Novel Manganese (II) Acetate Complex for Nitrite Anion

Seema Sharma[1] and K K Sharma[2]

[1]Assistant Director of Education, Department of Education, East Delhi Municipal Corporation, [2]DGM NTPC INDIA

Abstract: *A novel potentiometric membrane sensor has been developed and optimized based on 3,5,13,15-tetramethyl-4,14-diethyl-2,6,12,16,21,22-hexaazatricyclo [15.3. I $^{1-17}$ I $^{7-11}$] dicosa-1,(21)2,5,7,19,11(22),12,15,17,19-decaene Manganese acetate ionophore in poly vinyl chloride matrix membrane (PVC) plasticized with o-nitrophenyloctyl ether (NPOE) for high selective determination of nitrite ion. The sensor works well in a linear range: $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M with a Nernstian slope of -59.8 ±0.1 mV/decade and its detection limit is 5.0×10^{-7} M. The sensor shows working range over the pH 2.0-9.5 and is stable for a period of 3 months with response time <10 s. The selectivity coefficient values as determined by fixed interference method indicate a good selectivity for ions over a wide variety of other tested anions.*
Keywords: Sensor, Ion Selective Electrode, PVC, Potentiometry.

I. Introduction

Interest in sensors with enhanced selectivity for nitrite has increased recently owing the discovery of the endogenous enzyme nitric oxide synthase (NOS) which catalyzes the oxidation of arginine to nitric oxide and citrulline in a variety of human cells. The liberated NO reacts rapidly with water and oxygen to generate nitrite and nitrate ions [1-2].

Nitrite is present ubiquitously in soils, waters, foods and physiological systems and has been reported as a human health-hazard. The excess uptake of nitrite would cause gastric cancer [3] and blue body [4]. Therefore, it is necessary to develop a reliable and sensitive sensor to detect nitrite in food, drinking water and environmental samples.

In recent decade some electrochemically modified electrodes of nitrite have been explored to lower the operating potentials for nitrite oxidation [5].

In this work, we describe **[MnL](ac)₂ [Figure 1]** as a novel ionophore used in PVC polymeric nitrite selective electrode.
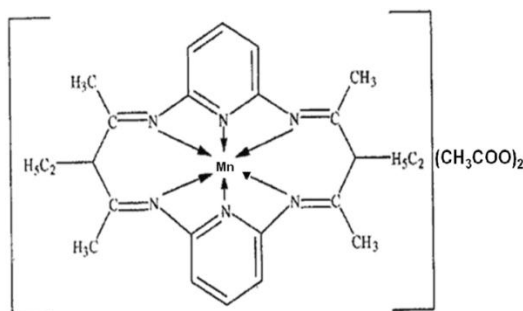

Figure 1 Ionophore [MnL](ac)₂

II. Experimental

2.1 Reagents and Instruments

PVC of high relative molecular weight, hexadecyltri-methylammonium chloride (HTAC), dibutyl phthalate (DBP), Tri-n-butylphosphate(TBP), o-nitrophenyloctyl ether (NPOE), n-butylacetate(BA), and metallic salts used were of the highest purity available from Merck and were used without further purification except for vacuum drying over P_4O_{10}. THF was used as received. All aqueous solutions were prepared with deionized, distilled water. Solution of anionic interferences, for selectivity studies, were prepared mostly from sodium salts in the water. Working solutions were prepared by successive dilutions with water. Potentials were measured with digital potentiometer EQ-602 Equiptronics (accuracy, 0.001 V, India). The pH measurements were carried out on digital pH meter (LabIndia pH Conmeter, India). Auto ranging Conductivity meter/TDS meter TCM-15 (Toshniwal Instruments Mfg. Pvt. Ltd Ajmer).

