MANGANESE(II)-ION-SELECTIVE ELECTRODE BASED ON 2,2′-BIS(SALICYLIDENEAMINO)AZOBENZENE INCORPORATED IN POLY(VINYL CHLORIDE) MATRIX

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A new PVC membrane electrode highly selective to Mn(II), based on 2,2′-bis(salicylideneamino)azobenzene as an ionophore. The electrode exhibits a Nernstian response to Mn(II) ions over a concentration range 0.8×10^{-1}–1.1×10^{-7} mol l^{-1} with a slope of 30.5 ± 0.5 mV per decade and detection limit 5.5×10^{-8} mol l^{-1}. The electrode was used for 45 days at the minimum without any measurable potential divergence. Also, the electrode revealed a fairly good discrimination ability between Mn(II) ions and some cations and anions. The electrode was also utilized as indicator electrode in the potentiometric titration of Mn(II) with EDTA and in determination of Mn(II) in drug as well as tape and river water.

Keywords: Ion-selective electrodes; Manganese(II) sensor; 2,2′-Bis(salicylideneamino)azobenzene; Potentiometry; Electrochemistry.

Manganese ores are an important raw material for production of steel, ferromanganese, non-ferrous alloys, dry cell batteries, paints and other chemicals. Thus, because of increasing industrial uses of manganese compounds, its determination is the subject of considerable efforts. Potentiometric detection based on ion-selective electrodes (ISEs) as a simple method offers great advantages such as speed and ease of preparation and procedures, relatively fast response, reasonable selectivity, wide linear dynamic range, and low cost. These characteristics have inevitably led to sensors for several ionic species, and the list of available electrodes has grown substantially over the past years[1]. Also, the ISEs allow non-destructive and on-line monitoring of particular ions in a small volume of sample without any pretreatment.

The Schiff bases derived from salicylaldehyde (salens) as polydentate ligands are known to form very stable complexes with transition metal ions[2,3].

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The resulting 1:1 complexes have been frequently used as catalysts in diverse processes such as oxygen and atom transfer[4], enantioselective epoxidation[5] and mediating organic redox reactions[6]. However, despite extensive scientific reports on the synthesis, characterization and crystal structure of transition metal–salen complexes, reports on analytical application of these ligands are quite spare. Recently some of these polydentate ligands were used for construction of ion-selective electrodes[7], optical sensors[8], ion transport[9] and solid-phase extraction[10] in our group. In this paper we introduce a selective and sensitive manganese ion-selective membrane electrode for potentiometric monitoring of trace amounts of Mn^{2+} by using 2,2′-bis(salicylideneamino)azobenzene as the ionophore (Fig. 1). To the best of our knowledge, there are only three reports on a carrier-based ion-selective membrane electrode for manganese ions[11–13]. The sensor exhibits a Nernstian response to manganese ions over a wide concentration range and a low detection limit in comparison with other reports[11–13]. The proposed electrode was used for determination of manganese in natural water and drugs.

EXPERIMENTAL

Reagents

All reagents used were of analytical grade. High-molecular-weight poly(vinyl chloride), sodium tetraphenylborate (NaTPB), dibutyl phthalate (DBP), dioctyl phthalate (DOP), tris(2-ethylhexyl)phosphate (TEHP) and tetrahydrofuran (THF) were purchased from Fluka and used as received. All nitrates and chlorides were of the highest purity available (from Merck or Fluka) and used without any further purification. Double-distilled water was used throughout.

Preparation of 2,2′-Bis(salicylideneamino)azobenzene (BSAAB)

A solution of 1,2-phenylenediamine (10.8 g, 100 mmol) in dry toluene (50 ml) was added under nitrogen into a 250-ml three-necked flask, equipped with a stirrer, thermometer,

