Binuclear Schiff Base Complex of Manganese(III) as a Neutral Carrier for a Highly Selective Iodide Electrode

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A new highly selective iodide electrode incorporating a binuclear manganese(III) complex, bis(salicylaldehyde-aminopropanol)dichloroaceticdimanganese(III) [Mn(III)₂-BSAPDCA], as a neutral carrier is described. The electrode displays an anti-Hofmeister selectivity sequence: iodide $\gg$ perchlorate $>$ salicylate $>$ thiocyanate $>$ nitrate $>$ bromide $>$ nitrite $>$ chloride $>$ sulfate. The excellent selectivity for iodide is related to a direct interaction between the central Mn(III) atom and iodide and a steric effect associated with the structure of the carrier, which is supported by UV spectroscopy and AC impedance techniques. The electrode exhibits a near-Nernstian potentiometric linear response range to iodide from 1.0×10^{-1} to 2.0×10^{-5} mol/L with a detection limit of 8.0×10^{-6} mol/L and a slope of -60.3 mV/decade in pH 3.0 of phosphate buffer solutions at 20°C. From a comparison of the potentiometric response characteristics between a binuclear manganese(III) complex, Mn(III)₂-BSAPDCA, and a mononuclear manganese(III) complex, Mn(III)-BSAPB, an enhanced response towards iodide from a binuclear metallic complex-based electrode was observed. The electrode, based on binuclear manganese(III) complex, was successfully applied to the determination of inorganic total iodine in iodized table salt with satisfactory results.

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Introduction

Carrier-based ion-selective electrodes perform simple procedures, with a fast response, high selectivity and sensitivity, wide linear range and low cost, and can be widely applied to direct and rapid detection in chemical, clinical and environmental analyses.¹

Traditional liquid-membrane electrodes for anions based on ion exchangers, such as lipophilic quaternary ammonium or phosphonium salts, always display the classical Hofmeister selectivity sequence: perchlorate $>$ thiocyanate $>$ iodide $\approx$ salicylate $>$ nitrate $>$ bromide $>$ nitrite $>$ chloride $>$ sulfate, in which the membrane selectivity is mainly dominated by the free energy of hydration of the ions involved.^{2,3} It is difficult to prepare useful electrodes for anions behind perchlorate in the Hofmeister selectivity sequence. Thus, research on anti-Hofmeister sensing materials with high selectivity for given anions is an expeditiously expanding domain in chemical sensors. Recently, electrodes using plasticized poly(vinyl chloride) (PVC) membranes incorporating derivatives of vitamin B₁₂, organotin species, metalloporphyrins, metallophthalocyanines and other transitional metal complexes demonstrated potentiometric anion selectivity sequences that were remarkably different from the Hofmeister pattern; the mechanism of these deviations was involved in a specific interaction between the central metal and the analyte anion.⁴⁻¹² Most of these electrodes exhibited priority of response to thiocyanate, salicylate and nitrite, respectively.⁴⁻¹²

The determination of iodide in food, medicine and

environment samples is very important, because iodine is an indispensable microelement to humans. Recent studies in our laboratory showed that solvent polymeric membrane electrodes incorporating some Schiff-base complexes of cobalt(II) as carriers exhibited high selectivity for iodide.¹³⁻¹⁶ However, Schiff-base complexes of cobalt(II) can reversibly coordinate oxygen, and as ionophores they will be influenced by oxygen in air.¹³⁻¹⁹ Because Schiff-base complexes of manganese(III) are more stable than Schiff-base complexes of cobalt(II), an electrode incorporating a Schiff-base complex of manganese(III) with a substantial improvement in good stability, long lifetime, oxygen independence and high selectivity towards iodide is of considerable interest.

On the other hand, many of the electrodes were based on mononuclear metallic complexes as carriers.⁴⁻¹⁶ An enhanced response towards the analyte anion from a binuclear metallic complex-based electrode was observed, showing that binuclear metallic complexes may become a new promising class of carriers for anion electrodes.²⁰⁻²²

In this paper, a binuclear Schiff-base complex of manganese(III) bis(salicylaldehydeaminopropanol)dichloroaceticdimanganese(III) [Mn(III)₂-BSAPDCA] (Fig. 1(a)) synthesized in our laboratory was incorporated into a plasticized PVC membrane with 2-nitrophenyl octyl ether (*o*-NPOE) as a plasticizer to prepare a highly selective iodide electrode. A comparison of the potentiometric response characteristics between the binuclear and mononuclear manganese(III) complexes was made, exhibiting that the electrode based on a binuclear manganese(III) complex, Mn(III)₂-BSAPDCA, demonstrated a highly selective response to iodide with a wider linear range and lower detection limit.

