We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

β-Cyclodextrin as an Ionophore for Membrane Electrode

Mohsen M. Zareh

Additional information is available at the end of the chapter

Abstract

This chapter included an explanation of the role of cyclodextrin as an ionophore for the preparation of voltammetric and potentiometric sensors for different compounds. There was a surveying of the different recorded cyclodextrin-based sensors for drug, organic, or inorganic cations. It also explained the performance characteristics for the first reported sensor for nickel based on β-cyclodextrin as an example.

Keywords: cyclodextrin, sensors, membrane electrodes, potentiometric, voltammetric

1. Introduction

The ion-selective membrane electrodes are based on selecting an appropriate matter which works like a sensing part. The sensing materials are the main component of the potentiometric ion sensors. They are responsible for forming a type of discrimination in the electrode behavior toward one ion rather than others. There are several types of the sensing material. They might have host-guest structure, which allows the inclusion of the analyzed ionic material. Another type is able to form a complex with the analyte ion. The third type is based on ion exchange reaction with the ion under investigation.

A potential difference will be aroused when the analyte ion can penetrate across the phase boundary between the two phases (analyte solution and internal reference solution) (**Figure 1**). Accordingly, an electrochemical equilibrium will be formed due to different potentials at both sides of the membrane. The potential difference (E) across the membrane is described by the Nernst equation:

$$E = E^{\circ} + (RT/ZF) \ln a \qquad (1)$$

where E° is the standard cell potential, R is the general gas constant, Z is the valency of the analyte ion, F is the Faraday constant, and a is the activity of the analyte ion.

Cyclodextrin is produced from starch by enzymatic conversion. They are formed of a cycle of oligosaccharides. There are three types of cyclodextrin according to the size of the ring. They may be composed of 5-, 6-, or 7-membered ring. They are named like α, β, and γ, respectively (**Figure 2**).

Typical cyclodextrins contain a number of glucose monomers ranging between 6 and 8. They create a cone shape, which is suitable for the inclusion of different cations (**Figure 3**).

Many researches were recorded where cyclodextrin was used for preparing sensor membrane electrode for the determination of organic compounds. The studies about the application of CD as an ionophore for sensors of inorganic cations were rarely found. The recorded sensors were either voltammetric sensors or potentiometric sensors.
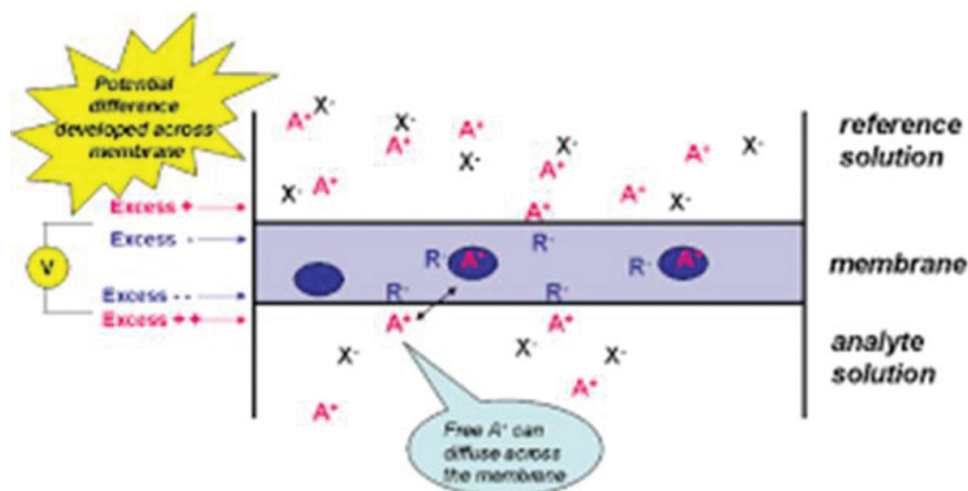
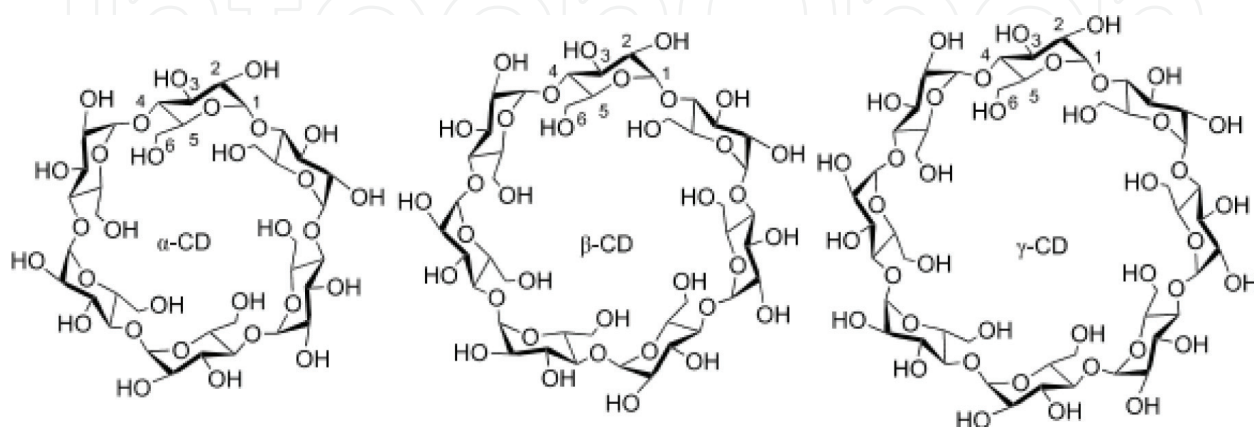