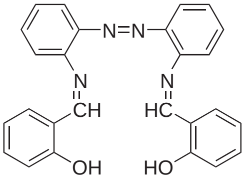

FIG. 1
The structure of ionophore

dropping funnel and a nitrogen gas inlet and maintained under nitrogen atmosphere. The flask was cooled to –5 °C (ice-salt bath) and then BaO_2 (20 g, 120 mmol) was added in small portions. The reaction mixture was stirred for 1 h and then was allowed to slowly warm up. Stirring was continued for additional 6 h. Unreacted excess of BaO_2 was removed on addition of distilled water with caution. The organic phase was extracted with toluene (3 × 5 ml). The organic phases were combined and concentrated on a rotary evaporator and then purified by flash chromatography. The red crystals were collected and characterized as 2,2′-diaminoazobenzene; m.p. 135 °C, yield 9.22 g (87%). In the second step, a solution of 2,2′-diaminoazobenzene (8.5 g, 40 mmol) in ethanol (100 ml) was added dropwise to excess salicylaldehyde (5.0 ml, 47.9 mmol). The reaction mixture was refluxed for 12 h. Progress of the reaction was monitored by TLC chromatography (*n*-heptane/ethyl acetate 2:1). The reaction mixture was cooled, a yellowish-orange solid precipitated from the red solution. The solid was separated by filtration, washed with cold ethanol (5 × 5 ml) to remove unreacted salicylaldehyde and dried in vacuo (7.6 g). The ethanolic washings were added to the mother liquor and the solution was dried on a rotary evaporator. A second crop of the product was produced which was recrystallized from hot ethanol (m.p. 221–223 °C). In addition to the melting point, thin layer chromatography (*n*-heptane/ethyl acetate 2:1), ^{1}H NMR (δ, ppm; *J*, Hz) and FTIR (ν, cm^{-1}) spectroscopies were utilized to confirm the disappearance of spectroscopic signals of starting material ((N–H) and (C=O) in FTIR; amine and aldehyde protons in NMR and appearance of new bands (C=N) in FTIR; imine proton in NMR). ^{1}H NMR ($CDCl_3$): 13.20 (s, OH, 2); 8.49 (s, HC=N, 2); 6.83–7.47 (m, aromatic protons, 16). FTIR (KBr): 1610 (C=N); 2105 (N=N); 3315 (OH). For $C_{26}H_{20}N_4O_2$ calculated: 74.27% C, 4.79% H, 6.66% N; found: 74.76% C, 5.02% H, 6.23% N.

Electrode Preparation

Powdered PVC (32.5 mg), DBP (64.5 mg), NaTPB (1.0 mg) and ionophore (2.0 mg) were mixed in 2.5 ml of THF. The resulting clear mixture was transferred into a glass dish. The solvent was slowly evaporated until an oily concentrate was obtained. A Pyrex tube (5.0 mm o.d.) was dipped into the mixture for about 10 s, so that a nontransparent membrane of about 0.3 mm thickness was formed. Then, the tube was pulled out from the solution and kept at room temperature for 1 h. The tube was then filled with internal filling solution (1×10^{-3} M $Mn(NO_3)_2$). The electrode was finally conditioned for 24 h by soaking in 1×10^{-3} M $Mn(NO_3)_2$ solution. Ag|AgCl was used as an internal reference electrode. The ratio of various components of the equilibrating solution and time of contact were optimized to provide a membrane with reproducible, noiseless and stable potentials.

EMF Measurements

All electromotive force (emf) measurements were carried out with the following cell assembly:

Ag|AgCl | 3 M KCl | 1×10^{-3} M $Mn(NO_3)_2$, 1.0×10^{-3} M KCl | PVC membrane |
measured solution | Hg_2Cl_2|Hg|saturated KCl.

A HANA302 ion analyzer pH/mV meter (made in Portugal) was used for potential measurements at 25.0 ± 0.1 °C. Activities were calculated using the Debye–Hückel procedure[14].

RESULTS AND DISCUSSION

Schiff bases seem to be potential ionophores for metal ions in the PVC membrane electrodes because of their excellent metal-binding properties, rapid exchange kinetics, and insolubility in water[7,15,16]. Due to the presence of oxygen and nitrogen donors in 2,2′-bis(salicylideneamino)azobenzene, this ligand was expected to act as a suitable ion carrier in the sensor based on PVC membrane. Thus, this ligand was used, in preliminary experiments, as a neutral carrier to prepare polymeric membrane electrodes for a variety of metal ions. As it can be seen in Fig. 2, of the different tested cations, Mn^{2+} with its most sensitive response seems to be suitable for the PVC membrane based on the ligand. The emf responses obtained for all other cation-selective electrodes are much lower than those predicted by the Nernst equation. The results might indicate that the selectivity to these ions is masked by the low detection limit of the electrode, which is most probably due to the transport of Mn(II) ions from the measured solution to the boundary between the membrane and solution as discussed by Bakker et al.[17,18]. Several parameters were investigated in order to evaluate the performance of the Mn(II) electrode such as membrane composition, response time, pH, calibration graph, reproducibility, selectivity and sample analysis.

