Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 5 (4) 203-208
(J.Phys.Theor.Chem.IAU Iran: Winter 2009)
ISSN: 1735-2126

Manganese (II)-selective PVC membrane electrode based on N-(2-picolinamido ethyl)-Picolinamide as ionophore

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ABSTRACT

In this research, a PVC membrane electrode for Manganese (II) ions based on N-(2-Picolinamido ethyl)Picolinamide as neutral carrier was prepared. The electrode exhibits a Nernstian response over Mn(II) concentration range of (1.0×10^{-5} to1.0×10^{-1}M) with a slope of 29.3±0.5 mV per decade of concentration with a working pH range of 4.0-9.0. It has a fast response time (≤15s) and can be used for at least two months without any considerable divergence in the potential. The proposed sensor shows a fairly good discriminating ability towards Mn^{2+} ion in comparison to some hard and soft metal ions. Selectivity coefficients determined by the matched potential method (MPM). The electrode was applied to the determination of Manganese (II) ions in real samples.

Keywords: Manganese(II)-selective electrode; PVC membrane; N-(2-Picolinamido ethyl)- Picolinamide; Potentiometry

INTRODUCTION

Manganese is an essential element, which plays an important role in the activation of many enzymes involved in metabolic processes of man, animals and plants [1–6]. Manganese is used in various products such as batteries, fertilizers, pesticides, ceramics, and dietary supplements [7] Eleven oxidation states of manganese are known, from −3 to +7, but the most abundant species both in mammals and plants is Mn^{2+}, followed by Mn^{3+} and Mn^{4+} [8].

Human kind can provide themselves the required manganese for body via sources like drinking water, vegetables, grains and etc. [9, 10]. Though, manganese is an essential micronutrient for various organisms [7], yet is toxic at higher concentration level [11]. Acute exposure to manganese containing dust may lead to chemical pneumonitis while chronic exposure may lead to a Parkinson-like dementia [12]. The maximum allowed content in waters varies according to its proposed use: for domestic water it is 0.05 $mgmL^{-1}$ and for irrigation water is 2.0 $mgmL^{-1}$ [13]. Consequently, the determination of manganese in environmental samples becomes important to monitor manganese in environmental resources. Various techniques have been used for the determination of trace manganese in biochemical and environmental resources [14]. Ion selective sensors are the best tools as they permit quick and convenient determination at low cost.

In this paper we reported that a new ISE for

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determination of Mn^{2+} ion based on N-(2-Picolinamido ethyl)-Picolinamide (2NPEP) as a new ionophore, has a wide working concentration range, fast response time and gives reproducible results.

EXPERIMENTAL

1. Reagents and materials

All the reagents, with the exception of 2NPEP were of analytical reagent grade. 2NPEP (Fig. 1.) was synthesized. Reagent grade dibutyl phthalate(DBP), acetophenone(AP), 2-nitrophenyl octyl ether (O-NPOE), oleic acid(OA), sodium tetraphenylborate(NaTPB), Potassium tetrakis[p-cholorophenyl]borate (KTpClPB), tetrahydrofuran(THF) and high relative molecular weight PVC (all from Fluka) were used as received. Nitrate and chloride salt of all cations used were of the highest purity available (all from Merck or Fluka) and used without any further purification. Double distilled deionized water was used throughout.

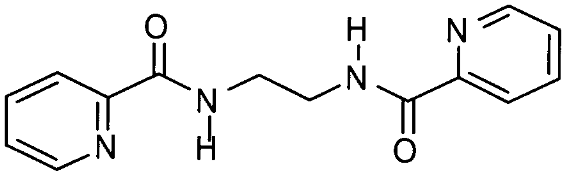

Fig.1. Structure of N-(2-Picolinamido ethyl)-Picolinamide as ionophore.

2. Preparation of the electrodes

The general procedure used to prepare the PVC membrane was mixed thoroughly 28 mg of powdered PVC, 5 mg of ionophore (2NPEP), 62 mg of plasticizer O-NPOE and 5 mg of additive KTpClPB until the PVC was wet. The mixture was then dissolved in 3 ml of dry freshly distilled THF. The resulting clear mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5mm o.d.) was dipped into the mixture for about 10s so that a non-transparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out of the mixture and kept at room temperature for about 2h before filling with internal solution 1.0×10^{-3}M $MnCl_2$. The electrode was finally conditioned for 10h by soaking in a 1.0×10^{-2} M $MnCl_2$ solution.

3. Emf measurements

All emf measurements were carried out with the following assembly:

Ag-AgCl | KCl(3M) | internal solution 1×10^{-3}M MnCl$_2$ | PVC membrane | test solution | Hg-Hg$_2$Cl$_2$,KCl(standard)

The potentials were measured by varying the concentration of the test solution in the range 1.0×10^{-7} to 1.0×10^{-1}M.