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Fig. 1 Structures of $\text{Mn(III)}_2\text{-BSAPDCA}$ (a) and Mn(III)-BSAPB (b).

Experimental

Apparatus

All potentiometric and pH measurements were made with a pH meter (MP 230, Mettler-Toledo, Switzerland) and a digital ion analyzer (Model PHS-3C, Dazhong Instruments, Shanghai, China). The cells used for mV measurements were of the following type: $\text{Hg, Hg}_2\text{Cl}_2$; KCl (satd.), sample solution; membrane, 0.1 mol/L KCl ; AgCl, Ag . Organometallic complexes synthesized were characterized by elemental analysis with a C-H-N-O-S-Rapid Elemental Analyzer (D-6450, Heracus, Germany). UV absorption spectra were obtained on a UV/VIS spectrophotometer (Lambda 17, Perkin-Elmer, USA). The AC impedance of the electrode membrane was recorded with an impedance-measurement unit (IM6e, ZAHNER Elektrik, Germany) equipped with THALES software 6.88.

Reagents and chemicals

Bis(salicylaldehydeaminopropanol)dichloroaceticdimanganese(III) [$\text{Mn(III)}_2\text{-BSAPDCA}$] and bis(salicylaldehydeaminopropanol)bromomanganese(III) [Mn(III)-BSAPB] (Fig. 1(b)) were prepared as described in a reference.²³ A plasticizer, 2-nitrophenyl octyl ether (*o*-NPOE), was synthesized as described by Horning.²⁴ Poly(vinyl chloride) (PVC) powder of chromatographic grade was supplied by Shanghai Chemical Co. (Shanghai, China). All other chemicals used were of analytical-reagent grade, and water used throughout was purified by a double distillation and deionization system. The solutions were buffered with 0.01 mol/L H_3PO_4 and adjusted to pH 3.0 with a concentrated NaOH solution.

Sensor construction

The membrane composition was optimized by using an orthogonal experimental design with the electrode linear response range for iodide as the object function for optimization. The optimum composition found was 2.5% (w/w) in ionophore, 31% (w/w) in PVC and 66.5% (w/w) in *o*-NPOE. The PVC membrane electrodes were fabricated from various carriers and assembled according to Thomas and his coworkers.^{25,26}

UV absorption spectra

The UV absorption spectra of the $\text{Mn(III)}_2\text{-BSAPDCA}$

Fig. 2 Potentiometric response curves of electrodes doped with $\text{Mn(III)}_2\text{-BSAPDCA}$ (●) and Mn(III)-BSAPB (▲) in 0.01 mol/L phosphate-buffered solutions, pH 3.0.

chloroform solutions were recorded after shaking them with aqueous 0.1 mol/L KI (pH 3.0) and a blank buffer solution for 30 min, respectively.

AC impedance

The AC impedance of the electrode membrane containing $\text{Mn(III)}_2\text{-BSAPDCA}$ was recorded. The working electrode was a Ag/AgCl foil with a 0.5-cm^2 area. A saturated calomel electrode (SCE) and a Pt foil with 0.5-cm^2 area were used as a reference electrode and a counter electrode, respectively. The frequency region used was 10^{-2} – 10^6 Hz and the AC amplitude was 50 mV (20°C).

Results and Discussion

Potentiometric response characteristics of electrodes

The potentiometric response characteristics of electrodes containing different carriers toward iodide are shown in Fig. 2. An electrode incorporating a binuclear manganese(III) complex, $\text{Mn(III)}_2\text{-BSAPDCA}$, exhibited a near-Nernstian potentiometric linear response range to iodide from 1.0×10^{-1} to 2.0×10^{-5} mol/L with a detection limit of 8.0×10^{-6} mol/L and a slope of -60.3 mV/decade in pH 3.0 of phosphate buffer solutions at 20°C . The time required for the electrode to reach 95% response was less than 30 s. The DC resistance of the electrode membrane was $940\text{ k}\Omega$ ($n = 6$). The standard deviation of the electrode potential readings over a period of 10 h in 0.01 mol/L phosphate-buffered solution (pH 3.0) containing 1.0×10^{-3} mol/L KI was 0.51 mV ($n = 36$), and the potential readings for the electrode dipped alternately into stirred solutions of 1.0×10^{-3} and 1.0×10^{-4} mol/L KI showed a standard deviation of 0.74 mV over 2 h ($n = 6$). The electrode could be used continuously for more than 2 months, and did not show any detectable loss of its performance characteristics. The potentiometric response characteristics of an electrode incorporating a mononuclear manganese(III) complex, Mn(III)-BSAPB , are rather poor (Fig. 2). An electrode incorporating Mn(III)-BSAPB showed a relatively narrow response linear range, high detection limit, and low response slope.