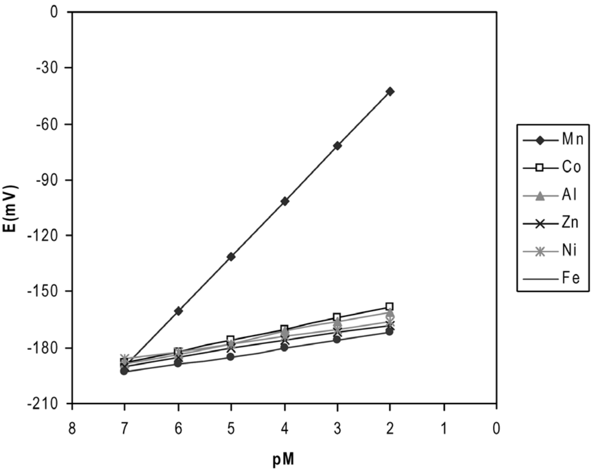

FIG. 2
Potential response of various ion-selective electrodes based on the Schiff-base ionophore

Study of Complexation

To the best of our knowledge, there is no report on the stability of BSAAB complexes with different cations. In order to determine the stoichiometry and stability of the resulting metal–BSAAB complexes, the interactions between the ion-carrier (BSAAB) and different cations in an acetonitrile solution were tested conductometrically. In typical experiments 15 cm^3 of cation nitrate solution (1.0×10^{-5} mol l^{-1}) was placed in a water-jacketed cell equipped with a magnetic stirrer and connected to thermostat. In order to keep the electrolyte concentration constant during titrations, both the starting solution and titrant had the same cation concentration. Then, a known amount of the BSAAB (1.0×10^{-3} mol l^{-1}) solution was successively added with a micropipette. The conductance of the solution was measured after each addition. Addition of BSAAB was continued until the desired BSAAB/cation mole ratio was achieved. The resulting molar conductivity versus ligand/cation mole ratio (Fig. 3) showed the formation of the 1:1 complex of BSAAB and manganese. The 1:1 binding of the cations with BSAAB can be expressed by the equilibrium

$$M^{n+} + L = ML^{n+}. \tag{1}$$

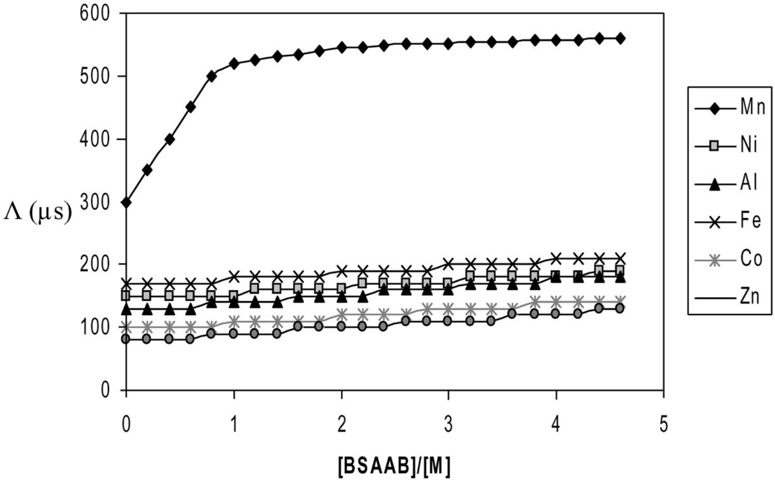

FIG. 3
Molar conductivity versus [BSAAB]/[M^{n+}] curves for metal ions in acetonitrile at 25 °C

The corresponding formation constant, K_f, is given by

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} \frac{f(\mathrm{ML}^{n+})}{f(\mathrm{M}^{n+})f(\mathrm{L})} \qquad (2)$$

where $[\mathrm{ML}^{n+}]$, $[\mathrm{M}^{n+}]$, [L] and f are the equilibrium molar concentration of complexes, free cation, free BSAAB and the activity coefficient of the species indicated, respectively. Under the dilute conditions we used, the activity coefficient of the uncharged ligand, $f(\mathrm{L})$, can be reasonably assumed to be unity[19]. The use of the Debye–Hückel limiting law for 1:1 electrolytes[20] leads to the conclusion that $f(\mathrm{M}^{n+}) \sim f(\mathrm{ML}^{n+})$, and hence the activity coefficients in Eq. (*2*) cancel out. Thus, the formation constant of the complex in term of the molar conductivity can be expressed as[21]

