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Fabrication and Characterization of Solid-Contact Anion-Selective Electrodes Based on Macrocyclic Receptors

Master´s thesis

Material Science

30 EAP

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Abbreviations

CP	Conducting polymer
CTRL	Control (membrane or electrodes)
DOS	Dioctyl sebacate
DMSO	Dimethyl sulfoxide
EIS	Electrochemical impedance spectroscopy
GC	Glassy carbon
HMW	High molecular weight
ISE	Ion-selective electrode
ISM	Ion-selective membrane
$\log a_{LLL}$	Logarithm of the lower limit of linear range
$\log a_{LOD}$	Logarithm of the limit of detection
NaOAc	Sodium acetate
NPOE	2-nitrophenyl octyl ether
PCTFE	Poly(chlorotrifluoroethylene)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEEK	Poly(ether ether ketone)
PVC	Poly(vinyl chloride)
SSM	Separate solution method
THF	Tetrahydrofuran

Introduction

The science of chemical sensors is a vast and rapidly developing field of study. A large number of substances in nature are in the form of ions. Thus, determining these ions easily is of great importance. Among different types of sensors solid-contact ion-selective electrodes are some of the most fascinating as they are quite robust and cheap, while often providing necessary performance (selectivity, accuracy, limit of detection, etc) for monitoring.

There are several challenges to be faced when developing these kinds of sensors since they consist of several components that affect their performance. The most important component is usually the receptor, capable of selective ion binding. Therefore, it has become a widespread field of study to develop different kinds of synthetic receptors for ions. However, the work usually stops after synthesizing and characterizing these receptors as individual molecules. As a result, only modest progress is made towards producing working chemical sensors. If working sensors are nevertheless desired, then it is also paramount to focus on the other half of the work – implementing the receptor molecules into real sensors.

The purpose of this thesis is to investigate the process of making and the performance of these sensors using a series of macrocyclic receptors as the “active agents” and providers of selectivity. Macrocyclic receptors with different pocket sizes were chosen because their structure can provide steric benefits to the binding process that also influence the selectivity of the sensor. Overall, the whole manufacturing and characterizing process of these sensors is thoroughly described as to provide a future guideline for making similar sensor systems. In the discussion part, rather than addressing only the results obtained with the electrodes, the focus is on why some of the results are the way they are and what are additionally important considerations to keep in mind during the process of making potentiometric solid-contact ion-selective electrodes.

On a larger scale, this thesis describes the final part of a several years long project, which was meant to cover the whole process from the design and synthesis of these macrocyclic receptors to finally using them in real sensors. This directs the focus on proof-of-concept rather than producing sensors that should be made commercial immediately after the research.

1. Literature overview

1.1 Ion-selective electrodes

Ion-selective electrodes (ISEs) are one of the most important and widely used classes of chemical sensors[1,2]. Often also referred to as potentiometric ion sensors, they work under zero current conditions, producing a voltage change that is in correlation to analyte species concentration (more accurately activity) in the sample solution[3]. Because of the relative simplicity of potentiometry, ISEs can be made rather small and portable, while having low energy consumption and low overall production costs[4].

Among the ISEs, the most notable and well-known group are the glass electrodes for pH measurement, which have been used over 100 years by now. However, the development of ISEs for detecting other ionic analytes is also of great importance and has exponentially increased over the course of the last few decades[5]. Some important fields of applications of ISEs include medical analysis[6], in which they are used for detecting blood electrolytes (K^+, Na^+, Cl^- and HCO_3^-) as well as for environmental and industrial monitoring[7], where they allow remote sensing and possibly automated process control.

Overall, both cation and anion sensing can be achieved with ISEs, although the former is usually easier to achieve and therefore currently there are more ISEs for cations than for anions[8]. The reasons behind this are that anions are relatively larger and more hydrated as well as many common anions are with different geometries (NO_3^-, $H_2PO_4^-$) or present only in narrow pH ranges ($H_2PO_4^-$, CO_3^{2-}). Nevertheless, the work done for developing anion sensitive ISEs has significantly advanced in the last two decades and there are already several quite good ISEs for many common anions.[9]

As already stated, the ISE's working principle relies on potentiometry, which requires a two-electrode system, where the potential is measured between the working and reference electrode. The ISE is the working electrode, which is in the ideal case selective towards one specific analyte ion. This selectivity is achieved with an ion-selective membrane (ISM) that recognizes the ions of interest. For this, the ISM must be in contact with the sample from one side, while the other side of ISM is either in connection with the ISE's inner solution that helps to convert ionic information into electrical signal or with a solid ion-to-electron transducer also referred to as the solid contact[3]. Based on this, ISEs can be divided into conventional ISEs, which have an inner filling solution, and solid-contact ISEs that have a solid state ion-to-electron transducer (**Figure 1**). The advantages of the latter are that they are more robust, easier to miniaturize as well as to maintain. At the same time their long-term stability is currently a key issue in their development[10,11].

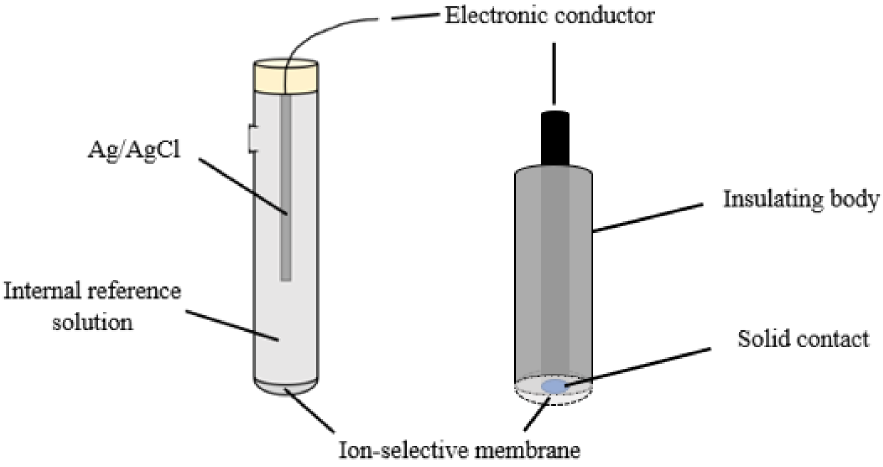


Figure 1. Structures of conventional (left) and solid contact (right) ion-selective electrodes.

Additionally, ISEs are classified based on the type and material of the ISM, which are usually glass, crystalline, liquid or polymeric[1]. In context of the current thesis, only polymeric membranes are considered and discussed.

Ion-to-electron transducers

The first prototypes of solid-contact ISEs were demonstrated in the 1970s with the coated-wire electrode[12]. However, one serious drawback of these sensors was poor potential stability resulting from the interface between the electronic (metal wire) and ionic (ISM) conductor. Nowadays one way to easily overcome this problem is to use electroactive material with ionic and electronic conductivity that serves as the ion-to-electron transducer. These kinds of materials are for example lipophilic silver complexes, ferrocene, Prussian blue and conducting polymers (CP)[3]. From the viewpoint of the current thesis, only the use of the latter is looked at in more detail.

To achieve electrical conductivity in polymers, they must form a π-conjugated system, where single and double bonds alternate. Additionally, either p- or n-doping is required to give the polymer real electrical conductivity. This is achieved by partially oxidizing or reducing the polymer[13]. This oxidation also provides the polymer with charged sites that make the polymer ionically conductive, which therefore enables the transduction of an ionic signal into an electronic one in the solid state. The doping of the CP depends on several factors and the specifics of the desired outcome. For instance, when cationic exchange is required, then large immobile polyelectrolytes with anionic centers in the polymeric backbone are used, e.g. polystyrene sulfonate. For anion exchange, the CP is doped with small mobile anions that can be either the primary ions themselves or easily replaced later with the analyte ions.[3]

For a polymer to be suitable for use as a solid contact, it must have in addition to ionic and electronic conductivity also high redox capacitance and possess good stability in the oxidized state[3]. Additionally, using CPs is favored because of easy manufacturing process that offers variability as they can be either deposited on the substrate by electropolymerization or simply by solution-casting of the soluble polymer. Electrochemical polymerization is mostly used when it is necessary to deposit thin films with controlled thickness. Furthermore, since polymers can be functionalized, using CPs gives the possibility of designing them for specific purpose or for binding covalently other components to the CP.[14]

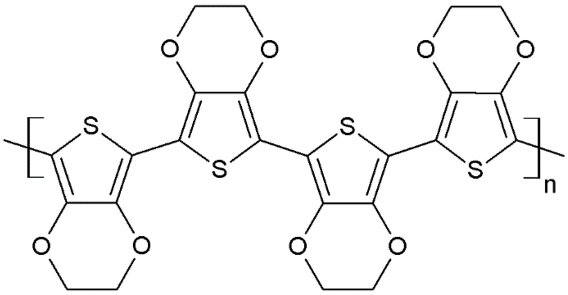


Figure 2. Molecular structure of poly(3,4-ethylenedioxythiophene).

Some of the most notable groups of conducting polymers used as the solid contact in ISEs involve polypyrroles, polythiophenes and polyanilines[4]. Among polythiophenes, poly(3,4-ethylenedioxythiophene) or simply PEDOT (**Figure 2**) is one of the most used and studied conducting polymer in the recent years as it is highly electroactive and also shows good environmental stability[4,13].

Ion-selective membranes

The selectivity and main working principle of ISEs is attributed to a selectively permeable ion-selective membrane (ISM) through which ideally only a single type of ions can penetrate. Therefore, the ISM’s composition usually determines the species to which the electrode is selective. The ISM is typically composed of a polymeric matrix (e.g. PVC), with or without plasticizer, into which different dopants such as ionophores and lipophilic ion exchangers have been added.[5]

The lipophilic ion-exchangers give membranes permselective properties and are also necessary for keeping the concentration of analyte in the bulk of the membrane phase relatively fixed[5]. In the case of anion sensing, the selectivity achieved with these ion-exchangers follows the Hofmeister series in the order:

$$SCN^- > I^- > NO_3^- > Br^- > Cl^- > OAc^- > F^- > H_2PO_4^- > SO_4^{2-}$$

, where lipophilic anions are preferred over hydrophilic ones[15]. However, the exact structure of the ion-exchanger can influence the observed selectivity pattern even more, making them not always nonspecific. Some examples of the most commonly used ion-exchangers are tridodecylmethylammonium chloride for anion-selective and potassium tetrakis (4-chlorophenyl) borate for cation-selective electrodes[5].

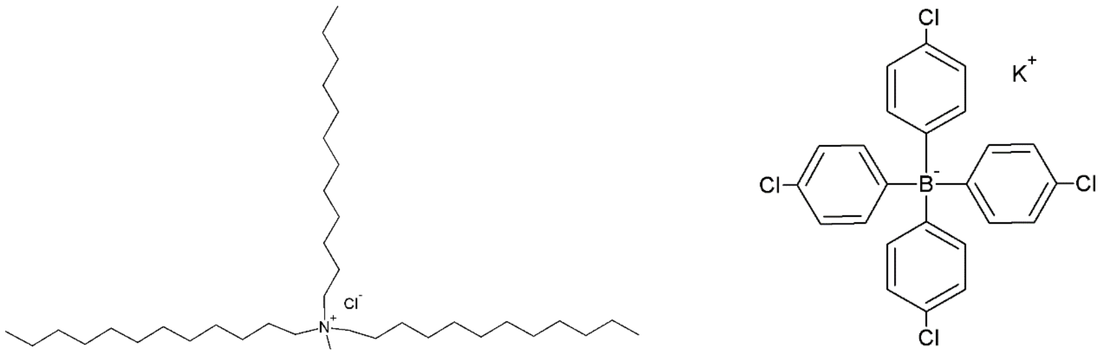


Figure 3. Examples of ion exchangers: tridodecylmethylamonium chloride; potassium tetrakis (4-chlorophenyl) borate.

The second main type of dopants are ionophores that can selectively recognize the ionic species of interest. These ionophores are structurally very diverse molecular receptors, which can provide a selectivity pattern that differs from the Hofmeister sequence[1]. They interact with the analyte in various ways among which hydrogen bonding, electrostatic interactions as well as the geometry of the host and guest molecules are important. In addition, solvation energies can play significant role here, especially for very hydrophilic ions, making it easier to design ionophores for cations rather than anions.[5]

Most commonly ionophores are neutral, highly lipophilic molecules that can freely move around in the membrane. Also, structurally they often have cavities or binding pockets, which can greatly improve their selectivity[5]. Some examples of successful ionophores for anions are presented in **Figure 4**.

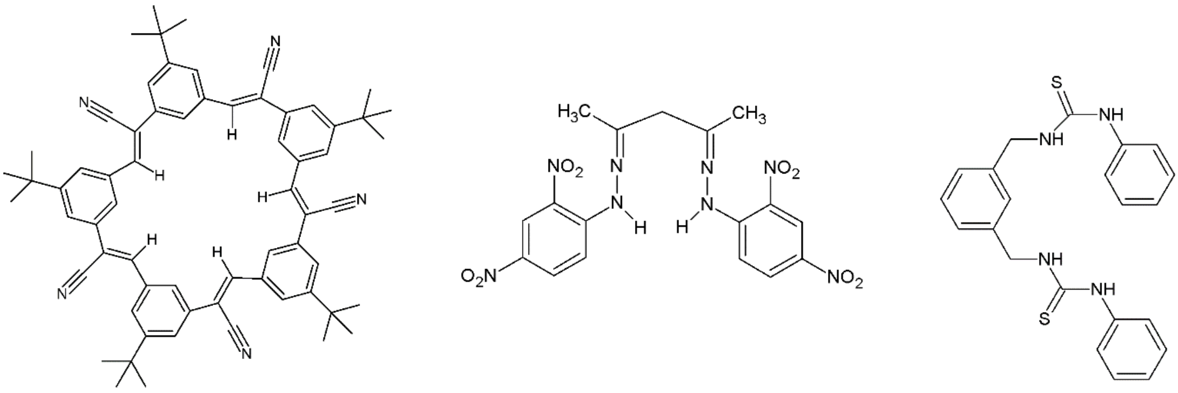


Figure 4. Examples of different ionophores (from left to right): perchlorate ionophore[16], acetate ionophore[17], sulphate ionophore[18]

In addition to ionophores, plasticizers also play an important part in achieving selectivity of the membrane. For instance, nonpolar plasticizers such as dioctyl sebacate are mostly used when working with monovalent ions and plasticizers of high polarity (2-nitrophenyl octyl ether) are more suitable for divalent ions[19]. Moreover, changing the ratio of membrane components can also significantly alter the performance of ISEs and it is often something that needs to be tried out experimentally to get the best results[5,20].