Figure 1. The response of membrane toward different ions.

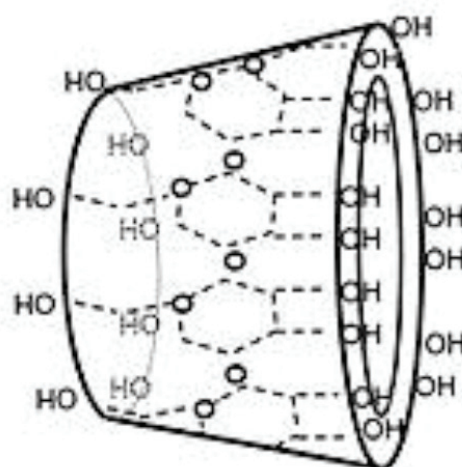**Figure 2.** Structure formula of α, β, and γ-cyclodextrin.

Figure 3. γ-CD toroid structure showing spatial arrangement.

1.1. Voltammetric sensors

Voltammetric sensors are an electrochemical sensor based on measurements of the diffusion current at polarization potential. Several examples of voltammetric sensors were recorded in the literature. They were used for the determination of amine-containing organic/pharmaceutical compounds.

Komiyama [1] prepared cyclodextrin electrode for the determination of p-nitrophenolate. The electrode was prepared by dipping Pt-wire into cyclodextrin polymer. Stefan et al. [2] used a multidextrin as a sensor for preparing selective membrane for *S*-captopril. Lenik and Nieszporek [3] constructed a modified glassy carbon ibuprofen electrode.. The electrode was based on multi-walled carbon nanotubes and β-cyclodextrins. It showed wider linear range (3.2×10^{-5} –1×10^{-2} mol L^{-1}) and lower limit of detection (1.25×10^{-5} mol L^{-1}). It was applied like a sensor for GC. The determination of some neurotransmitters such as dopamine (DA), epinephrine (EP), norepinephrine (NEP), levodopa (L-DOPA), 3,4-dihydroxy-phenyl acetic acid (DOPAC) and serotonin (ST) was applied by reduced graphene oxide (RGO) composite glassy carbon electrode modified with ionic liquid crystal (ILC), 1-butyl-1-methylpi-peridinium hexa-fluoro-phosphate, and cyclodextrin [4].

CD-based sensor was applied for the determination of an antibiotic chloramphenicol by Sun et al. [5]. They used a voltammetric sensor on mesoporous carbon @polydopamine and β-CD. It showed a response for chloramphenicol in the range of $5 \times 10^{-7} - 5 \times 10^{-5}$ M. Li et al. [6] determined o- and p-nitrophenol by using reduced graphene oxide-CD-Chitosan electrochemical sensor. It was based on the host-guest recognition sites on CD and abundant functional groups of Chitosan. It showed linear range for 0.12–0.2 and 4–50 μM for NPH. But for pNPh it was from 0.06 to 0.16 μM and 5 to 40 μM. Yi et al. [7] applied electropolymerization for βCD and L-arginin on the surface of carbon nanotubes @graphene nanoribbons (CNTs@GNRs) for preparing a modified electrode for 2- and 4-aminophenols (AP). A linear response ranging from 25.0 to 1300.0 nM for both 2- and 4-AP and the detection limits (DLs) of 2- and 4-AP obtained in this work were 6.2 and 3.5 nM, respectively.

1.2. Potentiometric sensors

They are a type of sensors based on measuring the potential changes with concentration in accordance with the Nernst equation.

