

# 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<sup>+</sup> ions concentration determination. PEDOT with PSS, Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> 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.

**Keywords:** bis(benzo-15-crown-5) derivatives, ion-selective electrode (ISE), potassium detection conductive polymer, PEDOT

## 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<sup>+</sup> 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<sup>+</sup> and Na<sup>+</sup> 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<sup>+</sup> determination, the most commonly used crown ionophores are derivatives of benzo-15-crown-5. Bis(15-crown-5) ethers react differently with Na<sup>+</sup> and

$K^+$  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.  $Pb^{2+}$  [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

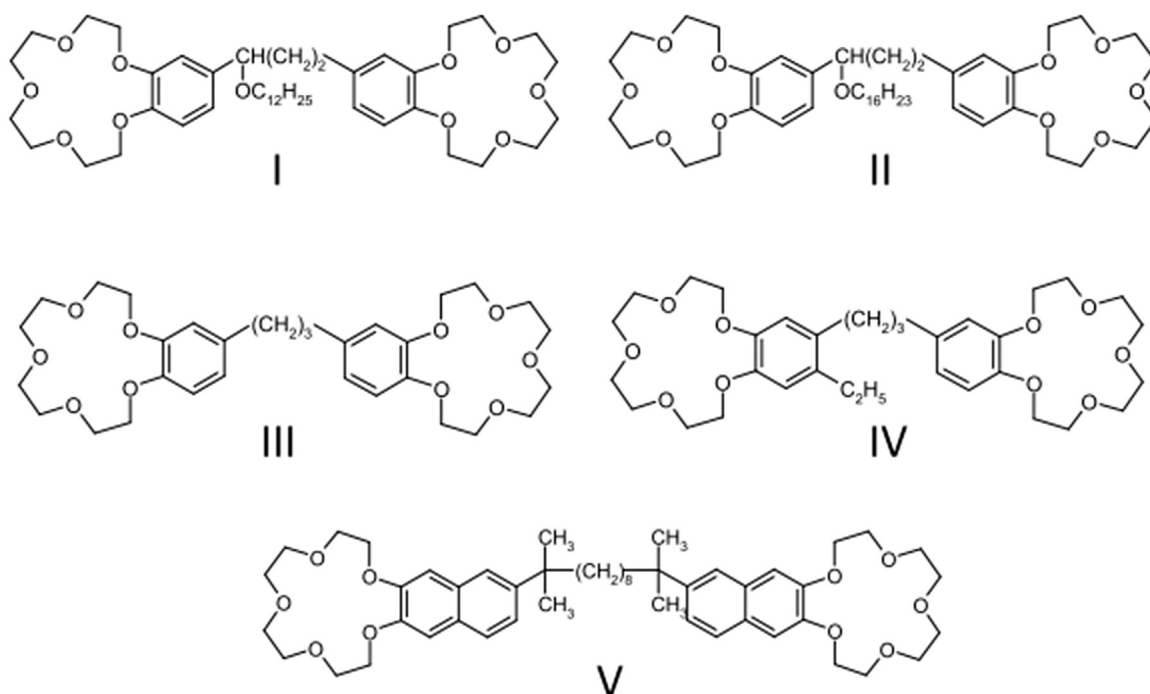


Fig. 1. Biscrowns used as ionophores in the investigated sensors.



**Table 1**

The composition of the ion-selective membranes.

membrane	ionophore (wt %)	PVC (wt %)	plasticizer <i>o</i> -NPOE (wt %)	ion-exchanger KTpClPB (wt %)
1	4.7	31.4	63.8	0.1
2	4.75	31.7	63.4	0.15
3	1.1.17 1	31.7	67	0.3

will be discussed based on the selectivity coefficients, lower detection limits and  $E$  vs.  $f(a_{K^+})$  slope ( $S$ ). The SEM images of the electrodes surface will be presented.

## 2. Experimental

### 2.1. Chemicals

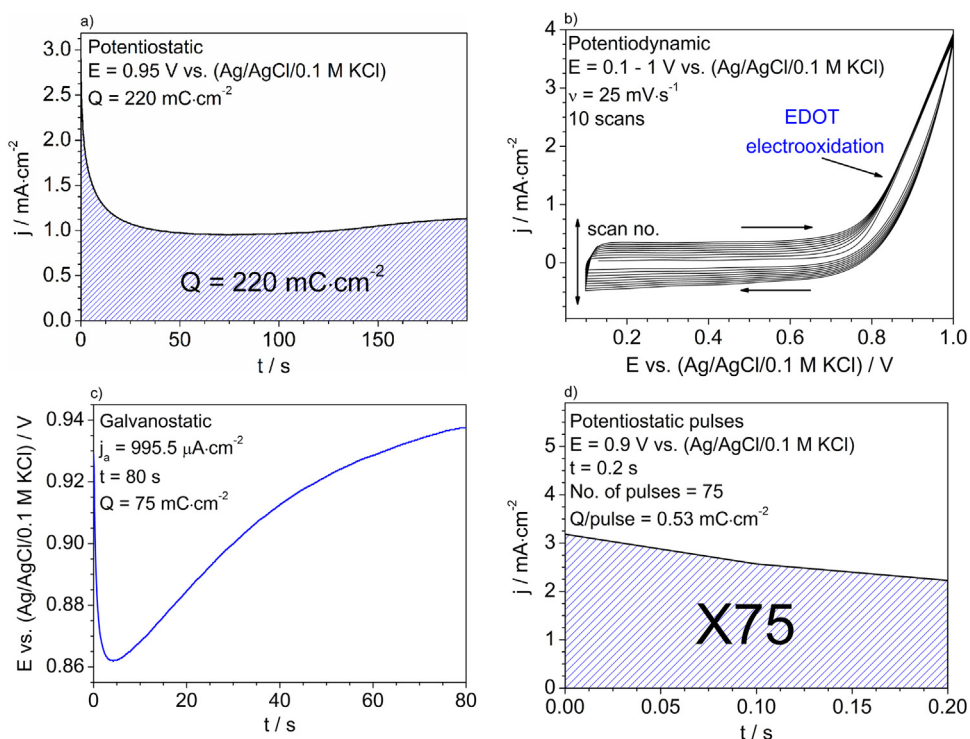
Biscrowns (**I-V**) used as the ionophores were obtained by synthesis. Synthesis of **I-IV** was described in the earlier paper [13]. Ionophore **V** was synthesized *via* the alkylation reaction of naphtho-15-crown-5 of the appropriate diol [14]. Valinomycin was purchased from Sigma-Aldrich. The other chemicals for membrane preparation: poly(vinyl chloride) (PVC, high molecular weight), 2-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB), tetrahydrofuran (THF, Selectophore) were purchased from Sigma-Aldrich. The chemicals used for electropolymerization: 3,4-ethylenedioxythiophene (EDOT), poly(sodium 4-styrenesulfonate) (NaPSS) ( $M_w \approx 70,000$ ) and  $LiClO_4$  were purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) blend (PEDOT/PSS, used as 1.3% (w/w) dispersion in water (conductive grade)) used as reference was purchased from Sigma-Aldrich.  $KCl$ ,  $CaCl_2$ ,  $MgCl_2$  and  $NH_4Cl$  (POCH) and  $LiNO_3$  (Sigma Aldrich) were used for model aqueous solutions preparation. The aqueous solutions were prepared with

