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Novel Polymeric Membrane Sensor for Nickel Ions using Meloxicam Drug as Electroactive Material in a PVC Matrix

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Abstract

A novel PVC membrane sensor based on Meloxicam drug which is used as an electro active substance. Meloxicam has been used as ionophore for Nickel Ion Selective PVC Membrane Electrode. The electrode reveals a Nernstian response for Ni^{2+} *over a wide pH range with linear portion (* 3.9×10^{-7}*-*10^{-2} *M) The sensor also shows a stable and selective potential response towards Nickel ions with a detection limit of* 6.1×10^{-7} *M and anionic slope of 27.4 mV/ decade at 25 ○C. The selectivity coefficients of various interfering ions were determined the membrane reveals good selectivity for nickel ions over the other metal ions investigated. The lifetime of this electrode is about two months. This electrode has been applied to the determination of nickel ions in wastewater from the electroplating industry and alloy.*

Keywords: *PVC membrane sensor, Meloxicam drug etc.*

1. Introduction

Nickel is a heavy metal which Human exposure, in the last 30 years the exponential increase in the use of nickel in industrial processes and products [1–4]. The toxicity of nickel has been known for a very long time, thus its use has been limited where it could be inhaled or ingested in soluble form. The most serious effects of nickel, such as cancer of the lung and nasal sinus, have occurred in people who have inhaled nickel dust while working in nickel refineries or in nickel processing plants. The levels of nickel in the workplace were much higher than background levels [5, 6].

The determination of trace amounts of nickel is becoming ever more important because of the in- creased interest in environmental pollution. The amount of nickel in various samples such as natural waters and wastewaters, food products, industrial materials, and industrial effluents, has been determined by different analytical methods [7, 8]. Usually, these methods are very costly and require heavy apparatus. Hence, extensive efforts have been made over the last decade to develop new potentiometric and optical sensors for the determination of metal ions in different real samples [9–13]. Among them, ISEs can provide reasonable selectivity over a wide con- centration range, fast response, low cost, and speed of installation and operation. A sensitive nickel ion sensor could find application in industrial wastes from electroplating, environmental monitoring and chemical manufacturing. A few papers have reported nickel ion-selective electrodes using organic and inorganic ion-exchangers as sensor materials. Meloxicam is a nonsteroidal antinflammatory drug used to relieve the symptoms of arthritis, primary dysmenorrheal, fever, and as an analgesic, especially where there is an inflammation. In Europe it is marketed under the trade names Movalis, Melox, and Recoxa.

In rare situations, it could cause serious liver disease. If there is a sensation of fatigue and/or liver pain, intake must be ceased. Meloxicam is licensed in Europe for treatment of rheumatoid arthritis, for short term use in osteoarthritis and for enclosing spondylitis. It has been approved for use in treating osteoarthritis in the United States of America (14). Meloxicam Adverse effects, can be summarized in the fallowing, its use can result in gastrointestinal toxicity and bleeding, tinnitus, headache, rash, very dark or black stool (sign of intestinal bleeding).

Experimental

Reagents and material

All chemicals were of analytical reagent grade. Dioctyl phthalate (DOP), dioctyl sebacate (DOS), dibutyl sebacate (DBS) and orthonitrophenyloctyl ether (o-NPOE) were purchased from Fluka Chemika-Biochemika (Ronkonkoma, NY). High molecular weight poly (vinyl chloride) powder (PVC) of molecular mass 100,000, tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Aldrich chemical company, and the other chemicals used are from Merck. They were of the highest purity available and used without any further purification extract for vacuum drying over P2O5. Doubly distilled water was used throughout this work. The stock solution (10-1M) nickel chloride was prepared. Also, the working solutions (1.0×10-2 - 1.0×10-7 M) were prepared by successive dilution with water and the pH was adjusted using 0.01 M HCl or NaOH according to the pH required.

Apparatus

Potentiometric measurements were performed at 25 ± 1°C with an Orion digital pH/mV meter (Model SA720) using the PVC membrane sensors in conjunction with an Orion Ag/AgCl double junction reference electrode (Model 90-02) filled with 10% (w/v) KNO_3. A combination Ross glass-pH electrode (Orion 81-02) was used for pH measurements. The cell used for EMF measurements is of the type: Ag/AgCl/ KCl (0.1 M)/sample test solution //sensor membrane //internal filling solution /AgCl/Ag. The potential readings of stirred 10^{-2} M - 10^{-7} M working solutions were measured,recorded after stabilization to ±0.5 mV and a calibration graph was constructed.