Odashima et al. [8] used a long derivative chain of β-cyclodextrin for preparing a new sensory element for the determination of organic amines. Stefan et al. [9] used either α or γ-cyclodextrin-based electrodes for the determination of R-baclofen. The detection limits were $7 \times 10^{-9}\,mol^{-1}\,L^{-1}$ for α-cyclodextrin-based electrode and $1.44 \times 10^{-10}\,mol^{-1}\,L^{-1}$ for γ-cyclodextrin-based electrode. (2-hydroxypropyl)-β-cyclodextrin, heptakis(2,3,6-tri-O-methyl)-β-cyclodextrins and heptakis(2,3,6-tri-O-benzoyl)-β-cyclodextrin were applied for preparing diclofenac electrode by Lenik [10]. Staden and Nejem [11] determined L-vesamicol by CD derivative-based potentiometric sensor. The detection limit was of the order of 10^{-10} M. They showed a linear range between 10^{-9} and 10^{-7} M. Lenik and Łyszczek [12] determined naproxen by functionalized β-CD. It is based on inclusion complex of naproxen with β-CD-derivative. The linear range was 5.0×10^{-5}–1.0×10^{-2} mol L^{-1}. Staden and Holo [13] determined L-histidine by an entioselective potentiometric membrane electrode based on CD. They applied carbon paste impregnated with α-, β-, 2-hydroxyl-3-trimethylammoniopropyl-β-(as chloride salt) and γ-cyclodextrins (γ-CDs). The recovery of L-his in the presence of D-his was higher than 99.10%. L-proline electrode was constructed based on carbon paste impregnated with α, β, or γ cyclodextrin [14]. The detection limit of the membrane was in the region of 10^{-10}–10^{-9} M.

All the aforementioned cyclodextrin applications were examples of sensors for drug analysis. The application of cyclodextrin for sensors for inorganic cations is rarely found. We choose one of these sensors that was sensing for nickel which was constructed by Zareh et al. [15], to study as an example of CD sensors. Two membrane compositions (**Table 1**) were prepared for the optimization to get the best. Electrode type I comprised DEP, while II comprised NPOE. The behavior of DEP-containing electrodes showed better Nernstian slope value than NOPE-containing membrane electrode. Both electrode types showed the same linear range of 5.01×10^{-5}–10^{-2} M. **Figure 4** shows the calibration graphs for each electrode type.

The effect of inner filling (IF) solution was studied by the application of the electrode type I containing three types of IF-solutions (A, B, and C). They were corresponding to compositions (0.1 M KCl + 0.1 M NiCl$_2$), (0.01 M KCl + 0.01 M NiCl$_2$), and (0.001 M KCl + 0.001 M NiCl$_2$), respectively. The slopes of Ni electrode were 30.9, 28.17, and 29.7 mV/decade, for electrodes with IF A, B, and C, respectively. When A and B IF was applied, the lower linear range reached 5.0×10^{-5} M. In the case of IF solution type C, the linear range was not less than 5×10^{-4} M. **Table 2** summarizes the obtained results.

The response time was estimated according to the IUPAC definition [16]. It is defined as the time between the instant when the Ni electrode was brought into contact with sample solution and the first instant when emf/time slope becomes equal to the limiting value selected on the basis of experimental conditions. Dynamic response was studied for both electrode types containing DEP or NPOE. From **Figures 5** and **6**, the response times for electrode types I and II were between 2 and 3 s for both types of electrodes for the tested concentrations 10^{-2}–10^{-4} M. This fast response for both types will help in the application of both electrode types for real measurements.
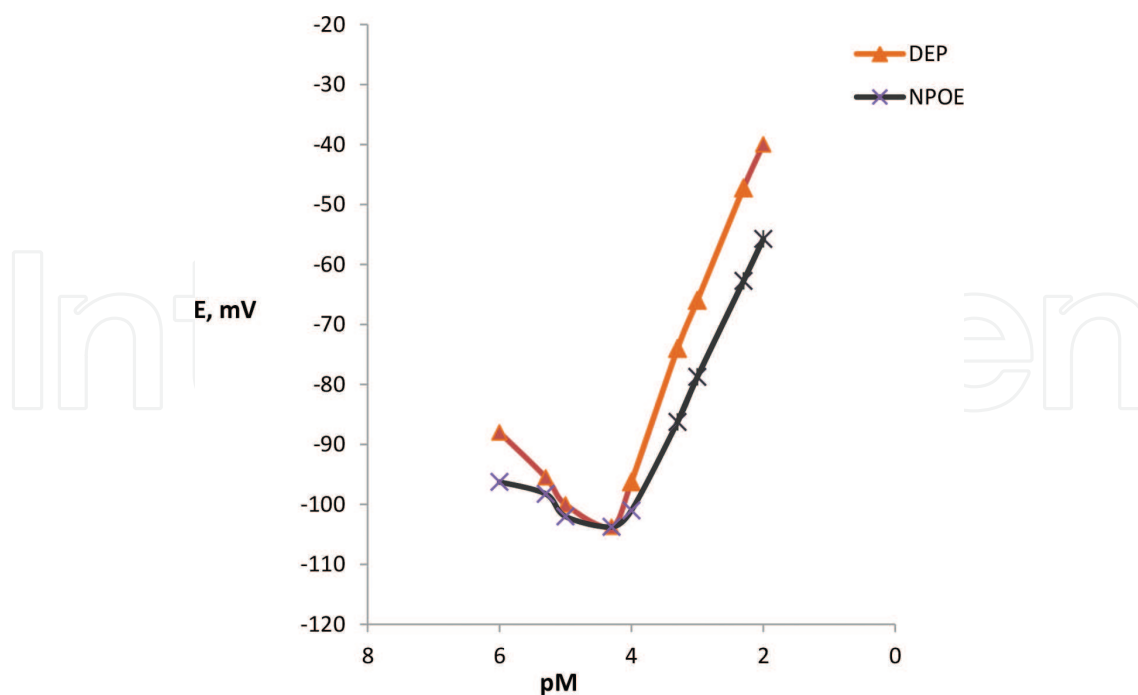
Figure 4. Calibration graphs for Ni-selective electrodes with membrane contains either (a) DEP or (b) NPOE plasticizers.

