Determination of Mn (II) by Poly (vinyl chloride) based Ion-selective using Schiff base of Furfuryl Aldehyde

**Aishwarya Singh[1], Arpit Singh[1], Kailash Chandra Yadav[1]
and Gyanendra Singh[2,*]**

Department of Chemistry
[1]Mewar University, Chittorgarh, Rajasthan-312901, India
[2]M.M.H. (PG) College, Ghaziabad, U.P.-2001001, India
*Corresponding Author E-mail: dr.singh20@yahool.com

Abstract

This study related with the development of Mn (II) selective membrane sensor using N,N' - bis(furfurylidene)-3-oxa-1,5diaminopentane as a neutral carrier. The sensor having membrane composition 33% PVC, 54% plasticizer *o*-NPOE, 8% NaTPB and 5% ionophore in 20 ml THF. The proposed sensor exhibits a Nernstian response for Mn (II) ion, in a wide concentration range of $5.0 \times 10^{-9}-1.0 \times 10^{-2}$ mol/L with a detection limit of 3.1×10^{-7} mol/L and slope of 29.8 ± 0.3 mV decade^{-1} of activity within pH range 3.0–7.0 and fast response time of 10s. The sensor has been found to work satisfactorily in partially non-aqueous media up to 25% (v/v) content of methanol, ethanol or acetone and could be used for a period of 8 months without any change in response characteristics. The Mn (II) selective electrode was also as an indicator electrode for the titration of 8 ml 1x 10^{-3} M EDTA solution.

Keywords: Manganese, Ionophore, N,N' - bis(furfurylidene)-3-oxa-1,5diaminopentane

Introduction

Manganese belongs to the VIIth group of periodic table. Manganese is widespread in nature, but is found only in compounds; it makes up 0.092% of the earth's crust. It is the third most abundant transition element, after iron and titanium. The most important manganese ores are brownstone and braunite [1-2]. Large quantities of manganese are also found in manganese nodules on the ocean floor, which are formed

by agglomeration of metal oxide colloids. Manganese (Mn^{2+}) found as a free element in nature (often in combination with iron), and in many minerals. Due to free existence in nature it has many industrial applications [3-7]

Manganese is an essential trace element which, in compound from, is found in all living cells. The human body contains about 0.3 mg / kg, mainly in the mitochondria, cell nuclei and bones. The recommended daily intake is 3 mg manganese. Manganese is present in many human and animal enzymes; it is needed in the synthesis of cholesterol, mucopolysaccharides, blood clotting factors and respiratory chain phosphrylation. Manganese deficiency can lead to sterility, among other symptoms [8]. Excess of manganese can cause irritation of the respiratory passages and impairment of movement. In the human brain the manganese is bound to manganese metalloproteins most notably glutamine synthetase in astrocytes. In plants Mn has an important function in photosynthesis and a deficiency causes retardation of growth [9].

After extensive studies in the field of potentiometric sensors the determination of alkali, alkaline earth metals, halides, nitrates, *etc* become possible. Efforts are required to develop ion-selective electrodes for heavy metal ions, which are toxic in very low concentration. The EPA recommends 0.05 mg/L as the maximum allowable manganese concentration in drinking water. Consequently, the determination of manganese in environmental resources becomes an important task. Various techniques have been used for the determination of trace manganese in biochemical and environmental resources. Most of techniques have problems such as, high detection limit, narrow working concentration range, high response time, poor selectivity and significant interfering cations. For this purpose, ion selective sensors are the best tools as they permit quick and convenient determination at low cost. In spite of this important requirement, only little work on manganese selective electrodes has been done [10]

This work, involved the development and comparative study of a manganese(II) selective PVC membrane electrodes based on newly synthesized schiff bases N,N´-bis(furfurylidene)-3-oxa-1,5diaminopentane. The values of formation constants show that the proposed ligand form stronger complex with manganese (III) and weaker complex with other metal ions.

Experimental
Reagents and Equipments
All the analytical grade reagents were used as purchased. 1,5-dimino-3oxapentane and furfuryl aldehyde were purchased from Sigma Aldrich. High molecular weight poly(vinyl chloride) (PVC), oleic acid (OA), dibutyl-butylphosphonate (DBBP), dioctylphthalate (DOP), dibutylphthalate (DBP), *o*-nitrophenyl octyl ether (*o*-NPOE), tris(2-ethylhexyl)phosphate (TEP), sodium tetraphenylborate (NaTPB) tetrahydrofuran (THF), acetone and chloroform were purchased from Merck. All metal nitrates were also brought from Merck and the stock solution of metal nitrates was obtained by dissolving weighed amounts of corresponding salt in double distilled water.

