroatom, connectivity, and flexibility of linkage in crown ether derivatives affects electrochemical selectivity of the electrodes based on them. Moody et al. tested different biscrown ether in the ISEs used to K^+ and Na^+ determination in human blood plasma [3]. Xia et al. used biscrown ether as ionophore and studied the effect of conformationally constrained bridge in ionophore for Ion-Selective Electrodes performance [4]. In the case of K^+ determination, the most commonly used crown ionophores are derivatives of benzo-15-crown-5. Bis(15-crown-5) ethers react differently with Na^+ and

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K^+ ions, forming sandwich complexes only with K^+ but not with Na^+ ions [5]. The selectivity of electrodes based on derivatives of benzo-15-crown-5 is mainly determined by stoichiometry of formed ionophore-ion complexes: 2:1 for sandwich type with potassium ions (diameter of ion is slightly larger than crown gap) and 1:1 in the case of sodium ions (diameter of ion fits to the crown gap) [6,7].

The combination of two monocrowns and form biscrown is very often advantageous for properties of ionophore. The structure of complex with ions characterized by slightly larger diameter than gap of the crowns depends on the length and nature of the linking bridge between two crowns. In the case of appropriate long chain capable to rotation, complex with stoichiometry 1:1 (biscrown: ion) can be formed. For shorter and rigid bridge is more likely formation of a complex double sandwich type (stoichiometry 2:2) [8–11], however it was suggested that *open clam* type complex is also likely [12].

Synthesized by our group, highly lipophilic derivatives of bis (benzo-15-crown-5) (Fig. 1) have been already tested as potassium ionophores for classic electrodes [13,14]. However, obtained selectivity coefficients ($\log K_{K/Na}$) were sufficient only to analyze concentration of potassium ions in urine (required $\log K_{K/Na} < -3.1$), but were not fully satisfactory to analyze concentration of K^+ in human blood plasma (required $\log K_{K/Na} < -3.6$), according to requirement indicated by U. Oesch et al. [15]. Thus, effort has been taken to further improve properties of ISEs based on derivatives of bis(benzo-15-crown-5).

There are many methods of ion-selective electrodes (ISEs) modification that utilize conductive polymers (CPs) [16]. One of the possibility is to deposit a conductive polymer interlayer between the substrate (*e.g.* glassy carbon or graphite) and membrane with ionophore and use it as an ion-to-electron transducer [17]. This method is versatile and allows to enhance sensing properties of sensors based on almost all known ionophores [18,19]. Conductive polymer can be also dissolved in the same solution as components of ion-selective membrane and then be deposited onto the electrode substrate [20]. In this case, the CPs, which act as ion-to-electron transducer, are built in the membrane matrix [21]. There is a possibility to direct bond ionophore to CP chains by specific functional groups [22]. Appropriate combination of ionophore and conductive polymer may allow the covalent bond between polymer and ionophore to occur [23]. The usage of conductive polymer as interlayer between membrane with ionophore and glassy carbon substrate does not require any sophisticated ionophore and CP modification and it has been applied in this report.

The presence of the CPs, positively affects the ISE properties. It was reported that modification of the electrodes with poly (pyrrole), poly(*N*-methylpyrrole) and poly(3,4-ethylenedioxythiophene) (PEDOT) allows to achieve lower detection limit (LDL) of K^+ ions [24]. It was also shown that the type of CP and the method of deposition strongly affect the ISE properties. One of the most promising polymer is PEDOT, because it is stable in a wide range of pH and in the presence of oxygen and carbon dioxide [25]. PEDOT and carbon nanotubes deposited onto glassy carbon electrode enhanced long-term stability of ISE based on the potassium ionophore – valinomycin [26]. Mir et al. reported that the miniature electrodes based on tridodecylamine and modified by PEDOT deposited on gold were stable in acidic pH, thus they can be the good candidates *e.g.* for endoscopic sensing in the stomach [27]. ISEs modified by PEDOT were successfully used for *e.g.* Pb^+[28], K^+, Na^+, H^+ [29], Ag^+ [30,31] and Cl^- [32] ions determination that confirms its versatility.

In this work, PEDOT deposited on glassy carbon was tested as ion-to-electron transducer in the ion selective electrodes for K^+ ions determination. Derivatives of bis(benzo-15-crown-5) – compounds **I**-**V** (Fig. 1) were used as the ionophores [13,14]. Prepared electrodes were tested in the presence of disturbing ions (Na^+, NH_4^+, Li^+, Mg^{2+} and Ca^{2+}) and also in the various pH. The influence of conductive polymer and method of electrodeposition

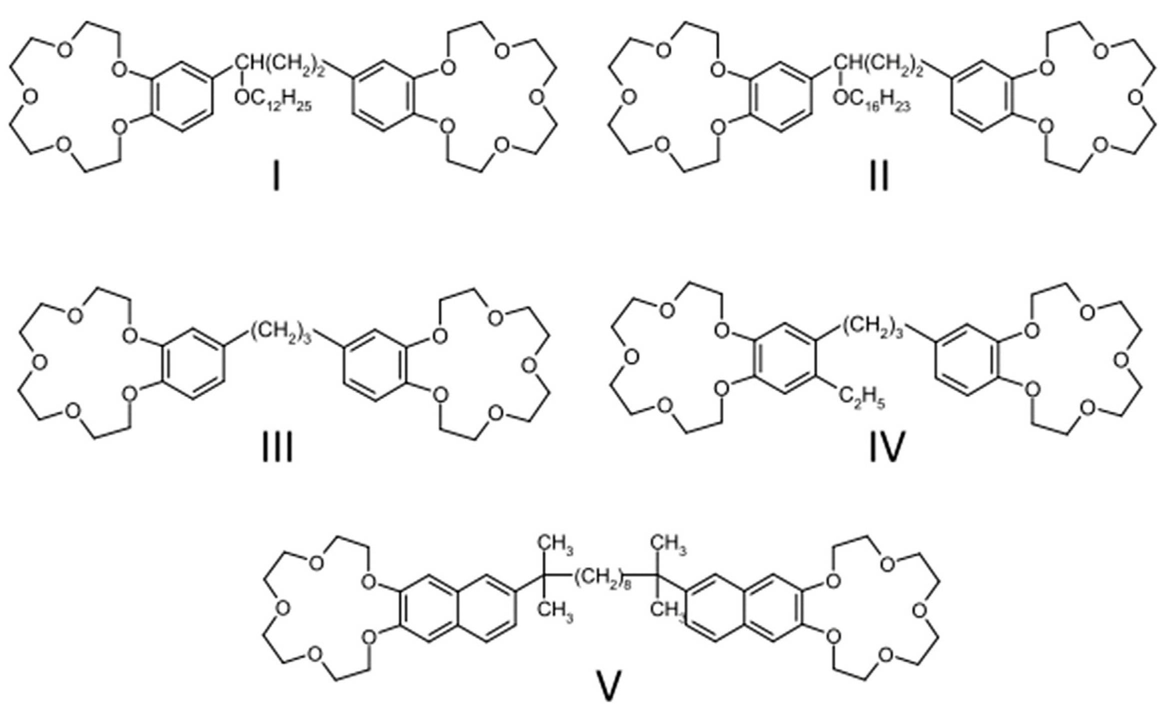

Fig. 1. Biscrowns used as ionophores in the investigated sensors.