$18.2 M\Omega \cdot cm$  resistivity deionized water from Millipore Milli-Q A10 system.

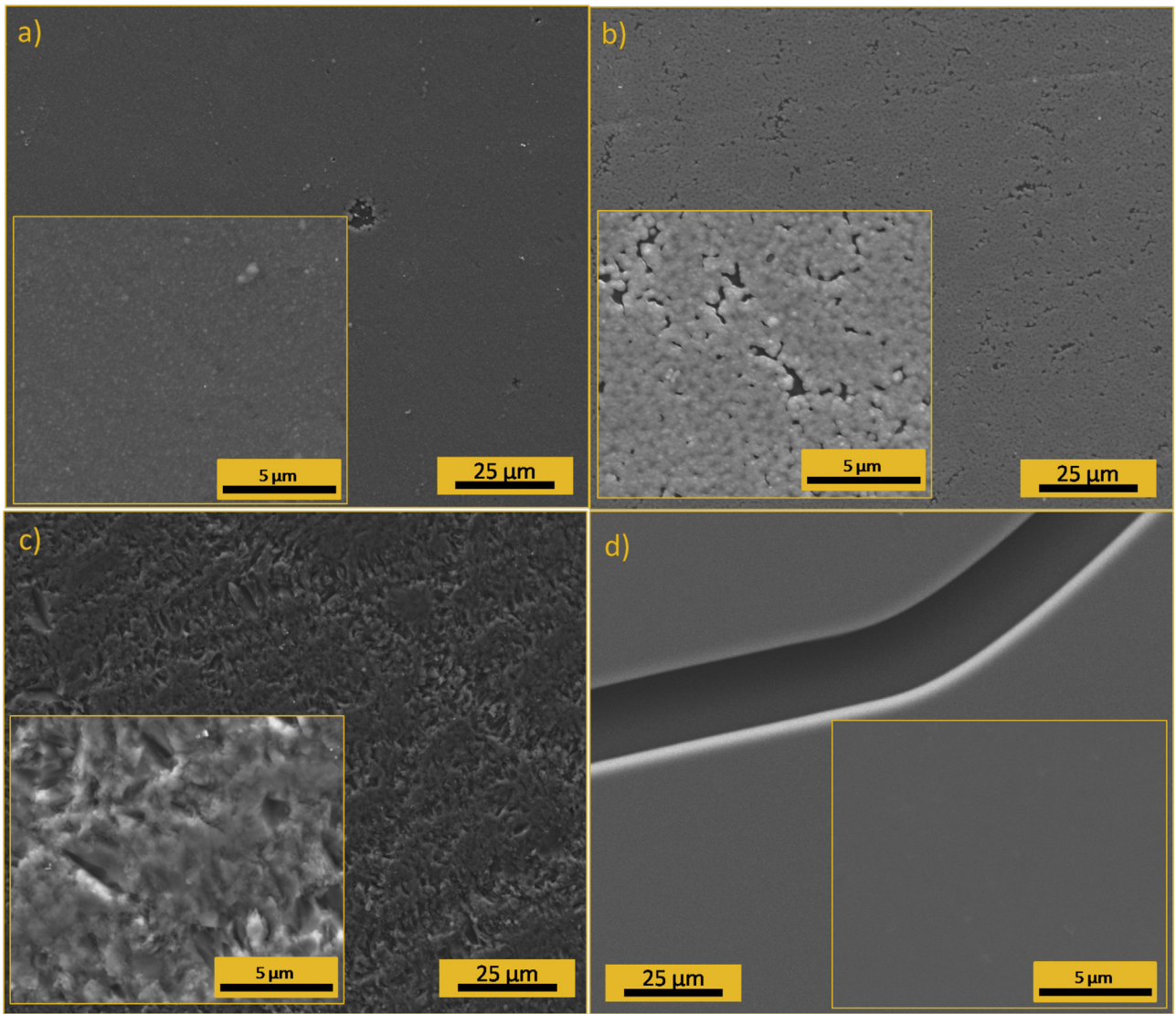
### 2.2. Apparatus

The potentiometric measurements were performed at room temperature using a 16-channel system (Lawson Lab Inc., Malvern, PA), which has been connected to computer equipped with the EMF Suite version 1.03 program. As a reference electrode an Philips double junction  $Ag|AgCl$  was used with 3 M  $KCl$  and 1 M  $CH_3COOLi$  as inner and outer filling solutions. The *solid contact* electrodes based on glassy carbon (outer diameter 2 mm) were purchased from MINERALS<sup>®</sup> (Poland). Automatic micropipettes (20–200  $\mu l$ ) were purchased from LABMATE+HTL. The morphology of the samples was investigated by Schottky field emission scanning electron microscopy (FEI Quanta FEG 250) with an ET secondary electron detector. Beam accelerating voltage was kept at 10 kV.