1.2 Potentiometric response

The ISEs work on the principle of electrochemical equilibrium, where an electrical potential difference develops at the boundary of ISM and the sample solution. This is to counteract the analyte ions from partitioning into or out of the membrane as the concentration of ionic exchanger remains the same. The partitioning of ions depends mainly on their and ISM's lipophilicity as well as on the solution concentration.[5]

To measure this potentiometric response, an indicator electrode (ISE) and a reference electrode against which the ISE's potential is measured is needed. In addition, a liquid junction potential (E_{lj}) that develops at the interface between the reference electrode and the sample solution must be eliminated or accounted for. Accounting for the liquid junction potential can be done with the Henderson equation[21]. However, more commonly the liquid junction potential is eliminated via cancellation. This is achieved by using a reference electrode with concentrated internal solution of an equitransferent electrolyte (anion and cation having the same mobility), which will generate very similar liquid junction potentials in the case calibration and measurement. Overall, the measured cell potential forms from the following components[22]:

$$E_{\mathrm{cell}} = E_{\mathrm{ind}} - E_{\mathrm{ref}} + E_{\mathrm{lj}} \tag{1}$$

In the perfect scenario, where ion-selective electrodes respond to only one specific type of ion this response can be linked to the ion's activity in solution with the Nernst equation[23]:

$$E_{\mathrm{cell}} = E_{\mathrm{I}}^{0} + \left(\frac{RT}{z_{\mathrm{I}}F}\right) \ln a_{\mathrm{I}} \tag{2}$$

E_{cell} is the measured cell potential, E_{I}^{0} is the standard potential of the ISE incorporating all the constant contributors to the potential, a_{I} and z_{I} are the activity and the charge of the measured ion and *R, T, F* have their universal meanings.

In practice, decadic logarithmic term is used and assuming that measurement is conducted at 25 °C while using mV as the unit of measurement, **Equation 2** can be simplified to:

$$E_{\mathrm{cell}} = E_{\mathrm{I}}^{0} + \frac{59.2\ \mathrm{mV}}{z_{\mathrm{I}}} \log a_{\mathrm{I}} \tag{3}$$

This means that for a monovalent ion such as sodium, potassium or chloride ion, for every 10-fold change in activity the potential changes by 59.2 mV, which correspond to the so-called theoretical or "Nernstian" slope. Depending on whether the analytes are cations or anions, the potential change when activity increases is either +59.2 mV/dec or -59.2mV/dec, respectively. In practice the absolute values of slopes are often below theoretical. In this thesis slopes with absolute values below 56 mV/dec are termed "sub-Nernstian", slopes in the range of 56-58 mV/dec are termed "near-Nernstian" and slopes above 58 mV/dec are termed "Nernstian".

Selectivity coefficients and their measurement

In real world situations when the solution contains more than one species of ions to which the ISEs may respond to or in the case of selectivity measurements, the Nikolsky-Eisenman equation is used:[24]

$$E_{\mathrm{cell}} = E_{0} + S \ln[a_{\mathrm{A}} + \textstyle\sum_{\mathrm{B}} K_{\mathrm{A,B}}^{\mathrm{pot}} (\,a_{\mathrm{B}})^{z_{\mathrm{A}}/z_{\mathrm{B}}}] \tag{4}$$

E_{cell} is here the measured potential, E_{0} is the standard potential, z_{A} and z_{B} are the charges of the primary (A) and the interfering (B) ion while a_{A} and a_{B} are the corresponding activities, *S* is the experimentally obtained slope from the calibration curve.

$K_{\mathrm{A,B}}^{\mathrm{pot}}$ is the potentiometric selectivity coefficient for the primary ion against the interfering ion. For a potassium selective electrode with possible interference from sodium it would be presented as $K_{\mathrm{K,\ Na}}^{\mathrm{pot}}$. If the $K_{\mathrm{A,B}}^{\mathrm{pot}}$ is larger than 1, the ISE responds more strongly to the interfering ions than to the primary ions and if the value is smaller than 1 then it is vice versa. Moreover, often the logarithmic values of the selectivity coefficients are used instead.[5]

There are several different approaches for determining selectivity coefficients, among which the two main groups are the mixed solution methods (MSM) and separate solution methods (SSM)[24]. Most of these methods rely on the Nikolsky-Eisenman equation and ideally the results obtained using different methods should give similar selectivity coefficients. However, depending on the exact conditions and measurement protocols even the results for similar membrane compositions by different authors often disagree[25]. This means that when publishing obtained selectivity coefficient values it is also important to specify the details of the measurement protocol.

For the current research, the most common separate solution method was applied. This SSM involves measuring two separate solutions with the same setup, where in one of them, only the primary ion A with the activity a_A is present while the other one contains only the interfering ion (B), but with the same activity as in previous case so that $a_\mathrm{B}= a_\mathrm{A}$[24]. Additionally, the exact time that the ISE spends in the measurement solution is recorded, which makes the use of improved SSM selectivity coefficient calculation method possible if needed to.

The $\log K_{\mathrm{A,B}}^{\mathrm{pot}}$ values are calculated for the common SSM by dividing the difference between potentials in interfering (E_B) and primary (E_A) ion solutions with the slope of the electrode. In addition, in case the charges of primary and interfering ions are different, this must be accounted for[24]:

$$log\ (K_{\mathrm{A,B}}^{\mathrm{pot}}) = \frac{E_\mathrm{B}-E_\mathrm{A}}{S} + (1-\frac{z_\mathrm{A}}{z_\mathrm{B}}) log a_\mathrm{A} \qquad (5)$$

Equation 5 relies only on two measurement points and may be of limited accuracy if the equilibrium has not been properly established. Because of this, several improved techniques have been published that take into account the time dependency of the equilibration processes[25,26]. This is especially important if the selectivity of the electrode to the primary ion is several orders of magnitude larger than to the interfering ions. In this thesis, however, it was decided not to use the time-dependent approach. There are two reasons for this: (1) in the case of electrodes prepared in this thesis interfering ions are not too discriminated and (2) using time-dependent approach may under used experimental conditions even increase the uncertainty as it cannot differentiate between the time-dependency of the ISE's response and the effect caused by a slow increase in the concentration of chloride in the cell.

2. Experimental part

2.1 Used chemicals and instruments

The chemicals used to make membrane cocktails: 2-nitrophenyl octyl ether (NPOE), di(2-ethylhexyl) sebacate (DOS), tridodecylmethylammonium chloride (TDMACl), high molecular weight poly(vinyl chloride) (PVC) and tetrahydrofuran (THF, ≥99.5%) were Selectophore^{TM} grade reagents from Fluka. 3,4-ethylenedioxythiophene (EDOT, 97%) was obtained from Sigma-Aldrich and all the other chemicals used (sodium salts, sodium hydroxide, potassium chloride, acetic and nitric acid) were analytical-reagent grade. Deionized water from ELGA Purelab Ultra (resistivity 16 - 18 MΩcm) was used in all experiments.

The primarily used reference electrode was a commercial double-junction Ag/AgCl electrode from Metrohm. During all the measurements, a 3 M KCl was used for the inner solution. In the outer compartment, initially 1 M KCl solution was used, but it was later changed for 0.1 M KCl to minimize the effect of KCl leaking in the sample solution. The inner and outer solutions were replaced periodically, outer solution every day and inner on weekly basis. In addition, a double-junction Ag/AgCl electrode from Elmetron with saturated KCl inner solution and the same outer solutions as with the Metrohm reference electrode was used a few times, when it was required to conduct simultaneous measurements and only one of the Metrohm reference electrodes was available.

A Thermo Scientific Orion Star A111 pH meter was used for monitoring the pH and temperature of the solutions. Prior to each use, it was calibrated with buffer solutions of pH 4.00 and 7.00. Furthermore, to observe the deposited ISMs and polished electrode surfaces, a Leica MZ125 optical microscope with a Leica DC 300 digital camera was used.

For the electropolymerization, cyclic voltammetry and electrochemical impedance measurements an Autolab General Purpose Electrochemical System and Autolab Frequency Response Analyzer System were used. For the potentiometric measurements a 16-channel Lawson EMF16 potentiometer and Metrohms' 800 Dosino pumps were used.

2.2 Fabrication of the electrodes

Commercially available SIGRADUR® G glassy carbon (GC) rods (3 mm diameter) encased in PVC shells (8 mm outer diameter) from Simona AG were used as electrode bodies (**Figure 1**). In addition to PVC electrode bodies, several electrode bodies with PCTFE shells and some with

PEEK shells (both 6 mm outer diameter) were tested. However, because of the compatibility with the membrane material PVC remained the preferred shell material throughout the work.

The PVC electrodes were polished first with wet sanding, using sandpaper with grit sizes from 100 to 4000. Using rough sandpaper in the beginning was necessary, because the electrode bodies are reusable and as the previous membrane components can diffuse into the PVC shell. Thus, it is important to make sure that no previous membrane components remain. After sandpaper, the polishing continued with diamond paste (particle size 1-15 μm).

As a quality control during the process, the surfaces of the electrodes were visually examined and some were also investigated with an optical microscope to detect defects that might occur – especially at the interface between the GC rod and the PVC shell. In addition, in this phase cyclic voltammetry was conducted with all the electrodes, to check whether any traces of the former membrane or other interfering substances were present. It also gave an estimate of the smoothness of the electrode surface.

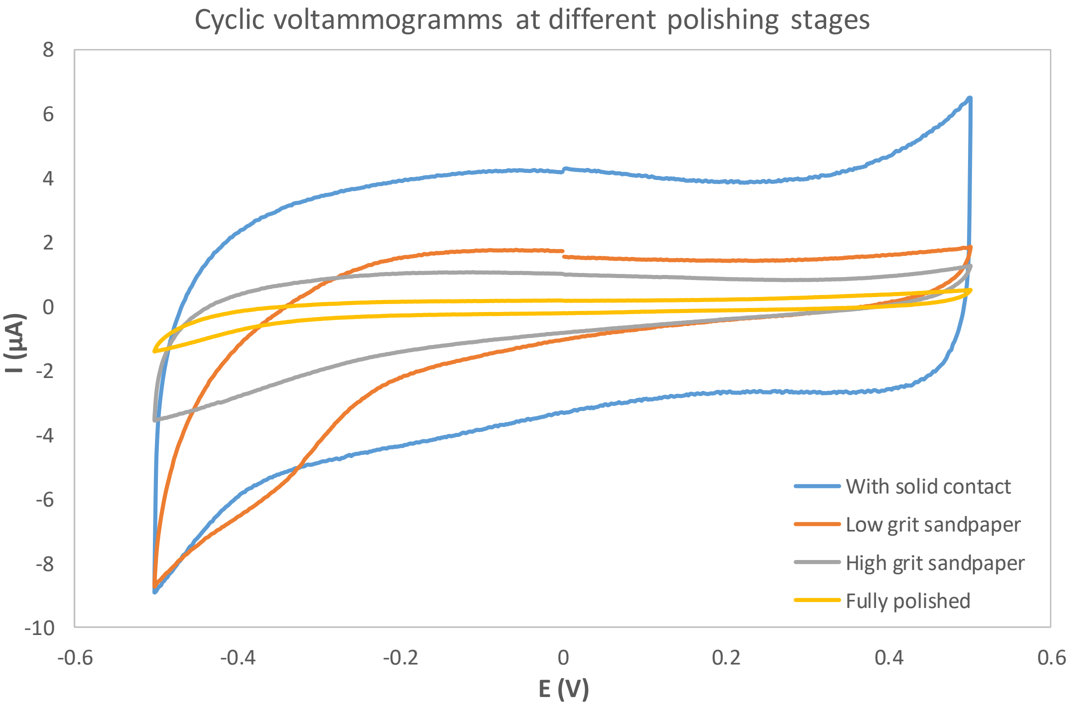


Figure 5. Examples of voltammograms at different polishing stages for the same electrode. Potential scan rate = 0.1 V/s.

If the observed currents were in desirable limits (less than 1 μA) and no noticeable peaks were detected in the voltammogram, then the polishing was completed with 0.3 μm Al_2O_3 paste. Alumina paste was also the only polishing step used for PEEK and PCTFE electrodes as there was no strong interference from the previous membrane in their case. Following the polishing process, the electrodes were thoroughly cleaned – first ultrasonically for 5 minutes both in deionized water and in ethanol and then chemically for 2 minutes in 1 M HNO_3 after which they were once more put to ultrasonic bath in deionized water for 5 minutes.

Electrochemical synthesis of PEDOT(Cl)

Galvanostatic electropolymerization was carried out using a single-compartment three-electrode system. The electrode bodies described in the previous section were used as working electrodes. The polished glassy carbon (GC) disk with an area of 0.07 cm^2 (it was the same for PVC, PCTFE and PEEK electrode bodies) acted as the active surface. The reference electrode was a double-junction Metrohm Ag/AgCl electrode and a GC rod was used as the counter electrode.

