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NICKEL ION SELECTIVE POLY VINYL CHLORIDE MEMBRANE ELECTRODE BASED ON LIX 54

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Abstract

PVC based ion selective electrode, which was selective and sensitive to Ni (II) ions, was developed using 1- phenyldecane - 1,3 - diones (LIX 54) as a carrier. The electrode exhibited a good potentiometric response for Ni (II) over a wide concentration range (1.0×10^{-5} – 1.0×10^{-1} M) with a slope 29.1 ± 1.6 mV/decade. The proposed electrode has a response time about 25 s. The electrode is suitable for use in aqueous solutions in a wide pH range of 8.0 to 9.5. The proposed electrode was used in two different applications such as the determination of nickel concentration in nickel-cadmium battery and as an indicator electrode for potentiometric titration of Ni^{2+}ion with EDTA.

Keywords: Nickel ion selective electrode, LIX 54, Potentiometry

1. Introduction

Since 1930, nickel has been regarded as a potentially toxic metal [1]. The main source of nickel in aquatic systems is decomposition or degradation of rocks and soil, biological cycles and especially industrial processes, and water disposal [2].The maximum recommended concentration of Ni(II) ions in drinking water for livestock is 2.5 mg/ml [3]. Nickel is well known as a toxic metal that can cause cancer of nasal lungs, dermatitis, asthma, and disorders of central nervous system [4].

A number of techniques, such as atomic absorption spectrometry (AAS), flame atomic absorption spectrometry-electrothermal atomization (AAS-ETA) [5], inductively coupled plasma-atomic emission spectroscopy (ICP-AES), and flame photometry [6], can be used for determination of nickel. However, these methods generally require sample pretreatment and infrastructure backup and are, therefore, not very convenient for routine analysis of large number of environmental samples [7]. Thus, there is critical need for the development of selective, portable, inexpensive diagnostic tool for the determination of nickel such as ion selective electtrode.

Polymer membrane, particularly PVC, can easily trap the ionophore based liquid membrane system. So a great deal of interest has been focused on the PVC based membranes [8].

In this work, results on the PVC based membrane sensor incorporating 1- phenyldecane - 1,3 - diones (LIX 54) as an ionophore have been presented and discussed for the determination of Ni(II) in aqueous solutions.

2. Experimental

2.1. Reagents

The chemicals used are of analytical grade and used without any further purification. Doubly distilled water was used for preparing all aqueous solutions. High molecular weight polyvinyl chloride powder (PVC), dioctyl phthalate (DOP), dibutyl phthalate (DBP), Chloronaphthalene (CN) and ethylenediaminetetraacetic acid (EDTA) were obtained from Aldrich. Tetrahydrofuran (THF) and salts of metal nitrate or chloride were obtained from Fluka.

2.2. Apparatus and emf measurements

Potentials were measured with a digital Hanna pH / mV meter (model 8417) made in Romania. All potential measurements were carried out at 25° C. Double junction Ag/AgCl electrode from Hanna made in Italy was used as reference electrode. The electrode cell assembly of the following type was used [9]:

Reference electrode | test solution | PVC membrane | internal solution (1.0×10^{-2} M Ni^{2+}) | AgCl | Ag

2.3. Electrode preparation

The ionophore polymeric solution was prepared by dissolving 0.7 g of high molecular weight polyvinylchloride (PVC), 0.05 g of ionophore (LIX 54) and 1 g of dioctylphthalate (DOP) as plasticizer in 6 ml of tetrahydrofuran (THF). The resulting solution was poured into flat bottom petridish with diameter of 6 cm. The petridish was covered with a filter paper and allowed to evaporate the solvent in air for about 24 h [10,11]. A transparent membrane with an average thickness of 0.3 mm was obtained.

The fabricated membrane was brought to room temperature, and conditioned in a solution containing a mixture of 10^{-2} M Ni^{2+} ion and 0.3 M $(NH_4)_2SO_4$ at pH = 9 for 24 h. The membrane was incorporated into sensor body and when not in use the electrode was stored in the same solution.