Membrane preparation and sensor construction

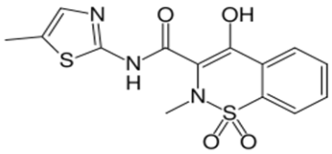

Fig.1 Chemical structure of Meloxicam

Systematic (IUPAC) name 4-hydroxy-2-methyl-N-(5-methyl-2-thiazolyl)-2H-1,2-benzothiazine-3-carboxamide-1,1-dioxide.

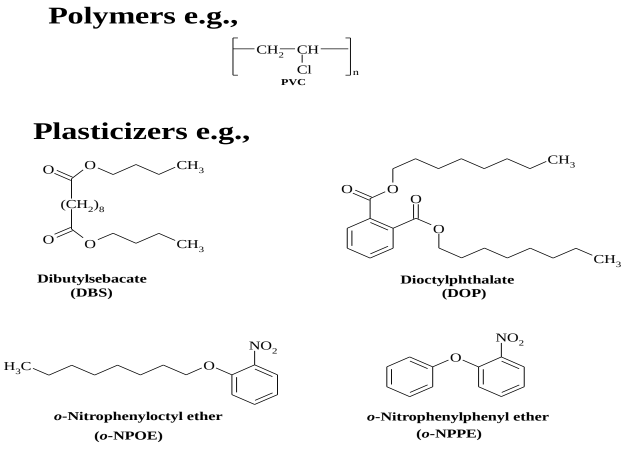

Fig.2 Structures of membrane components

The emf and pH measurements

All the potential measurements were carried out at 25 ±1˚C with Orion pH/meter (Model SA720) using Nickel membrane sensor in conjunction with a double junction Ag/AgCl reference electrode (Orion Model 90–02) containing 10% w/v potassium nitrate in the outer compartment. A combination Ross glass pH electrode (Orion 81-02) was used for all pH measurements. Before starting the measurements, the electrode was preconditioned in stirred water until a steady potential was obtained. The potential build up across the membrane electrode was measured using the cell: Ag / AgCl / KCl 10^{-3} M, $NiCl_2$ 10^{-3} M // PVC membrane//internal filling solution /AgCl / Ag double junction reference electrode**.**

Response of the sensor was made by measuring its potentials in 1.0×10^{-7} to 1.0×10^{-2} M $NiCl_2$ solution. Nickal membrane sensors Fig.(2.1).based on TMP ionophore and Ag/AgCl double junction reference electrode were immersed in a 25 ml beaker containing 10 ml of 10^{-2} M potassium phosphate buffer of pH 6. Portions (1.0 ml) of 10^{-7} to 10^{-2} M standard Nickel solutions were successively added and the potential response of the sensor was measured after stabilization(±0.2 mV).

A calibration graph was constructed by plotting the potential change against the logarithm of the Nickel ions concentration. The plot was used for subsequent determination of unknown Nickel solutions.

Effect of different plasticizer

The effect of pH on the sensor potential was tested by measuring the potential at different pH values over the range 2-10 in solutions containing 10^{-3} and 10^{-4} M Nickel (II) ions. The pH of the solutions was adjusted by using NaOH or HCl solutions. The corresponding mV readings were recorded after each addition.

Three different membrane sensors were prepared using DOP, DOS and DBS plasticizers and calibration experiments were carried out using these Nickel sensors. The potentiometric characteristics of the three plasticizers were compared and the results were tabulated.

Effect of thickness and Response time

The membrane is prepared in three Petri dishes 2,3 and 5 cm in diameter to obtained three different thicknesses. Plotting the relation between mV measurements and the concentration of Ni^{2+} , and comparing the three calibration curves obtained.

Dynamic response time of the sensor was measured in consequently stirred solutions of varying Nickel (II) concentrations. The time needed for the stability of the potential needing was measured for the different concentrations of Ni^{2+} during a 240 second period for concentration. The relation between the mV readings and time was plotted.

Sensor Selectivity

Potentiomctric selectivity coefficients were evaluated using the separate solutions method (SSM) (17-20) according to the following equation:

$$\log K_{A,B}^{pot} = \frac{(E_B - E_A)Z_A F}{2.303RT} + (1 - Z_A/Z_B)\log a_A$$

Where,

$\log K_{Cd,B}^{POT}$ is the potentiometric selectivity coefficient,
EA is the potential of the primary Ni2+ ion,
EB: potential of the interfering ion,
ZA: charge of the primary
Ni ion,
ZB: charge of the interfering ion,
R : molar gas constant (8.314 JK-1 mole-1),
aA: activity of the primary ion of charge Z2, mol l-1,
aB : activity of the primary ion of charge Z1, mol l-1,
T: absolute temperature, and F: Faraday's constant (96487 C mole-1).