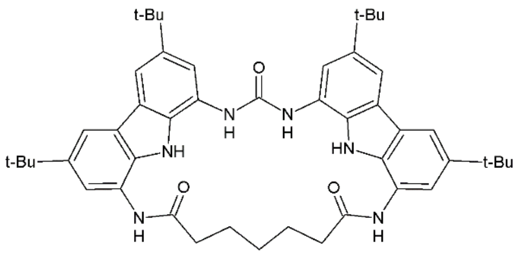
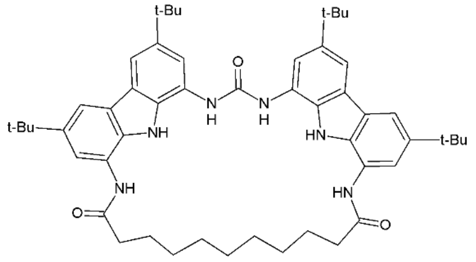
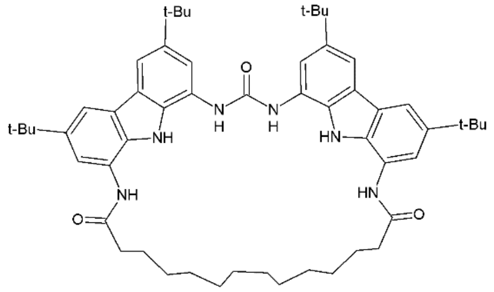
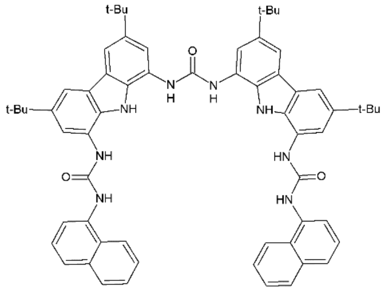
For polymerization, an aqueous solution of 0.01 M EDOT and 0.1 M KCl was prepared and then purged for 15 min with nitrogen prior to the process. During the polymerization a constant current of 14 µA was applied for 714 s while a nitrogen flow was kept over the solution surface. As a result, a slightly blueish film was visible on the surface of electrodes giving a proof that polymerization was successful. After the PEDOT layer had been electrodeposited on the GC surface, the electrodes were left for conditioning in a 0.01 M NaOAc solution overnight.

Making and applying the membrane

Five different ion-selective membranes were made with each plasticizer. As approximate values, the dry fraction of the membrane consisted of the following components in mass percentages: 65 % plasticizer (NPOE or DOS), 32 % HMW PVC, 2 % ionophore and 0.6 % TDMACl (50 % of mole fraction of the used ionophore). The total mass of the “dry” part corresponded to approximately 17 % of total membrane cocktail weight after being dissolved in THF. After adding THF, membrane cocktails were left on a mixer overnight and were stored in the refrigerator afterwards.

In total, four different ionophores, synthesized in Tartu University by Sandip A. Kadam and Mihkel Ilisson, that are presented in **Table 1** were used, three of which were macrocyclic molecules with different carbonyl ring sizes (MC0XX). The fourth one was a 1,3-bis(carbazolyl)urea derivative (CZ007) previously also used in a similar study by Kerli Martin.[27] Lastly, the fifth membrane cocktail had all the ingredients with the corresponding fractions except the ionophore and it was made to serve as a control membrane (CTRL).

Table 1. The structures of the used ionophores and their code names.

Name	MC005	MC009
Structure		
Name	MC012	CZ007
Structure		

The membrane cocktail was applied on the surface of a dried electrode via drop-casting with an automatic pipette. In case of PVC electrodes, 100 µl of the membrane cocktail was deposited in two additions with 30 minutes between them to let the solvent evaporate. For PCTFE electrodes 20 µl was used both times, because of the smaller diameter of electrode body. For the same reasons, for PEEK electrodes only one time 50 µl addition was done. Following the process, the electrodes were left to dry until next day, after which they were immersed into 0.1 M NaOAc conditioning solution for at least two days.

Planning and timetable

The initial plan for measurements was to focus on three novel macrocyclic receptors and to see whether there is any difference in their behavior in the sensor. The non-cyclic receptor with naphthalene groups CZ007 was added to serve as an additional reference to enable comparison with the previous work of Kerli Martin[27]. Because of this, the same membrane compositions and similar measurement techniques were used. However, during the experimental work several stages were improved and complemented with additional steps.

Similarly to Kerli Martin’s work, acetate was chosen as the primary ion because the measurements with similar receptors in DMSO-water systems suggested that out of simple carboxylates, acetate is among those that are most strongly bound[28]. Moreover, it is a common anion in nature as well as in food industry, making it an important analyte to be detected.

For the first measurement series 14 electrodes were made using the five different membrane compositions and with NPOE as the plasticizer. There were three of each electrode except for the ones containing CZ007 and the measurements with those electrodes lasted for about two months.

Following the initial set of electrodes, the effect of the plasticizer was investigated by replacing NPOE with DOS, which is considered more suitable for monovalent ions[19]. For that, 15 PVC electrodes with DOS as the plasticizer were made and the measurements with these electrodes lasted for about three weeks. After that, electrodes were remade using the same membrane cocktails and three electrodes with PEEK bodies were added, one with each of the macrocycles (see below). Additionally, after measurements with DOS, a small series of six electrodes (two for each macrocycle) with the old NPOE membrane cocktails was made, having three PVC and three PEEK electrodes.

Finally, after receiving new chemicals and analyzing all the previous data, a repeated set of measurements for DOS and NPOE was conducted, using 10 new PVC and 10 new PCTFE electrodes. The selectivity measurements with these electrodes were carried out with the help of Åbo Akademi University’s PhD student Ville Yrjänä in order to shorten measurements’ time as well as to eliminate possible operator errors by measuring two sets of five electrodes at the same time. Among all the results, these last measurements are expected to be most trustworthy.

Overall, all the measurements were done over the course of 15 months and in total 93 sensors were made and tested during that time.

2.3 Characterization of the electrodes

To characterize the prepared ISEs electrochemical impedance spectroscopy (EIS) and potentiometry were used. For all series, four different types of measurements were done in the following order. Firstly, EIS was conducted to determine the resistance and the overall condition of the membrane. Following that, at least two repetitions of calibration measurements were done to see the potentiometric response to the change of primary ion activity in the solution. After that, measurements observing the effect of pH on the performance of the ISEs were done. Finally, the most diverse set of measurements consisted of determining the selectivity coefficients for 14 potentially interfering anions. In addition, after selectivity experiments, calibration measurements were repeated to see whether and how much electrodes’ performance had changed over the course of time and because of other measurements.

Electrochemical impedance spectroscopy

Similarly to polymerization, a three-electrode cell with the same equipment including nitrogen purging was used. However, the measurements were conducted in a 0.1 M NaOAc solution. The impedance measurements were performed at an open-circuit potential by applying a sinusoidal potential modulation with an amplitude of 100 mV in the frequency range going from 100 kHz to 100 mHz while 61 points were recorded.

The purpose of the impedance measurements was to get qualitative rather than quantitative information about the quality and performance of the membranes. The high-frequency range should provide a semicircle, which can be assigned to the bulk resistance in parallel with the geometric capacitance of the ion-selective membrane. The lower frequency part should show a diffusion line that is related to the diffusion of ions in the ISM (and PEDOT) layers. Additionally, the imaginary impedance at the lowest frequencies should correlate with the redox capacitance of PEDOT[10]. Examples of the recorded impedance spectra are presented in **Figures 6** and **7**.

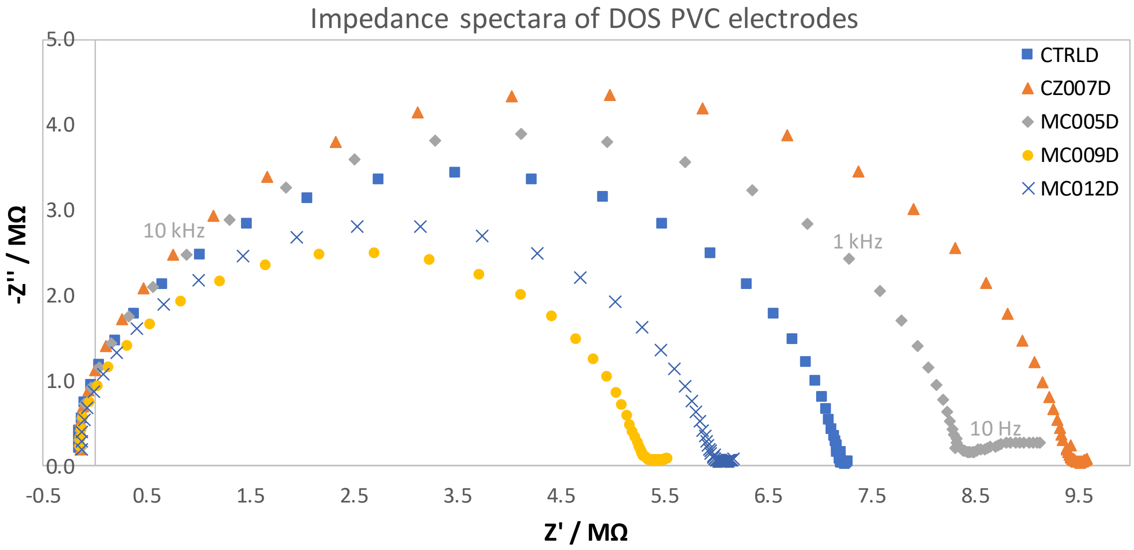


Figure 6. Example of the typical impedance spectra for one of each different PVC electrodes with DOS as the plasticizer.

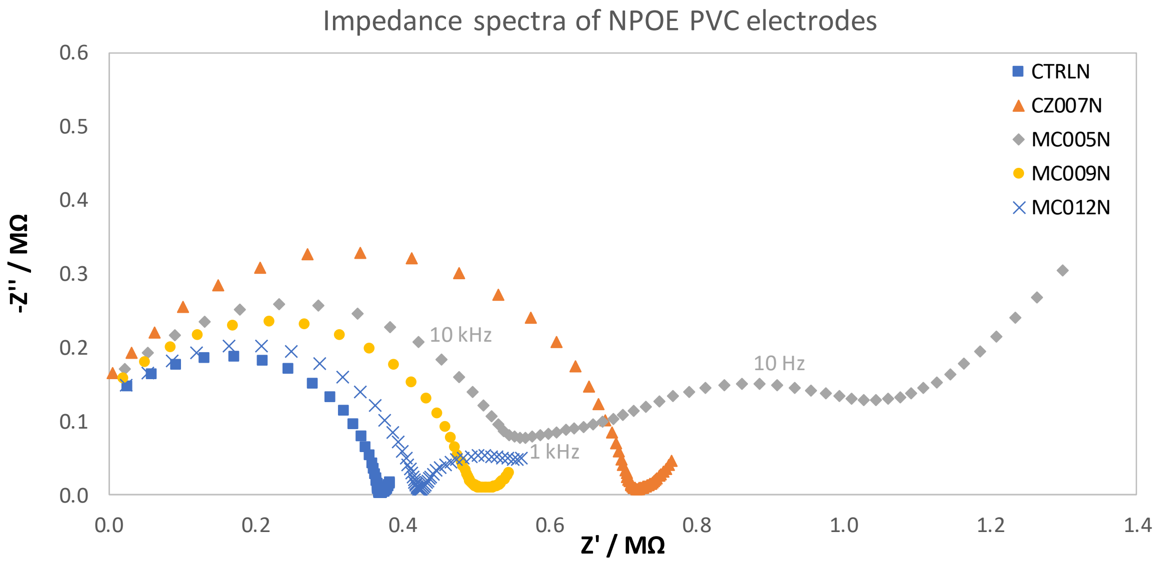


Figure 7. Example of the typical impedance spectra for one of each different PVC electrodes with NPOE as the plasticizer.

It can be said for all the cases that the impedance spectra had an initial semicircle and there was also a rise in impedance at low frequency corresponding to the diffusion process. On the other hand, processes taking part in the middle to low frequency range (1 kHz – 1 Hz) of the spectra are more complicated to exhaustively describe especially in the case of NPOE as the plasticizer. They are most likely the result of additional processes in the membrane or at different interfaces that might become visible under certain circumstances. Moreover, the shapes of the impedance spectra appeared to be strongly connected with the ionophore used in the membrane. Because of that, it was also possible to determine which ionophore was in the membrane based on the spectra. This analysis however was not regarded too important in context of this work and will not be discussed further.

From the quantitative side, the values of the bulk resistance varied from series to series and were heavily influenced by the plasticizer, since it makes up the biggest part of the ISM. In case of NPOE for PVC electrodes, they were around 400 – 800 kΩ and for DOS and PVC electrodes they were between 5 and 15 MΩ. The variations in case of the same plasticizer can be accounted for by the small differences in the thicknesses of the ISMs as well as the slightly different ages of the membranes (and therefore to differences in water uptake). The differences in thicknesses are also the main reason why the bulk resistance was a bit lower for PCTFE and PEEK electrodes.

Potentiometric measurements

To determine the potentiometric response towards the change of acetate ion's activity, calibration measurements were conducted. For that, 10 ISEs (usually two for each membrane composition) were immersed in 60 ml of 0.1 M NaOAc solution. In addition, the cell contained the reference electrode and two tubes that were connected to the automated dilution system. The dilution system pumped out a certain amount of the solution from the sample cell and then added the same amount of deionized water, diluting the solution by half-decade at a time. In total, usually 12 dilutions were done, making the concentration of the last solution 10^{-7} M.

The time between dilution steps was six or seven minutes (depending on the measurement series) and based on the average observed response time that was enough for the solution to mix and potentials to stabilize. No additional stirring was used as the flow from the dilution pumps already provided mixing of the solution. Another reason behind trying to avoid using magnetic stirrer was to prevent amplification of diffusion of the KCl from the reference electrode into the solution. Without stirring, the potential drift over time for the electrode that was most sensitive towards chloride ions was minimal.

All measurements were performed at ambient temperatures and the temperature and pH of the sample solutions were monitored by measuring the solutions that the dilution system had pumped out of the sample cell. The pH of those samples remained in the range between 6.5 and 8.5. This slightly depended on the amount of time the solution had been exposed to air, therefore being mostly caused by the dissolution of carbon dioxide from the air. However, it probably varied significantly less in the sample cell during the measurement, because the cell was rather closed to surrounding atmosphere. Furthermore, for calibration and selectivity measurements' data calculation, the Henderson equation[21] was used to estimate the liquid junction potential[29].

pH measurements

To assess the effect of pH on the produced ISEs, acid-base titration measurements were conducted. Starting with a 0.01 M acetic acid solution, the potential response of the electrodes as well as the pH of the solution were recorded. In three- to five-minute intervals, depending on how quickly the potentials stabilized, small amounts of 0.25 M NaOH solution were added. The NaOH solution also contained 0.01 M NaOAc to keep the acetate concentration constant during the measurement. The acetic acid solution was purged for 15 min prior to measurement and constant nitrogen flow was kept on top of the solution surface. Constant stirring was used during the entire measurement.