$$K_f = \frac{[\mathrm{ML}^{n+}]}{[\mathrm{M}^{n+}][\mathrm{L}]} = \frac{(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{obs}})}{(\Lambda_{\mathrm{obs}} - \Lambda_{\mathrm{ML}})[\mathrm{L}]} \qquad (3)$$

where

$$[\mathrm{L}] = C_{\mathrm{L}} - \frac{C_{\mathrm{M}}(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{obs}})}{(\Lambda_{\mathrm{M}} - \Lambda_{\mathrm{ML}})} . \qquad (4)$$

Here, Λ_M is the molar conductivity of the cation before addition of BSAAB, Λ_{ML} the molar conductance of the complexed, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the BSAAB added, and C_M the analytical concentration of the cation salt. The complex formation constant, K_f, and the molar conductance of complex, Λ_{ML}, were obtained by computer fitting of Eqs (*3*) and (*4*) to the molar conductance versus mole ratio data using a nonlinear least-squares program KINFIT[22]. The results showed that the stability constant of the Mn^{2+}–BSAAB complex ($\log K_f = 5.7$) was at least 10^4-fold greater than those obtained with the other cations tested, Zn^{2+}, Ni^{2+}, Cd^{2+}, Hg^{2+}, Co^{2+}, Ag^+, Li^+, Mg^{2+}, Ba^{2+}, Fe^{2+}, and Al^{3+}. Thus, BSAAB may be used as a suitable selective ionophore in construction of a Mn^{2+} ion-selective membrane electrode.

Effect of Membrane Composition

In general, the sensitivity and selectivity of an ion-selective electrode is strongly influenced by the nature and amount of the plasticizer and lipophilic additive. The effect of plasticizer on the characteristics of the Mn^{2+}-

selective electrode was investigated by using three kinds of plasticizers – DBP, DOP and TEHP. The best calibration parameters and mechanical characteristics of the membranes were observed in the case of DBP; hence, this plasticizer was used in further studies. Although membranes based on neutral carriers may work properly even if they contain only a very small amount of ionic sites (e.g., as impurities), the addition of a salt of lipophilic ion is advisable and beneficial for various other reasons as well. In fact, it has been demonstrated that the presence of lipophilic negatively charged additives improves the potentiometric behavior of certain cation-selective electrodes by reducing the Ohmic resistance, improving the response behavior and selectivity[23–26] and, in some cases, by catalyzing the exchange kinetics at the sample–membrane interface[27]. From the data presented in Table I, it can be seen that the addition of NaTPB considerably increases the sensitivity of the electrode response. Use of 1.0% (w/w) NaTPB resulted in a Nernstian behavior of the electrode (No. 5). The results thus obtained indicate that the best sensitivity and linear range is obtained for membrane No. 5 with the PVC/DBP/BSAAB/NaTPB per cent ratio 32.5:64.5:2:1 which resulted in a Nernstian behavior of the membrane electrode over a wide concentration range (0.8×10^{-1} to 1.1×10^{-7} mol l^{-1}). The optimum equilibration time for the proposed sensor in the presence of 1.0×10^{-3} M manganese nitrate is 24 h. After this time, the electrode based on BSAAB generates stable potentials in contact with manganese ion solutions.

TABLE I
Optimization of membrane composition

Membrane No.	Component, %				Slope mV/decade	Linear range mol l^{-1}
	PVC	plasticizer	ligand	additive		
1	33	66 (DOP)	1	0	9.5 ± 0.3	1.2×10^{-4}–1.1×10^{-2}
2	33	66 (TEHP)	1	0	12.3 ± 0.6	2.3×10^{-3}–1.3×10^{-1}
3	33	66 (DBP)	1	0	13.1 ± 0.4	7.3×10^{-4}–1.5×10^{-2}
4	33	65 (DBP)	1	1 (NaTPB)	22.1 ± 0.2	0.5×10^{-5}–2.2×10^{-1}
5	32.5	64.5 (DBP)	2	1 (NaTPB)	30.5 ± 0.5	1.1×10^{-7}–0.8×10^{-1}
6	32.5	63.5 (DBP)	3	1 (NaTPB)	25.2 ± 0.2	3.1×10^{-5}–4.2×10^{-2}
7	32.5	63.5 (DBP)	2	2 (NaTPB)	24.4 ± 0.3	2.4×10^{-5}–2.3×10^{-2}
8	34	66 (DBP)	0	0 (NaTPB)	6.3 ± 0.1	8.5×10^{-4}–3.2×10^{-2}

