

Full Length Research Paper

Design, construction and investigating functionality of a nickel (II) ion selective electrode

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Ni²⁺ ion-selective electrode (Ni-ISE) based on plasticized poly(vinyl chloride) (PVC) membrane with 25, 26, 27 tri propoxy 28, Amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene as ionophore and dibutyl phthalate (DBP) as plasticizer was designed and constructed. The Ni-ISE showed a linear reply in the concentration range of 1.0×10^{-1} to 1.0×10^{-4} M with slope of 29.3 ± 0.5 mV/decad. The Ni-ISE response time was ≤ 6 s and was used for two months with no deviation in the pH range 4 to 9. The best performance was obtained with a membrane composition of 30% PVC, 62% DBP, 3% 25, 26, 27- tripropoxy-28, amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene and 5% potassium tetrakis[p-cholorophenyl]borate

(KTpCIPB). Its detection limit was 1.0×10^{-5} M. The selectivity coefficients (K_{ij}^{pot}) for different cations were calculated by the matched potential method (MPM). The scanning electron microscopy (SEM) of the Ni-ISE's membranes showed some morphological changes during its life span, probably due to both the reaction between the Ni²⁺ ion and / or less of the membrane parts by permeation.

Key words: Ni²⁺ ion-selective electrode, 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene; scanning electron microscopy (SEM).

INTRODUCTION

The construction of sensitive and correct appliances based on electrochemical sensors, capable of quantifying and detecting the concentration of contaminating substances in different ecosystems has been the subject of growing significance in recent years (Malinowska et al., 2000; Pineros et al., 1998; Perez-Marín et al., 2001; Arada Perez et al., 2003). Because ion selective electrodes show good selectivity for different ions, so they are very suitable for measuring the content of the considered ions. They are built easily and the results are obtained speedily. They are of comparatively low cost and can be applied in various applications. There are varieties of commercial electrodes manufactured based on alkali, alkaline earth metals, nitrates and are available

in the market. Researchers have recently reported the new ion selective membrane sensors to detect Cu²⁺, Ag⁺ and Mn²⁺ ions (Jeong et al., 2010; Seo et al., 2010; Aghaie et al., 2010). However, much more studies are needed in developing ion selective electrodes to detect heavy metal ions which are poisonous even at very low concentrations. Various techniques have been used for the determination of heavy metal ions in biochemical and environmental sources (Maniasso and Zagatto, 1998). The majority of techniques have inadequacies such as narrow working concentration range, high detection limit, poor selectivity, high response time and interference by other cations (Midgley and Mulcahy, 1985). It is therefore believed that some types of ion selective electrodes are the best tools for a convenient, quick and cheap determination of ions concentration.

In the present study, a new sensor based on 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23-tetra-tert-butyl-

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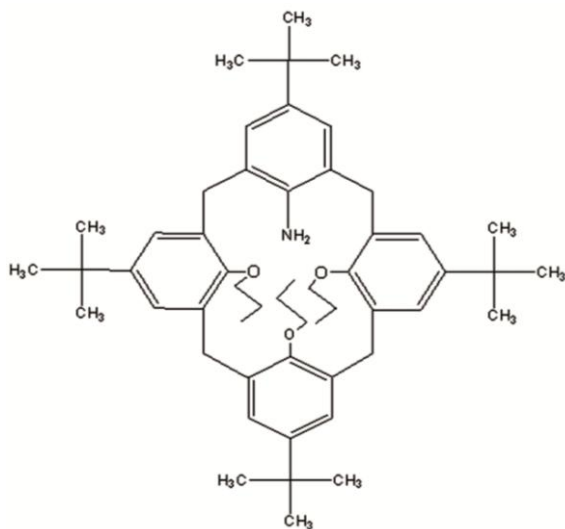


Figure 1. Structure of 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene.