3. Results and discussion

3.1. Effect of membrane composition

Several membranes of different compositions were prepared. The ratios of PVC, ionophore, and plasticizer were varied [12]. Some of the results of this study are summarized in table 1. It is clear from these results that the composition of the membrane highly affects the response and performance of the electrode. The ratios of all constituents should be optimized for best performance of the sensor.

The membrane composition which is suitable with regard to Nernstian's slope [13,14] was found to contain 40% PVC, 3% ionophore and 57% plasticizer.

3.2. Effect of pH

The behavior of the membrane was studied in 1.0×10^{-3} and 1.0×10^{-4} M of Ni^{2+} ion solution containing 0.3 M $(NH_4)_2SO_4$ at different pH values, Fig. 1. The electrode potential was found to be independent on pH in the range (8 - 9.5).

However, the decrease in the observed potential at pH values higher than 9.5 may be due to the formation of some hydroxy complexes of Ni^{2+} ion in solution. On the other hand, its decrease at pH values lower than 8 may be due to the liberation of protons from LIX 54 in the basic medium which helps on nickel complex formation [15]. Accordingly, it was decided to perform all measurements at pH = 9.

Table 1: Optimization of membrane ingredients:

.No	Composition (wt. %)					Slope, mV/decade of activity	Linear range (mol L^{-1})
	ionophore (LIX 54)	PVC	Plasticizer				
			DBP	DOP	CN		
1	20	80				10.5 ± 1.0	$\times10^{-3}$-1.0×2.0 10^{-1}
2	03	40			57	15.3 ± 1.0	$\times10^{-5}$-1.0×3.0 10^{-2}
3	**03**	**40**		**57**		**1.6 ± 29.1**	**10^{-5}-$\times1.0$ $10^{-1}\times1.0$**
4	03	40	57			18.0 ± 2.0	$\times10^{-4}$-1.0×5.0 10^{-1}
5	05	30		65		20.0 ± 3.0	$\times10^{-4}$-1.0×1.0 10^{-1}

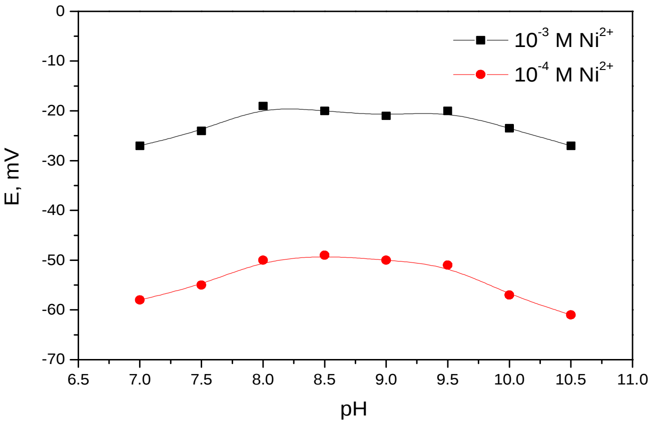

Fig.1 Effect of pH of the test solution on the potential response of PVC based nickel ion selective electrode

3.3. Calibration curve and statistical data

According to the linear working range of the electrode prepared with 40 % PVC, 3 % LIX 54 and 57 % DOP, the slope was found to be 29.1 ± 1.6 mV/dec., which is very close to the Nernstian slope value [16].

Using a series of nickel ion concentrations in the range of ($1.0\text{x}10^{-6}$ - $1.0\text{x}10^{-1}$ M), the potential of the cell was measured. The mV values were plotted against the negative logarithm of nickel ion concentrations to obtain the calibration curves as shown in Fig. 2. The working range and the slope of the nickel ion selective electrode were obtained from the linear part of the calibration curve.

The electrode was found to have a linear range from 1.0×10^{-5} to 1.0×10^{-1} M of nickel ion concentration. The detection limit, as determined from the intersection of the two extrapolated segments of the calibration graph, was 7.3×10^{-6} M.