Calibration Curve and Statistical Data

The potential response of the electrode at varying concentration of Mn(II) ions displays a linear response to the concentration of Mn^{2+} ions in the range 1.1×10^{-7}–0.8×10^{-1} mol l^{-1} (Fig. 4). The slope of calibration graph was 30.0 ± 0.5 mV per decade of the activity of Mn^{2+} ions. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph was 5.5×10^{-8} mol l^{-1}. The standard deviation of 10 replicate measurements is ±0.5 mV.

Effect of pH

The pH dependence of the potentials of the proposed electrode was investigated for two concentrations of manganese ion (1.0×10^{-4} and 1.0×10^{-3} mol l^{-1}) over the pH range 1.0–9.0. The results are shown in Fig. 5. pH was adjusted by nitric acid or sodium hydroxide solution. As can be seen, the potential response remains almost constant over the pH range 1.5–5.0, which can be taken as the working pH range of the electrode. The increased potential of the electrode at pH < 1.5 is most probably due to the response of the membrane to the hydrogen ions. The diminished potential of the electrode at pH > 5.0 can be ascribed to the formation of some manganese hydroxide species.

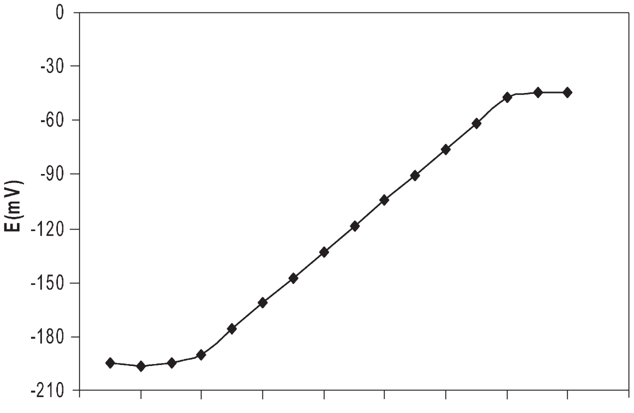

FIG. 4
Calibration curve for ion-selective electrode based on a Schiff-base ionophore at pH ~ 3.5 (see No. 5)

Response Time

For any ion-selective electrode, the response time is one of the most important factors. In this study, the practical response time of the sensor was recorded by changing the Mn^{2+} concentration in solution over a concentra-

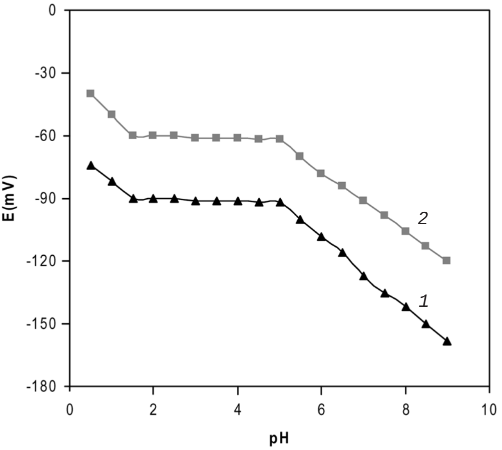

FIG. 5
Effect of pH on the response of the Mn^{2+} ion-selective electrode (composition, see No. 5) for concentrations of test solutions: 1×10^{-4} (*1*) and 1×10^{-3} (*2*) M Mn^{2+} solutions

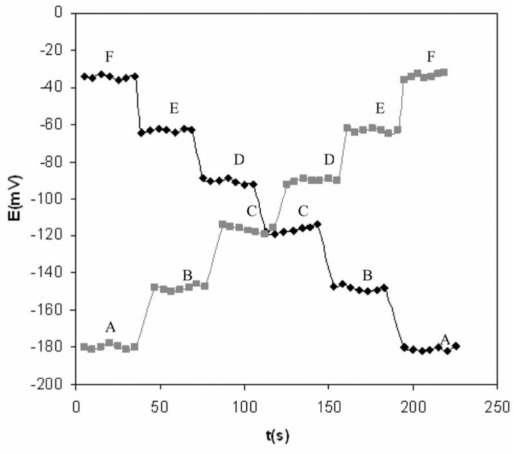

FIG. 6
Dynamic response time of the membrane electrode for step changes in Mn^{2+} concentration (increasing and decreasing): 1.0×10^{-7} (A), 1.0×10^{-6} (B), 1.0×10^{-5} (C), 1.0×10^{-4} (D), 1.0×10^{-3} (E) and 1.0×10^{-2} (F) mol l^{-1}