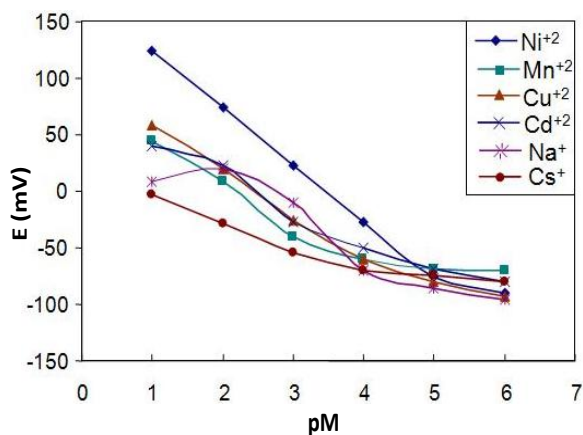


Figure 2. Potential response of various metal electrodes based on 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23 tetra-tert-butyl-calix[4]arene.

calix[4]arene as neutral carrier for the determination of Ni^{2+} ion in the concentration range of the 1.0×10^{-1} to $1.0 \times 10^{-4} \text{ M}$ was designed, built and tested. The structure of 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene is shown in Figure 1.

MATERIALS AND METHODS

Reagents

All reagents used in this work were of analytical grade, with the exception of 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23 tetra-tert-butyl-calix[4]arene. Reagent grade DBP, oleic acid (OA), o-

nitrophenyl octyl ether (o-NPOE), acetophenone (AP), sodium tetraphenyl borate (NaTPB), KTpCIPB, tetrahydrofuran (THF) and high relative molecular weight PVC were purchased from Fluka or Merck Companies. Nitrate and chloride salt of all cations were of the highest purity available (all from Fluka or Merck) and used without any further purification. Double distilled di-ionized water was used throughout.

Experimental section

Construction of the electrode

The PVC membrane was prepared by mixing thoroughly 30 mg of PVC, 3 mg of 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene, 62 mg of plasticizer DBP and 5 mg of additive KTpCIPB. This was followed by dissolving the admixture in 2 ml of dry freshly distilled THF. The resulting clear mixture was vaporized slowly until an oily concentrated product was obtained. A pyrex tubule with 5 mm i.d was dipped into the concentrated product for about 7 s for which an opaque membrane thickness of approximately 0.3 mm was formed. The tubule was then pulled out of the admixture and kept at room temperature for about 10 h. The electrode was then filled with a solution containing $1.0 \times 10^{-3} \text{ M}$ $\text{Ni}(\text{NO}_3)_2$ solution. The sensor was finally conditioned for 17 h by soaking into a solution containing $1.0 \times 10^{-2} \text{ M}$ $\text{Ni}(\text{NO}_3)_2$ solution.

Electromotive force (emf) measurements

All emf measurements were carried out with the following assembly: $\text{Ag} - \text{AgCl} \mid \text{KCl} (3 \text{ M}) \mid \text{internal solution } 1.0 \times 10^{-2} \text{ M } \text{Ni}(\text{NO}_3)_2 \mid \text{PVC membrane} \mid \text{test solution} \mid \text{Hg} - \text{Hg}_2\text{Cl}_2, \text{KCl (satd)}$.

Potentiometer DEC model 330 FC was used for the potential measurements. The potentials were measured by varying the concentration of the test solution in the range of 1.0×10^{-1} to $1.0 \times 10^{-7} \text{ M}$. The emf observations were made comparative to the double-junction saturated calomel electrode (SCE, Philips). Activities were measured according to the Debye-Huckel procedure (Kamata et al., 1988).