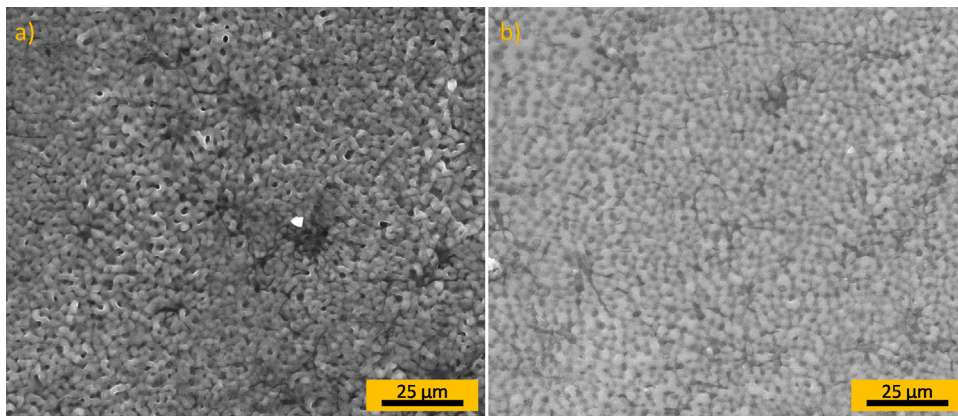
Conductive polymers electrodeposition were performed using the potentiostat–galvanostat system AutoLab PGStat10 under GPES 4.9 software control. Electrochemical experiments were carried out in a 3 electrode cell system with  $Ag/AgCl/0.1 KCl$  used as a reference electrode and platinum mesh acting as counter electrode.



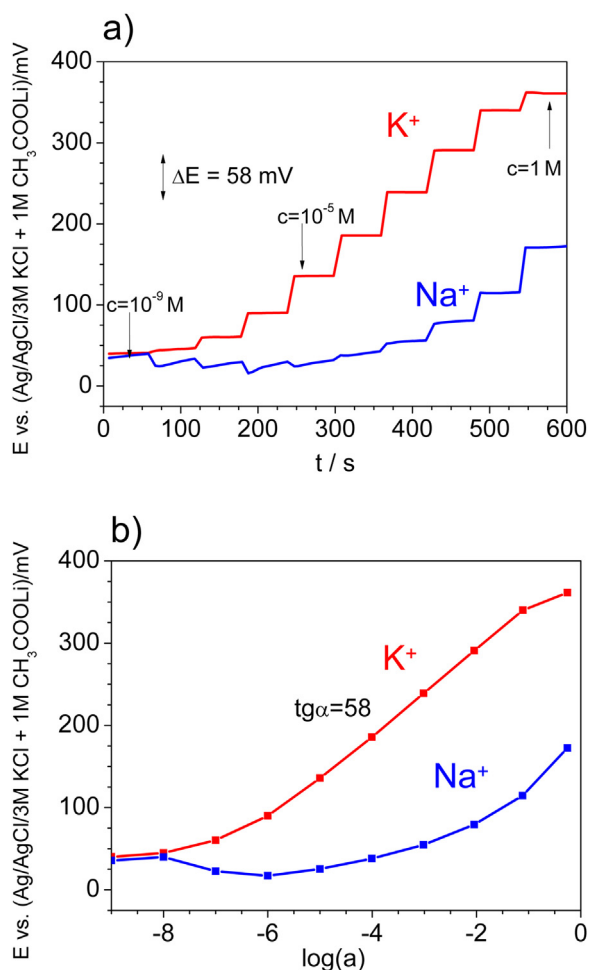
**Fig. 2.** Exemplary curves recorded during PEDOT:PSS electrodeposition: a) – potentiostatic, b) – potentiodynamic, c) – galvanostatic, d) – potentiostatic pulses.



**Fig. 3.** The SEM images of PEDOT:PSS surfaces deposited by a) galvanostatic, b) potentiostatic, c) potentiostatic pulses, and d) drop-casting methods.



**Fig. 4.** The SEM images of the drop-casted membrane deposited on the PEDOT:PSS surfaces deposited via a) potentiostatic pulses and b) potentiostatic method.



**Fig. 5.** Response of the electrode PEDOT/PSS/a/I/1 to various concentrations of  $K^+$  and  $Na^+$  ions: a) dynamic responses, b) resulting calibration curves  $E = f(\log(a))$ .

### 2.3. Membrane deposition

Membrane, which is the main element of the properly functioning potentiometric sensor was formed with typical components of membranes which contain: macrocyclic ionophore, plasticizer (*o*-NPOE), PVC and salt with lipophilic anion (potassium tetrakis(4-chlorophenyl) borate). The composition of the ion-selective membranes is specified in Table 1. The membrane components (~48 mg total mass) were dissolved in 0.375 ml of THF to prepare a membrane cocktail for drop-casting. The volume of the drop-casted membrane cocktail was equal to 20  $\mu$ l. After deposition, electrodes were kept under the protective glass cover for at least 24 h, until the complete evaporation of THF. Each electrode was conditioned in a solution containing the primary ion – KCl  $10^{-3}$  M, for 24 hours.

### 2.4. Polymer electrodeposition

PEDOT was electrochemically deposited from a electrolyte containing monomer (0.0066 M EDOT) and the source of counter ion (0.05 M NaPSS,  $LiClO_4$  or KCl). Four methods of electrodeposition were tested: potentiostatic, galvanostatic, potentiodynamic and potentiostatic pulses. PEDOT films were electrosynthesized directly on the glassy carbon disc electrodes with 2 mm in a diameter. The details of electropolymerization conditions are presented in Fig. 2.

Comparative electrodes with PEDOT/PSS blend were prepared via drop-casting method using 5  $\mu$ l of aqueous suspension of PEDOT/PSS onto glassy carbon electrode and dried overnight at room temperature.

### 2.5. Methods of measurements

The experiments were conducted with the use of model water solutions for the measured ( $K^+$ ) and disturbing ( $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $NH_4^+$ ,  $Li^+$ ) ions in selected ranges of activities. The characteristics of the electrodes were determined for the model activities from 1 M to  $10^{-9}$  M. The selectivity coefficients have been determined with the use of Separate Solution Method (SSM) [33] for the  $\log(a) = 0$  (extrapolated to 1 M excluding data recorded for 1 M in extrapolation due to the anionic effect) and  $\log(a) = -1$ . For the better characterization of sensors, selectivity coefficients were determined using Fixed Interference Method (FIM) as well [33]. Both methods (SSM and FIM, 0.1M) are recommended by International Union of Pure and Applied Chemistry (IUPAC) [33]. Single-ion activity coefficients were calculated theoretically by using the Debye–Hückel equation [34]. HCl and LiOH were used for pH adjustment.