Selectivity measurements

The selectivity coefficients ($\log K_{\mathrm{A,B}}^{\mathrm{pot}}$) were determined for 14 different anions. For that, the following sodium salts were used: Na_2HPO_4, Na_2SO_4, NaH_2PO_4, $NaHCO_3$, $NaNO_3$, NaSCN, NaF, NaCl, NaBr, NaI, sodium formate, sodium lactate, sodium pivalate and sodium benzoate. These anions were chosen, because they are quite common substances, while presenting a wide range of different properties (size, geometry, lipophilicity). The main protocol of the SSM method that was introduced in **Section 1.2** was used, where for all of the prepared solutions the activity of the interfering anion was equal to the anion activity in the 0.01 M NaOAc solution.

The setup consisted of a cell with five ISEs (one for each of the ISMs) that were measured against the reference electrode in 60 ml of sample solution. All the solutions apart from sodium bicarbonate were purged for 15 minutes prior to measurement, while during the measurement, a nitrogen layer was kept above their surface. Furthermore, all the ISEs were immersed in the solution together a few seconds after starting the recording of potentials to get the exact beginning time for the measurement. Potential values recorded seven minutes into each measurement with the interfering ions were used in the calculations.

During the measurement, constant stirring was used to speed up the time it takes for equilibria to establish in between the membrane composition and sample solution. A negative side effect of this was the increased flow of KCl into the solution from the reference electrode. This was also occasionally visible during the measurement of the anions that were bound the weakest to the receptor, therefore increasing the uncertainty of those values.

For the first measurement of each day, all the ISEs were measured in 0.01 M NaOAc solution and the obtained values were used for that day's selectivity coefficients calculations. This was necessary because of slight drifts of the electrodes' standard potentials over time. The order of interfering ion solutions in which the measurements took place went from those with the lowest selectivity coefficients towards those with the highest selectivity coefficients (both referring to the selectivity of the control electrodes).

Each measurement lasted for 8 minutes after which the ISEs were rinsed and put back into 0.01 M NaOAc conditioning solution and the measured solution was replaced with a fresh one. Also, the conditioning solutions were replaced with the change of interfering ion to avoid any accumulation of different interferants. Between measurements, the electrodes spent at least three times longer in the conditioning solution than they spent in the interfering ion solution, giving them enough time to recover.

3. Results and discussion

3.1 Potentiometric response of the prepared ISEs

As stated in the first part, the ideal change of potential (slope) for an ISE would be -59.2 mV per ten-fold increase in a monovalent anion activity in the sample solution at 25 degrees. However, the initial results with NPOE as the plasticizer led to sub-Nernstian slopes. The results of these electrodes are summarized in **Table 2** and the examples of the calibration curves are presented in **Figure 8**. For the results in **Table 2** and for all later calibration data, an average from all the electrodes' results with the same membrane in that series is presented. The slopes for individual ISEs are in turn calculated from at least two separate calibration measurements for that electrode. The standard uncertainties of these values are expressed as pooled standard deviations. Furthermore, the upper limit of the linear range is always $10^{-1.11}$ M as activities greater than that were not measured.

Table 2. Response characteristics of the first set of NPOE electrodes (N1).

	CTRLN1	CZ007N1	MC005N1	MC009N1	MC012N1
Slope (mV/dec)	-54.2 ± 1.2	-47.8 ± 3.4	-47.8 ± 5.2	-44.0 ± 1.8	-47.6 ± 1.5
log a_{LLL}[a]	-2.77 ± 0.21	-3.69 ± 0.02	-3.49 ± 0.16	-4.00[c]	-4.00[c]
log a_{LOD}[b]	-3.88 ± 0.53	-4.72 ± 0.11	-4.44 ± 0.23	-4.82 ± 0.18	-4.91 ± 0.09

[a] – lower limit of the linear range, [b] – limit of detection, [c] – The lower limit of the linear range was chosen to stretch to $10^{-4.00}$ M to keep the comparison between different sets more universal. Therefore, only results from $10^{-1.11}$ M to $10^{-4.00}$ M are used in calculation of the slope unless the R^2 value dropped below 0.999 before that. This is also the reason why the uncertainty values are only present in case log a_{LLL} is less negative than -4.00.

In the case of NPOE as plasticizer the best slopes were achieved with electrodes without ionophores and they were around -54 mV per decade. For ionophore containing membranes, the slopes were in most cases less negative than -50 mV per decade, however a few individual electrodes reached -52 mV at least in the beginning. When looking at the relatively large uncertainty values, then although it is mainly derived from pooling the results from several electrodes, another important contributor is the age of the ISE. More explicitly, the time between the first and the last calibration measurement was about a month, during which time the slope of most electrodes became less negative by several millivolts.

Another important factor in observing the performance of ISEs is their working range. The linear range ($R^2 \geq 0.999$), for the prepared electrodes extended in most cases from $10^{-1.11}$ M to $10^{-4.00}$ M, although for controls and electrodes with MC005 it often did not reach $10^{-3.50}$ M or even $10^{-3.01}$ M. This was mainly attributed to chloride contamination form the reference electrode rather than the ISEs' own poorer performance. Moreover, as it took over a month to complete these measurements, then during that time, the linear range of the electrodes decreased as well. This is the reason why for CZ007, the presented lower limit of linear range is less than $10^{-4.00}$ M. In conclusion, despite being less than theoretical, these responses were quite similar to the ones previously published by Kerli Martin *et al*[27].

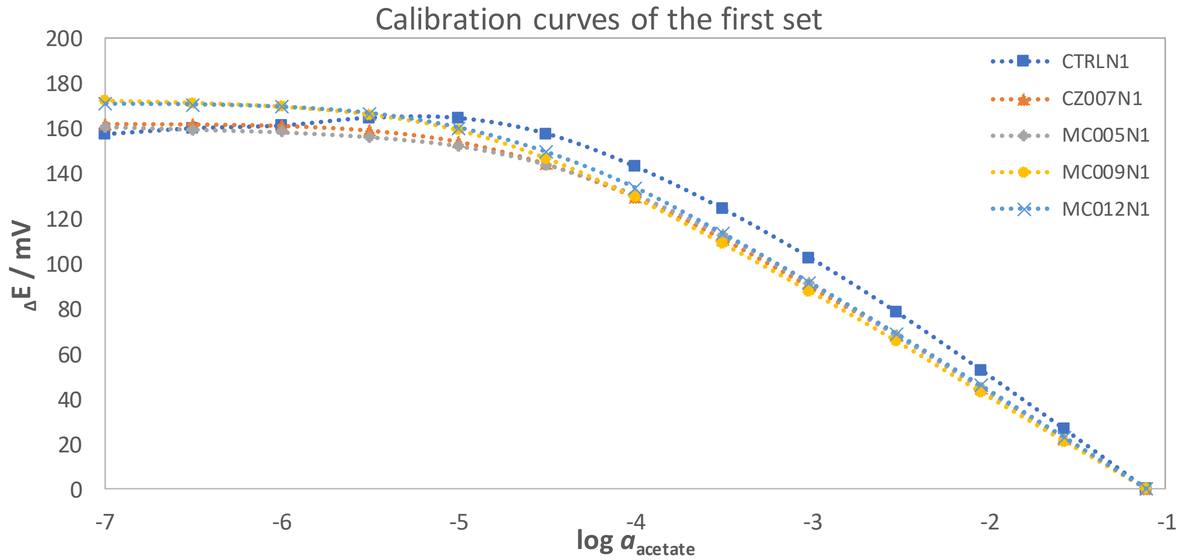


Figure 8. Examples of calibration curves from the first measurement series. The potentials have been shifted on the y-axis in order to start all curves at $_{\Delta}$E = 0.00 mV at log *a* = -1.11.

With the change of plasticizer to DOS, the slopes improved. Several of the electrodes with ionophores were able to reach slopes near-Nernstian slopes of -56 mV per decade. On the other hand, there were several electrodes with even poorer slopes than before, although the membrane on top of them was the same. In **Table 10** in **Appendix 1**, all the calculated slope values from two different measurement sets with DOS are presented. In **Table 3**, a summary of all the results, with slope more negative than -50mV/dec is given and presented as one measurement series and that also includes results from the three PEEK electrodes.

Table 3. Response characteristics of first two sets of DOS electrodes (D1). A summary from **Table 10** in **Appendix 1.**

	CTRLD1	CZ007D1	MC005D1	MC009D1	MC012D1
Slope (mV/dec)	-52.14 ± 0.77	-55.97 ± 0.82	-54.57 ± 0.70	-55.70 ± 0.30	-56.33 ± 0.43
log a_{LLL}	-2.77 ± 0.37	-4.00[a]	-3.29 ± 0.41	-4.00[a]	-4.00[a]
log a_{LOD}	-3.82 ± 0.42	-4.92 ± 0.11	-4.30 ± 0.38	-5.02 ± 0.12	-5.19 ± 0.14

[a] See footnote [c] to **Table 2**.

When looking at the results in **Table 3**, then although the slopes in most cases remain sub-Nernstian, overall those electrodes can be considered quite good. Especially, when taking into account that the measurement temperature was about one to two degrees lower than 25°C, which slightly lowers the theoretical slope. Furthermore, as the measurements were made over a shorter period of time per series and as some problems with electrode bodies can already be disregarded in this summary, then the uncertainties are much smaller than for NPOE.

Although not explicitly presented in **Table 3**, the linear ranges for these electrodes improved as well. This is mainly apparent with the detection limits of the electrodes with MC009, MC012 and CZ007 ionophores. The control and MC005 electrodes do not display improvements and this evidences the possible chloride contamination as the reference electrode remained the same.

The results from the small repeated measurement series with NPOE as the plasticizer are not separately presented as they comprise only a few of the membrane compositions and have just two electrodes per ionophore. Overall, the slopes for MC005 and MC012 were around -56 mV per decade with the linear range similar to those with DOS, showing that these electrodes had almost Nernstian response and allowing the use of their selectivity results. For MC009, the results were even worse than during the first measurement series, which implies that there must have been something wrong with the membrane composition at least by that time.

For the final measurements done with fresh chemicals as well as using ten PVC and ten PCTFE electrodes, the results with both NPOE and DOS as plasticizers improved further. These results are presented in **Tables 4** and **5**.

Table 4. Response characteristics of final set of DOS electrodes (D2).

	CTRLD2	CZ007D2	MC005D2	MC009D2	MC012D2
Slope (mV/dec)	-54.81 ± 0.68	-57.57 ± 0.71	-55.60 ± 0.63	-57.57 ± 0.88	-57.85 ± 0.64
log a_{LLL}	-3.92 ± 0.12	-4.00[a]	-3.92 ± 0.12	-4.00[a]	-4.00[a]
log a_{LOD}	-4.84 ± 0.12	-5.07 ± 0.04	-4.81 ± 0.11	-5.02 ± 0.04	-5.28 ± 0.15

[a] See footnote [c] to **Table 2**.

In the case of the final DOS series, the slopes reached -58 mv per decade for several individual electrodes, which can be regarded as Nernstian responses considering the solution temperatures and slight possible deviations in solution concentrations. For control electrodes and the ones containing MC005 as the ionophore the slopes remained slightly lower, but this might be once again caused by the chloride flow from the reference electrode. However, because of lower outer filling solution concentration this is clearly diminished now as the detection limit and lower limit of linearity have greatly increased.

In this series, there were also two outliers – one PCTFE electrode for control and one for MC005. Both had initially good responses that quickly deteriorated after the first measurement. It appeared as if the response time for these electrodes increased several times and because of this, the same protocol was not useable anymore. A possible reason for this is that the adhesion between the electrode body and the membrane was not good enough. Therefore, all the results (including selectivity coefficients) from these two electrodes were excluded from further analysis.

Table 5. Response characteristics of final set of NPOE electrodes (N2).

	CTRLN2	CZ007N2	MC005N2	MC009N2	MC012N2
Slope (mV/dec)	-55.18 ± 0.66	-58.36 ± 0.32	-55.90 ± 0.43	-58.09 ± 0.20	-58.28 ± 0.17
log a_{LLL}	-4.00[a]	-4.00[a]	-3.69 ± 0.09	-4.00[a]	-4.00[a]
log a_{LOD}	-4.93 ± 0.08	-5.26 ± 0.03	-4.63 ± 0.08	-5.21 ± 0.04	-5.31 ± 0.03

[a] See footnote [c] to **Table 2**.

The results of the final NPOE series of electrodes were the best ones achieved with overall slopes for three ionophores between -58 and -59 mV per decade. For control and MC005, these are also the best results, although in case of the latter, the linear range and detection limit are not as good as with DOS as the plasticizer.

Based on all the results from the calibration measurements, it can be concluded that a Nernstian response is achievable for this kind of sensors if other sources of error are brought down to a minimum. The response ranges of the ISEs can then also easily span over four orders of magnitude.

3.2 pH sensitivity of the produced ISEs

The main purpose of pH measurements was to find whether in the pH ranges of the calibration and selectivity measurements, there is dependence of the potential on the solution pH. The potential of the ISEs is expected to change up until pH 6.8 due to the deprotonation of acetic acid (rise in acetate activity), while at higher pH values the potential should remain approximately constant.

The results from the first set of electrodes with NPOE as the plasticizer are presented in **Figure 9**, from which a strong pH dependence throughout the whole measured pH range for ionophore containing ISEs can be seen. This raised several concerns as to what exactly is the reason behind this behavior and whether it was also affecting calibration measurements. Possible explanations were sensitivity to hydroxide ions as well as response to chloride leaching out of the reference electrode. The latter however appeared to be unlikely as the control electrodes reached rather stable potentials after pH 6.5 with only slight declines that could be attributed to chloride sensitivity.