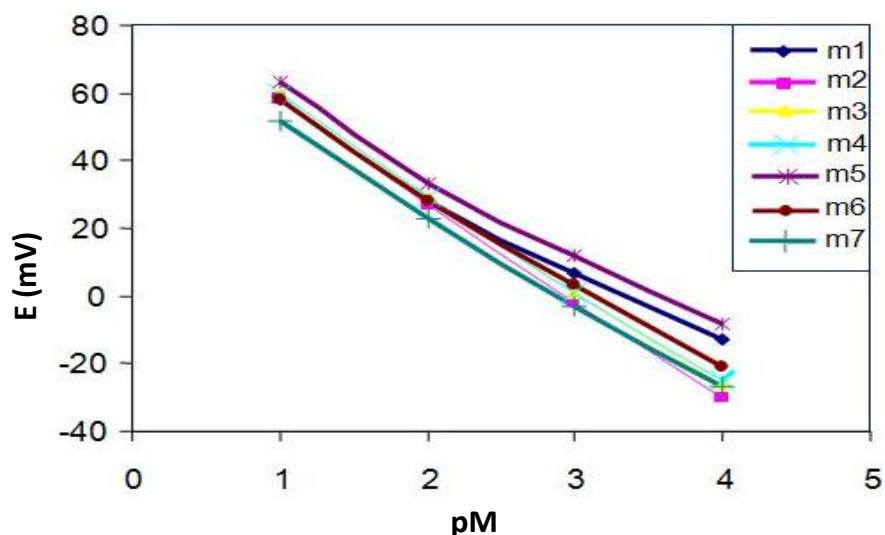
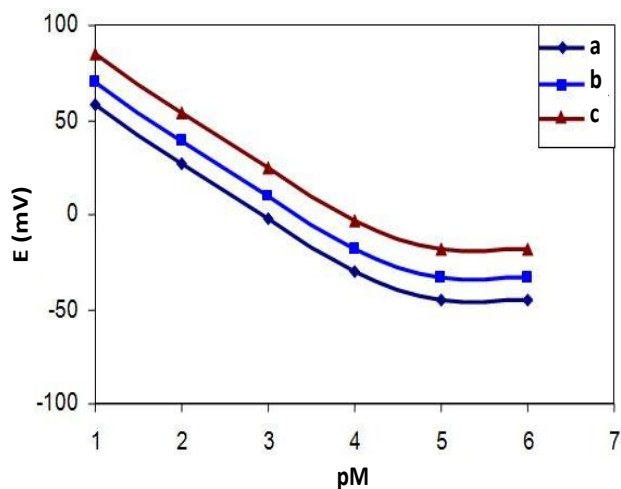
RESULTS AND DISCUSSION

The effect of membrane composition

In the over previous work 25, 26, 27 tri propoxy 28, amino 5, 11, 17, 23-tetra-tert-butyl-calix[4]arene was used as an ion carrier to prepare PVC membrane electrodes for some common metal ions (Fekri et al., 2011). The potential response of these sensors is shown in Figure 2. The constructed Ni-ISE responds to Ni^{2+} ion with linear trend in the concentration range of 1.0×10^{-1} to $1.0 \times 10^{-4} \text{ M}$ as compared to its response to other cations. The selectivity and sensitivity of an ion-selective sensor not only depend on the nature of the ion carrier used, but also considerably on the membrane composition and the

Table 1. Effect of membrane composition on response of Ni²⁺ ion-selective electrode.

Membrane No.	Composition (wt%)				Slope (mV/decade)
	Ionophore	PVC	Plasticizer	Additive	
1	3	30	62, NPOE	5, KTpCIPB	23.4
2	3	30	62, DBP	5, KTpCIPB	29.3
3	3	30	61, DBP	6, KTpCIPB	28.6
4	3	30	64, DBP	3, KTpCIPB	28.7
5	5	30	60, NPOE	5, KTpCIPB	23.4
6	5	30	62, DBP	3, NaTPB	26.2
7	3	30	62, AP	5, OA	26.3

**Figure 3.** The potential responses of different membrane.**Figure 4.** Effect of internal filling solution on the potential response of the Ni²⁺ ion-selective electrode. The Ni(NO₃)₂ concentration is: (a) 1.0×10^{-2} M, (b) 1.0×10^{-3} M, (c) 1.0×10^{-4} M.

characteristics of solvent intermediates and the additive used (Poursaberi et al., 2001, 2002; Ganjali et al., 2001, 2002; Shamsipur et al., 2001, 2002). Furthermore, the influence of the membrane composition, nature and amount of solvent intermediates, additives and ionophore on the potential response of the Ni²⁺ electrode were investigated (Table 1 and Figure 3). It was observed that the use of 62% (w/w) DBP in presence of 30% (w/w) PVC, 3% (w/w) ionophore and 5% (w/w) KTpCIPB (Table 1), resulted in obtaining the best sensitivity and Nernstian slope for the Ni-ISE (29.3 ± 0.5 mV/decade) indicating the best combination as being the electrode. The effect of the concentration of internal solution on the potential response of the Ni²⁺ ion-selective sensor was examined. The concentration of Ni(NO₃)₂ was altered between 1.0×10^{-2} to 1.0×10^{-4} M and the plots of measured emf, versus pNi²⁺ were drawn (Figure 4). It was found that the alteration of the concentration of the internal solution has no influence on Ni-ISE's potential response, except for an anticipated change in the intercept in the