Composition, w/w %	PVC, mg	βCDX, mg	DEP, mg	NPOE, mg	% Ionophore	Slope, mV/ Decade	Detection limit, M
I-Membrane	63.6	12.8	126.4	0	6.31	28.76	3.98×10^{-5}
II-Membrane	60	14	0	121	7.18	23.33	6.3×10^{-5}

Table 1. Composition of membrane types I and II used for preparing Ni^{2+}-selective electrode.

Inner filling solution	Slope, mV/Decade	Linear range, M	R^2
A-(10^{-1} M $NiCl_2$ + 10^{-1} M KCl)	30.89	10^{-2}–5×10^{-5}	0.9987
B-(10^{-2} M $NiCl_2$ + 10^{-2} M KCl)	28.17	10^{-2}–5×10^{-5}	0.9986
C-(10^{-3} M $NiCl_2$ + 10^{-3} M KCl)	29.68	10^{-2}–5×10^{-4}	0.9931

Table 2. Effect of inner filling on the performance of Ni-selective electrode based on β-CDX with DEP plasticizer.

The detection limit (DL) of an ISE can be defined as the cross point of line segments fitted to linear segments of *emf* versus *log a_{Ni2+}* [16]. For membrane types I and II, the values of the detection limits were 3.98×10^{-5} and 6.3×10^{-5} M.