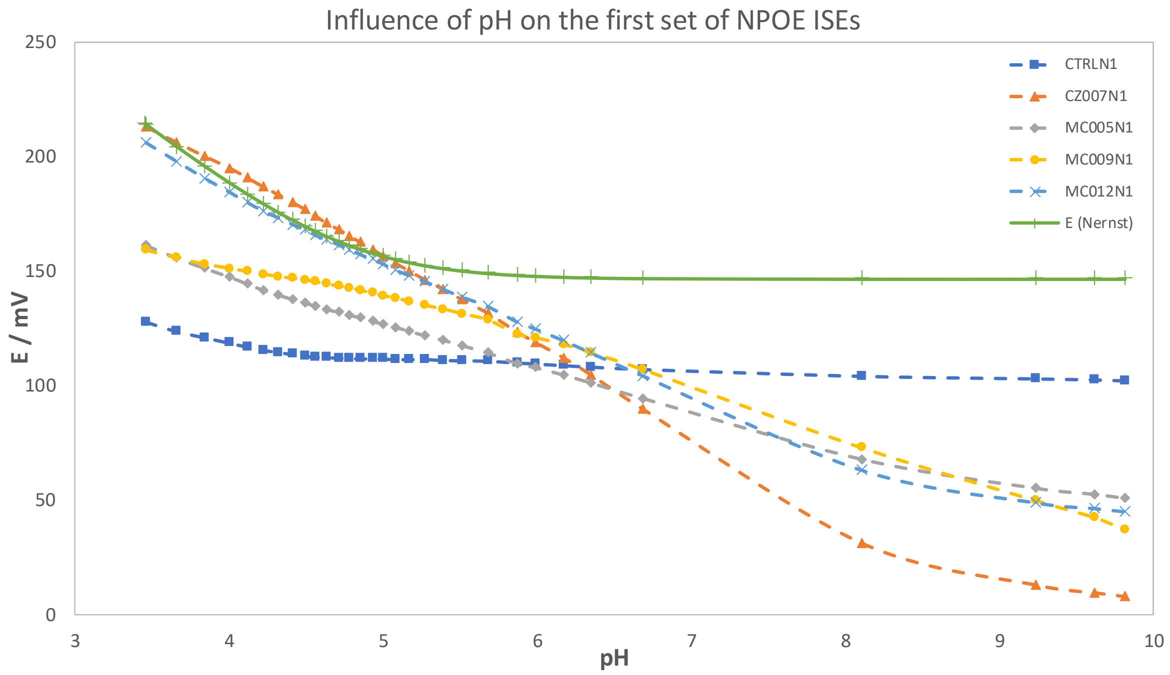


Figure 9. Examples of pH response from the first set of NPOE containing ISE. Green line represents the calculated theoretical response.

In the following measurement series with DOS as the plasticizer, several electrodes from each of the different membrane compositions had no pH sensitivity or only slight potential decrease at high pH values. On the other hand, for all the membrane compositions, there were some electrodes that had constant and strong pH dependencies. Examples of both cases are demonstrated in **Figure 10**. Similarly to the first NPOE results, constant declines and lower starting potentials for controls and MC005 electrodes are apparent and they are caused by the constant chloride flow from the reference (amplified by stirring).

Combining the results from calibration and pH measurements showed that there were some electrode bodies which had no pH sensitivity and provided much better slopes while the use of other electrode bodies resulted in poor slopes and strong pH dependency. The pH measurements became therefore an important additional way in determining the reliability of the ISEs.

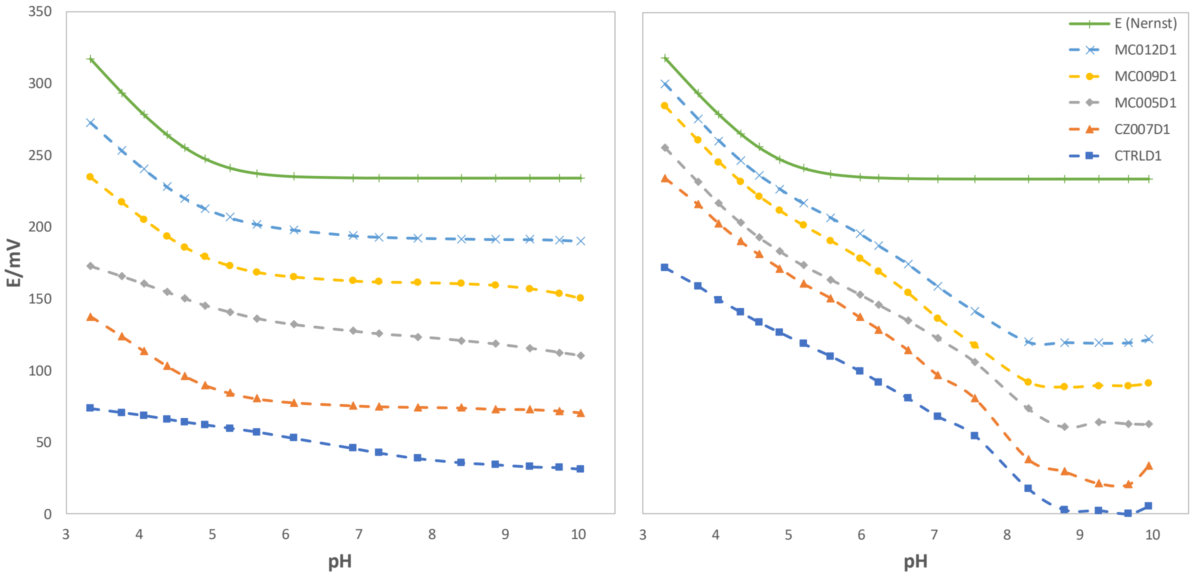


Figure 10. Examples of pH response of the DOS containing ISEs. With green, the theoretical response is displayed. On the left is minimal pH dependence and on the right is extremely strong pH dependence. Standard potentials of the electrodes have been adjusted for the graphs.

In the final measurement series, the pH sensitivity was also minimal with the only exception being for MC005 with NPOE as the plastizer in which case the PVC electrodes had again strong pH dependency while the potentials of PCTFE electrodes started to decline at pH values over 7.5. The exact reasons behind this remain unknown, but can most likely be attributed to the specifics of that membrane composition. This is because the electrode bodies used, did not present any issues with other membranes and as said, even in case of PCTFE the drop in potential was quite noticeable. It is possible that the age of ionophore (MC005) also contributed, but as this was not seen with DOS it is unlikely to be the primary reason.

3.3 Selectivity of the prepared ISEs

The selectivity measurements involved the biggest and most important part of the experiments and the resulting data are also rather voluminous. Therefore, only the averaged results from the main measurement series are presented and analyzed here. Some additional data tables are presented in the appendices.

Selectivity results with electrodes using NPOE as the plasticizer

During the initial selectivity measurements with NPOE as the plasticizer, the same electrodes were measured twice for each of the interfering ions to decrease the uncertainty of the results. The repeated measurements took place two weeks after the initial measurements, however the results differed strongly for several cases for the same electrodes. Furthermore, when comparing to the previously published data by Kerli Martin *et al*[27], then although the control electrodes have similar trends and close enough values, it is not the case for electrodes containing CZ007, used also by Martin *et al*. Combined results from these measurements are presented in **Table 6**.

Table 6. Selectivity coefficients for the first set of NPOE electrodes. The uncertainties express standard deviations between measurement series and between replicate electrodes.

	$\mathbf{log}\boldsymbol{K}^{\mathbf{pot}}_{\mathbf{acetate,j}}$				
ion *j*	CTRLN1	CZ007N1	MC005N1	MC009N1	MC012N1
Thiocyanate	6.11 ± 0.10	-0.04 ± 0.11	2.08 ± 0.18	4.27 ± 0.10	0.35 ± 0.15
Iodide	5.53 ± 0.06	0.02 ± 0.10	1.97 ± 0.08	3.90 ± 0.11	0.56 ± 0.18
Nitrate	4.28 ± 0.09	-0.61 ± 0.18	0.75 ± 0.22	2.42 ± 0.11	-0.49 ± 0.11
Bromide	3.25 ± 0.08	-0.65 ± 0.17	1.17 ± 0.18	1.41 ± 0.19	-0.67 ± 0.16
Benzoate	2.74 ± 0.09	1.32 ± 0.09	1.97 ± 0.22	1.88 ± 0.10	1.34 ± 0.07
Chloride	1.63 ± 0.12	-0.98 ± 0.16	0.46 ± 0.21	-0.12 ± 0.16	-1.35 ± 0.11
Pivalate	1.32 ± 0.07	1.08 ± 0.09	1.25 ± 0.19	1.00 ± 0.11	0.81 ± 0.11
Lactate	0.76 ± 0.15	-0.54 ± 0.18	-0.19 ± 0.15	0.11 ± 0.06	-0.47 ± 0.07
Formate	0.46 ± 0.13	-0.59 ± 0.13	-0.10 ± 0.27	-0.20 ± 0.13	-0.56 ± 0.11
Bicarbonate	0.08 ± 0.13	0.86 ± 0.32	0.62 ± 0.26	0.82 ± 0.34	0.40 ± 0.20
Dihydrogen phosphate	-0.63 ± 0.20	-2.69 ± 0.06	-1.65 ± 0.41	-0.77 ± 0.19	-2.52 ± 0.15
Sulphate	-0.62 ± 0.10	-1.46 ± 0.11	-0.52 ± 0.31	0.45 ± 0.11	-2.11 ± 0.07
Hydrogen phosphate	-0.99 ± 0.10	0.07 ± 0.11	-0.31 ± 0.35	-0.02 ± 0.20	-0.69 ± 0.39
Fluoride	-0.94 ± 0.19	-0.85 ± 0.11	-0.99 ± 0.22	-0.87 ± 0.18	-1.04 ± 0.23

The standard deviations between measurement series and replicate electrodes are quite large in the case of all ionophore containing membranes. This uncertainty comes mainly from the difference between results from different measurement series rather than from differences between replicate electrodes in the same measurement series. In addition to large uncertainties and differences with previously published data, it seemed strange for the middle-sized macrocycle MC009 to have much lower selectivity for acetate when compared to the other macrocycles. Because of this, these first selectivity measurements left several problems and questions hanging about using these kinds of ISE systems.

To answer some of them and to see whether the problem was in some specific electrode bodies, a verification series with six electrodes (three PVC and three PEEK bodies) was done after the measurements with DOS as the plasticizer. The results regarding these measurements are not presented separately as they only involved a small selection of the membrane compositions. Overall, for MC005 and MC012 it was plausible that these new selectivity results were more accurate as the slopes and pH response were considerably better. For MC009, the slopes and pH response were both abysmal and the selectivity for acetate was now even worse than before. All in all, although there was a lot of data for ISEs with NPOE as the plasticizer, several issues with the reliability of these results remained and no concrete conclusions could be made at that point.

Selectivity results with electrodes using DOS as the plasticizer

All the selectivity coefficient results from the first two sets of electrodes with DOS are presented in **Table 11 Appendix 2**. Similarly as with the calibration data, there is a considerable difference between some of the results. Therefore, when combining information from different types of measurements, then electrodes that had better slopes (more negative than -50 mV/dec) and low pH sensitivity also gave similar selectivity coefficients with much less scatter. Based on these criteria, in **Table 7**, the selectivity results from electrodes with reasonable slopes from the two measurements sets with standard deviation are presented. However, for **Table 7** only results from PVC electrodes are used, as only the macrocycles had PEEK electrodes. In addition, although the trend between "good" PVC and PEEK was the same, there were still occasionally discrepancies between the two, which would increase the uncertainty and limit the comparability of the values with the two other membrane compositions.

Table 7. Selectivity coefficients of only PVC electrodes for the first two sets with DOS. The uncertainties express standard deviations between replicate electrodes.

	$\log K^{\mathrm{pot}}_{\mathrm{acetate},j}$				
ion *j*	CTRLD1	CZ007D1	MC005D1	MC009D1	MC012D1
Thiocyanate	5.71 ± 0.08	1.19 ± 0.09	1.90 ± 0.03	1.18 ± 0.04	0.87 ± 0.04
Iodide	5.06 ± 0.07	0.95 ± 0.07	1.91 ± 0.06	1.28 ± 0.05	0.82 ± 0.02
Nitrate	3.60 ± 0.04	0.18 ± 0.04	0.89 ± 0.06	0.49 ± 0.02	0.04 ± 0.04
Bromide	2.79 ± 0.06	0.19 ± 0.04	1.34 ± 0.03	0.11 ± 0.04	-0.21 ± 0.01
Benzoate	2.77 ± 0.09	2.16 ± 0.03	2.44 ± 0.12	2.13 ± 0.13	1.95 ± 0.07
Chloride	1.48 ± 0.10	-0.17 ± 0.01	0.84 ± 0.11	-0.52 ± 0.05	-0.85 ± 0.02
Pivalate	1.42 ± 0.07	1.50 ± 0.01	1.61 ± 0.08	1.16 ± 0.05	1.12 ± 0.03
Lactate	0.50 ± 0.08	-0.36 ± 0.02	-0.16 ± 0.04	-0.27 ± 0.01	-0.30 ± 0.01
Formate	0.50 ± 0.11	-0.20 ± 0.01	0.13 ± 0.08	0.12 ± 0.02	-0.26 ± 0.01
Bicarbonate	0.40 ± 0.05	0.17 ± 0.02	0.73 ± 0.16	0.34 ± 0.05	-0.12 ± 0.04
Dihydrogen phosphate	0.04 ± 0.03	-0.74 ± 0.08	-0.97 ± 0.21	-0.89 ± 0.02	-1.49 ± 0.05
Sulphate	0.17 ± 0.06	0.41 ± 0.09	-0.60 ± 0.09	-0.28 ± 0.02	-0.93 ± 0.07
Hydrogen phosphate	-0.08 ± 0.05	-0.61 ± 0.06	-1.39 ± 0.10	-1.10 ± 0.02	-1.68 ± 0.02
Fluoride	-0.27 ± 0.24	-1.56 ± 0.10	-0.85 ± 0.21	-1.86 ± 0.10	-2.24 ± 0.08

The uncertainties are in this case rather small and exceed 0.10 only on few occasions. This is especially good considering that the values incorporate two separate measurement sets, which shows that over the course of at least one month, these membrane cocktails have retained their properties. The only exception is with fluoride, in which case during one single measurement there was most likely very strong leaching of KCl from the reference electrode. This mainly affected control and MC005 however it still had some impact on all the electrodes.

Overall, as there were some trustworthy results with DOS as the plasticizer, the same could not be said about NPOE. This was the reason that lead to the final redoing of both measurement series, using all new chemicals and with also having ten PCTFE electrodes in the mix to ensure that the electrode body itself does not affect the outcome.