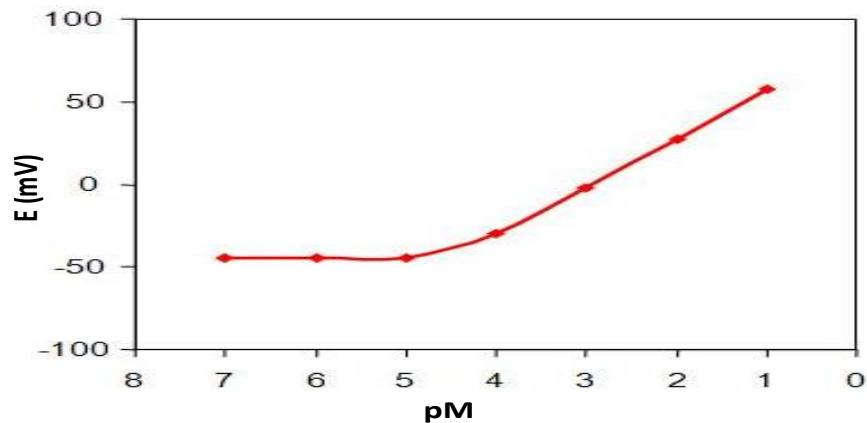


Figure 5. Calibration curve for the proposed Ni^{2+} ion-selective electrode.

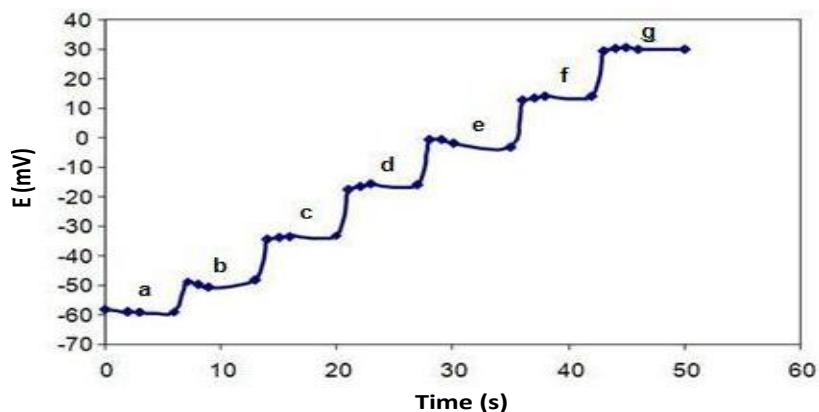


Figure 6. Dynamic response of the Ni^{2+} ion-selective electrode for step changes in concentration of Ni^{2+} (a) 1.0×10^{-5} M, (b) 5.0×10^{-5} M, (c) 1.0×10^{-4} M, (d) 5.0×10^{-4} M, (e) 1.0×10^{-3} M, (f) 5.0×10^{-3} M, (g) 1.0×10^{-2} M.

vicinity of Nernstian curves. The reference solution with concentration of 1.0×10^{-2} M was relatively suitable for smooth functioning of the Ni-ISE system.

Calibration curve and statistical analysis

The measurements were carried out in the concentration range of 1.0×10^{-1} to 1.0×10^{-7} M. The critical response characteristics of the proposed electrode were evaluated according to International Union of Pure and Applied Chemistry (IUPAC) recommendation (IUPAC Analytical Chemistry Division, 1976). The emf response of the polymeric membrane (Figure 5) showed practically Nernstian slope of 29.3 ± 0.5 mV/decade in the concentration range 1.0×10^{-1} to 1.0×10^{-4} M for $\text{Ni}(\text{NO}_3)_2$ solutions. The detection limit was defined as the

concentration of Ni^{2+} ion obtained from the intersection of two extrapolated segments of the calibration graph was found to be 1.0×10^{-5} M.