### 2.6. Measurement in human blood plasma

Previously presented comparison between different types of tested electrodes allows the best sensor for  $K^+$  ions to be choose. The PEDOT/PSS/d/I/1 was utilized to determine  $K^+$  in biological sample – human blood plasma rich in potassium and sodium ions. Standard addition method (SAM) [35] and equation 1 was used for determination of the potassium ions concentration. As a standard, 10 ml of 1 M KCl was added to 50 ml of human blood plasma.

$$C = \frac{C_s \cdot V_s}{(V_x + V_s) \cdot 10^{\frac{\Delta E}{S}} - V_s} \quad (1)$$

$C_s$  – standard concentration;  $V_s$  – standard volume;  $V_x$  – source volume,  $\Delta E$  – potential difference before and after the addition of KCl;  $S$  – slope of the KCl characterization  $10^{-4}$ – $10^{-1}$  M.

## 3. Results and discussion

### 3.1. Morphology of conductive polymer and membrane

The method and conditions of conductive polymers electrodeposition affects the properties and morphology of resulting layers [36–38]. Four methods of PEDOT electrosynthesis were applied: a) – potentiostatic, b) – potentiodynamic, c) – galvanostatic, d) – potentiostatic pulses. Exemplary curves registered during PEDOT: PSS electrodeposition are presented in Fig. 2. The parameters of deposition are added to the graphs.

The morphology of such prepared electrodes were investigated using scanning electron microscopy technique (SEM). Examples of SEM images of the electrodes surfaces are presented in Fig. 3a-c. The morphology of drop-casted PEDOT is presented in Fig. 3d. The galvanostatic approach lead to the uniform polymer layer, that covered whole surface of glassy carbon, see Fig. 3a. Easy control of consumed charge for electrodeposition and quality of the obtained polymers film makes this method the most convenient and most commonly used [25,39]. In the case of the potentiostatic method, polymer grew in a form of humps. The main drawback of this method is the fact, that obtained layers did not closely cover the conductive substrate as it is presented in Fig. 3b. Films of polymers obtained via short, 0.2 s potentiostatic pulses were characterized by completely different morphology. Deposited layer was very rough, but covered the glassy carbon surface, see Fig. 3c. In the case

**Table 2**

The resulting log LDL, slopes and selectivity coefficients for potassium selective glassy carbon ISEs ( $\log K_{K,x}$ , SSM, 1 M/ $\log K_{K,x}$ , SSM, 0.1 M)/( $\log K_{K,x}$ , FIM) with derivatives of bis (benzo-15-crown-5) as ionophores (I-V as in Fig. 1); methods of polymer electrodeposition (a-d as in Fig. 2).

Electrode code	PEDOT/PSS/a/I/1	PEDOT/PSS/a/II/1	PEDOT/PSS/a/III/1	PEDOT/PSS/a/IV/2	PEDOT/PSS/a/V/2	
log LDL	-6.9	-6.5	-6.2	-5.8	-5.8	
S[mV/dec]	52.5	55.4	51.2	52.7	51.0	
$\log K_{K/Na}$	-5.0/-4.6/-4.4	-4/-3.6/-3.7	-4/-3.8/-3.5	-4.1/-3.9/-3.8	-4.5/-4.1/-3.8	
$\log K_{K/Ca}$	-4.5/-4.8/-5.0	-5.7/-5.5/-5.0	-5.5/-5.3/-5.0	-4.1/-4.3/-4.8	-5/-4.9/-4.2	
$\log K_{K/Mg}$	-4.7/-5.1/-4.9	-5.6/-5.1/-4.9	-5.8/-5.4/-5.0	-6.2/-5.3/-5.0	-6/-5.7/-4.8	
$\log K_{K/Li}$	-5.2/-4.9/-4.8	-5.4/-5.0/-4.7	-5.1/-4.8/-4.3	-5.4/-5.1/-4.6	-5.9/-5.1/-4.7	
$\log K_{K/NH_4}$	-2.8/-2.6/-3.1	-2.1/-2.0/-3.0	-2/-1.9/-3.0	-3.5/-3.2/-2.8	-3.8/-3.3/-3.4	
$\log K_{K/H}$	-/-4.0	-/-4.1	-/-4.0	-/-4.8	-/-3.2	
Electrode code	PEDOT/Cl <sup>-</sup> /d/I/1	PEDOT/PSS/d/II/1	PEDOT/ClO <sub>4</sub> <sup>-</sup> /d/II/1	PEDOT/PSS/b/I/1	PEDOT/PSS/c/II/1	PEDOT/PSS/A (without membrane)
log LDL	-7.3	-7.2	-6.4	-6	-6.2	-4.2
S[mV/dec]	54.3	58.1	53.1	51.4	51.1	52.3
$\log K_{K/Na}$	-5.6/-5.2/-4.7	-5/-4.8/-5.1	-5.2/-4.9/-4.4	-4.4/-4.0/-3.8	-4.3/-4.1/-3.9	-1.5/-1.7/-1.9
$\log K_{K/Ca}$	-5.8/-5.1/-4.8	-5.1/-4.8/-4.4	-4.1/-3.9/-3.6	-4.4/-4.3/-4.1	-4.3/-4.2/-4.1	-2.8/-2.7/-3.2
$\log K_{K/Mg}$	-6.7/-5.5/-5.2	-6.1/-5.1/-4.8	-4.5/-4.4/-4.2	-5.2/-4.7/-4.3	-5/-4.7/-4.3	-3.2/-3.2/-3.3
$\log K_{K/Li}$	-5.9/-5.3/-4.7	-5.7/-5.2/-4.9	-3.9/-3.9/-3.0	-4.5/-4.2/-4.1	-4.3/-4.2/-4.1	-2.8/-3.0/-3.2
$\log K_{K/NH_4}$	-2.8/-2.7/-3.0	-2.9/-2.9/-3.0	-2.8/-2.7/-3.0	-2/-2.2/-2.8	-1.9/-2.1/-2.2	-1.6/-1.4/-1.1
$\log K_{K/H}$	-/-3.2	-/-3.9	-/-3.4	-/-3.1	-/-3.2	-/-1.5
Electrode code	PEDOT/PSS/drop-casted/I	PEDOT/PSS/drop-casted/II	PEDOT/PSS/drop-casted/III	PEDOT/PSS/drop-casted/IV	PEDOT/PSS/drop-casted/V	PEDOT/PSS/d/Valinomycin/3
log LDL	-6.5	-6.6	-6.0	-7.2	-5.6	-6.1
S[mV/dec]	53.4	57.1	56.3	53.1	58.4	58.2
$\log K_{K/Na}$	-4.0/-/-	-3.5/-/-	-3.2/-/-	-3.8/-/-	-3.5/-/-	-4.6/-4.5/-4.2
$\log K_{K/Ca}$	-4.5/-/-	-5.4/-/-	-4.3/-/-	-5.1/-/-	-4.5/-/-	-4.9/-4.7/-4.3
$\log K_{K/Mg}$	-4.6/-/-	-4.4/-/-	-4.8/-/-	-5.7/-/-	-4.3/-/-	-5.1/- 4.6/-4.8
$\log K_{K/Li}$	-3.5/-/-	-3.2/-/-	-3.4/-/-	-3.5/-/-	-3.5/-/-	-5.3/-5.0/-5.0
$\log K_{K/NH_4}$	-2.2/-/-	-2.4/-/-	-2.3/-/-	-2.4/-/-	-2.5/-/-	-2.5/- 2.4/-2.1