Complete selectivity results

The results from the final measurement series for DOS are presented in **Table 12** in **Appendix 2** and the spread of those new results is quite small. There are some differences between results with PCTFE and PVC electrodes, however when putting them all together, the combined uncertainty still remains low. Additionally, the results match up quite well with some of the previous results with DOS. Therefore, all of the data from the ISEs with DOS can be combined and is presented in **Table 8** and in **Figure 11**.

Table 8. Final selectivity coefficients for DOS as the plasticizer. The uncertainties express standard deviations between replicate electrodes over different measurement series.

	$\log K^{\mathrm{pot}}_{\mathrm{acetate,j}}$				
ion *j*	CTRLD	CZ007D	MC005D	MC009D	MC012D
Thiocyanate	5.66 ± 0.09	1.22 ± 0.07	2.09 ± 0.19	1.30 ± 0.13	1.07 ± 0.17
Iodide	5.02 ± 0.07	0.97 ± 0.06	2.09 ± 0.17	1.44 ± 0.15	0.99 ± 0.15
Nitrate	3.61 ± 0.03	0.20 ± 0.04	1.01 ± 0.12	0.63 ± 0.12	0.15 ± 0.10
Bromide	2.85 ± 0.08	0.23 ± 0.07	1.49 ± 0.15	0.22 ± 0.10	-0.08 ± 0.11
Benzoate	2.81 ± 0.08	2.18 ± 0.03	2.57 ± 0.15	2.19 ± 0.11	2.04 ± 0.09
Chloride	1.50 ± 0.07	-0.16 ± 0.04	0.91 ± 0.10	-0.54 ± 0.05	-0.83 ± 0.03
Pivalate	1.43 ± 0.05	1.50 ± 0.01	1.64 ± 0.06	1.08 ± 0.11	1.11 ± 0.02
Lactate	0.50 ± 0.05	-0.35 ± 0.03	-0.13 ± 0.04	-0.25 ± 0.02	-0.28 ± 0.02
Formate	0.47 ± 0.08	-0.20 ± 0.02	0.16 ± 0.07	0.15 ± 0.04	-0.23 ± 0.03
Bicarbonate	0.41 ± 0.03	0.15 ± 0.03	0.70 ± 0.14	0.33 ± 0.05	-0.09 ± 0.05
Dihydrogen phosphate	0.09 ± 0.09	-0.72 ± 0.07	-0.90 ± 0.16	-0.74 ± 0.13	-1.35 ± 0.13
Sulphate	0.19 ± 0.08	0.36 ± 0.08	-0.56 ± 0.09	-0.22 ± 0.10	-0.83 ± 0.10
Hydrogen phosphate	-0.08 ± 0.06	-0.63 ± 0.05	-1.36 ± 0.14	-1.06 ± 0.06	-1.66 ± 0.05
Fluoride	-0.33 ± 0.11	-1.55 ± 0.09	-1.09 ± 0.14	-1.97 ± 0.09	-2.23 ± 0.09

The results in **Table 8** are a combination from at least 6 different electrodes over three measurement sets. The uncertainties remain below 0.15 in most cases and are always less than 0.20. The biggest standard deviations arise in the cases of lipophilic interfering ions, where the main contributor is the type of electrode body (PCTFE or PVC) and in case of the less strongly bound ions, where the leaching out of the reference electrode's filling solution starts to affect the results. The results for fluoride from one of the previously mentioned measurements with the first DOS series are disregarded here as they differed considerably from all the other data.

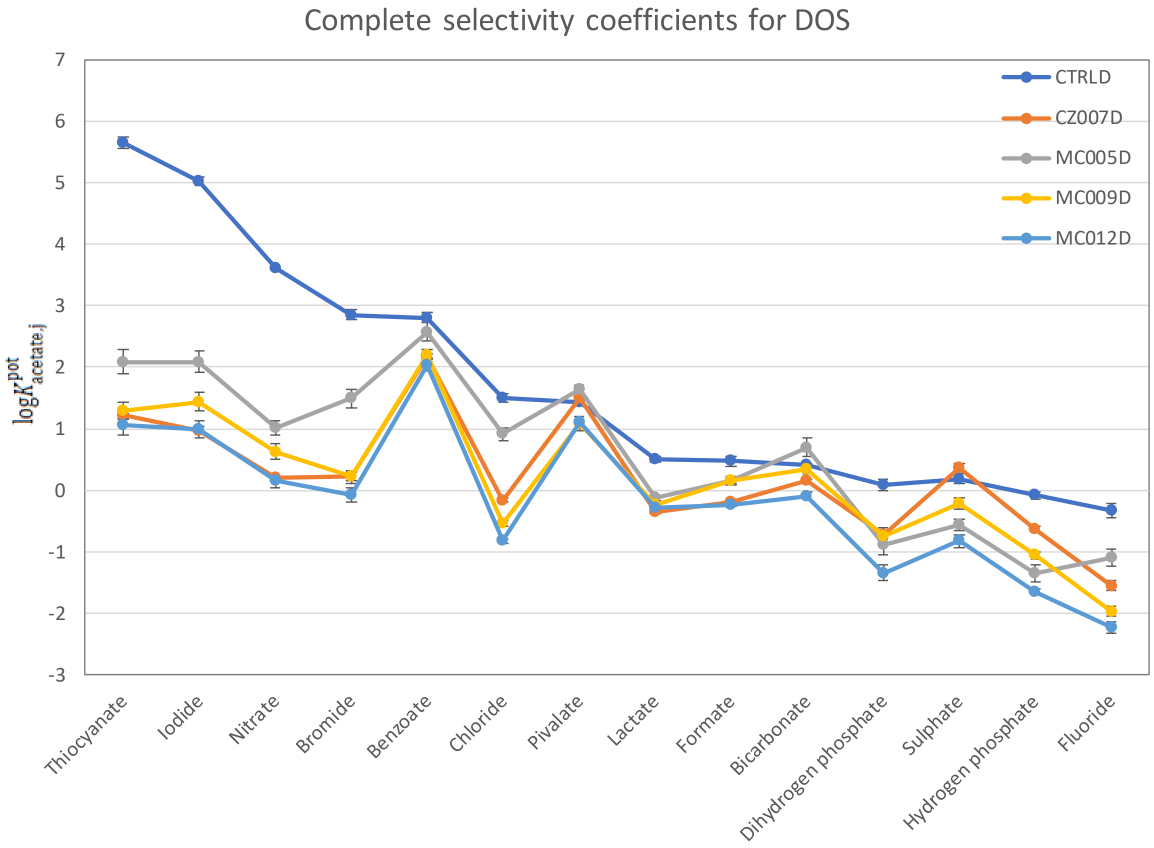


Figure 11. Final potentiometric selectivity coefficients towards all studied interfering anions with DOS as the plasticizer.

Overall, there are clear differences between controls and ionophore-containing ISEs, although the differences between ionophore ISEs themselves are not very big. The selectivity for controls follows the Hofmeister series and is therefore mainly determined by the lipophilicity of the interfering ion, while adding an ionophore to the membrane can improve the selectivity of the ISEs by over four orders of magnitude.

For the final repeated measurement with NPOE, the in-series matching between electrodes is also very good, although some differences between PVC and PCTFE are even larger. These results are presented in **Table 13** in **Appendix 2**. When comparing with the initial NPOE results, there are not many similarities as the only results from that series that can be considered are those of the controls. In addition, the selectivity coefficients determined for the MC012 and MC005 ISEs during the small NPOE measurement series should also be included in the final presentation of the results. The combined selectivity results for NPOE containing ISE are presented in **Table 9** and in **Figure 12**.

Table 9. Final selectivity coefficients for NPOE as the plasticizer. The uncertainties express standard deviations between replicate electrodes over different measurement series.

	$\mathbf{log}\boldsymbol{K}^{\mathbf{pot}}_{\mathbf{acetate,j}}$				
ion *j*	CTRLN	CZ007N	MC005N	MC009N	MC012N
Thiocyanate	6.12 ± 0.09	0.99 ± 0.03	2.55 ± 0.14	1.10 ± 0.11	1.17 ± 0.28
Iodide	5.55 ± 0.06	0.87 ± 0.03	2.54 ± 0.09	1.58 ± 0.11	1.20 ± 0.19
Nitrate	4.25 ± 0.08	0.27 ± 0.03	1.26 ± 0.10	0.87 ± 0.08	0.30 ± 0.12
Bromide	3.26 ± 0.06	0.02 ± 0.02	1.88 ± 0.07	0.12 ± 0.04	-0.11 ± 0.08
Benzoate	2.77 ± 0.09	2.07 ± 0.05	2.59 ± 0.11	2.10 ± 0.08	2.00 ± 0.07
Chloride	1.66 ± 0.10	-0.43 ± 0.03	1.12 ± 0.06	-0.82 ± 0.02	-1.05 ± 0.04
Pivalate	1.30 ± 0.06	1.29 ± 0.01	1.46 ± 0.06	0.96 ± 0.01	1.12 ± 0.03
Lactate	0.73 ± 0.12	-0.49 ± 0.02	-0.13 ± 0.06	-0.30 ± 0.01	-0.32 ± 0.02
Formate	0.53 ± 0.13	-0.25 ± 0.02	0.28 ± 0.06	0.25 ± 0.03	-0.16 ± 0.03
Bicarbonate	0.14 ± 0.13	-0.30 ± 0.04	0.64 ± 0.07	0.23 ± 0.02	-0.07 ± 0.05
Dihydrogen phosphate	-0.47 ± 0.26	-1.40 ± 0.03	-0.94 ± 0.19	-1.28 ± 0.05	-2.04 ± 0.13
Sulphate	-0.42 ± 0.28	-0.27 ± 0.04	0.20 ± 0.18	-0.89 ± 0.06	-1.43 ± 0.26
Hydrogen phosphate	-0.78 ± 0.28	-1.32 ± 0.01	-0.73 ± 0.15	-1.78 ± 0.02	-2.28 ± 0.14
Fluoride	-0.85 ± 0.20	-1.91 ± 0.07	-1.12 ± 0.14	-2.18 ± 0.05	-2.32 ± 0.11

The uncertainties here are bigger than in the case of DOS. For controls it is because of the spread of the results from the first measurement series for interferents that are being bound less strongly than acetate. This is similar for MC005 and could be explained by differences in KCl contamination as the first measurements had 1 M and later ones 0.1 M reference filling solutions. Another reason could also be the age of NPOE itself as it was several years old during the first measurements. For MC009 and CZ007 the maximum standard deviation is 0.11, however only results from the latest measurement series are included here. Finally, in the case of MC012, the main contributor to the uncertainty is the difference between results with PCTFE electrodes and electrodes with other body types of electrodes and it is biggest in the cases of thiocyanate, iodide and sulphate.

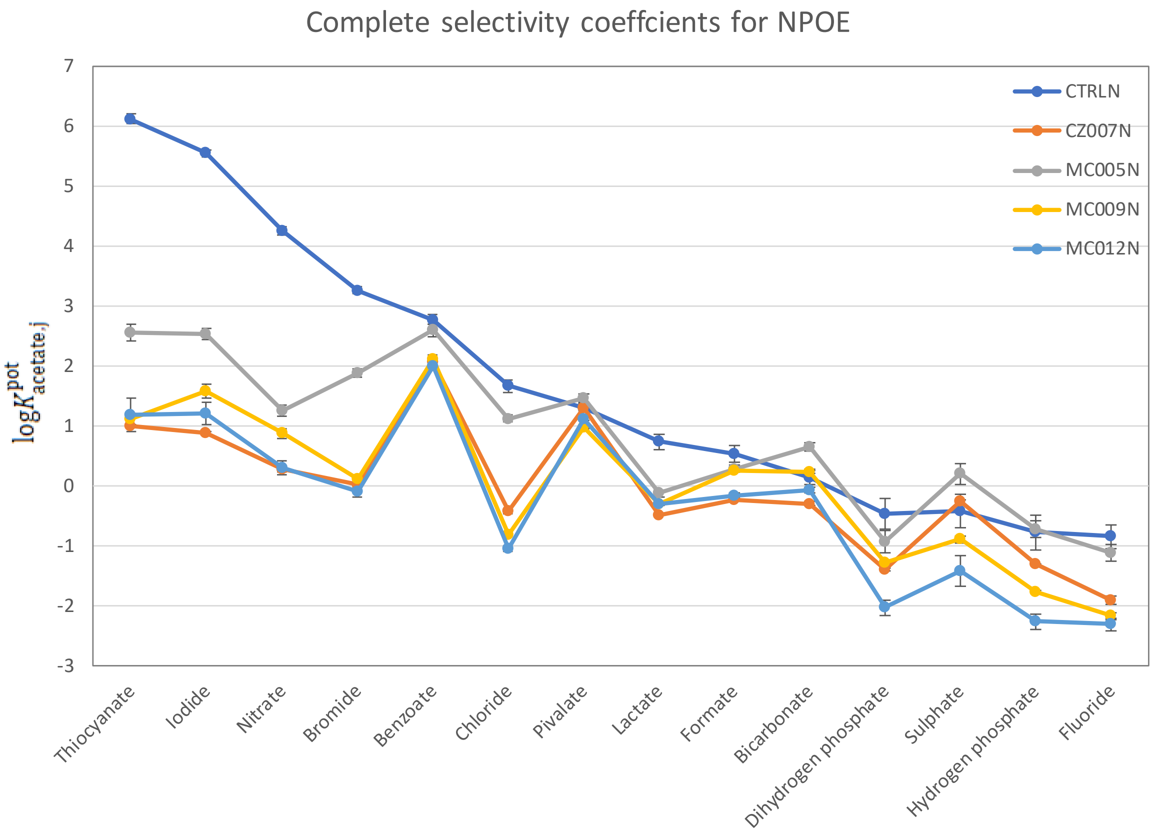


Figure 12. Potentiometric selectivity coefficients towards all studied interfering anions with NPOE as the plasticizer.

Comparing all the results between the two plasticizers, shows that the trends as well as the selectivity coefficient values themselves look rather similar. There do not seem to be any specific interactions and the ring size of the cyclic receptors does not affect the selectivity very much. MC005 appears to behave slightly differently and is less selective for acetate than the other ionophores, however it still follows the same trend. MC005 is also the ionophore with which the selectivity for interfering ions in several cases is higher especially with NPOE as the plasticizer than for controls. Furthermore, concerning the combination of MC005 and NPOE, then in the case of all the measurements, including EIS, these sensors behaved slightly differently. This could mean that some specific interactions between the two have considerable impact on the performance of the sensors.