Double distilled water was used throughout the investigation. All potentiometric measurements were made at 25 ± 1ºC with a digital potentiometer using Mn (II) selective membrane sensor in conjunction with Ag/AgCl reference electrode containing 10% (w/w) potassium nitrate solution in the outer compartment.

Synthesis of ionophore

The ionophore (Fig.1) N,N´- bis(furfurylidene)-3-oxa-1,5diaminopentane was synthesized by stirring 1,5-diamino-3-oxapentane (1 mmol in 20 mL absolute acetone) and furfuryl aldehyde (1 mmol in 20 mL acetone) in reflux for 17 hrs. Evaporation of the solution in vacuum gave crystalline ligand which were washed with 5 mL of cooled absolute ethanol and then recrystallized from acetone-/chloroform (68% yield).
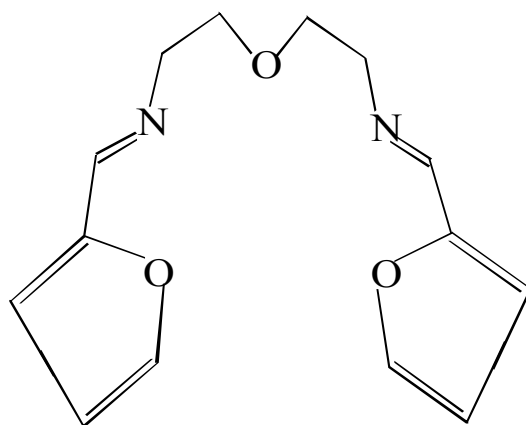

Figure 1: N,N´ - bis(furfurylidene)-3-oxa-1,5diaminopentane

Preparation of Electrode

The PVC-membrane have been prepared by dissolving a mixture of 33% PVC, 54% plasticizer (DBBP, DBP, OA, DOP *o*-NPOE respectively), 8% NaTPB, and 5% ionophore dissolved in THF. After complete evaporation of THF a membrane sheet about 0.5 mm of thickness and 8 mm diameter was cut away and glued at one end of a glass tube with the help of araldite and M-seal to avoid leakage. The membrane electrode was finally conditioned by soaking in a 0.1 M Mn(NO$_3$)$_2$ solution for 2 days. A saturated silver electrode was inserted in the tube for electrical contact and another saturated silver electrode was used as an external reference electrode.

The Emf measurements were carried out with the cell assembly given below:

Internal reference Silver electrode	Internal reference solution (0.01 M Mn^{2+})	Mn^{2+}ion Selective Membrane	Test solution of Mn^{2+} ion	External reference Silver electrode

Results and discussion

In this research work we have tested ionophore N,N´- bis(furfurylidene)-3-oxa-1,5diaminopentane as neutral carrier for Mn (II) ion with or without plasticizers. The six membranes of different composition were fabricated by using different type of plasticizers *i.e.* DOP, DBP, DBBP, TEP, o-NPOE and OA keeping PVC, ionophore and NaTPB in fixed composition. Membrane without plasticizer worked in the linear concentration range of 3.2 x 10^{-8} – 1 x 10^{-4} M with the nernstian slope of 21.502± 1.0 mV/decade. The results in table 1 indicate that the plasticizer plays the significant role in membrane characterization and result improvement. The best result was obtained by membrane No. 1 (Table 1) using o-NPOE as plasticizer in the composition of *o*-NPOE: NaTPB: ionophore: PVC of 54: 8: 5: 33 (%, w/w). The membrane No.1 exhibits significantly enhanced selectivity towards Mn (II) ion over the concentration range $5.0×10^{-9}$ to $1.0×10^{-2}$ M Mn (II) ion with a limit of detection $3.1 × 10^{-7}$M and a Nernstian compliance (29.8.± $0.3mVdecade^{-1}$ of activity) (Fig. 2) within pH range 30–7.0 and fast response time of 10s.