of drop-casted layer of PEDOT, the surface after solvent evaporation is very smooth. However, obtained layer is characterized by long cracks causing the pieces of material detachment from the electrode. As it can be concluded, the method of PEDOT deposition affects the morphology and surface area of deposited films. Moreover, layers deposited using electrochemical route are characterized by better adhesion of the polymer to the substrate in comparison with drop-casted material. Noteworthy, surface of the polymer acts as a template for membrane deposition. As it is presented in Fig. 4, morphology of the membrane surface prepared by drop-casting method depends on the morphology of the polymer interlayer. The pseudo liquid membrane drop-casted onto the rough surface of polymer (deposited via potentiostatic pulses) was characterized by higher roughness in comparison with membrane deposited onto smoother film deposited via potentiostatic method, see Fig. 4a and b. The influence of polymer and membrane morphology on the ISE parameters was tested.

### 3.2. Ion selective electrodes performance

Obtained electrodes were tested as ion selective electrodes for K<sup>+</sup> activity determination. The exemplary potentiometry

calibration curves showing the change of the electrode potential depend on K<sup>+</sup> and Na<sup>+</sup> activity (E vs. log(a)) in aqueous solutions are presented in Fig. 5. In the case of K<sup>+</sup> solution, there is a range of activities ( $\sim 10^{-5} - 10^{-1}$  M) where the slope is close to Nernstian. The anionic effect in the case of K<sup>+</sup> containing electrolyte was observed for concentration higher than  $10^{-1}$  M. Noteworthy, Nernstian slope is observed only for high activities ( $10^{-1}$  M to 1 M) in the case of sodium ions. Such analysis were performed for all tested electrodes to determine: selectivity coefficients, lower detection limits and E vs.  $f(a_{K^+})$  slopes. Obtained results are collected in Table 2 and compared with results obtained for electrodes based on commercially available ionophore – valinomycin.

Additional experiment was performed for GC/PEDOT:PSS electrode without membrane. Electrodes were coded as: polymer (PEDOT)/counter ion (PSS, Cl<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>)/deposition method (a-d as in Fig. 2)/ionophore (I-V as in Fig. 1)/membrane composition (1-3 as in Table 1).

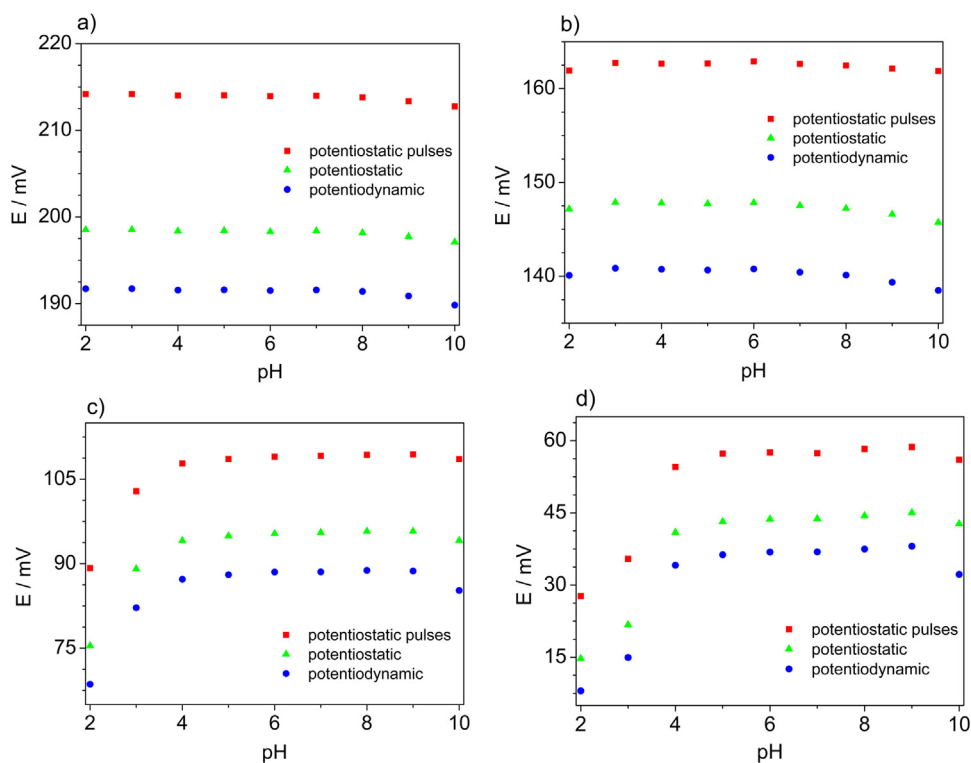
The values of log(LDL) for electrodes modified with PEDOT varies in a range between -5.6 and -7.3. However, polymer electrode without PVC membrane with ionophore exhibited the worst detection limit (log LDL = -4.2). The best value of detection

**Table 3**

Comparison our biscrown ethers with other non-commercial ionophores.