Response time

Dynamic response time is a significant factor for an ion selective sensor (Matysik et al., 1998). In this study, the practicable response time of the proposed electrode was recorded by the immediate changing solution of the diverse Ni^{2+} concentration ranging from 1.0×10^{-2} to 1.0×10^{-5} M. The actual potential – time trace is shown in Figure 6. Over the proposed concentration range, the Ni-ISE reached the equilibrium response in less than 6 s. To evaluate reversibility of Ni-ISE, a similar process but in the opposite direction was followed. The measurements

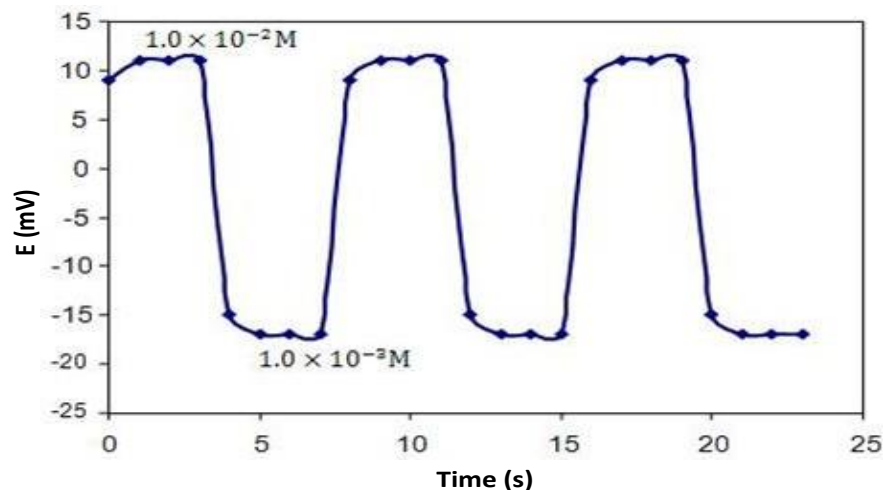


Figure 7. Dynamic response characteristics of the Ni^{2+} ion-selective electrode for several high-to-low sample cycles.

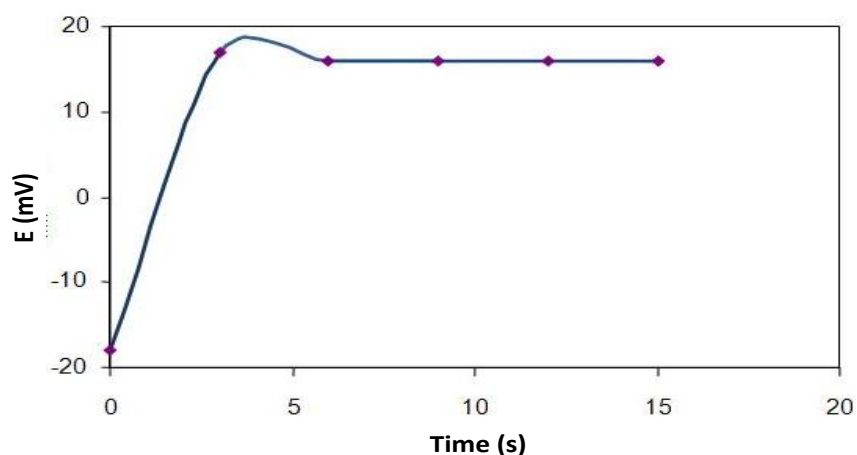


Figure 8. Statistical response time of the Ni^{2+} ion-selective electrode.

were accomplished in the sequence of high-to-low sample concentration cycles (Figure 7). It was observed that the electrode's potentiometric response is reversible and had no memory effect (Bakker et al., 2000). It was concluded experimentally that the constructed Ni-ISE was responsive to Ni^{2+} ion in less than 6 s. The Ni-ISE is therefore may be categorized as fast responding electrode (Figure 8) (Pranitis et al., 1992).

Influence of pH

A Ni^{2+} solution with concentration of $1.0 \times 10^{-3} \text{ M}$ was used for this study. The pH dependence of the Ni-ISE potential was examined by varying the pH in the range of

1.0 to 10. The tentative results showed that the potentials remained constant in the pH range 4.0 to 9.0 (Figure 9) and the same may be taken as the working pH range of the Ni-ISE. This showed that electrode No.2 in Table 1 can be used to measure a wide range of industrial and environmental water samples without pH modification. The sharp changes in potential below pH 4.0 may be due to H^+ co-fluxing.