pH effect on the electrode response

Figure 3 illustrates the influence of the pH on the potentiometric response characteristics of an electrode doped with $\text{Mn(III)}_2\text{-BSAPDCA}$ toward iodide. The linear-response range and the slope deteriorating with increasing solution pH can be explained by coordination competition between I^- and OH^- , and increasing competition of OH^- at higher pH values. A similar effect of the pH on the potentiometric response for electrodes based on porphyrin and vitamin B_{12} derivatives was observed previously.^{27,28}

Selectivity

The potentiometric selectivity coefficients, $\log K_{\text{I}^+}^{\text{pot}}$ of the electrodes containing $\text{Mn(III)}_2\text{-BSAPDCA}$ and Mn(III)-BSAPB were determined by a separate solution method and compared with that of an electrode containing a quaternary ammonium salt, hexadecyltriethylammonium iodide (HTOAI)¹³ (Table 1). The electrode containing $\text{Mn(III)}_2\text{-BSAPDCA}$ exhibited excellent selectivity to iodide, and displayed an anti-Hofmeister selectivity sequence: iodide $\gg$ perchlorate $>$ salicylate $>$ thiocyanate $>$ nitrate $>$ bromide $>$ nitrite $>$ chloride $>$ sulfate. An electrode incorporating a mononuclear manganese(III)

complex, Mn(III)-BSAPB , showed poor selectivity to iodide.

Mechanism to iodide response

That PVC membrane electrodes incorporating some organometallic compounds as carriers exhibited an anti-Hofmeister selective behavior was mainly based on the geometric configuration of the carrier and a specific interaction between the central metal in an organometallic compound and the analyte anion, rather than the lipophilicity of the anion or a simple electrostatic interaction with the anion.²⁸ An electrode doped with $\text{Mn(III)}_2\text{-BSAPDCA}$ exhibited excellent potentiometric selectivity for iodide, which is mainly related to a direct interaction between the central Mn(III) atom and iodide and a steric effect associated with the structure of the carrier. In the complex $\text{Mn(III)}_2\text{-BSAPDCA}$, the Mn(III) atom is six-coordinated and the coordination sphere can be described as a distorted octahedron, due to the Jahn-Teller effect.²³ The elongated Mn-O bonds in the axial direction are longer and weaker than the Mn-O and Mn-N bonds in the equatorial plane. On the other hand, the chelation strength of the carbonyl group is relatively weak in solution, and the coordinate carbonyl group in $\text{Mn(III)}_2\text{-BSAPDCA}$ may be replaced by I^- in the solution reversely. This agrees with the results obtained by Gopinathan²⁹ and Li.³⁰ Therefore, the response mechanism of an electrode doped with $\text{Mn(III)}_2\text{-BSAPDCA}$ is suggested to involve the central Mn(III) atom serving as a coordinate site for iodide, and the coordinate replacement may take place in the axial direction (Fig. 4). Compared with the mononuclear manganese(III) complex, Mn(III)-BSAPB , the response towards iodide from a binuclear manganese(III) complex, $\text{Mn(III)}_2\text{-BSAPDCA}$, based electrode is enhanced, which can be explained as follows: on the one hand, the binuclear complex possesses a higher lipophilicity ($\log P = 2.74$) than mononuclear complex ($\log P = 2.01$), which is favorable to increase the solubility of the carrier in the membrane; on the other hand, because $\text{Mn(III)}_2\text{-BSAPDCA}$ has two central metals, the chance of an interaction towards iodide from the central metal Mn(III) is improved. The coordination numbers and association constants of the axial coordination reaction of complexes $\text{Mn(III)}_2\text{-BSAPDCA}$ and Mn(III)-BSAPB towards iodide were measured by means of a spectra technique.³¹ The coordination numbers for $\text{Mn(III)}_2\text{-BSAPDCA}$ and Mn(III)-BSAPB were all 1. The association constant $\ln K^0$ of iodide to $\text{Mn(III)}_2\text{-BSAPDCA}$ was 12.75, and

Fig. 3 Potentiometric response curves of an electrode doped with $\text{Mn(III)}_2\text{-BSAPDCA}$ at different pH values of 0.01 mol/L phosphate-buffered solutions: (●) pH 3.0, (▲) pH 4.0 and (■) pH 6.0.

Fig. 4 Suggested coordination scheme of $\text{Mn(III)}_2\text{-BSAPDCA}$ with iodide.