2.2 Electrode preparation

Different compositions of membrane ingredients, including ionophore, the plasticizers NPOE, DBP, BA, TBP, the additive HTAC and PVC **as shown in Table 1** were thoroughly dissolved in 10 ml THF. The resulting solution was carefully cast in to a glass dish of 2 cm diameter for slow evaporation at room temperature to obtain membrane of about 0.3 mm thickness with optimum composition and behavior. The membrane was cut and pasted to the one end of pyrex tube with the help of araldite. The electrode was then filled with an internal solution of 1.0×10^{-2} M nitrite. The prepared electrodes were finally conditioned by soaking in a 1.0×10^{-2} M nitrite solution for 24 h.

2.3 EMF Measurements

EMF measurements with the polymeric membrane were carried out
with the following cell assemblies:
Ag–AgCl │ internal solution, 1.0×10^{-2} M NaNO$_2$ │ PVC membrane
│ test solution │ Hg–Hg$_2$Cl$_2$│ KCl (satd).
The activities were calculated according to the Debye-Huckel procedure [6].

III. Results and Discussion

3.1 Potential response

In preliminary experiments, the ionophore [MnL](ac)$_2$ was applied in the construction of a number of membrane sensors for different anions. The potential responses for different anionic species are shown in [**Figure 2**]. As it is seen except for the NO$_2^-$ ion-selective electrode the slope of the corresponding potential pA^{n-} plots is much lower than the expected Nernstian slope and the plots suffer from a limited linear range. However, the nitrite ion resulted in a Nernstian response over a wide concentration range ($1.0 \times 10^{-6} - 1.0 \times 10^{-1}$M). This is, most probably, due to both the selective behaviour of the ionophore against NO$_2^-$ in comparison to other anions tested and the rapid exchange kinetics of the anion, between the aqueous and membrane phases.
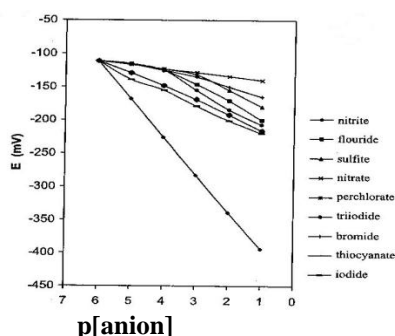

Figure 2 Potential response of various membrane sensors based on [MnL](ac)$_2$

3.2 UV-Vis. spectra

To obtain a clue about the interaction mechanism of [MnL](ac)$_2$ with nitrite, the UV-Vis. spectra of 1.0×10^{-4} mol L^{-1} [MnL](ac)$_2$ in DMSO were obtained without and with the presence of 1.0×10^{-4} mol L^{-1} nitrite and the results are shown in [**Figure 3**]. The decrease in the absorbance of the Soret band at 475 nm, accompanying an 8 nm red shift after the contact of [MnL](ac)$_2$ with nitrite ion, indicated that there is a specific interaction between the **NO$_2^-$** and Mn(II) of the studied ionophore.

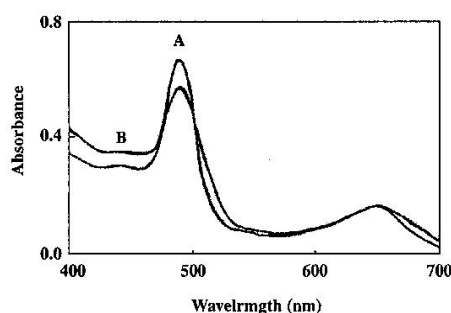**Figure 3 UV-Vis absorption spectra of [MnL](ac)$_2$ in DMSO solution (A)without and (B) with 1.0×10^{-4}M NO$_2^-$**

3.3 Effect of Plasticizer

As shown in [**Figure 4**], among the four solvent mediators used, o-NPOE shows best results than dibutyl phthalate, TBP or benzyl acetate in preparing the nitrite sensor.