Influence of temperature

The resulting changes of Ni-ISE functionality with temperature, for the test solutions at 20, 25, 30, 35, 40, 45°C for the Ni^{2+} electrodes are showed in Table 2. The

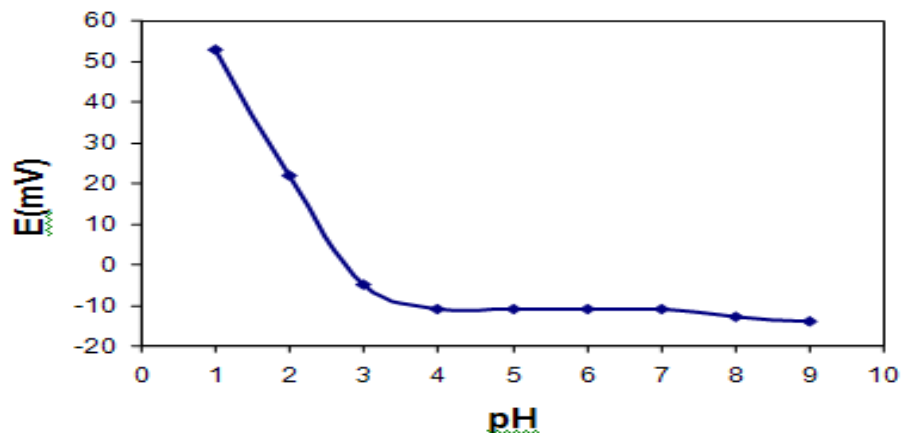


Figure 9. Variation of potential as function of pH.

Table 2. Variation of functionality of Ni-ISE with temperature.

Temperature (°C)	Slope (mV/decade)	E° (mV)	Linear range [M]
20	31.3	97.5	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$
25	29.3	86.5	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$
30	29.2	80.5	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$
35	28.9	78.3	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$
40	28.3	75.3	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$
45	27.4	70.9	$1.0 \times 10^{-1} - 1.0 \times 10^{-4}$

electrode showed a good Nernstian behavior in the temperature range 20 to 45°C. The Nernstian slopes were decreased with increasing temperature. The standard cell potentials (E_{cell}°) were established at different temperatures from the respective calibration plots as the intercept of these plots at $\text{pNi}^{2+} = 0$, and were used to conclude the isothermal temperature coefficient (dE°/dt) of the cell with the help of the following equation (Antropov, 1972):

$$E_{\text{cell}}^{\circ} = E_{\text{cell}(25^{\circ}\text{C})}^{\circ} + (dE^{\circ}/dt)_{\text{cell}}(t - 25)^{\circ}\text{C} \quad (1)$$

Plot of (E_{cell}°) versus $(t-25)^{\circ}\text{C}$ produced a beeline as shown in Figure 10. Then, the isothermal temperature coefficient of the cell was taken from the slope of this line.

It amounts to $-9.56 \times 10^{-4} \text{ V}/^{\circ}\text{C}$. The standard potential to the saturated calomel electrode (SCE) were computed using the following equation:

$$E_{\text{Hg}/\text{Hg}_2\text{Cl}_2}^{\circ} = 0.241 - 6.60 \times 10^{-4}(t - 25)^{\circ}\text{C} \quad (2)$$

The values of standard potential of Ni^{2+} ion-selective

electrode (E_{elec}°) were calculated at the different temperatures from the following relation:

$$E_{\text{cell}}^{\circ} + E_{\text{ref}}^{\circ} = E_{\text{elec}}^{\circ} \quad (3)$$

Plot of E_{elec}° versus $(t-25)^{\circ}\text{C}$ gave a beeline, as shown in Figure 10. The slope of the line was taken as the isothermal temperature coefficient of the Ni^{2+} ion-selective electrode. It amounts to $-1.56 \times 10^{-3} \text{ V}/^{\circ}\text{C}$. The small values of $(dE^{\circ}/dt)_{\text{cell}}$ and $(dE^{\circ}/dt)_{\text{elec}}$ exhibit the high thermal stability of electrode in the inspected temperature range.