Ionophore used in membrane construction	carbosilane 1 [41]	poly(benzyl-eugenol) [42]	rifamycin [43]	dbdb-18-6 [44]	calix[4]azacrown ether [45]
Slope [mV/dec]	58.3	56.3	56.7	58.2	55.3
$\log K_{K/Na}$	-4.7 [FIM]	-1.3 [SSM]	-2.4 [SSM]	-2.7 [SSM]	-3.8 [MPM*]
$\log K_{K/Ca}$	-3.4 [FIM]	-2.5 [SSM]	-3.4 [SSM]	-3.9 [SSM]	-4.5 [MPM*]
$\log K_{K/Mg}$	-3.5 [FIM]	-3.2 [SSM]	-3.4 [SSM]	-2.4 [SSM]	-4.8 [MPM*]
$\log K_{K/NH_4}$	-5.0 [FIM]	-0.2 [SSM]	-2.5 [SSM]	-	-1.4 [MPM*]

\*MPM – matched potential method.



**Fig. 6.** The influence of pH on potentiometric response of electrodes based on ionophore I and modified with electrodeposited PEDOT/PSS in a)  $10^{-1}$  M, b)  $10^{-2}$  M, c)  $10^{-3}$  M and  $10^{-4}$  M solutions of KCl.

limit ( $\log LDL = -7.3$ ) was registered for electrode with ionophore I coded as PEDOT/Cl<sup>-</sup>/d/I/1. The slopes were determined for linear range of  $E = \log(a)$  results. The  $E = \log(a)$  slopes for PEDOT/PSS with ionophore I and PEDOT/PSS with ionophore V deposited *via* potentiostatic pulses and drop-casting method, respectively were the closest to the Nernstian slope. Noteworthy, all sensors with PEDOT layer exhibited satisfactory *S* values. Obtained results were compared to previous literature reports about sensors based on biscrown ethers. Prepared biscrown ethers-containing sensors exhibited the best sensing properties (slope, selectivity coefficient, detection limit) among previously presented electrodes based on the biscrown ethers [2–4,13,14]. The main challenge of the K<sup>+</sup> sensors construction is to achieve electrode with the lowest as possible value selectivity coefficient relative to the Na<sup>+</sup> ions. Problem of the Na<sup>+</sup> disturbing ions presence is observed due to the common occurrence in a biological samples [40]. As it is presented in Table 2, in the most cases, the presence of electrodeposited conductive polymer improves the values of selectivity coefficients  $\log K_{K,Na}$  in comparison with electrodes modified with drop-casted PEDOT/PSS. Values of selectivity coefficients of the best PEDOT modified electrode (PEDOT/Cl<sup>-</sup>/d/I/1) were compared with other non-commercial ionophores in a form of a table (see Table 3). As it can be concluded, modification of ISE with PEDOT interlayer is a very promising way of selectivity coefficient improvement. However, it was also shown that the method of polymer deposition strongly affected these values. Since the specific surface area of polymer (and membrane) was higher for PEDOT deposited *via* potentiostatic pulses (as shown in Fig. 3 and 4), improved selectivity coefficients may result from more efficient complexation of ions on the electrode/solution interface.

All modified, miniature electrodes exhibited improved sensing properties in comparison with the same ionophores in the classic electrodes without CP [13]. Taking into account all determined

parameters, the best characteristics was obtained for electrode with ionophore I with PEDOT/PSS deposited using short, potentiostatic pulses.

### 3.3. pH influence

The stability of the ion-selective electrodes in a wide range of pH is crucial for biomedical applications. Thus, the influence of pH in a range from 2 to 10 on the electrode potential was measured for different concentration of K<sup>+</sup> ions ( $10^{-4}$  M –  $10^{-1}$  M) for electrodes based on ionophore I (see Fig. 1) and modified by electrodeposited PEDOT/PSS. Obtained results are presented in Fig. 6a-d. The pH in whole measured range did not affect potential of electrodes in  $10^{-1}$  M KCl solution. However, lower concentration of KCl, higher impact of pH is observed. The clear change of potential was registered for pH lower than 4 for solutions with concentration  $10^{-2}$ ,  $10^{-3}$  and  $10^{-4}$  M. Decrease of electrode potential at pH 10 was observed for electrode prepared *via* potentiodynamic polarization. Thus, proposed electrodes can work as sensors in a range (4-9) of pH even at low concentration of KCl.

### 3.4. Performance in the biological fluids

1.1.23 Prepared electrodes can be successfully used as sensor in biological samples. The physiological concentration of potassium ions for an adult is in the range between 3.5 and 5.1 mmol/dm<sup>3</sup> [46]. The concentration of K<sup>+</sup> ions determined using proposed sensor was equal to 4.19 mmol/dm<sup>3</sup>. The results were compared with concentration determined by certificated laboratory which was equal to 4.11 mmol/dm<sup>3</sup>. Result obtained using PEDOT/PSS/d/I/1 electrode is in the given range and confirms possible applicability of proposed ISEs in clinic applications.

### 3.5. Comparison with other non-commercial ionophores

We compared our biscrown ethers with other non-commercial ionophores. As we can see, most of the best parameters show our derivative.

## 4. Conclusions

Presented work compares directly, based on derivatives of bis (benzo-15-crown-5), ion selective electrodes with conductive polymer as interlayer, prepared by different methods of electrodeposition. Electrodes were tested as sensors for  $K^+$  ions determination in aqueous solution. Both, detection limit and selectivity coefficient can be improved by polymer electrodeposition. Proposed method of polymer deposition (short 0.2 s potentiostatic pulses) allows to obtain improved properties of tested sensors. It was shown, that method of polymer synthesis affects the morphology of polymer film and membrane with ionophore deposited onto the polymer. The improved properties of electrode prepared *via* potentiostatic pulses may result from higher specific area of electrode surface. Tested electrodes based on synthesized ionophores exhibited even better sensing properties than electrode based on commercially available valinomyacin.