RESULTS AND DISCUSSION

1. Effect of membrane composition

It is well known that the sensitivity and selectivity obtained for a given ionophore significantly depend on the membrane composition and the nature of solvent mediator and additives used [15]. Thus, the influences of the membrane composition, nature and amount of plasticizer and additive on the potential response of the Mn(II) sensor were investigated and the results are summarized in Table 1. It is seen that, the use of 62% (w/w) O-NPOE in the presence of 28% (w/w) PVC, 5% (w/w) ionophore and 5% (w/w) KTpClPB (No. 10, Table 1) resulted in the best sensitivity, with a Nernstian slope of 29.3 ± 0.5 mV/decade over a wide dynamic range.

2. Calibration curve and statistical data

The potential responses of different ion–selective electrodes based on (2NPEP) are shown in (Fig. 2.) As it is seen, among different cations tested, the largest sensitivity was obtained for Mn^{+2} ions. The emf vs.–log a of the PVC membrane based on (2NPEP), prepared under optimal composition, indicated a rectilinear range from 1.0×10^{-5} to 1.0×10^{-1} M. The slope of the calibrations curve was 29.3 ± 0.5 mV per decade of Mn concentration. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration graph, was 8×10^{-6} M. The standard deviation of 7 replicate measurements is ±0.5 mV.

The membrane electrodes prepared could be used for more than 2 months without any measurable change in potential.

Table 1. Optimization of the membrane ingredients

	Composition (%)					
No	PVC (mg)	Ionophore (mg)	Additive (mg)	Plasticizer (mg)	Slope (mV/decade)	Linear Range [M]
1	30	5	5 (OA)	60 (AP)	8.12	$1.0\times10^{-4} - 1.0\times10^{-1}$
2	30	5	5 (OA)	60 (DBP)	9.05	$1.0\times10^{-4} - 1.0\times10^{-1}$
3	30	5	5 (NaTPB)	60 (O-NPOE)	24.8	$1.0\times10^{-5} - 1.0\times10^{-1}$
4	30	5	5 KTpClPB	60 (O-NPOE)	29.1	$1.0\times10^{-5} - 1.0\times10^{-1}$
5	30	5	3 KTpClPB	62 (O-NPOE)	28.1	$1.0\times10^{-5} - 1.0\times10^{-1}$
6	30	3	5 KTpClPB	62 (O-NPOE)	26.8	$1.0\times10^{-4} - 1.0\times10^{-1}$
7	30	1	5 KTpClPB	64 (O-NPOE)	23.1	$1.0\times10^{-4} - 1.0\times10^{-1}$
8	30	-	5 KTpClPB	65 (O-NPOE)	18.5	$1.0\times10^{-4} - 1.0\times10^{-1}$
9	30	5	5 (OA)	60 (O-NPOE)	17.2	$1.0\times10^{-4} - 1.0\times10^{-1}$
10	28	5	5 KTpClPB	62 (O-NPOE)	29.3	$1.0\times10^{-5} - 1.0\times10^{-1}$
11	30	5	5 KTpClPB	60 (DBP)	20.5	$1.0\times10^{-4} - 1.0\times10^{-1}$
12	30	5	5 KTpClPB	60 (AP)	19.9	$1.0\times10^{-4} - 1.0\times10^{-1}$

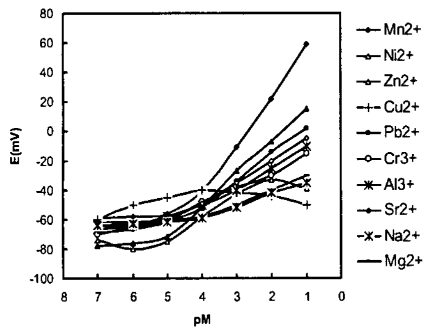

Fig.2. Potential response of various metal ion-selective electrodes based on (2NPEP).

3. Response time

The critical response characteristic of the electrode was assessed according to IUPAK a recommendation (Fig. 3.) illustrates the static response time of the membrane electrode. As it is seen the static response time is less than 15 s for Mn^{2+} concentration $\leq 1.0\times10^{-3}$M and the response of the electrode was remained constant for more than 5 min after which only a very slow divergence was recorded (±1 mV).

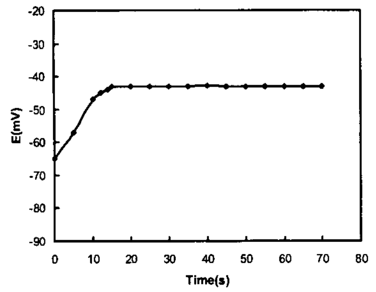

Fig.3. Static response time of proposed electrode by changing the Mn^{2+} concentration from 1.0×10^{-4} to 1.0×10^{-3}M.

4. Effect of pH

The pH dependence of the electrode potentials was tested at1.0×10^{-2}M and1.0×10^{-3} M Mn^{2+} solution by varying the pH in the range 2.0–10.0. The potentials remained constant in the pH range 4.0–9.0 (Fig. 4) and the same may be taken as the working pH range of the sensor. The sharp changes in potential below pH 4.0 may be ascribed to H+ co-fluxing and above pH 9.0 may be due to the hydrolysis of Mn^{2+} ions.