Table 1: Membrane optimization with different plasticizers.

| Membrane No.	Composition of membrane (%)									Working Concentration Range (M)	Slope *(mV decade^{-1} of activity)*	Response Time (sec)
	0-NPOE	DBP	DOP	DBBP	TEP	OA	NaTPB	Ionophore	PVC			
1	54						8	5	33	$5.0 ×10^{-9}$- $1.0 × 10^{-2}$	29.8 ± 0.30	10
2		54					8	5	33	$1.5 × 1 0^{-9}$- $1.0 × 10^{-2}$	26.00 ± 1.0	13
3			54				8	5	33	$2.6 × 1 0^{-9}$- $1.0 × 10^{-2}$	23.00 ± 0.1	18
4				54			8	5	33	$2.2 × 1 0^{-9}$- $1.0 × 10^{-2}$	23.60 ± 1.0	16
5					54		8	5	33	$1.4 × 1 0^{-9}$- $1.0 × 10^{-2}$	22.50 ± 0.1	16
6						54	8	5	33	$2.8 × 1 0^{-9}$- $1.0 × 10^{-2}$	24.50 ± 0.1	11
7. Without plastisizer							8	5	33	$3.2 × 1 0^{-8}$- $1.0 × 10^{-4}$	21.02 ± 1.0	21
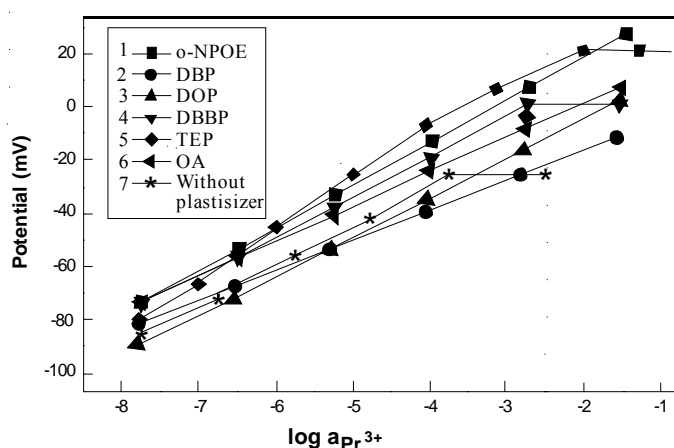
Figure 2: Variation of potential of Mn (II) Selective membrane with different plasticizers

The complexetion between metal cations and the ionophore were measured in terms of formation constant (K_f) using molar conductance ratio (equation 1 and 2) in acetonitrile solution at $25 \pm 0.50\ ^0C$.

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (1)$$

where

$$[L] = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \qquad (2)$$

Here, Λ_M is the molar conductance of the cation before addition of ligand, Λ_{ML} the molar conductance of the complex, Λ_{obs} the molar conductance of thesolution during titration, C_L the analytical concentration of the ionophoreadded, and C_M the analytical concentration of the cation. The complex formation constants, K_f, and the molar conductance of complex, Λ_{obs}, were obtained by using a nonlinear least squares program KINFIT [11-12], and the results are summarized in table 2. The value of $\log K_f$ is highest for Mn^{2+} thus the stability of complex of ionophore with the tested cations follow the order of $Mn^{2+} > Ce^{3+} > Hg^{2+} > Cu^{2+} > Co^{2+} > Eu^{3+} > Nd^{3+} > Al^{3+} > Ni^{2+} > Th^{4+} > Fe^{3+} > Zn^{2+} > Ag^+ > Pb^{2+} > Mg^{2+}$.

A number of metal ion selective electrodes were prepared by using the prposed schiff's base as an ionophore, but after extensive work it has cleared that the present ionophoric membrane electrode is extremely selective to Mn (II) cations.

Table 2: Formation constant of metal ions-ligand N,N' - bis(furfurylidene)-3-oxa-1,5-diaminopentane

Cation	Log K_f
Mn^{2+}	6.32 ± 0.12
Ce^{3+}	2.82 ± 0.30
Nd^{3+}	2.32 ± 0.11
Th^{4+}	2.18 ± 0.80
Eu^{3+}	2.35 ± 0.14
Cu^{2+}	2.56 ± 0.07
Zn^{2+}	1.84 ± 0.18
Mg^{2+}	1.65 ± 0.15
Co^{2+}	2.38 ± 0.12
Ni^{2+}	2.19 ± 0.09
Pb^{2+}	1.69 ± 0.11
Hg^{2+}	2.72 ± 0.13
Ag^+	1.73 ± 0.12
Fe^{3+}	2.13 ± 0.14
Al^{3+}	2.18 ± 0.05

The influence of pH of the test solution (A) 1.0×10^{-2} M, (B) 1.0×10^{-3} M, (C)1.0×10^{-4} M, (D) 1.0×10^{-5} M of Mn (II) ion on the potentiometric response of the membrane electrode was examined in the range of 2-10. The proposed electrode work satisfactorily in the pH range of $3.0 - 7.0$.