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## References

- [1] U.E. Spichiger-Keller, Chemical sensors and biosensors for medical and biological applications, Wiley-VCH, 1998.
- [2] K. Kimura, T. Maeda, H. Tamura, T. Shono, Potassium-Selective PVC Membrane Electrodes Based on Bis- and Poly(Crown Ether)s, *J. Electroanal. Chem.* 95 (1979) 91–101.
- [3] G.J. Moody, B.B. Saad, J.D.R. Thomas, Studies on Bis(crown ether)-based Ion-selective Electrodes for the Potentiometric Determination of Sodium and Potassium in Serum, *Analyst* 114 (1989) 15–20.
- [4] Z. Xia, I.H.A. Badr, S.L. Plummer, Lawrence Cullen, Leonidas G. Bachas, Synthesis and Evaluation of a Bis(crown ether) Ionophore with a Conformationally Constrained Bridge in Ion-Selective Electrodes, *Analytical Sciences* 14 (1998) 169–173.
- [5] J.L. Atwood, J.E. Davies, D.D. Macnicol, F. Vögtle, *Comprehensive Supramolecular Chemistry, Molecular Recognition: Receptors for Cationic Guests*, vol. 1 (1996), pp. p.605.
- [6] M.A. Bush, M.R. Truter, Crystal structures of complexes between alkali-metal salts and cyclic polyethers. Part III. Aquo-(2,3-benzo-1,4,7,10,13-pentaoxacyclopentadec-2-ene)sodium iodide, *J. Chem. Soc., Perkin Trans. 2* (1972) 341–344.
- [7] P.R. Mallison, M.R. Truter, Crystal structures of complexes between alkali-metal salts and cyclic polyethers. Part V. The 1: 2 complex formed between potassium iodide and 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin (benzo-15-crown-5), *J. Chem. Soc., Perkin Trans. 2* (1972) 1818–1823.
- [8] M. Bourgoin, K.H. Wong, J.Y. Hui, J. Smid, Interactions of macrobicyclic polyethers with ions and ion pairs of picrate salts, *J. Am. Chem. Soc.* 97 (1975) 3462–3467.
- [9] E. Kleinpeter, I. Starke, D. Ströhl, H.J. Holdt, NMR Spectroscopic Study of Solution Structure and Complexational Behaviour of bis-benzo crown ethers, *Journal of Molecular Structure* 404 (1997) 273–290.
- [10] S. Fery-Forgues, F. Al-Ali, Bis(azacrown ether) and bis(benzocrown ether) Dyes: Butterflies Tweezers And Rods In Cation Binding, *J. Photochem. Photobiol. C: Photochemistry Reviews* 5 (2004) 139–153.
- [11] M. Szarmach, E. Wagner-Wysiecka, M.S. Fonari, E. Luboch, Bis(azobenzocrown ether)s – Synthesis and Ionophoric Properties, *Tetrahedron* 68 (2012) 507–515.
- [12] Y. Inoue, T. Hakushi, Y. Liu, L.-H. Tong, J. Hu, G.-D. Zhao, S. Huang, B.-Z. Tian, Complexation Thermodynamics of Bis(crown ether)s. Calorimetric Titration of Complexation of Potassium Ion with Bis(benzocrown ether)s: Enthalpy-Entropy Compensation, *J. Phys. Chem.* 92 (1988) 2371–2374.
- [13] E. Luboch, A. Cygan, J.F. Biernat, Bis(benzocrown ether)s with Polymethylene Bridges and Their Application in Ion-Selective Electrodes, *Tetrahedron* 47 (1991) 4101–4112.
- [14] E. Luboch, A. Cygan, J.F. Biernat, A. Yu. Simonov, A.A. Dvorkin, XVII International Symposium on Macrocyclic Chemistry, (1992) Provo, Utah, USA P10.
- [15] E. Pungor, Ion-Selective Electrodes. 4. (1984) 82, U. Oesch, P., Anker, D. Ammann and W. Simon, Membrane Technological Optimization of Ion-Selective Electrodes Based on Solvent Polymeric Membranes for Clinical Applications, 4th Symposium of Ion-Selective Electrodes, Mátrafüred, 1984.
- [16] J. Bobacka, A. Ivaska, A. Lewenstam, Potentiometric Ion Sensors Based on Conducting Polymers, *Electroanalysis* 15 (2003) 366–374.
- [17] A. Cadogan, Z. Gao, A. Lewenstam, A. Ivaska, D. Diamond, All-solid-state Sodium-Selective Electrode Based on a Calixarene Ionophore in a Poly(Vinyl Chloride) Membrane With a Polypyrrole Solid Contact, *Anal. Chem.* 64 (1992) 2496–2501.
- [18] E. Bakker, P. Buhlmann, E. Pretsch, Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 1. General Characteristics, *Chem. Rev.* 97 (1997) 3083–3132.
- [19] P. Buhlmann, E. Pretsch, E. Bakker, Carrier-Based Ion-Selective Electrodes and Bulk Optodes. 2. Ionophores for Potentiometric and Optical Sensors, *Chem. Rev.* 98 (1998) 1593–1688.
- [20] F. Garnier, Functionalized Conducting Polymers-Towards Intelligent Materials, *Angew. Chem.* 101 (1989) 529–533.
- [21] J. Bobacka, T. Lindfors, M. McCarrick, A. Ivaska, A. Lewenstam, Single-Piece all-Solid-State Ion-Selective Electrode, *Anal. Chem.* 67 (1995) 3819–3823.
- [22] L.Y. Heng, E.A.H. Hall, One-Step Synthesis of  $K^+$ -Selective Methacrylic-Acrylic Copolymers Containing Grafted Ionophore and Requiring No Plasticizer, *Electroanalysis* 12 (2000) 178–186.
- [23] J. Bobacka, Conducting Polymer-Based Solid-State Ion-Selective Electrodes, *Electroanalysis* 18 (2006) 7–18.
- [24] A. Michalska, K. Maksymiuk, Conducting Polymer Membranes for Low Activity Potentiometric Ion Sensing, *Talanta* 63 (2004) 109–117.
- [25] M. Vazquez, J. Bobacka, A. Ivaska, A. Lewenstam, Influence of Oxygen and Carbon Dioxide on the Electrochemical Stability of Poly(3,4-Ethylenedioxythiophene) Used as Ion-to-Electron Transducer in all-Solid-State Ion-Selective Electrodes, *Sens. Actuators B* 82 (2002) 7–13.
- [26] Z. Mousavi, J. Bobacka, A. Lewenstam, A. Ivaska, Poly(3,4-ethylenedioxythiophene) (PEDOT) Doped with Carbon Nanotubes as Ion-to-Electron Transducer in Polymer Membrane-Based Potassium Ion-Selective Electrodes, *Journal of Electroanalytical Chemistry* 633 (2009) 246–252.
- [27] M. Mir, R. Lugo, I.B. Tahirbegi, J. Samitier, Miniaturizable Ion-Selective Arrays Based on Highly Stable Polymer Membranes for Biomedical Applications, *Sensors* 14 (2014) 11844–11854.
- [28] M. Guziński, G. Lisak, T. Sokalski, J. Bobacka, A. Ivaska, M. Bocheńska, A. Lewenstam, Solid-Contact Ion-Selective Electrodes with Highly Selective Thioamide Derivatives of p-tert-Butylcalix[4] arene for the Determination of Lead(II) in Environmental Samples, *Anal. Chem.* 85 (2013) 1555–1561.
- [29] M. Guziński, J.M. Jarvis, B.D. Pendley, E. Lindner, Equilibration Time of Solid Contact Ion-Selective Electrodes, *Anal. Chem.* 87 (2015) 6654–6659.
- [30] Z. Mousavi, J. Bobacka, A. Ivaska, Potentiometric  $Ag^+$  Sensors Based on Conducting Polymers: A Comparison between Poly(3,4-ethylenedioxythiophene) and Polypyrrole Doped with Sulfonated Calixarenes, *Electroanalysis* 17 (2005) 1609–1615.
- [31] M. Vazquez, J. Bobacka, M. Luostarinen, K. Rissanen, A. Lewenstam, A. Ivaska, Potentiometric Sensors Based on Poly(3,4-Ethylenedioxy-Thiophene) (PEDOT) Doped with Sulfonated calix[4] arene and calix[4] resorcarenes, *J. Solid State Electrochem.* 9 (2005) 312–319.
- [32] A. Michalska, A. Gałuszkiewicz, M. Ogonowska, M. Ocypa, K. Maksymiuk, PEDOT films: multifunctional membranes for electrochemical ion sensing, *J. Solid State Electrochem.* 8 (2004) 381–389.
- [33] E. Lindner, Y. Umezawa, Performance Evaluation Criteria For Preparation and Measurement of Macro- and Microfabricated Ion-Selective Electrodes, *Pure Appl. Chem.* 80 (2008) 85–104.
- [34] P.C. Meier, Two-Parameter Debye-Hueckel Approximation for the Evaluation of Mean Activity Coefficients of 109 Electrolytes, *Anal. Chim. Acta* 136 (1982) 363–368.
- [35] B.E.H. Saxberg, R. Kowalski, Generalized Standard Addition Method, *Analytical Chemistry* 51 (1979) 1031–1038.
- [36] K. Trzcinski, M. Szkoda, K. Siuzdak, M. Sawczak, A. Lisowska-Oleksiak, Enhanced Photoelectrochemical Performance of Inorganic–Organic Hybrid Consisting of Bivo<sub>4</sub> and PEDOT:PSS, *Appl. Surf. Sci.* 388 (2016) 753–761.
- [37] J.A. Cobos-Murcia, L. Galicia, A. Rojas-Hernández, M.T. Ramírez-Silva, R. Álvarez-Bustamante, M. Romero-Romo, G. Rosquete-Pina, M. Palomar-Pardave, Electrochemical Polymerisation of 5-Amino-1, 10-Phenanthroline onto Different Substrates, Experimental and Theoretical Study, *Polymer (Guildf.)* 46 (2005) 9053.
- [38] E. Garfias-García, M. Romero-Romo, M.T. Ramírez-Silva, J. Morales, M. Palomar-Pardave, Electrochemical Nucleation of Polypyrrole onto Different Substrates, *Int. J. Electrochem. Sci.* 5 (2010) 763–773.
- [39] J. Bobacka, Potential Stability of All-Solid-State Ion-Selective Electrodes Using Conducting Polymers as Ion-to-Electron Transducers, *Anal. Chem.* 71 (1999) 4932–4937.
- [40] G.J. Moody, Bahruddin B. Saad, J.D.R. Thomas, Studies on Bis(Crown Ether)-Based Ion-Selective Electrodes for the Potentiometric Determination of Sodium and Potassium in Serum, *Analyst* 114 (1989) 15–20.