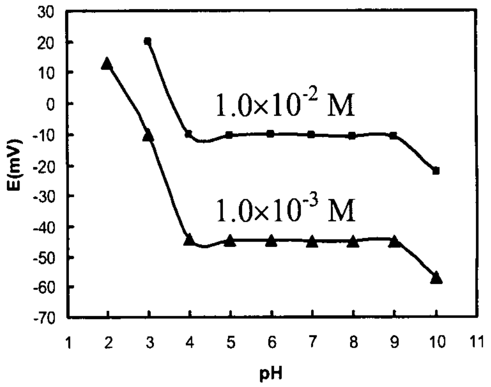

Fig.4. Effect of pH 1.0×10^{-2}and1.0×10^{-3}M Mn^{2+} solutions on the potential response of Mn^{2+} ion-selective electrode.

5. Potentiometric selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measurement in the target sample is possible [15,16]. The selectivity coefficients of the proposed membrane selective electrode were determined against a number of interfering ions by using of the matched potential method (MPM) [17]. MPM is a recently recommended procedure by IUPAC, which gets rid of the limitations of the corresponding methods based on the Nicolski-Eisenman equation for the determination of potentiometric selectivity coefficients. These limitations include non–Nernstian behavior of interfering ions and inequality of charges of primary and interfering ions. The obtained results for the $K^{pot}_{Mn^{2+}}$ of Mn^{2+} ion-selective electrode are summarized in Table 2.

Table 2. Selectivity coefficient of various interfering cations

M^{n+}	$K^{pot}_{Mn,M}$
Na^+	5.2×10^{-3}
Mg^{2+}	4.7×10^{-3}
Cu^{2+}	1.01×10^{-1}
Cr^{3+}	7.5×10^{-2}
K^+	9.2×10^{-3}
Al^{3+}	1.8×10^{-2}
Ni^{2+}	2.17×10^{-1}
Pb^{2+}	6.8×10^{-2}
Cd^{2+}	1.04×10^{-1}
Zn^{2+}	3.2×10^{-1}
Ca^{2+}	6.3×10^{-3}
Sr^{2+}	8.6×10^{-3}

As seen from Table 2, with the exception of Zn^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} ions, the selectivity coefficients obtained for all other cations were in the order of 10^{-2} or smaller, indicating that these ions do not disturb the functioning of the Mn^{2+} ion–selective electrode significantly.

6. Reversibility of the electrode response

To evaluate the reversibility of the electrode, a similar procedure with opposite direction was adopted. The measurements were performed in the sequence of high-to-low sample concentrations and the results are shown in (Fig. 5.) It shows that the potentiometric response of the electrode is reversible and had no memory effect [16].

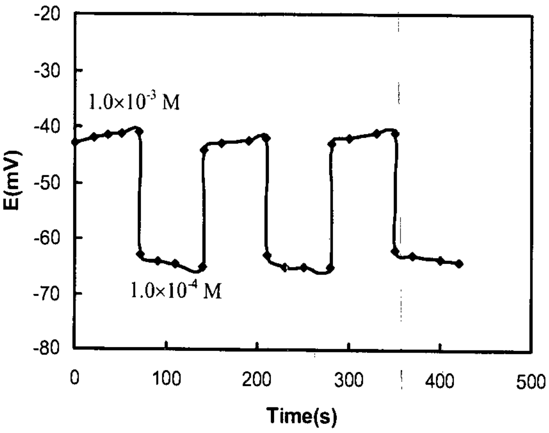

Fig. 5. Dynamic response characteristics of the Mn^{2+}-electrode for several high-to-low sample cycles.

Analytical application

The proposed electrode was successfully applied to the determination of Manganese(II) ions in the multiple vitamins with minerals tablet by standard addition method. An electrode was immersed into a sample of 10 cm^3 with unknown concentration (Cx) and the equilibrium potential of E_1 was recorded. Then 0.1 cm^3 of 1.0×10^{-2} M of Mn(II) standard was added into the testing solution and the equilibrium potential of E2 were obtained. From the potential change of ΔE (E_2 - E_1) one can determine the concentration of the testing sample using the equation given below:

$$C_X = \frac{C_S V_S}{(V_X + V_S)10^{-\Delta E/S} - V_X}$$

Here Cx is the Mn(II) concentration of testing sample, Cs the concentration of the standard, Vx and Vs are the corresponding volumes, S is the slope of the electrode response, and ΔE the change in potential [18]. The concentration of Mn^{2+} in the test sample (Cx) obtained by official method was 6.37×10^{-4} M [19] and the value obtained by the proposed electrode was 6.28×10^{-4} M The results have good agreement with each other.

CONCLUSION

The membrane sensor incorporating (2NPEP) as an ionophore can be used to determine Mn(II) in the wide concentration range. The manganese(II) ion-selective electrode which was designed in this work has many advantages including: easy preparation, low cost, wide dynamic range, low detection limit, good selectivity and long life time of more than two months. The selectivity of the electrode towards Mn^{2+} is quite good over other cations. The functional pH range of sensor is 4-9. The proposed sensor was successfully applied to direct determination of Mn(II) in real samples.

Acknowledgments

We gratefully acknowledge the support of this work by Islamic Azad University, Science and Research Campus, Tehran.

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