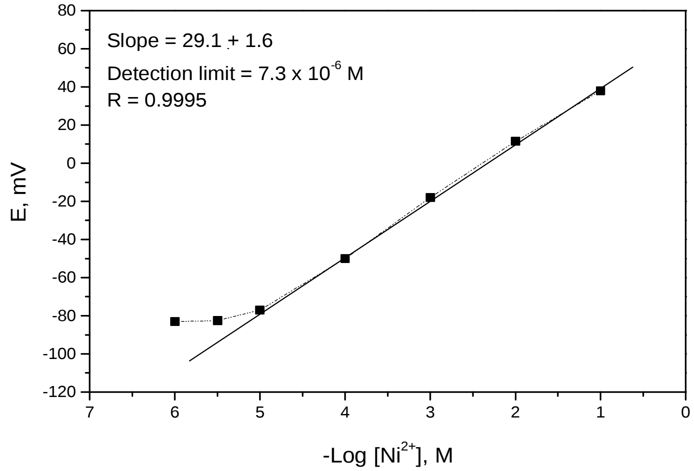

Fig. 2 Calibration graph for PVC based nickel ion selective electrode uses membrane contains 40% PVC, 3% LIX 54 and 57% DOP (**No.** 3, see **Table** 1)

3.4. Response time

This was evaluated by potential reading for the electrode dipped alternatively into two stirred solutions of nickel ions 1.0×10^{-5} and 1.0×10^{-1} M [17,18]. The results are given in Fig. 3 showed that the sensing behavior of the membrane remained unchanged when the potentials were recorded either from the low to the high concentrations or vice versa.

The response time of the electrode was about 25 s. This means that the response time of electrode is rapid and reversible. The membrane electrode prepared could be used for at least 35 day without observing any considerable change in response characteristics.

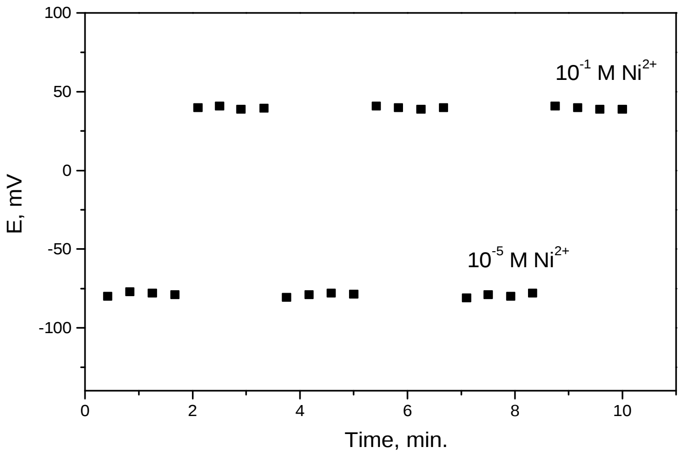

Fig. 3 Dynamic response time of the electrode membrane for two concentrations (from low to high and vice versa)

3.5. Selectivity

The potentiometric selectivity coefficients for a variety of cations were tested using the separate solution method (SSM). According to this method the potentiometric selectivity coefficients, $K^{pot.}_{Ni^{2+}, B}$ can be evaluated using the following equation [19]:

$$\text{Log } K^{pot.}_{Ni^{2+}, B} = \frac{E_B - E_{Ni^{2+}}}{2.303\ RT/Z_{Ni^{2+}}F} + \left(1 - \frac{Z_{Ni^{2+}}}{Z_B}\right) \text{Log } a_{Ni^{2+}}$$

Where E_{Ni}^{2+} and E_B are the observed potentials (mV) for the same concentration of Ni^{2+} ion and interfering ions, respectively, a_{Ni}^{2+} is the activity of Ni^{2+}, $Z_{Ni}^{2+}$and Z_B are the charge number of nickel and interfering ion B, respectively. Results obtained from this study are summarized in table 2. These results show a good selectivity of the prepared membrane over most ions tested.

Table 2: Selectivity coefficients $K^{pot.}_{Ni^{2+},\ B}$ of pvc based conventional electrode using separate solution method.