tion range 1.0 × 10^{-2}–1.0 × 10^{-7} mol l^{-1}. The potentials versus time curves are shown in Fig. 6. Over the whole concentration range, the plasticized membrane electrode reaches its equilibrium response in a very short time (about 10 s). This is most probably due to the fast exchange kinetics of Mn^{2+} complexation–decomplexation with the ionophore at the test solution–membrane interface. To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was used. The measurements were performed in the order of decreasing Mn^{2+} concentrations. The results showed that the potentiometric response of the sensor is reversible, although the time needed to reach the equilibrium values was longer than that for the opposite concentration order (50 s). It is well documented that, in the case of decreasing Mn^{2+} concentrations, the time needed to attain a stable potential is ca. 100 times larger than that required for the case of increasing concentrations (for a ten-fold change in the cation concentration)[27]. The lifetime of the proposed electrode was determined by performing periodic calibration (twice in a week) with standard solutions and calculating the response and slope over the range 1.1 × 10^{-7}–0.8 × 10^{-1} M Mn^{2+} solution. It was found that the electrode worked well over the period more than 45 days without showing any significant divergence in concentration ranges, slopes and response times.

Selectivity

The selectivity behavior is obviously one of the most important characteristics of an ion-selective electrode, determining whether a reliable measure-

TABLE II
Selectivity coefficient for interfering ions

Interfering ion	$-\log K^{pot}_{Mn,M}$	Interfering ion	$-\log K^{pot}_{Mn,M}$
Ag^+	2.32	Fe^{2+}	2.72
Cr^{3+}	2.51	Zn^{2+}	3.32
Ni^{2+}	2.93	Co^{2+}	3.95
Al^{3+}	3.77	Na^+	2.78
K^+	3.52	Ce^{3+}	2.42
Cu^{2+}	2.24	Pd^{2+}	2.18
Cd^{2+}	2.98	Ca^{2+}	2.34
Sn^{2+}	2.12	Hg^{2+}	2.06

ment of the target sample is possible. The potentiometric selectivity coefficients of the electrode ($K^{\mathrm{pot}}_{\mathrm{Mn,M}}$) for different cationic species were determined by an IUPAC recommended fixed interference method[28] by adding a fixed amount (fixed concentration) of interfering ions to various concentrations of manganese. The resulting selectivity coefficients are summarized in Table II. It indicates that the sensor is selective for Mn^{2+} ion in the presence of interfering ions. As can be seen for most ions the used log $K^{\mathrm{pot}}_{\mathrm{Mn,M}}$ values were of the order of 1.0×10^{-2} or smaller, indicating that they would not significantly disturb the functioning of the Mn^{2+} ion-selective electrode.

Examination of the selectivity data for the electrodes employed in this study indicates that the extent of formation of complex of ionophore and metal ion, the geometrical structure, and rigidity of ionophores are the major factors determining the selectivity. The other determining factor is the kind of plasticizer used in PVC. The result indicates that the geometry and ligating cavity of the 2,2′-bis(salicylideneamino)azobenzene is a significant factor for determining selectivity to other metals. Based on the data for electrode No. 5 in Tables I and II, the good sensitivity and highest selectivity to manganese ion are attributed to its strong complexation of manganese ion with 2,2′-bis(salicylideneamino)azobenzene which has a proper cavity for coordination of the ligand.