Regarding the matter of acetate sensing, none of the used receptors are especially selective for it. The best of them would be MC012 in the case of both plasticizers. If, however, the sensors would be made using benzoate as the primary ion then it is possible that they could have real applications. In the case of MC012, the selectivity towards benzoate is almost ten times higher than towards any other tested interfering ion.

Several things should be noted when focusing only on the binding of carboxylates. For instance, the selectivity coefficient values towards carboxylates are grouped much closer together for all the ionophore-containing ISEs and the standard deviation of these results is almost always considerably lower than for other anions. This shows, as expected, that these ionophores preferentially bind carboxylates, although the differences in ionophore structure do little to improve the selectivity of the ISEs towards specific carboxylates.

3.4 Further discussion

To highlight the main discovered problems that otherwise would have remained unnoticed some more discussion about substrate effects, aging of different ISE components and also influence from reference electrode's outer filling solution is presented below.

Influences from the electrode body

One of the most surprising discoveries during this research was how much the electrode body in the case of PVC electrodes influenced the results. During the first measurements no such effect was heard of and because of this, it remained unnoticed. However, when the electrodes were reused and the bodies reshuffled then it became apparent that some electrode bodies gave significantly better results than others. It was also observed then that there was a difference between the appearance of some of the electrode shells (**Figure 13**). Some of them were considerably more porous than others and a few also had pores in a spiral pattern.

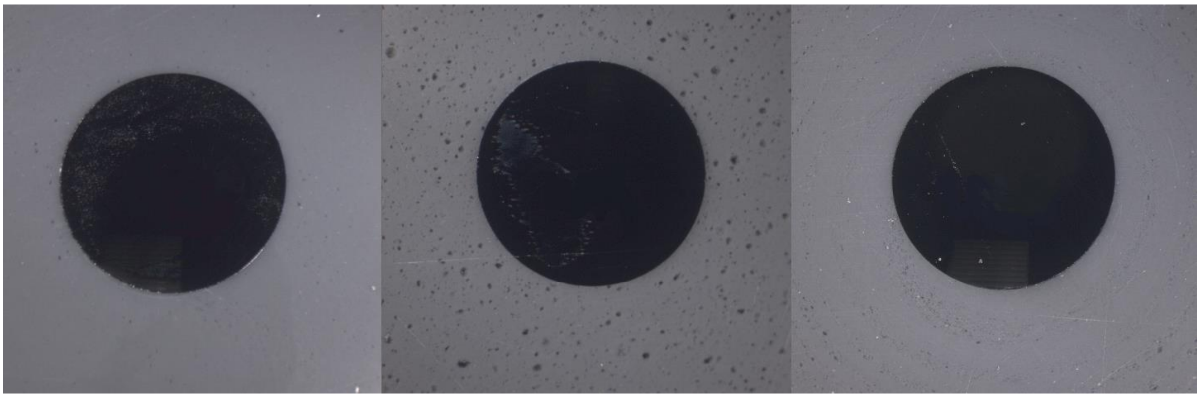


Figure 13. Photos of the bottoms of PVC electrodes with differing shells. The black disks in the middle are the cross-sections of GC rods (diameter 3 mm). From left to right: slightly porous, very porous, moderately porous with a spiral pattern.

The main difference between the electrode bodies came from different time of manufacture and it was also verified later by the company that there might have been some small differences between the PVC bodies. The more porous electrode bodies were brand-new and arrived in the beginning of the first measurement series, while the other PVC shells originated from previous batch(es). Overall, when trying to explain the difference in their behavior, then one explanation could be that some compounds are either introduced into the PVC shells over multiple drop-castings of the membrane or some substances originally present in the shells diffuse into the membrane and therefore negatively alter the performance of the electrodes.

To determine whether this was the case, additional types of shells were used. Firstly, a few electrodes with PEEK as the shell material were tested in which case there should be no interaction between the membrane and electrode body as PEEK can withstand THF without dissolving. In later measurements, they were replaced with PCTFE shell electrodes with similar properties as there were more of these kinds of electrodes available. Additionally, IR-spectroscopy was conducted by Åbo Akademi University PhD student Ville Yrjänä to determine differences between membranes deposited on different substrates. It was apparent from the recorded spectra that there were some differences between membranes drop-casted on PEEK and glass from those deposited on PVC. However, no conclusions could be made about the membranes deposited on different PVC shells.

In conclusion, the newer more porous PVC electrode bodies gave results similar to the electrodes with PEEK or PCTFE bodies allowing one to trust these results over the ones obtained with older PVC electrode bodies. However, there were still some differences especially with selectivity, which would lead one to believe that some minimal diffusion of components between membrane and electrode body still took place. Therefore, it is important to note down the types of electrodes used and maybe even their manufacturer when comparing the results between different sources. Overall, the PVC shell electrodes were preferred in this research due to the strong adhesion of the membrane, which provided that the membrane would not accidently come off or allow significant water uptake along the interface between the shell and the membrane.

Aging of chemicals and membrane cocktails

Another important contributor to the reliability of the results was the age of different components. In the initial measurements most of the chemicals used to make the membrane and conducting polymer were several years old, among them most noticeably NPOE.

Furthermore, as the membrane cocktails were not remade each time during the first measurement series, their composition could also change. For instance, reopening the vial for drop-casting can result in partial evaporation of THF, making the cocktail more and more concentrated after each use. Additionally, there are possible reactions that take place over time such as the formation of peroxides, which can thereafter react with other compounds in the solution. This can be a prominent reason why for the mid-sized macrocycle (MC009) the initial and secondary results with NPOE differed between themselves as well as from the repeated measurements with fresh chemicals. Also, because the receptor batch itself was several years old by that point and as it ran out, then for the last measurement series an entirely new batch was synthesized, which improved the trustworthiness of the most recent results even more.

In addition, the first measurement series took much longer time (almost a month longer) than the later experiments, thus leaching of the plasticizer and other components out of the membrane or water uptake could have taken place. To get some insight into this process, for the last set of electrodes with NPOE, calibration and some selectivity measurements were repeated two weeks after the end of the initial measurements, making the electrodes a month old by that time. However, although there were slight changes in selectivity and the slopes for PVC electrodes had become by up to two mV per decade less negative, these changes were not as drastic as during the first batch. Therefore, it could be said that when these ISEs are made with fresh chemicals, they should easily be useable for one month.

Influence from the reference electrode

One additional contributor to the uncertainty of some of the results was the reference electrode. Since the outer filling solution contained 1 M KCl during the first measurements, the process of KCl leaching into samples that were ten or more times more dilute had noticeable effects. It was especially prominent for electrodes that had higher selectivity for chloride such as the control electrodes or the ones containing MC005. A good example here are the pH measurements, during which controls to a large extent reacted to chloride flow rather than pH. However, it was apparent in selectivity measurements for several strongly discriminated interfering ions as well. Because of this, 0.1 M KCl solution was used in the outer compartment instead in the later measurements to decrease this uncertainty source. For the most recent measurements, no noticeable drift in potential was detected anymore for control electrodes during selectivity measurements, which might lead one to believe that the KCl leaching out had a much lower effect in those measurements.

Possibly even better results could be achieved by using solid state reference electrodes from which any kind of leakage should be extremely minimal[30]. However, these electrodes are currently still in the prototype phase and because of this was not tried out in the current study.

Summary

In the current thesis, the process of fabricating and the performance of solid-contact acetate-selective electrodes was investigated. These ion sensors were based on novel macrocyclic receptors for which acetate had previously shown to be the most strongly bound carboxylate. The purpose of the thesis was to prepare and characterize these sensors as well as to see how or whether differences in membrane composition and ionophore structure affect the results acquired with the sensors.

The main electrode type used in this work was PVC coated glassy carbon electrodes, however electrodes with other shell materials were additionally included for comparison. Furthermore, to get a more detailed picture of the effects of membrane composition on the performance of these sensors, two different plasticizers were used in the course of this work. In addition to determining the sensitivity of the prepared sensors, their pH dependence and selectivity against 14 common interfering ions was exhaustively studied.

Over the course of this work, several issues ranging from the influence of the commercial electrode bodies to the age of different components arose and needed to be solved. These problems were initially not expected and to this extent have neither been published or analyzed before. However, the sensors made during the final phase of this work had sensitivities close to the theoretical as well as stable potentials in a wide pH range and provided results with low uncertainty. The produced sensors had modest to good selectivity towards acetate, however, some of them could possibly be investigated for use in benzoate determination.

This thesis played a key part in a project lasting several years, with the goal of designing and developing new synthetic receptor molecules for a real-world working carboxylate sensor. Moreover, the detailed experimental protocol and observations presented in this work, could serve as a future guideline in making similar sensor systems.

Kokkuvõte

Makrotsüklilistel retseptoritel põhinevate tahk-kontaktsete anioonitundlike sensorite valmistamine ja karakteriseerimine

Indrek Saar

Käesolevas magistritöös uuriti tahk-kontaktsete atestaadi-selektiivsete elektroodide valmistamist ning nende karakteriseerimist. Need ioon-selektiivsed sensorid baseerusid uudsetel makrotsüklilistel retseptoritel (ionofooridel), mille jaoks oli eelnevalt just atsetaatioon osutunud kõige tugevamini seonduvaks karboksülaadiks. Töö eesmärgiks oli lisaks nende sensorite valmistamisele ja karakteriseerimisele uurida, kuidas muutused ioon-selektiivse membraani koostises ning ionofooride struktuuris mõjutavad nende sensorite toimimist.

Töös kasutati peamiselt PVC kattega klaassüsinikust elektroode, kuid peale nende uuriti ja testiti ka teistsuguse ümbrismaterjaliga elektroode. Selleks, et kindlaks teha paremini membraani koostise mõju sensori toimimisele, kasutati nende valmistamiseks kahte erinevat plastifikaatorit. Lisaks valmistatud sensorite tundlikkuse uurimisele, määrati nende pH sõltuvus ning selektiivsus 14 levinud ja potentsiaalselt segava aniooni suhtes.

Eksperimentide käigus kerkisid esile mitmed seni laialdast kajastust mitte pälvinud probleemid, mille kirjeldamisele ja analüüsile on samuti antud töös palju tähelepanu pööratud. Neist olulisemad olid elektrooditoorikute mõju ning kasutatud kemikaalide ja membraanilahuste vanusega kaasnevad efektid sensoritega mõõdetud tulemustele. Kokkuvõttes võib aga väita, et need probleemid õnnestus edukalt ületada, sest töö lõppfaasis valmistatud sensorid saavutasid peaaegu teoreetilise eeldatud tundlikkuse ning olid stabiilsed laias pH vahemikus, andes samas madala mõõtemääramatusega tulemusi. Üldiselt oli valmistatud sensorite selektiivsus atsetaadi suhtes keskmine, küll aga võiks neist osasid kaaluda bensoaadi määramiseks.

Antud tööl oli võtmeroll praeguseks mitu aastat kestnud projektis, mille eesmärgiks oli jõuda uute aniooniretseptorite disainist ja sünteesist päris maailmas toimivate karboksülaat-anioonide sensoriteni. Lisaks võib öelda, et siin töös esitatud detailne eksperimentide kirjeldus ja tehtud tähelepanekud võiksid saada tulevikus lähtepunktiks teiste taoliste sensorsüsteemide valmistamisel.

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Appendices

Appendix 1. Slopes of the electrodes

Table 10. Slopes (in mV/dec) for all the electrodes in the first series of electrodes with DOS as the plasticizer. The uncertainties express standard deviations. The shaded values are used for **Table 3**.

	Nr.	CTRLD1	CZ007D1	MC005D1	MC009D1	MC012D1
First set	1	-52.25 ± 0.43	-56.10 ± 0.94	-38.87 ± 0.72	-42.4 ± 1.0	-41.3 ± 1.4
	2	-52.70 ± 0.34	-56.18 ± 0.62	-54.77 ± 0.77	-55.89 ± 0.26	-56.72 ± 0.16
	3	-38.6 ± 3.3	-55.79 ± 0.50	-41.7 ± 3.0	-44.72 ± 0.72	-44.9 ± 1.1
Second set	4	-51.48 ± 0.94	-55.80 ± 0.30	-54.42 ± 0.26	-55.49 ± 0.22	-56.20 ± 0.21
	5	-45.0 ± 1.4	-46.5 ± 1.4	-54.57 ± 0.14	-55.83 ± 0.20	-56.44 ± 0.53
	6	-42.4 ± 1.7	-44.6 ± 1.2	-44.92 ± 0.58	-49.9 ± 1.3	-46.5 ± 1.4
	7 (PEEK)			-54.54 ± 0.64	-55.60 ± 0.29	-55.94 ± 0.12

Appendix 2. Selectivity coefficients values

Table 11. Determined selectivity coefficients ($\log K^{\mathrm{pot}}_{\mathrm{acetate,j}}$) for the first series of DOS electrodes. Values from „good“ PVC and PEEK electrodes are presented in light and dark gray, respectively.