Interfering cations (10^{-2} M)	Selectivity coefficients ($K^{pot.}_{Ni^{2+},\ B}$)
Na^+	5.0×10^{-4}
K^+	2.0×10^{-3}
Li^+	1.0×10^{-4}
Cu^{2+}	8.6×10^{-4}
Cd^{2+}	3.3×10^{-4}
Zn^{2+}	4.7×10^{-4}
Mn^{2+}	3.1×10^{-4}
Fe^{2+}, Hg^{2+}, Pb^{2+}, Ag^+, Mg^{2+}	P*

*P, precipitation.

3.6. The analytical applications of the developed electrode

3.6.1. Potentiometric titration

The proposed electrode was used as an indicator electrode for the titration of 10 ml of 1.0×10^{-2} M of Ni^{2+} ion with 1.0×10^{-2} M of (EDTA) [20]. The results obtained are presented in Fig. 4. As can be seen, the amount of nickel ions in solution can be determined using the electrode.

3.6.2. Determination of Ni^{2+} ion concentration in a spent Ni-Cd battery

The electrode was also used for the potentiometric measurement of nickel ion in a spent AA-size Ni-Cd battery. 0.3 g of anode from Ni-Cd battery was dissolved in a beaker containing 25 ml of 4 M HCl. The sample was heated at a temperature of 60° C with stirring for 2 hour [21]. After filtration, The filtrate was completed to 50 ml by distilled water after addition of 2 g $(NH_4)_2SO_4$ and its pH was reached to 9.

The nickel content was determined potentiometrically and its concentration was 3.5×10^{-2} M, also by atomic absorption spectrometry (AAS), as a reference method and the concentration of Ni^{2+} ion was 4×10^{-2} M. the results show a satisfactory agreement between the two methods.

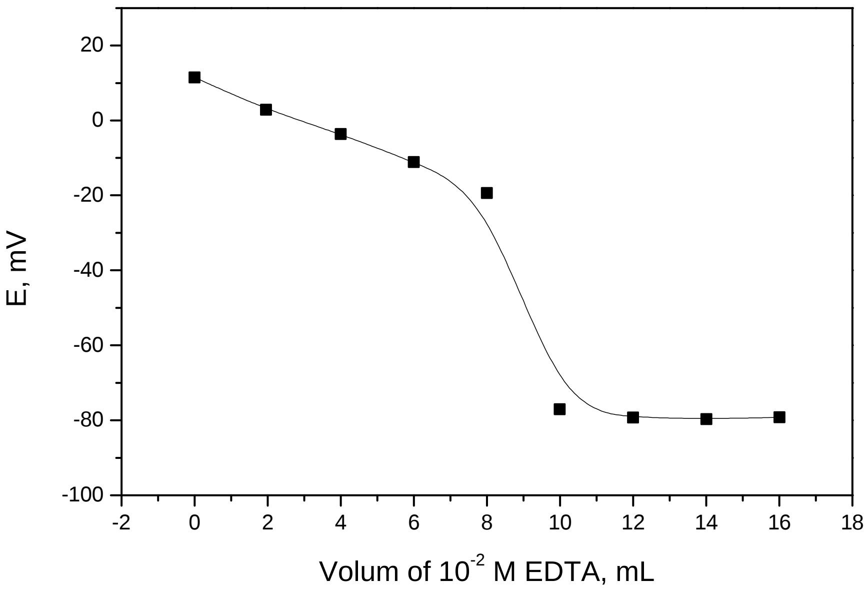

Fig. 4 Titration of 10 ml of 10^{-2} M Ni^{2+} ion with 10^{-2} M EDTA by the use of the proposed nickel ion selective electrode (**No.** 3) as an indicator electrode.

4. Conclusions

The proposed electrode has been shown to have good operating characteristics (sensitivity, stability, response time, detection limit and a wide linear range). The electrode was successfully applied for the determination of nickel content in potentiometric titration and real sample.

5. List of abbreviations

Atomic absorption spectrometry (AAS)
Flame atomic absorption spectrometry - electrothermal atomization (AAS-ETA)
Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

Poly vinyl chloride (PVC)
1- phenyldecane - 1,3 - diones (LIX 54)
Dioctyl phtalate (DOP)
Dibutyl phthalate (DBP)
Chloronaphthalene (CN)
Ethylenediaminetetraacetic acid (EDTA)
Tetrahydrofuran (THF)

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