- [41] S. Chandra, R. Buschbeck, H. Lang, Triethylene Glycol Ether End-grafted Carbosilane Dendrimer: A Potential Ionophore for Potassium Ion Recognition, *Analytical Sciences* 22 (2006) 1327–1332.
- [42] D. Siswanta, Y.D. Wulandari, J. Jumina, Synthesis of Poly(Benzyl-eugenol) and Its Application as an Ionophore for a Potassium Ion-Selective Electrode, *Eurasian Journal of Analytical Chemistry* 11 (2016) 115–125.
- [43] S.S.M. Hassan, W.H. Mahmoud, A.H.M. Othman, A Novel Potassium Ion Membrane Sensor Based on Rifamycin Neutral Ionophore, *Talanta* 44 (1997) 1087–1094.
- [44] W.S. Han, Y.H. Lee, K.J. Jung, S.Y. Ly, T.K. Hong, M.H. Kim, Potassium Ion-Selective Polyaniline Solid-Contact Electrodes Based on 4',4(5)-Di-tert butyldibenzo-18-crown-6-ether Ionophore, *Journal of Analytical Chemistry* 63 (2008) 987–993.
- [45] S. Kim, H. Kim, K.H. Noh, S.H. Lee, S.K. Kim, J.S. Kim, Potassium Ion-Selective Membrane Electrodes Based on 1,3-alternate calix[4] crown-5-azacrown-5, *Talanta* 61 (2003) 709–716.
- [46] H.J. Adrouge, N.E. Madias, *Am. J. Med.* 71 (1981) 456.