Potentiometric selectivity

One of the most important characteristic of any ion selective electrode is its relative response to the main ion over other ions existent in solution, which is described in terms of potentiometric selectivity coefficients.

Potentiometric selectivity coefficient ($K_{i,j}^{\text{pot}}$), expressing the preference by the membrane for an interfering ion

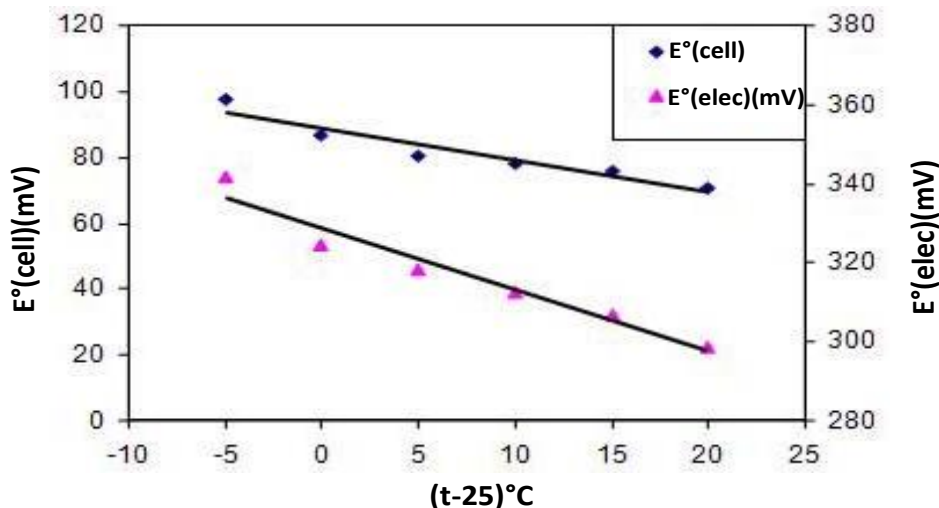


Figure 10. Modification of standard potential of the cell and the electrode with changes of test solution temperatures.

Table 3. Selectivity coefficient of various interfering cations.

Interfering cation	$K_{Ni^{2+},M}^{pot}$
Zn ²⁺	1.24×10^{-3}
Cu ²⁺	1.96×10^{-2}
Cd ²⁺	1.98×10^{-3}
Mn ²⁺	6.51×10^{-3}
Co ²⁺	2.08×10^{-1}
Cs ²⁺	7.08×10^{-3}
Na ²⁺	1.32×10^{-3}

(A^{n+}) relative to Ni^{2+} , were established by the IUPAC recommended MPM (Umezawa et al., 1995; Bakker, 1997b). The resulting selectivity coefficients summarized in Table 3 show that the electrode is selective for Ni^{2+} ion in the presence of the interfering ions and for most ions used ($K_{Ni^{2+},M}^{pot}$) values are in the order of $1.0 \times 10^{-2}M$ or smaller. However, Co^{2+} has comparatively higher values and may cause interference at higher concentrations.

Lifetime study

Lifetime studies were based on observing the change in the slope of the ion selective electrode with time. The prepared Ni^{2+} ion-selective electrode was used for more than 2 months and no measurable change in sensor potential was observed.

Studying made membranes by SEM

SEM micrographs of Ni^{2+} ion-selective electrode membranes at diverse steps of its operation are shown in Figure 11. In Figure 11a signifies the surface of membrane without activation, where smooth layers with irregular shapes were observed. Figure 11b shows the SEM picture of the activated membrane responding to Ni^{2+} ion, where the exterior of the membrane shows pores of different sizes together with white aggregates pointed to the formation of complex between the cation and ionophore and Figure 11c shows the SEM image of deactivated membrane, where the pores are much smaller than those of activated membrane and without the presence of white aggregates. The observed morphological changes could be due to both the reaction between the Ni^{2+} and the ionophore and/or loss of the membrane components by exudation. The loss of