The process of the electrode response is based on a nonpolarized electrochemical equilibrium. There are two equilibrium steps to explain the response mechanism of the proposed Ni-selective electrode. The first step is the equilibrium between Ni^{2+} in membrane and solution sites. The second step is the equilibrium of formation of Ni^{2+}-β-CDX into the membrane site. The steps of this mechanism can be represented below:
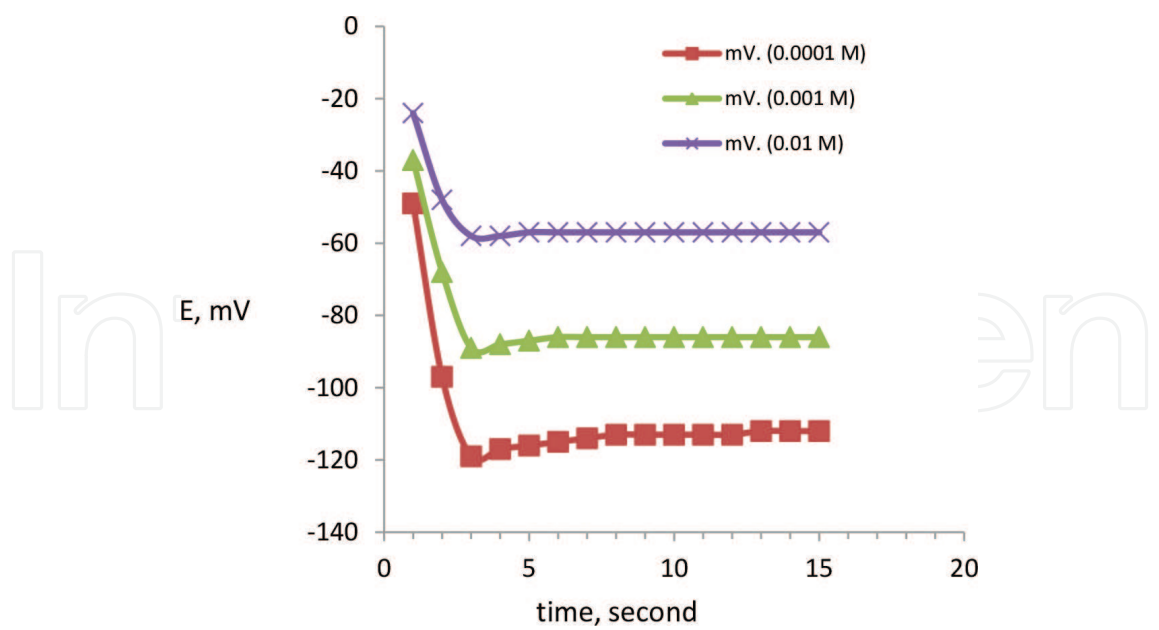
Figure 5. Dynamic response for Ni-selective electrodes with membrane type I containing DEP, for different concentrations (a) 0.01 M, (b) 0.001 M, and (c) 0.0001 M Ni^{2+} solutions.
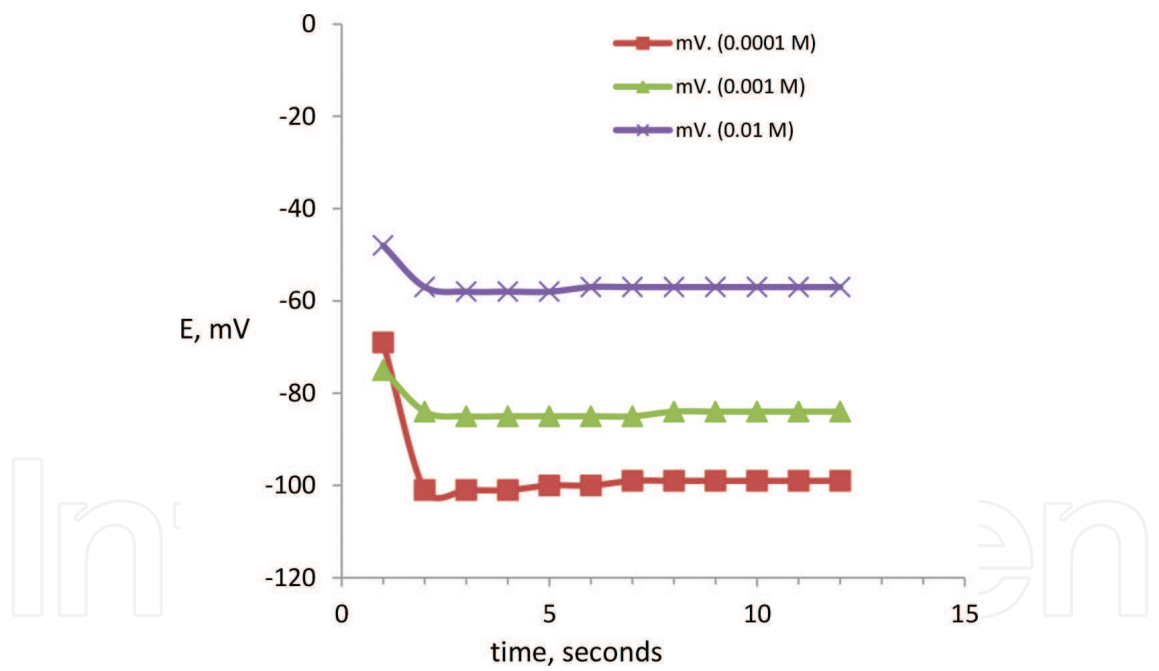

Figure 6. Dynamic response for Ni-selective electrodes with membrane type II containing NPOE, for different concentrations (a) 0.01 M, (b) 0.001 M, and (c) 0.0001 M Ni^{2+} solutions.

$$\left[Ni^{2+}\right]_s \rightleftharpoons \left[Ni^{2+}\right]_m$$

$$\left[Ni^{2+}\right]_m + \beta - CDX_m \rightleftharpoons \left[Ni^{2+} - \beta\text{-}CDX\right]^{2+}_m$$

$$\Delta E = E_m - E_s = (RT/F) \ln \left\{ k_i \, a_{Ni}^{2+} \left[1 + K_f \, (carrier)\right]/(sites) \right\}$$

2. pH-effect

The potential changes versus different pH values for the DEP-membrane electrode type I and type II were tested. In acidic part, the break was observed at pH values 3.8 and 3.2 for type I and II electrodes, respectively. The sensitivity of β-CDX toward the H^+ is the reason for the potential break in acidic medium. The break in acidic medium was due to the inclusion of H^+ into ionophore in the membrane site. Above pH 3.2 and 3.8, the potential was not changed whatever the pH value for types I and II, respectively. This was due to the absence of the H^+ ion concentration, which disturbs the equilibrium. Representative curves for nickel with membrane types I and II are shown in **Figure 7**.
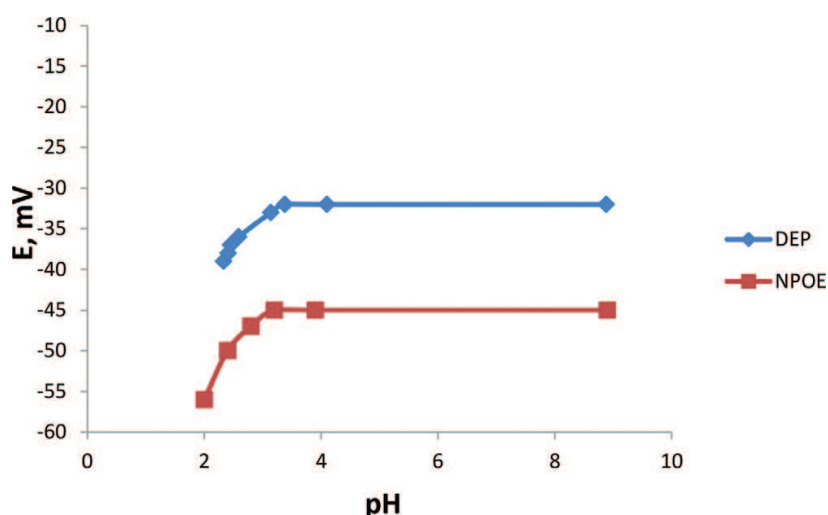