The potential of a cell comprising the membrane sensor and the reference electrode was measured in two separate solutions, one containing the Nickel ion (A) at the activity aA (but no B), the other containing the interfering ion (B) at the same activity aA = a B (but no A) and EA and EB are the measured potential values, respectively. Different interfering cations at a concentration of 10-3 M were used.

Results and Discussion

Response Characteristics of Nickel membrane sensor and Selectivity

The Nikel sensor prepared by mixing 1% ionophore, 33% PVC, and 66% plasticizer (DOP, DPS or DOS) offers the best sensitivity, which is obtained on using DOS as a plasticizer, Fig (3.1) as well as the linear potentiometric response over a wide range of Nickel ions concentration (3.9×10^{-7} -10^{-2} M) with a Nernstian slope of about 27.4 mV per decade. From the data given in the Table (1) it can be seen that the prepared sensor has a correlation coefficient of 0.9998. The slopes of the calibration graphs is Nernstian compared with the sub-Nernstian or over-Nernstian slopes given by some other sensors. The linear range of the sensor response for Ni^{2+} is about five decades of concentration, which is 1–2 decades greater than those reported for some other Nickel ions electrodes. The limits of detection, defined as the concentration of Nickel ions obtained when extrapolating the linear calibration region to the baseline potential, are given in Table (1).

As can be seen, the sensor showed detection limits of (6.1×10^{-7} -10^{-2}), which are better than those of most other Nickel sensors (21-22).

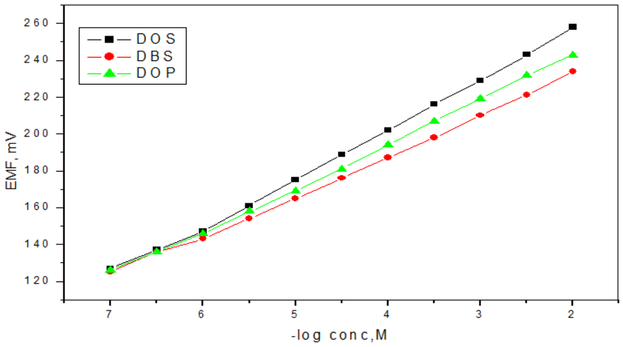

Fig.3 Potentimetric response curves of Nickel sensor using different plasticizers

Table 1 Potentiometric parameters of Nickel PVC membrane based on the ionophore and different plasticizers

Parameter	Value		
	DOS	DBS	DOP
Slope (mV/decade)	27.4	21.3	22.6
Intercept (mV)	309	253	261
Correlation coefficient(r)	0.999	0.999	0.999
Linear range (M)	3.90×10^{-7}-10^{-2}	5.01×10^{-6}-10^{-2}	3.98×10^{-6}-10^{-2}
Precision (%)	98	94.5	95
pH range	3.5-7. 5	3.5-7.5	3.5-7.5
Response time (sec)	30 ≥	40 ≥	40 ≥
Detection limit (M)	6.1×10^{-7}	4.9×10^{-6}	5.3×10^{-6}
Accuracy (%)	97	94	95

Selectivity is the most important characteristic of any membrane and is measured in terms of potentiometric selectivity coefficient ( ). The potentiometric selectivity coefficients, describing the preference by the PVC membrane incorporating an interfering ion, B, relative to Nickel ion, A, were determined by the separate solution method (SSM), which is recommended by IUPAC (23). In this method, the selectivity coefficient of Nickel sensor based on the TMP was evaluated graphically at fixed concentration of Nickel ion and interfering ions as shown in Excellent selectivity coefficients in the order of 10−3 M and lower are obtained for a large number of cations.