The values obtained for correlation coefficients evidenced the good linearity of the calibration curves for each plasticizer used as solvent mediator in this study.
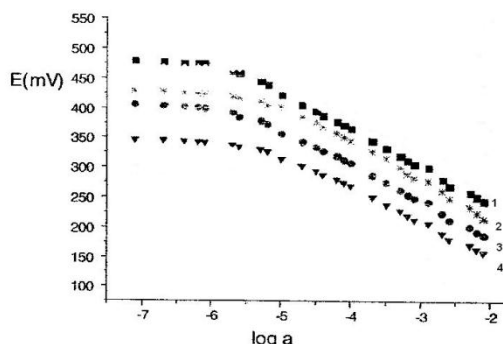

Figure 4 Calibration curves obtained by using different plasticizers as solvent mediators. (1) o-NPOE (2) BA (3) DBP (4) TBP.

3.4 Optimization of membrane ingredients

Apart from the critical role the nature of the ion carrier has in preparing membrane-selective sensors some other important features of the PVC membrane, such as the amount of ionophore, the nature of the solvent mediator, the plasticizer/PVC ratio, and especially the nature of additives used, are known to significantly influence the sensitivity and selectivity of the membranes **[7-14].**

The membrane composition based on ionophore $[MnL](ac)_2$ for nitrite ion-selective sensors were optimized, and the results are given in **Table 1.** As is obvious from

Table 1, among four solvent mediators used, o-NPOE is a more effective solvent mediator than dibutyl phthalate, TBP or benzyl acetate in preparing the nitrite sensor. It should be noted that the nature of the plasticizer influences both the dielectric constant of the membrane and the mobility of the ionophore and its complex.

The sensitivity of the electrode's response increases with increasing ionophore $[MnL](ac)_2$ content until a value of 2% is reached. Further addition of ionophore however, resulted in diminished response of the electrode, most probably due to some inhomogenieties and possible saturation of the membrane **[15].**

Table 1. Optimization of membrane ingredients.

| | | Composition % | | | | |
No.	PVC	Plasticizer	I	HTAC	Slope	Linear range
1	33	NPOE, 67	–	0	-5.3±0.2	1.0×10^{-4}–1.0×10^{-2}
2	33	NPOE, 65	2	0	-14.3±0.1	1.0×10^{-4}–1.0×10^{-2}
3	33	NPOE, 64	3	0	-30.9±0.3	1.0×10^{-5}–1.0×10^{-2}
4	33	NPOE, 62	4	1	-51.1±0.1	1.0×10^{-6}–1.0×10^{-2}
5	33	NPOE, 61	5	1	-47.9±0.2	1.0×10^{-6}–1.0×10^{-1}
6	33	NPOE, 60	5	2	-59.8±0.1	1.0×10^{-6}–1.0×10^{-1}
7	33	DBP, 60	5	2	-55.2±0.2	1.0×10^{-5}–1.0×10^{-1}
8	33	BA, 60	5	2	-52.2±0.2	1.0×10^{-5}–1.0×10^{-1}

The data given in **Table 1** reveals that the presence of an additive has a beneficial effect on the performance characteristics of the membrane electrode. Addition of 2% hexamethytrimethylammonium chloride (HTAC) as a suitable additive **[16-19]** increased the slope of the potential sensor response from a sub-Nernstian value of -51.1mV/decade (No. 4) to a Nernstian value of -59.8mV/decade (No. 6). The presence of cationic additives, such as HTAC, can reduce ohmic resistance and improve the response behavior and selectivity of the membrane electrodes. Moreover, the additives may catalyze the exchange kinetics at the sample-membrane interface.

As is seen from **Table 1,** the membrane obtained with the PVC:NPOE:I:HTAB percent ratio of 33:60:5:2 shows a Nernstian slope of -59.8 ± 0.1mV per decade over a wide nitrite concentration range.