		Ion *j*													
	nr	SCN^-	I^-	NO_3^-	Br^-	Benzoate	Cl^-	Pivalate	Lactate	Formate	HCO_3^-	$H_2PO_4^-$	SO_4^{2-}	HPO_4^{2-}	F^-
CTRLD1	1	5.78	5.11	3.60	2.82	2.78	1.58	1.43	0.57	0.53	0.45	0.06	0.22	-0.04	-0.41
	2	5.62	4.99	3.56	2.72	2.67	1.38	1.34	0.41	0.37	0.35	0.05	0.19	-0.06	-0.40
	3	6.47	5.60	3.35	2.45	2.59	1.03	1.26	0.42	-0.10	1.45	-1.04	-0.57	1.43	-0.46
	4	5.73	5.09	3.64	2.82	2.86	1.49	1.48	0.52	0.59	0.39	0.00	0.10	-0.14	0.01
	5	5.64	4.87	3.30	2.37	2.38	1.07	1.17	0.28	-0.04	1.20	-0.72	-0.40	0.05	-0.39
	6	6.08	5.26	3.55	2.71	2.60	1.14	1.37	0.30	-0.09	1.31	-0.88	-0.46	-0.09	-0.21
CZ007D1	1	1.21	0.99	0.18	0.20	2.17	-0.17	1.50	-0.35	-0.19	0.15	-0.74	0.41	-0.60	-1.68
	2	1.26	0.99	0.22	0.22	2.18	-0.16	1.49	-0.36	-0.19	0.17	-0.67	0.47	-0.58	-1.55
	3	1.23	0.99	0.18	0.22	2.18	-0.18	1.50	-0.35	-0.20	0.14	-0.69	0.46	-0.57	-1.57
	4	1.06	0.85	0.13	0.13	2.13	-0.18	1.52	-0.39	-0.21	0.20	-0.85	0.28	-0.70	-1.43
	5	0.16	-0.03	-0.81	-0.82	1.62	-0.65	1.16	-0.41	-0.56	0.53	-1.71	-0.46	-0.15	-0.92
	6	0.48	0.06	-0.59	-0.70	1.42	-0.94	1.28	-0.43	-0.69	1.28	-2.07	-0.73	-0.23	-0.66
MC005D1	1	1.12	1.25	-0.28	0.29	1.81	-0.38	1.30	-0.65	-0.48	1.24	-2.97	-1.78	0.19	-0.54
	2	1.86	1.84	0.85	1.31	2.30	0.72	1.52	-0.20	0.06	0.55	-1.21	-0.68	-1.43	-1.04
	3	1.26	1.17	-0.15	0.45	1.86	-0.04	1.22	-0.45	-0.41	1.22	-2.71	-1.57	-0.15	-0.76
	4	1.92	1.94	0.95	1.37	2.53	0.87	1.66	-0.15	0.21	0.85	-0.82	-0.51	-1.27	-0.62
	5	1.90	1.95	0.86	1.35	2.49	0.93	1.65	-0.13	0.13	0.80	-0.88	-0.61	-1.46	-0.88
	6	1.37	1.27	0.28	0.61	1.86	0.09	1.26	-0.37	-0.40	1.19	-2.09	-1.48	-0.19	-0.54
	7	2.19	2.18	1.11	1.58	2.72	1.01	1.71	-0.08	0.23	0.88	-0.68	-0.49	-1.16	-0.60
MC009D1	1	0.31	0.81	-0.51	-0.96	1.41	-1.33	0.89	-0.67	-0.44	1.00	-2.31	-1.37	-0.47	-0.64
	2	1.13	1.22	0.49	0.07	1.97	-0.57	1.11	-0.27	0.10	0.28	-0.89	-0.30	-1.08	-1.97
	3	0.56	0.51	-0.49	-0.81	1.42	-1.08	0.83	-0.45	-0.29	0.95	-1.95	-1.00	-0.28	-0.90
	4	1.20	1.30	0.48	0.12	2.20	-0.52	1.20	-0.27	0.13	0.37	-0.91	-0.29	-1.12	-1.78
	5	1.20	1.32	0.52	0.14	2.20	-0.48	1.18	-0.27	0.13	0.37	-0.88	-0.26	-1.11	-1.83
	6	1.25	1.36	0.60	0.16	1.70	-0.83	1.03	-0.36	-0.22	0.78	-1.57	-0.90	-0.53	-1.10
	7	1.52	1.61	0.69	0.31	2.36	-0.46	1.22	-0.23	0.17	0.44	-0.71	-0.04	-0.96	-1.88
MC012D1	1	0.15	0.14	-0.88	-1.24	1.29	-1.56	0.82	-0.72	-0.63	0.90	-2.78	-2.05	-0.42	-0.66
	2	0.92	0.83	0.09	-0.21	1.87	-0.87	1.08	-0.31	-0.26	-0.12	-1.44	-0.88	-1.66	-2.28
	3	-0.01	-0.08	-1.02	-1.16	1.20	-1.33	0.75	-0.46	-0.58	0.62	-2.26	-0.58	0.61	-0.87
	4	0.86	0.83	0.03	-0.20	2.00	-0.85	1.15	-0.30	-0.25	-0.08	-1.48	-0.92	-1.67	-2.15
	5	0.84	0.80	0.01	-0.22	1.97	-0.84	1.13	-0.31	-0.27	-0.15	-1.54	-1.01	-1.70	-2.30
	6	-0.14	-0.26	-1.09	-1.37	1.45	-1.18	0.87	-0.40	-0.59	1.06	-2.25	-1.65	-0.64	-0.76
	7	1.19	1.14	0.22	-0.03	2.14	-0.84	1.13	-0.30	-0.24	0.01	-1.32	-0.74	-1.69	-2.07

Table 12. Determined selectivity coefficients ($\log K^{\mathrm{pot}}_{\mathrm{acetate,j}}$) for the final series of DOS electrodes. Values from PCTFE electrodes are presented in dark gray.

		Ion *j*													
	nr	SCN^-	I^-	NO_3^-	Br^-	Benzoate	Cl^-	Pivalate	Lactate	Formate	HCO_3^-	$H_2PO_4^-$	SO_4^{2-}	HPO_4^{2-}	F^-
CTRLD2	1	5.71	5.05	3.65	2.96	2.90	1.55	1.45	0.49	0.43	0.41	0.11	0.21	-0.13	-0.36
	2	5.57	4.94	3.60	2.88	2.82	1.49	1.43	0.49	0.42	0.42	0.08	0.13	-0.15	-0.34
	3	5.58	4.95	3.62	2.89	2.80	1.50	1.44	0.52	0.47	0.43	0.25	0.32	0.00	-0.14
	4	3.37	2.85	1.78	1.83	1.64	0.93	1.03	0.52	0.58	0.39	0.44	-0.13	-0.42	-0.27
CZ007D2	1	1.20	0.96	0.22	0.21	2.16	-0.20	1.48	-0.37	-0.22	0.12	-0.78	0.26	-0.69	-1.61
	2	1.21	0.95	0.17	0.26	2.17	-0.18	1.49	-0.33	-0.16	0.12	-0.69	0.31	-0.66	-1.41
	3	1.28	1.02	0.23	0.31	2.22	-0.10	1.50	-0.32	-0.21	0.15	-0.68	0.37	-0.59	-1.47
	4	1.29	1.04	0.26	0.34	2.23	-0.08	1.50	-0.30	-0.20	0.16	-0.65	0.34	-0.63	-1.52
MC005D2	1	2.25	2.22	1.07	1.60	2.61	0.92	1.63	-0.13	0.14	0.63	-0.90	-0.53	-1.46	-1.18
	2	2.28	2.23	1.12	1.58	2.59	0.93	1.65	-0.10	0.24	0.53	-0.87	-0.67	-1.53	-1.12
	3	2.25	2.22	1.08	1.67	2.74	0.98	1.68	-0.09	0.12	0.67	-0.89	-0.45	-1.21	-1.25
	4	2.39	2.32	0.99	1.68	2.80	0.97	1.77	-0.11	0.14	0.77	-0.93	-0.70	-1.14	-1.13
MC009D2	1	1.27	1.44	0.63	0.27	2.18	-0.58	0.98	-0.23	0.14	0.30	-0.67	-0.27	-1.09	-1.98
	2	1.26	1.47	0.69	0.22	2.15	-0.59	0.99	-0.26	0.14	0.29	-0.72	-0.31	-1.13	-2.08
	3	1.41	1.60	0.83	0.35	2.29	-0.52	0.99	-0.23	0.16	0.30	-0.57	-0.12	-1.00	-2.07
	4	1.39	1.57	0.70	0.27	2.19	-0.57	1.00	-0.22	0.22	0.31	-0.60	-0.20	-1.04	-1.95
MC012D2	1	1.13	1.05	0.21	-0.06	2.04	-0.86	1.10	-0.28	-0.23	-0.10	-1.36	-0.83	-1.65	-2.33
	2	1.09	0.99	0.15	0.00	2.07	-0.79	1.10	-0.27	-0.17	-0.06	-1.29	-0.79	-1.61	-2.22
	3	1.27	1.13	0.23	0.01	2.10	-0.80	1.11	-0.24	-0.22	-0.10	-1.22	-0.79	-1.75	-2.25
	4	1.25	1.14	0.26	0.04	2.15	-0.80	1.10	-0.27	-0.23	-0.10	-1.19	-0.69	-1.58	-2.17

Table 13. Determined selectivity coefficients ($\log K_{\mathrm{acetate,j}}^{\mathrm{pot}}$) for the final series of NPOE electrodes. Values from PCTFE electrodes are presented in dark gray.

		Ion *j*													
	nr	SCN^-	I^-	NO_3^-	Br^-	Benzoate	Cl^-	Pivalate	Lactate	Formate	HCO_3^-	$H_2PO_4^-$	SO_4^{2-}	HPO_4^{2-}	F^-
CTRLN2	1	6.14	5.57	4.18	3.25	2.81	1.68	1.26	0.59	0.57	0.14	-0.38	-0.24	-0.57	-0.84
	2	6.26	5.66	4.23	3.25	2.85	1.75	1.29	0.68	0.63	0.22	-0.33	-0.17	-0.54	-0.83
	3	6.09	5.58	4.22	3.30	2.86	1.73	1.32	0.71	0.68	0.30	-0.13	-0.06	-0.40	-0.60
	4	6.07	5.56	4.21	3.29	2.75	1.66	1.24	0.70	0.64	0.26	-0.15	-0.02	-0.38	-0.61
CZ007N2	1	0.96	0.82	0.22	-0.01	2.02	-0.41	1.28	-0.49	-0.25	-0.32	-1.39	-0.30	-1.31	-1.82
	2	0.98	0.87	0.26	0.04	2.04	-0.40	1.30	-0.47	-0.26	-0.34	-1.44	-0.31	-1.33	-1.89
	3	1.02	0.90	0.29	0.03	2.14	-0.47	1.29	-0.48	-0.22	-0.25	-1.39	-0.25	-1.33	-1.98
	4	1.01	0.88	0.30	0.03	2.08	-0.45	1.28	-0.50	-0.27	-0.29	-1.38	-0.22	-1.31	-1.96
MC005N2	1	2.56	2.53	1.20	1.79	2.47	1.05	1.39	-0.15	0.27	0.73	-0.67	0.00	-0.88	-0.95
	2	2.58	2.45	1.23	1.79	2.46	1.04	1.39	-0.20	0.28	0.69	-0.80	-0.02	-0.72	-1.05
	3	2.64	2.61	1.34	1.88	2.74	1.14	1.48	-0.17	0.29	0.57	-1.17	0.36	-0.57	-1.24
	4	2.72	2.67	1.41	1.93	2.64	1.14	1.48	-0.14	0.36	0.63	-1.09	0.30	-0.64	-1.24
MC009N2	1	0.99	1.46	0.79	0.08	2.03	-0.80	0.95	-0.31	0.28	0.25	-1.30	-0.92	-1.76	-2.13
	2	1.03	1.50	0.82	0.09	2.05	-0.80	0.96	-0.31	0.22	0.20	-1.34	-0.95	-1.80	-2.14
	3	1.20	1.69	0.95	0.16	2.12	-0.82	0.97	-0.29	0.25	0.21	-1.22	-0.82	-1.76	-2.21
	4	1.17	1.67	0.93	0.13	2.20	-0.85	0.95	-0.30	0.27	0.24	-1.27	-0.88	-1.81	-2.24
MC012N2	1	1.02	1.03	0.21	-0.19	1.92	-1.02	1.09	-0.32	-0.18	-0.09	-2.16	-1.71	-2.39	-2.34
	2	1.01	1.06	0.24	-0.15	1.90	-1.03	1.07	-0.35	-0.13	-0.04	-2.19	-1.65	-2.38	-2.35
	3	1.50	1.43	0.45	0.00	2.04	-1.05	1.13	-0.32	-0.13	-0.01	-1.89	-1.11	-2.10	-2.45
	4	1.54	1.45	0.45	0.00	2.06	-1.02	1.14	-0.33	-0.15	-0.03	-1.88	-1.11	-2.11	-2.40

Fact sheet

Fabrication and Characterization of Solid-Contact Anion-Selective Electrodes Based on Macrocyclic Receptors

The purpose of this thesis was to investigate the process of fabricating and the performance of solid-contact carboxylate-selective electrodes. For that, three novel macrocyclic receptors and two common plasticizers were chosen with which the ion-selective membranes were made and drop-casted on to PVC coated glassy carbon electrodes. The sensitivity, pH dependence and selectivity against 14 common interfering ions of these sensors were studied.

During the experimental work, several unexpected and previously unpublished issues arose that had strong impact on the performance of the sensors. Most notable of them were the influences from the electrode bodies and age of different components. However, by the final phase of this work, these problems could be surpassed, and the last series of sensors provided almost theoretical sensitivities and low uncertainty values.

Keywords: supramolecular chemistry, electrochemistry, potentiometric sensors, carboxylate anions.

CERCS: P300 analytical chemistry

Makrotsüklilistel retseptoritel põhinevate tahk-kontaktsete anioonitundlike sensorite valmistamine ja karakteriseerimine

Käesoleva töö eesmärgiks oli uurida sünteetilistel retseptoritel põhinevate karboksülaat-selektiivsete elektroodide valmistamist ning neid karakteriseerida. Töös keskenduti kolmele erinevale makrotsüklilisele retseptorile ja kahele plastifikaatorile, millega valmistati PVC kattega klaassüsinikelektroodidele ioontundlikke membraane. Põhjalikult uuriti sensorite tundlikkust, pH sõltuvust ja selektiivsust 14 levinud ja potentsiaalselt segava aniooni suhtes.

Töö tulemusena ilmnesid mitmed seni laialdast kajastust mitte saanud probleemid, mis mõjutavad taoliste sensorite tööd. Neist peamisteks olid mõju elektrooditoorikutest ning erinevate membraanikomoponentide vanusest. Küll aga õnnestus töö lõppfaasis need raskused ületada ning valmistada peaaegu teoreetilise tundlikkuse ning madala mõõtemääramatusega sensorid.

Märksõnade loend: supramolekulaarkeemia, elektrokeemia, potentsiomeetrilised sensorid, karboksülaatanioonid.

CERCS: P300 analüütiline keemia

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