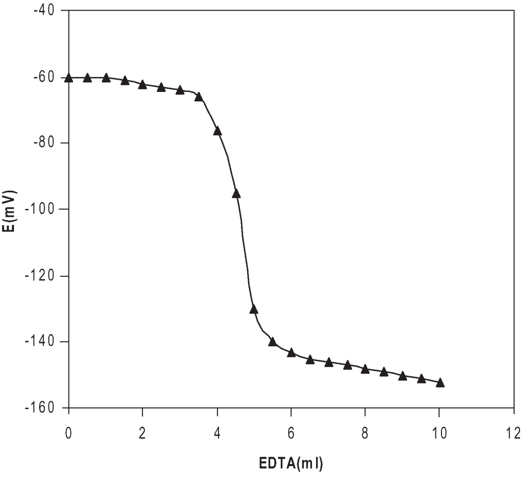

FIG. 7
Potentiometric titration for 50 ml of 1.0×10^{-3} M $Mn(NO_3)_2$ solution with 1.0×10^{-2} M EDTA using the proposed membrane electrode

Analytical Applications

In order to assess practical utility of the proposed manganese sensor, it was employed under optimum conditions. It can be used as an indicator electrode in titration of 50.0 ml of 1.0 × 10^{-3} M $Mn(NO_3)_2$ solution with 1.0 × 10^{-2} M EDTA. As can be seen from Fig. 7, the end-point on the graph (5.2 ml) corresponded to the calculated equivalent point (5.0 ml). The sensor was also successfully used in the direct determination of manganese ion in tap and river water samples. The proposed electrode showed a fair recovery of manganese ions (Table III). Furthermore, the applicability of the proposed sensor was also tested in determination of manganese in a drug (Teslascan). Teslascan is an intravenous paramagnetic contrast medium for

TABLE III
Determination of the manganese ions ($n = 5$)

Sample	Mn(II) ion added mol l^{-1}	Found mol l^{-1}	Recovery %
Tap water	0.00	0.00	–
	1.29	$(1.26 \pm 0.2) \times 10^{-4}$	98
	6.9	$(6.6 \pm 0.2) \times 10^{-3}$	96
	7.9	$(7.6 \pm 0.2) \times 10^{-3}$	96
	9.4	$(8.9 \pm 0.3) \times 10^{-3}$	95
River water (Gelerood river, Broujerd, Iran)	0.00	0.00	–
	1.03	$(1.0 \pm 0.1) \times 10^{-4}$	97
	1.18	$(1.14 \pm 0.3) \times 10^{-4}$	97
	1.28	$(1.22 \pm 0.2) \times 10^{-4}$	96
	9.3	$(9.0 \pm 0.2) \times 10^{-3}$	97

TABLE IV
Determination of manganese in a drug using the proposed electrode

Drug	Manganese, % w/w in the composition	Found by ISE % w/w	Recovery, %
Teslascan	7.25	7.15	99

MRI. The active substance of Teslascan is mangafodipir trisodium, a manganese (Mn(II)) chelate with the ligand fodipir (dipyridoxyl diphosphate or DPDP). The manganese content of drug is 7.26%. The results obtained using the proposed sensor were quantitative, precise and accurate (Table IV).

CONCLUSION

A new PVC-based membrane containing 2,2′-bis(salicylideneamino)azobenzene, sodium tetraphenylborate (NaTPB) as an anion excluder and DBP as a plasticizer, of the composition PVC/DBP/BSAAB/NaTPB 32.5:64.5:2:1%, exhibited the best performance for Mn^{2+} with a slope of 30.5 ± 0.5 mV per decade and a wide concentration range of 1.1×10^{-7}–0.8×10^{-1} mol l^{-1} at pH 1.5–5.0. The selectivity of the electrode to Mn^{2+} in the presence of other cations was good and the lifetime (stability) of the assembly was more than 45 days. This electrode is superior to the existing manganese electrodes[11–13] with regard to the linear range and detection limit (Table V). The electrode can be used to determine Mn^{2+} ions by direct potentiometry or titration. The proposed sensor was successful in determining Mn^{2+} in drugs and natural water.

TABLE V
Comparison of slope, linear and pH range of proposed electrode with previous works

Slope mV/decade	Linear range mol l^{-1}	pH-range	Ionophore	Ref.
27.9	1.25×10^{-5}–1.0×10^{-1}	3.0–8.0	Mn(II) complex of 14,16-dimethyl-1,4,7,10,13-pentaazacyclohexadeca-13,16-diene [Me_2(16)dieneN_5]	11
30.1	4.0×10^{-7}–1.8×10^{-2}	4.5–7.5		12
30.0	5.0×10^{-6}–1.0×10^{-1}	3.0–6.5	*N*,*N*′-bis[3-(salicylideneamino)ethane-1,2-diamine] (H_2L)	13
30.5	1.1×10^{-7}–0.8×10^{-1}	1.5–5.0	2,2′-(salicylideneamino)azobenzene (BSAAB)	this work

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