The effect of pH on the response characteristics can be explained by coordination competition between ionophore and hydroxide ion. A potential change was observed at pH > 7, which may be due to the formation of hydroxyl complex of the cation.

The proposed membrane sensor also work satisfactory in non-aqueous medium such as methanol, ethanol acetone up to 25% (v/v) solution (Table 3) But above 25 % of non-aqueous content, electrode sensor showed potential drift with time.

Table 3: Effect of partially non-aqueous medium on the working of Mn^{2+} sensor (No.1)

Non-aqueous content (%v/v)	Slope (mV /decade) of activity	Working Conc. Range (M)	Response time (Sec)
0	29.8 ± 0.3	$5.0 \times 1 0^{-9}$- 1.0×10^{-2}	07:00
Methanol			
10	21.70 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	07:00
20	21.50 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	07:00
25	21.10 ± 1.0	1.0×10^{-8}-1.0×10^{-2}	07:00
30	18.20 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	10:00
40	17.50 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	13:00
Ethanol			
10	22.30 ± 1.0	1.0×10^{-8}-1.0×10^{-2}	07:00
20	21.80 ± 1.0	1.0×10^{-8}-1.0×10^{-2}	07:00
25	21.7 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	07:00
30	18350 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	10:00
40	16.30 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	13:00
Acetone			
10	23.70 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	07:00
20	23.01 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	07:00
25	22.70 ± 1.0	1.0×10^{-8}-1.0×10^{-2}	07:00
30	18.50 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	12:00
40	16.80 ± 1.0	1.0×10^{-8}- 1.0×10^{-2}	14:00

The average time required for the electrode to produce the static potential known as static response time, which was found to be 10s over the entire concentration range. The membrane electrode will perform around 8 months without any considerable divergence in potentials. After this period, the slope and detection limit of membrane will decrease due to loss of plasticizer and/or ion-carrier from the polymeric membrane.

The relative response of proposed membrane for Mn (II) over the other ions present in the solution was detected using Fixed Interference Method (FIM), and the results was presented in terms potentiometric selectivity coefficients (log $K^{POT}_{Mn^{2+}, M^{n+}}$) which has been measured at 1×10^{-3} M concentration of interfering ions using the modified the Nicolsky equation (Eq. 3) [11].

$$K^{POT}_{Mn^{2+}, M^{n+}} = \frac{a_{Mn^{2+}}}{a_{M^{n+}}^{z_{Mn^{2+}}/z_{M^{n+}}}} \tag{3}$$

Where a Mn^{2+} is the activity of the primary ion and a $_{M}^{n+}$ is the activity of interfering ion z_{Mn}^{2+} and z_{M}^{n+} are their respective charges. The selectivity Coefficient pattern (Table 4) clearly indicates that the electrodes are efficiently selective to Mn (II) ions.

The performance characteristics of the proposed electrode and those of some reported electrodes [9-12] were compared and it was found that the proposed electrode has wide concentration range, fast response time (10s) and long life time (8 months).

The proposed membrane electrode was successfully applied as an indicator electrode for the titration of Mn(II) ion (1.0×10^{-3} M) with a standard EDTA solution (1.0×10^{-3} M). The resulting titration curve is shown in figure 3. It has a sharp inflection point, and the amount of Mn^{2+} ions in solution can be accurately determined.

In addition, the electrode was used successfully for determination of Mn(II) in different real samples. The obtained values are quite comparable to those obtained with AAS and ICP, thereby illustrating the utility of the sensor for determining the Mn (II) in real samples(Table5).