Figure 7. pH-effect for Ni electrode for 0.001 M Ni^{2+} solutions for electrodes comprising (a) DEP and (b) NPOE.

3. Selectivity properties

The selectivity of Ni electrode with different membrane types I and II was calculated according to the SSM [16]. **Table 3** shows the obtained values of the selectivity coefficient ($K^{Pot}_{Ni^{2+}, j^{z+}}$). From the results, it can be reported that most of the tested interferents for Ni-ISE type I showed perfect selectivity. When the electrode type I was used, the values of the selectivity coefficient toward divalent cations were so perfect to consider this electrode selective for Ni^{++} cation. The recorded values for most of the tested divalent cations were of the order of 10^{-3}. In case of trivalent cations, this type of electrode showed better selectivity coefficient values (of order 10^{-5}). When electrode type II was used, the selectivity coefficient values were higher than that for electrode type I. It showed values of order 10^{-2} for trivalent cations and 10^{-1} for most of the divalent cations. This can be attributed to that in type II electrode the NPOE has active sites to interact with cationic species which lowers the selectivity toward Ni^{++} [17]. The tested monovalent cations (Na^+, K^+, and NH_4^+) showed interference with the measurements with either type I or type II. Accordingly, it is recommended that measurements with the proposed electrodes should be conducted in the absence of these cations.

Interferent	$K^{Pot}_{Ni^{2+}, j^{z+}}$	
	I-DEP	II-NPOE
Ir^{3+}	7.67×10^{-5}	1.4×10^{-2}
Fe^{3+}	4.38×10^{-5}	1.3×10^{-2}
Zn^{2+}	1.1×10^{-3}	6.1×10^{-2}
Co^{2+}	1.8×10^{-3}	3.5×10^{-2}
Cu^{2+}	2.1×10^{-3}	3.0×10^{-1}
Ba^{2+}	2.2×10^{-3}	3.0×10^{-1}
Mg^{2+}	1.6×10^{-3}	1.5×10^{-1}
Ca^{2+}	2.2×10^{-3}	2.0×10^{-1}
Cd^{2+}	2.2×10^{-3}	1.6×10^{-1}
Hg^{2+}	1.7×10^{-3}	2.0×10^{-1}
Mn^{2+}	1.5×10^{-3}	1.7×10^{-1}
Pb^{2+}	2.9×10^{-3}	1.2×10^{-1}

Table 3. Selectivity coefficient values for nickel electrodes based on β-CDX incorporating (DEP) [I], and (NPOE) [II] as plasticizers.
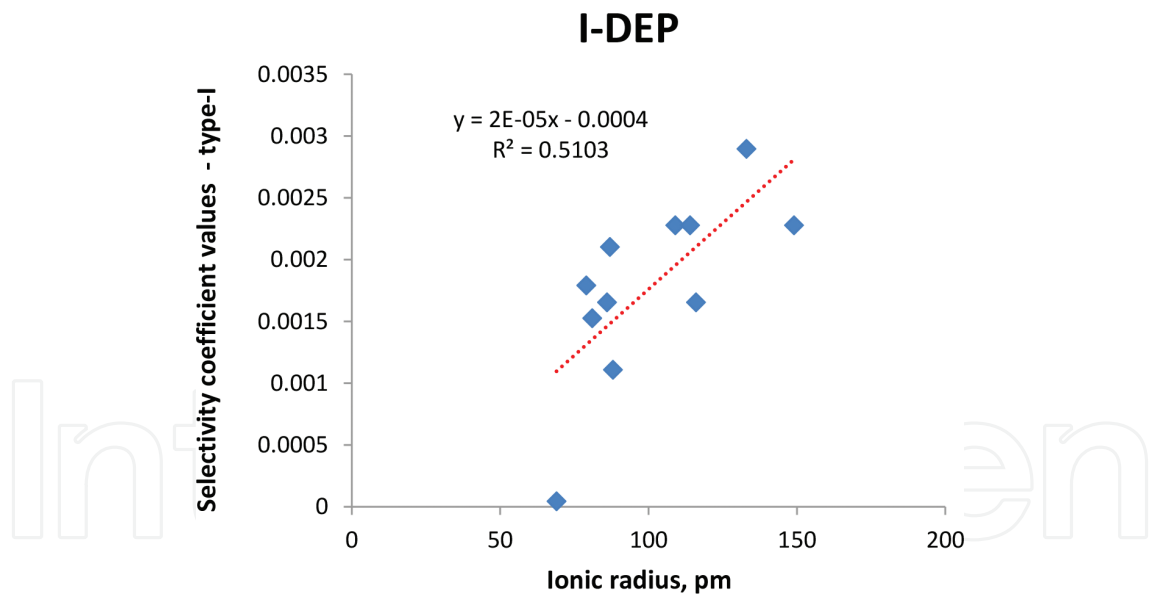