Table 2 Selectivity coefficients for Nickel PVC-membrane sensor

Interference	$\log K_{Cd,B}^{POT}$
Ni^{2+}	1.01×10^{-3}
Cd^{2+}	1.2×10^{-4}
Co^{2+}	3.90×10^{-3}
Ca^{2+}	7.26×10^{-4}
K^{+}	6.86×10^{-4}
Sr^{2+}	3.13×10^{-4}
Na^{+}	9.34×10^{-4}
Pb^{2+}	1.10×10^{-3}
Fe^{3+}	4.77×10^{-3}
Cu^{2+}	2.1×10^{-4}
Ag^{+}	2.56×10^{-3}
Hg^{2+}	8.59×10^{-4}
Al^{3+}	3.29×10^{-3}
Zn^{2+}	1.83×10^{-3}

(Table 2) indicating insignificant interfering effect of these cations on the Nickel ion determination by the proposed membrane sensor. So the electrode is highly selective towards Nickel ions over several cations.

The response time is defined as the time between the instant at which the ion-selective electrode and a reference electrode are dipped in the sample solution and the first instant at which the potential of the cell becomes equal to its steady-state value (within ±1 mV) or has reached 90% of the final value. The potentiometric response time of the proposed Nickel electrodes was determined by immersion of the electrode in conjugation with the reference electrode in a series of $NiCl_2$ solutions (10^{-6} – 10^{-2} M) and the potential was recorded after reaching a stable value within ±0.5 mV according to the IUPAC recommendation (24).

The electrode showed very fast response after times of 30-40 sec (Fig. 5). The membrane was found to be used efficient over a period of 2 months and this makes it suitable for the measuring the concentration of Nickel for a longer time, also it has very low cost.

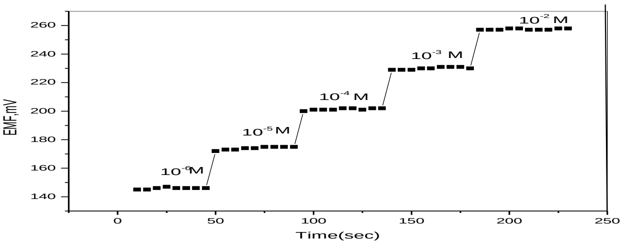

Fig.5 Dynamic response time of Nikal membrane sensor. Analytical Applications Determination of Nikal in alloys

The Nickel contents of some alloys was assessed. The alloys were digested with hydrochloric acid and their contents of Nickel were measured by direct potentiometry using the proposed membrane sensor. The mean standard deviation is ±0.5%. Similar results are obtained by using atomic absorption spectrometry Table (3).

Table 3 Determination of Nickel in some alloys

Type of alloy	Ni^{2+} content, mg1^{-1}	
	Potentiometry	Atomic absorption
Alloy1 (Cd^{2+}, Co^{2+}, Ni^{2+})	128 ± 0.4	129 ± 0.5
Alloy 2(Cd^{2+}, Cu^{2+})	195 ± 0.3	193 ± 0.2

Determination of Nickel in waste water

Potentiometric determination of Ni^{2+} ions in some industrial waste water samples obtained from plating factories using the proposed membrane sensor. The sample was boiled with nitric acid to dissociate the metal complex which may be found in the water sample, and the Ni^{2+} content was determined by direct potentiometry.Ni^{2+} content in the sample has also been determined using atomic absorption spectroscopy (AAS). The results obtained from both methods (Table 4) were compared by applying the F-test at 95% confidence level, were the result which obtained using potentiometry equals 167410.1400 (S_1^2) and the result which obtained using AAS equals 1762.212333 (S_2^2) and from the equation F = (S_1^2)/ (S_2^2) In all cases, the calculated *F*-test values did not exceed the theoretical values, indicating that there is no significant difference between the two methods in concerning precision and accuracy in the determination of Nickel.

Table 4 Determination of Nickel in some waste water samples

Samples	Ni^{2+} content, mg1^{-1}	
	Potentiometry	Atomic absorption
Sample 1	43.2 ± 0.1	43 ± 0.4
Sample 2	22.3 ± 0.5	22.4 ± 0.3
Sample 3	17.8 ± 0.5	18.1 ± 0.2

Conclusion

A new PVC membrane sensor based on, TMP, was prepared, characterized and used for ca Meloxicam Drug. The sensor is easily fabricated; it shows high selectivity and sensitivity over a wide dynamic range, with low detection limit and very short response time. These properties make the sensor suitable for measuring the concentration of Nickel in a wide variety of samples including some alloys and some kinds of electroplating waste water without pre- treatment steps. No significant interference from other cationic species present in the samples is observed. The sensor also shows a stable and selective potential response towards 3.9 x 10^{-7}-10^{-2} M Nickel ions with a detection limit of 6.1x 10^{-7} M and anionic slope of 27.4 mV/ decade.

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