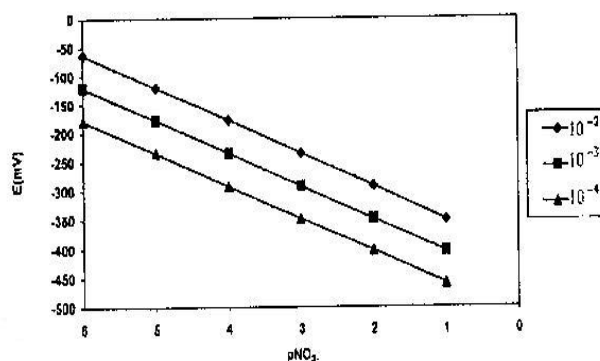### 3.5 Effect of the internal solution

Figure 5 Effect of the internal solution on the potential response of NO$_2^-$

The effect of the internal solution concentration on the potential response of the sensor was investigated [**Figure 5**]. The sodium nitrite concentration was changed from 1.0×10^{-4} to 1.0×10^{-2} M, and corresponding EMF versus pNO$_2^-$ plots were obtained. It was found that the concentration of the internal solution has a negligible effect on the potential response of the electrode, except for an expected shift in the intercept of the resulting plots. A 1.0×10^{-3} M concentration of the filling solution was used for further studies.

3.6 Limit of detection

The plot of EMF vs. pNO$_2^-$ obtained with optimal membrane ingredients for the sensor **[Figure 6]** indicate its Nernstian behavior over wide concentration ranges of nitrite ion. The slope and linear range of the resulting calibration graph are -59.8mV per decade and 1.0×10^{-6}–1.0×10^{-1} M, respectively. The limit of detection (LOD), defined as the concentration of nitrite ion obtained when the linear regions of the calibration graph are extrapolated to the base line potential, is 5.0×10^{-7}M (~40 mg mL^{-1}).
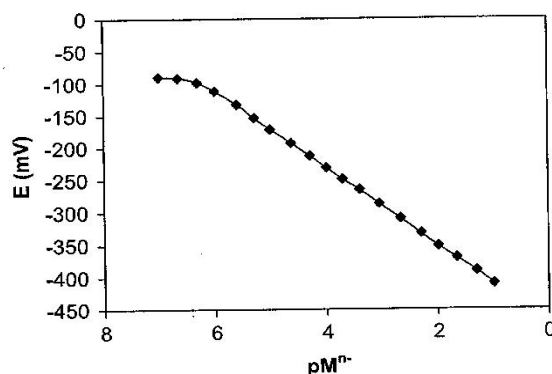
Figure 6 Calibration curve of nitrite electrode.

3.7 Effect of the pH

The potential response of the sensor based on [MnL](ac)$_2$ was found to be sensitive to pH changes. Thus, the pH dependence of the electrode was tested by measuring the potential response of a solution of varying pH over a range of 2.0 to 12.0 in the presence of 1.0×10^{-3} M of NaNO$_2$. The pH adjustments were carried out by nitric acid and sodium hydroxide solution. The sample potential pH plot for the sensor is shown in **[Figure 7].** The results show that the sensor is suitable for nitrite determination in wide pH range of 2.0–9.5. However, the increased potential of the electrode at pH>9.5 can be explained in terms of the increased interference from OH$^-$ ions which may have a strong competing ligation reaction with NO$_2^-$ ions for the central Mn(II) ion. At higher acidic media (pH<2.0), the drift in the potential may be due to the instability of the ionophore.

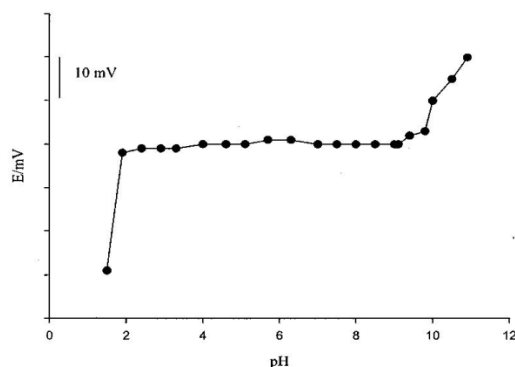**Figure 7 Effect of the pH of the test solutions on the potential response of the electrode.**

3.8 Optimum equilibration time

The optimum equilibration times for the membrane sensor in the presence of 1.0×10^{-3} M sodium nitrite were investigated and found to be 24 h, after which the electrode generated stable potentials in contact with nitrite ion solutions. The standard deviation of 10 replicate potential measurements for the proposed electrode was at the most ±0.4mV. The proposed electrode was very stable and could be used for at least 2 months without observing any change in response characteristics.

