



ORIGINAL ARTICLE

Asymmetric Schiff base as carrier in PVC membrane electrodes for manganese (II) ions

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Received 26 July 2010; accepted 30 August 2010

Available online 7 September 2010

KEYWORDS

Manganese;
Ion-selective electrode;
PVC membrane;
Schiff base;
Potentiometry

Abstract Manganese(II) complex of (E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol was synthesized and used as a suitable Mn(II) – selective membrane in PVC matrix. The plasticized membrane sensor exhibits a nersian response for Mn(II) ions over a wide concentration range of 6×10^{-6} – 2×10^{-2} M with slope of 29 ± 1 mV per decade. It has a response time of < 11 s and can be used for 2 months without any measurable divergence in potential. The response of the proposed sensor is independent of pH between 4 and 9.5. The proposed sensor shows a fairly good discriminating ability towards Mn(II) in comparison with some hard and soft metals. The electrode was used in the determination of Mn(II) in aqueous solutions and as an indicator electrode in potentiometer titration of manganese ions against EDTA.

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Peer review under responsibility of King Saud University.

doi:10.1016/j.arabjc.2010.08.013



1. Introduction

In recent decades many intensive studies have been introduced on the design and synthesis of highly selective ion-carrier as sensory molecules in the fabrication of ion-selective electrodes. There are many examples about the selective affinity of Schiff's bases toward metal ions, and hence their application in the construction of ion-selective electrodes (ISEs) Sadeghi et al., 2006; Mashhadizadeh et al., 2002; Gupta et al., 2007; Farhadi et al., 2004. Manganese is the twelfth most abundant element and the third most abundant transition element (exceeded only by iron and titanium). The most stable oxidation state of manganese is Mn(II), and in the group oxidation state of Mn(VII) it is even more strongly oxidizing than Cr(VI). Manganese liberates hydrogen from water and dissolves readily in dilute

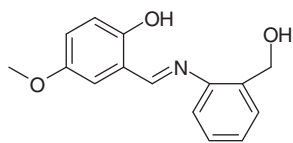


Figure 1 Structure of ionophor (E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol (HMP).

aqueous acids to form manganese(II) salts. With a non-metal it is not very reactive at ambient temperatures but frequently reacts vigorously when heated (Greenwood and Earnshaw, 1985). The major uses of manganese are in the iron and steel industries. Manganese dioxide is used quite extensively in alkaline batteries, and in the glass, paints, and drying industries. Other compounds of manganese are used as driers for paints, varnishes, oils, fertilizers, disinfectants, and as anti-clock compounds for internal combustion engines (Singh, 2005). Manganese is the essential trace element that has a complex role in many body functions. This element is toxic at higher levels for organisms and plants. In humans, chronic manganese poisoning affects the central nervous system (Kendzler and Turker, 2002; Malvankar and Shinde, 1991). Therefore, it is important from analytical point of view to develop sensitive, selective and economical method for the determination of the trace amounts of manganese (Wang and Lu, 1995; Afzali et al., 2008; Shamsipur and Mostafavi, 2009; Mashhadizadeh et al., 2007).

The Schiff base derived from salicylaldehyde (salens) polydentate ligands are known to form very stable complexes with transition metal ions (Ochiai, 1973; Tajmir-Riahi, 1983; Arena et al., 1986; Calligaris et al., 1987; Martell and Sawyer, 1988; Atwood, 1997; Shamsipur, 2009). The resulting salen complexes have attracted increasing attention, mainly due to their peculiar properties (Calligaris et al., 1987; Atwood, 1997) and their reactivity mainly in the area of binding small molecules (Martell and Sawyer, 1988). Chelating agents with moderate coordination sites like nitrogen seem to generate great affinity toward moderate metal ions such as Cu(II). Schiff bases are ligands containing mixed O, N-donor atoms, which have high bonding affinities with some metal ions such as Cu(II), Cd(II), and Pb(II) . . . ions.

The aim of this work is to use an asymmetrical tridentate Schiff base ligand E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol (Fig. 1) as an active material in PVC matrix for the fabrication of Mn(II) – selective sensor.

2. Experimental

2.1. Apparatus

All potentiometric measurements were made at 25.0 ± 0.1 °C with a pH/mV meter (Zag Chimi, Iran) using proposed sensor in conjunction with a double junction Ag/AgCl (Azar electrode, Iran) as reference electrode.

2.2. Reagents and solutions

Analytical reagent grade chemicals and doubly distilled water were used for preparing all aqueous solutions. High molecular weight polyvinyl chloride powder (PVC), dioctyl phthalate (DOP), dibutyl phthalate (DBP), dimethylsebacate (DMS), and tetrahydrofuran (THF) were obtained from Aldrich company. Sodium tetraphenylborate (NaTPB) and o-nitrophenyloctyl ether (NPOE) were obtained from Fluka. Salts of metal nitrates were of the highest purity available from Merck (Darmstadt, Germany) and were used as received.

2.3. Synthesis

(E)-2-(hydroxyl-5-methoxybenzylideneamino) phenol (HMP) was prepared by the standard method (22). A mixture of 2-hydroxy-5-methoxybenzaldehyde (0.001 mol, 0.152 g) and 2-amino benzyl alcohol (0.001 mol, 0.123 g) was mixed. The resulting mixture was boiled under reflux for 2 h and the solution was concentrated and allowed to cool at room temperature for 48 h. The yellow solid obtained was filtered, washed with cooled methanol, and recrystallized from ethanol–chloroform (1:1), m.p.:120–121 °C. Yield:69% IR (KBR) (ν_{\max} (cm^{-1})):1616 and 3100–3416 (OH).

Anal calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_3$ (257.29):C, 70.02%; H, 5.88%; N, 5.44% found: C, 69.9%; H, 5.9%; N, 5.35%.

^1H NMR (400 MHz, DMSO solutions); 3.71 (1H, s, OH), 3.89 (3H, s, CH₃), 4.63 (2H, s, CH₂), 5.41 (1H, s, OH), 6.83–7.34 (7H, m, 7CH), 8.61 (1H, s, CH).

^{13}C NMR (400 MHz, DMSO solutions):118.1, 132.4, 148.2, 153.3, 154.5 (5c), 111.5, 116.9, 117.4, 121.6, 120.3, 128.4, 132.6 (7ch), 59.7 (CH₂), 52.4 (CH₃), 158.6 (C=N).

2.4. Electrode preparation

The procedure to prepare the PVC membrane was to mix the powdered PVC, the plasticizer, the ionophore HMP and the

Table 1 Optimization of membrane ingredients.

No.	Composition (w/w)%			NaTPB	Slope (mV/dec)	Dynamic range (M)	
	PVC	HMP	Plasticizer				
1	31.5		62.4, DBP	3.1	3.2	19	1.0×10^{-5} – 1×10^{-3}
2	31.25		62.5, DOP	3.12	3.12	6.10	1.0×10^{-6} – 3.0×10^{-4}
3	29.8		61.9, DBP	5.1	3.3	9	1.0×10^{-5} – 1.0×10^{-3}
4	83.3		0	8.30	8.30	0.95	1.0×10^{-6} – 1.0×10^{-3}
5	29		61.9, DOP	0	4.1	21	2.0×10^{-6} – 1.0×10^{-2}
6	30		67, NPOE	3	0	10.9	2.0×10^{-5} – 1.0×10^{-3}
7	36.3		52.9, DBP	4.3	6.5	16	2.0×10^{-6} – 5.0×10^{-3}
8	28.6		62.4, DBP	5.2	3.7	28.6	6.0×10^{-6} – 2.0×10^{-2}

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