Table 4: Selectivity Coefficient values calculated by Fixed Interference Method

Interfering Ion	Selectivity Coefficient,$K^{POTZn^{2+}, M^{n+}}$
	Fixed Interference Method
Ce^{3+}	3.4×10^{-4}
Nd^{3+}	2.8×10^{-4}
Th^{4+}	3.6×10^{-4}
Eu^{3+}	2.7×10^{-4}
Cu^{2+}	4.3×10^{-4}
Zn^{2+}	3.7×10^{-4}
Mg^{2+}	3.2×10^{-4}
Co^{2+}	2.8×10^{-4}
Ni^{2+}	4.1×10^{-4}
Pb^{2+}	2.6×10^{-4}
Hg^{2+}	3.3×10^{-4}
Ag^{+}	4.2×10^{-4}
Fe^{3+}	3.6×10^{-4}
Al^{3+}	3.8×10^{-4}

Table 5: Practical Application of proposed electrode

Sample	Mn^{2+}-ISE (µg/L)	AAS (µg/L)	ICP (µg/L)
brownstone	2.4	2.2	2.1
Drinking water	12.5	12.4	12.5
Industrial waste water	11.4	11.2	11.3
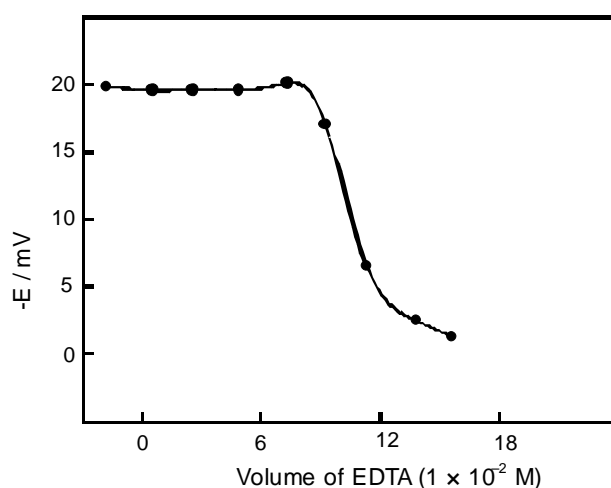
Figure 3: Potentiometric titration curve of 10^{-3} M Mn^{2+} ion solution with 8 ml, 1 x 10^{-3} M EDTA solution

Conclusion

The proposed ionophore was used as an excellent ionophore for Mn^{2+} selective membrane sensor. The proposed sensor is superior in terms of linear range, detection limit, selectivity coefficients, and response time to the previously reported ones.

The sensor no. 1 having membrane with composition o-NPOE:PVC:Ionophore:NaTPB in ratio of 54%:33%:8%:5% (w/w), was found to perform best. Membrane electrode has good potentiometric figures of merit for the determination of Mn (II) ions, including high sensitivity, low detection limit (3.1 × 10^{-7} M), fast response time (10 s), good Nernstian slope (29.8 mV/decade) and wide linear range (5.0 × 10^{-9} - 1.0 × 10^{-2} M) with respect to Mn^{2+} ion concentration.

References

[1] Inorganic chemistry Hollenman-wiberg, Academic Press, (2010) pp-1405
[2] R.D.W. Kemmitt, Manganese, Comprehensive Inorganic chemistry 3 (1973) 772-876.
[3] http://en.wikipedia.org/wiki/ Praseodymium
[4] http://www.lenntech.com/ periodic/elements/pr.htm#ixzz1OzGzPjnq

[5] R.J. Callow, "The Industrial Chemistry of the Lanthanons, Yttrium, Thorium and manganese

[6] US EPA (US Environmental Protection Agency). Integrated Risk Information System (IRIS) on Manganese, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati,OH, 1993.

[7] Maniasso, N.; Zagatto, E. A. G. *Anal. Chim. Acta* 1998, *366*, 87.

[8] Lal, U. S.; Chattopadhyaya, M. C.; Ghosh, K.; Dey, A. K. *Indian Agriculturist (Spec. vol.)* 1982, 139. Uranium", Pergamon Press, 1967.

[9] M. R. Ganjali, F. S. Mirnaghi, P. Norouzi and M. Adib *Sens. Actuators, B*, 2006, 115(1), 374-378

[10] F.J. Saez de Viteri and D. Diamond, Analyst, 119 (1994)

[11] Mahajan, R. K.; Kumar, M.; Sharma, V.; Kaur, I. *Talanta* 2002, *58*, 545.