3.9 Dynamic response time

The dynamic response time is an important factor in any ion-selective electrode. In this study, the practical response time was recorded by changing the nitrite concentration in the solution over a concentration range of 1×10^{-1} to 1.0×10^{-6} M. The results are shown in **[Figure 8].** As seen over the entire concentration range, the electrode reaches its equilibrium response in a very short time (<10 s). This is most probably due to the fast exchange kinetics of the complexation–decomplexation of nitrite ions with the $[MnL](ac)_2$ at the test solution-membrane interface.
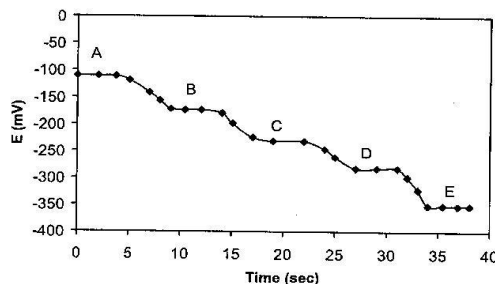
Figure 8 Dynamic response time of the nitrite electrode for step changes in concentration of NO_2^- (A) 1.0×10^{-6} M, (B) 1.0×10^{-5} M, (C) 1.0×10^{-4} M, (D) 1.0×10^{-3} M, (E) 1.0×10^{-2} M, 3.10   Life-Time

The long-term stability of the electrode was studied by periodically recalibrating in standard solutions and calculating the response slope over the range of 1.0×10^{-6} to 1.0×10^{-1}M [20, 21]. The slopes of the electrode response were reproducible to within 2.0-3.0mV per decade over a period of 3 months and the results are given in **Table 2.**

Table 2 Stability and reproducibility of the nitrite-selective electrode (n = 5)

Time (day)	Slope (mV per decade)	Linear range (M)
1	−59.8±0.4	1.0×10^{-6} to 1.0×10^{-1}
7	−59.8±0.4	1.0×10^{-6} to 1.0×10^{-1}
14	−59.8±0.4	1.0×10^{-6} to 1.0×10^{-1}
21	−59.0±1.0	1.0×10^{-6} to 1.0×10^{-1}
35	−58.5±1.0	1.0×10^{-6} to 1.0×10^{-1}
49	−58.5±1.0	1.0×10^{-6} to 1.0×10^{-1}
60	−58.0±1.5	1.0×10^{-6} to 1×10^{-1}
70	−57.5±1.5	1.0×10^{-6} to 1×10^{-1}
90	−57.0±1.5	1.0×10^{-6} to 1×10^{-1}

Table 5 Effect of partially non-aqueous media on the response of [MnL](ac)$_2$ nitrite selective polymeric membrane electrode.

Non-aqueous Content (%v/v)	Slope (mV/decade)	Linear range (mol L^{-1})
0	59.8	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
Methanol		
10	59.8	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
20	59.6	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
30	46.5	$1.5 \times 10^{-5} - 1.0 \times 10^{-1}$
Ethanol		
10	59.8	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
20	59.3	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
30	45.8	$2.0 \times 10^{-5} - 1.5 \times 10^{-1}$
Acetone		
10	59.8	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
20	59.0	$1.0 \times 10^{-6} - 1.0 \times 10^{-1}$
30	45.2	$7.2 \times 10^{-5} - 1.0 \times 10^{-1}$

IV.   Analytical Applications

Nitrites are widely used in the production and preservation of cured meat products, but are well known as toxic substances. The major effect of nitrites is the induction of methaemoglobinemia as a result of nitrite reduction with hemoglobin. They can also react with some amines or amides present in the stomach forming N-nitroso compounds with carcinogenic action. These are the reasons why, the nitrite content in food industry must be controlled and their determination must be currently done for checking the quality of meat products.