Figure 8. Correlation between ionic radius (pm) of the tested cations and selectivity coefficient ($K^{Pot}_{Ni^{2+}, j^{z+}}$) for Ni-ISE with membrane type I for 0.0001 M solutions.

The relation between ionic radius [18] of interferent cations and the values of selectivity coefficient for both electrode types is shown in **Figures 8** and **9**. It was found that there was an increase in the selectivity coefficient values with increasing the ionic radius of the tested cations. This was true for both electrode types I and II. The increment values in case of type I were less than those in case of type II. This was attributed to that the increase in ionic volume was suitable for the β-CDX cavity.
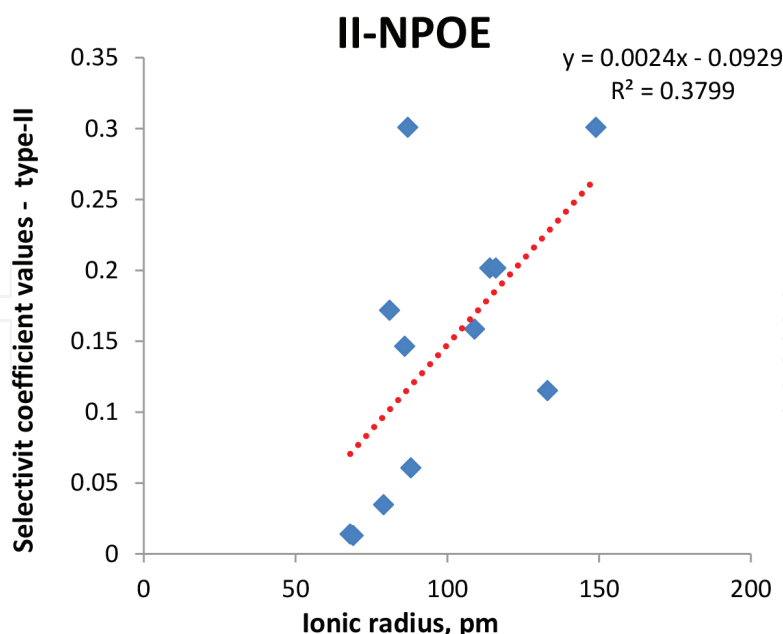
Figure 9. Correlation between ionic radius (pm) of the tested cations and selectivity coefficient ($K^{Pot}_{Ni^{2+}, j^{z+}}$) for Ni-ISE with membrane type II for 0.0001 M solutions.

4. Determination of nickel in its samples

In this chapter, two types of samples containing nickel were used. They were representative for food samples and stainless steel samples. Five steel samples (A–D) and one food (E) sample were chosen. On the one hand, 0.1 g of each stainless steel sample was dissolved into aqua-Regia, heated at 105°C, and diluted to 250 ml using bi-distilled water. This solution was measured directly. On the other hand, 0.5 g chocolate sample (E) was dissolved in 100 ml after digestion with HNO_3, $HClO_4$, and H_2O_2. In this case, 1 ml was diluted to 50 ml, and the result solution was subjected to potential measurements using the proposed Ni-selective electrode. The obtained Ni values into the stainless steel samples (A–D) were between 1.467 and 7.354 ppm. The chocolate sample E showed Ni content 14.707 ppm. All the obtained values agreed with the values given by AAS analysis of the same samples [19]. The obtained values of

No.	Sample	Ni^{2+}, ppm		RSD*, %
		AAS method	Ni-ISE method	
A	Test tube holder	1.437	1.467	1.95
B	Shaving blade	6.005	7.354	2.51
C	Screwdriver	4.181	4.640	2.13
D	Coin (1/4 pound)	4.61	3.686	1.81
E	Chocolate (Cadbury Dairy Milk)	12.158	14.707	2.34

*(4-determinations).

Table 4. Determination of nickel in its samples using the proposed Ni-ISE.

Ni in chocolate agreed with previously recorded values [20]. **Table 4** shows the obtained results for analysis by using both the proposed electrode and an AAS method for the same samples.