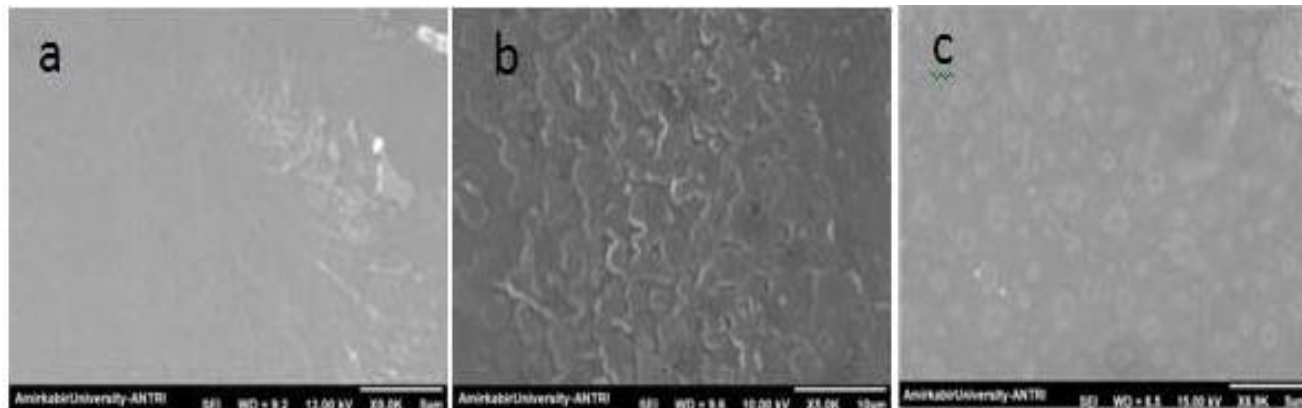


Figure 11. SEM micrographs Ni^{+2} ion-selective electrode membrane in (a) inactive, (b) activated membrane responding to Ni^{+2} , (c) membrane with loss of answer to Ni^{+2} .

components from ion selective electrode membranes with the result of their loss of response is previously reported in the literatures (Bakker et al, 1997a; Gibbons and Kusy 1996).

Analytical applications

The proposed sensor was successfully applied to the determination of Ni^{+2} ions in the sewage of a galvanization company by standard addition method. An ion selective electrode was plunged into a sample of 10 ml with unknown concentration (C_x) and the equilibrium potential of E_1 was recorded. Then 0.1 ml of $1.0 \times 10^{-2} \text{ M}$ of Ni^{+2} standard was added into the sample and the equilibrium potential of E_2 was attained. From the potential change of $\Delta E = E_2 - E_1$, the concentration of the testing sample was obtained using the subsequent equation:

$$C_x = \frac{C_s V_s}{10^{-\Delta E/S} (V_x - V_s) - V_x}$$

Where C_x and C_s are the Ni^{+2} concentrations in the test solution and the standard sample respectively, V_x and V_s are the corresponding volumes, S is the slope of the sensor response, and ΔE is the potential change (Buck and Lindner, 1994). The concentration of Ni^{+2} ion in the sample was determined by three following methods: (a) standard addition (b) atomic absorption Varian model Spectra AA-200 (c) calibration curve of Ni^{+2} ion-selective electrode. The results are given in Table 4. As we can see, the results of different methods were comparable.

Conclusions

The constructed membrane sensor can be used to

Table 4. Results of determination of Ni^{+2} ion concentration in sample of a galvanization company by different methods.

Applied method	Datum (mol L^{-1})
Standard addition	6.38×10^{-4}
Atomic absorption	6.42×10^{-4}
Calibration curve of Ni^{+2} ion-selective electrode	6.35×10^{-4}

determine Ni^{+2} ion concentration in the range of the 1.0×10^{-1} to $1.0 \times 10^{-4} \text{ M}$. This ISE has a slope of $29.3 \pm 0.5 \text{ mV/decade}$, responds sufficiently to Ni^{2+} and has a lifetime of two months. The main benefits of this electrode are its simplicity of preparation, Nernstian behavior, low detection limit, short conditioning time, good response and selectivity and low cost. This sensor was stable in a wide pH range and has a fast response time. The selectivity of the sensor to Ni^{+2} ion was rather good over other cations.

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