V.   Conclusion

The results of the present study show that electrodes having [MnL](ac)$_2$ as ionophore in o-nitrophenyloctylether plasticized polyvinyl chloride membranes, realized with an internal electric solid contact, exhibit a relatively high selectivity for nitrite over many anions. The most important characteristics of the electrodes having the optimum composition of the membrane are: slope: - (59.8 ±0.1) mV/decade; linear range: $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ M; detection limit: 5.0×10^{-7} M; response time: <10 s.

References
[1]   M.A. Marletta, A.Tayeh and J.M. Hevel, BioFactors, 2 (1990) 219.
[2]   S. Archer, J. FASEB, 7 (1993) 349.
[3]   W. Lijinsky, S. S. Epstein Nature, 225 (1970) 21–23.
[4]   E. Morcos, N.P. Wiklund, Electrophoresis, 22 (2001) 2763-2768.
[5]   X. Yang, N. Kumar, H. Chi, D. B. Hibbert, P.W. Alexander Electroanalysis, 9 (1997) 549–553.
[6]   M Shamsipur, M Yousefi, M Hosseini, M R Ganjali, Anal Lett:, 34 (2001) 2249–2261.
[7]   M. Shamsipur, A. Avanes, M. Javanbakht, M. R.Ganjali, H. Sharghi, Anal Sci., 18 (2002) 875–879.
[8]   M. R. Ganjali, M. Hosseini, F. Basiripour, M. Javanbakht, O. R. Hashemi, M. Rasteger Faal, M. Shamsipur, G. W. Buchanan Anal Chim Acta., 469 (2002) 181–186.
[9]   M Shamsipur, M Javanbakht, V Lippolis, A Garau, M R Ganjali, A Yari, Anal Chim Acta 462 (2002) 225–234.
[10]   M R Ganjali, M Yousefi, M Javanbakht, T Poursaberi, M Salavati-Niassari, L Hajiagha-Babaei, E Latifi, M Shamsipur, Anal Sci. 18 (2002) 887–892
[11]   M Shamsipur, M Yousefi, M Hosseini, M R Ganjali, H Sharghi, H Naeimi, Anal Chem 73 (2001) 2869–2874.
[12]   M R Ganjali, T Poursaberi, L Hagi-agha Babaei, M Yousefi, S Rouhani, M Shamsipur, Fresenius, J Anal Chem , 370 (2001) 1091–1095.
[13]   M Shamsipur, M Yousefi, M R Ganjali, Anal Chem, 72 (2000) 2344.
[14]   S Kamata, A Bhale, Y Fukanaga, H Murata, Anal Chem, 60 (1988) 2464–2467.
[15]   Y Umezawa, K Umezawa, H Sato, Pure Appl Chem, 67 (1995) 507–518.
[16]   M. R. Ganjali, M. Rezapour, M. R. Pourjavid, M. Salavati-Niasari, Anal. Sci., 19 (2003) 1127-1131.
[17]   M. R. Ganjali, S. Shirvani-Arani, P. Norouzi, M. Rezapour, M. Salavati-Niasari, Mikrochim. Acta., 146 (2004) 35-41.
[18]   M. Shamsipur, M. Javanbakht, A. R. Hassaninejad, H. Sharghi, M. R. Ganjali, M. F. Mousavi, Electroanalysis, 15 (2003) 1251-1259.
[19]   W.P. Hu, X.Z. Dong, Z.J. He, Chin. J. Anal. Chem., 32 (2004) 765-768.
[20]   A. Rawat, S. Chandra, A. Sarkar, Sensor Lett., 7 (2009) 1100–1105.
[21]   Coordination Chemistry Reviews, 392 (2012) 438.