5. Conclusions

Cyclodextrin (CD) is one of the important reagents that is able to form inclusion complex with a variety of compounds. This property helps its use as an ionophore for preparing electrochemical sensors for many organic pharmaceutical cations. The recorded electrochemical sensors were either potentiometric or voltammetric. Up to date, the application of CD for preparing inorganic sensors was rarely found.

Author details

Mohsen M. Zareh

Address all correspondence to: mohsenzareh@hotmail.com

Department of Chemistry, Faculty of Science, Zagazig University, Zagazig, Egypt

References

[1] Komiyama M. Preparation of cyclodextrin membrane-modified electrodes as sensor materials. Macromolecular Materials and Engineering. 1988;**163**:205-207

[2] Stefan R-I, van Staden JF, Aboul-Enein HY, van Staden JF. Maltodextrins as new chiral selectors in the design of potentiometric, enantioselective membrane electrodes. Fresenius' Journal of Analytical Chemistry. 2001;**370**:33-37

[3] Lenik J, Nieszporek J. Construction of a glassy carbon ibuprofen electrode modified with multi-walled carbon nanotubes and cyclodextrins. Sensors and Actuators B: Chemical. 2017;**255**:2282-2289

[4] AttaEkram NF, El-AdsYousef H, Galal MA. Determination of some neurotransmitters at cyclodextrin/ionic liquid crystal/graphene composite electrode. Electrochimica Acta. 2016;**199**:319-331

[5] Sun Y, Wei T, Jiang M, Xu L, Xu Z. Voltammetric sensor for chloramphenicol determination based on a dual signal enhancement strategy with ordered mesoporous carbon@polydopamine and β-cyclodextrin. Sensors & Actuators, B: Chemical. 2018;**255**:2155-2162

[6] Li C, Wu Z, Yang H, Deng L, Chen X. Reduced graphene oxide-cyclodextrin-chitosan electrochemical sensor: Effective and simultaneous determination of o- and p-nitrophenols. Sensors & Actuators, B: Chemical. 2017;**251**:446-454

[7] Yi Y, Zhu G, Wu X, Wang K. Highly sensitive and simultaneous electrochemical determination of 2-aminophenol and 4-aminophenol based on poly(l-arginine)-β-cyclodextrin/carbon nanotubes@graphene nanoribbons modified electrode. Biosensors and Bioelectronics. 2016;**77**:353-358

[8] Odashima K, Hashimoto H, Umezawa Y. Potentiometric discrimination of organic amines by liquid membrane electrodes based on a long alkyl chain derivative of β-cyclodextrin. Microchimica Acta. 1994;**113**:223-238

[9] Stefan R-I, van, Alexander S, Rat'ko A. Enantioselective, potentiometric membrane electrodes based on cyclodextrins: Application for the determination of R-baclofen in its pharmaceutical formulation. Talanta. 2006;**69**:1049-1053

[10] Lenik J. A new potentiometric electrode incorporating functionalized β-cyclodextrins for diclofenac determination. Materials Science and Engineering: C. 2014;**45**:109-116

[11] van Staden R-IS, Nejem RM. Cyclodextrins-based enantioselective, potentiometric membrane electrodes for l-vesamicol assay in serum samples. Sensors and Actuators B: Chemical. 2006;**117**:123-127

[12] Lenik J, Łyszczek R. Functionalized β-cyclodextrin based potentiometric sensor for naproxen determination. Materials Science and Engineering: C. 2016;**61**:149-157

[13] Stefan-van Staden R-I, Holo L. Enantioselective, potentiometric membrane electrodes based on cyclodextrins for the determination of L-histidine. Sensors and Actuators. 2007;**120**:399-402

[14] Kenneth I, Raluca O, Stefan I. Enantioselective potentiometric membrane electrodes based on α-, β- and γ-cyclodextrins as chiral selectors for the assay of L-proline. Talanta. 2005;**66**:501-504

[15] Zareh MM, Zordek W, Elgendy K, Zaky M, Keshk A, Abd-Alhady A. β-cyclodextrin as a selective Green-ionophore for determination of nickel by membrane electrode. Sensor Letters. 2017;**15**:1-7

[16] Buck RP, Lindner E. Recommendations for nomenclature of ionselective electrodes (IUPAC Recommendations 1994). Pure and Applied Chemistry. 1994;**66**:2527

[17] Zareh MM. Blank Membranes versus Ionophore-based Membranes for the Selective Determination of H^+. Analytical Sciences. 2009;**25**:1135-1131

[18] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst. 1976;**A32**:751-767

[19] Manual Book, Buck Scientific 210/211 VGP Atomic Absorption Spectroscopy

[20] Vivian Fern Andes and Daksesh Parikh. Toxicologist D.M. Saxena Finds Nickel Content Above Safety Limit in 11 Brands. December 31, 2012