Table 1 Selectivity coefficients, $\log K_{\text{I}^+}^{\text{pot}}$, for electrodes incorporating $\text{Mn(III)}_2\text{-BSAPDCA}$, Mn(III)-BSAPB and HTOAI, respectively

Carrier	Interfering ion								
	I^-	ClO_4^-	Sal^-	SCN^-	NO_3^-	Br^-	NO_2^-	Cl^-	SO_4^{2-}
$\text{Mn(III)}_2\text{-BSAPDCA}$	0	-1.9	-2.1	-2.2	-3.5	-3.7	-3.8	-4.1	-4.6
Mn(III)-BSAPB	0	-1.5	-1.1	-2.5	-3.2	-3.4	-3.0	-3.3	-4.3
HTOAI	0	1.9	0	0.5	-1.4	-2.0	-2.8	-3.1	-4.2

a. Selectivity coefficients obtained in 0.01 mol/L phosphate-buffered solutions (pH 3.0).

Fig. 5 UV absorption spectra of chloroform solutions of $\text{Mn(III)}_2\text{-BSAPDCA}$ (-----) and $\text{Mn(III)}_2\text{-BSAPDCA}$ treated with 0.1 mol/L KI (—).

Fig. 6 UV absorption spectra of chloroform solutions of $\text{Mn(III)}_2\text{-BSAPDCA}$ (-----) and $\text{Mn(III)}_2\text{-BSAPDCA}$ treated with 0.1 mol/L KClO_4 (—).

that to Mn(III)-BSAPB was 9.23. The experimental result that the association constant of iodide to $\text{Mn(III)}_2\text{-BSAPDCA}$ was higher than that of Mn(III)-BSAPB confirmed the enhanced selectivity of $\text{Mn(III)}_2\text{-BSAPDCA}$. Binuclear metallic complexes are promising as a new class of carrier for anion electrodes.²⁰⁻²²

In order to investigate the mechanism to the iodide response, UV absorption spectra and AC impedance were obtained. The UV absorption spectra of $\text{Mn(III)}_2\text{-BSAPDCA}$ in CHCl_3 (Fig. 5) confirm the interaction between the carrier and iodide. The peak showing a considerable red shift of about 12 nm and a substantial increase in absorbance between shaking the $\text{Mn(III)}_2\text{-BSAPDCA}$ chloroform solutions with aqueous 0.1 mol/L KI (pH 3.0) and a blank buffer solution for 30 min, respectively, suggests that the coordination between the carrier and iodide has taken place. At the same time, the effect of ClO_4^- (0.1 mol/L) on the UV absorption spectra of a $\text{Mn(III)}_2\text{-BSAPDCA}$ chloroform solution was also investigated, and no detectable change in the corresponding UV absorption spectra was observed (Fig. 6); similar spectra were also obtained when adding other anion solutions instead of a ClO_4^- solution. On the other hand, the iodide concentration decreased after the solvent extraction of iodide into a $\text{Mn(III)}_2\text{-BSAPDCA}$ chloroform solution, and the percentage of extraction was 62.07%. The other anion concentration had almost no detectable decrease. All of these observations seem to support the hypothesis that the excellent potentiometric selectivity for iodide of the electrode is correlated with the unique coordination of iodide to the $\text{Mn(III)}_2\text{-BSAPDCA}$.

Figure 7 illustrates the AC impedance of an electrode membrane incorporating $\text{Mn(III)}_2\text{-BSAPDCA}$ conditioned in

Fig. 7 Impedance plots of a PVC membrane containing $\text{Mn(III)}_2\text{-BSAPDCA}$ (frequency, 10^{-2} – 10^6 Hz; AC amplitude, 50 mV; temperature, 20°C).

Fig. 8 Bulk resistance of an electrode membrane containing $\text{Mn(III)}_2\text{-BSAPDCA}$ conditioned in 1.0×10^{-2} mol/L KI (pH 3.0) with different times.

pH 3.0 phosphate buffer solution containing different concentration of KI for 4 h. Perfect semicircle bulk impedance at high frequencies and Warburg impedance at low frequencies were observed. The bulk resistance of an electrode membrane containing $\text{Mn(III)}_2\text{-BSAPDCA}$ conditioned in 1.0×10^{-2} mol/L KI (pH 3.0) with different times is shown in Fig. 8. The bulk resistance decreased with an increase in time. When the time was more than 4 h, the decrease became very slow and the bulk resistance approached a plateau; 4 h was chosen as an appropriate time to be used for conditioning the electrode membrane in the AC impedance experiment. As can be seen in Fig. 7, when the concentration of KI was 1.0×10^{-4} , 1.0×10^{-3} , and 1.0×10^{-2} mol/L, respectively, the corresponding bulk impedance of the membrane was 0.107, 0.094, and 0.083 MΩ. The bulk resistance of the membrane incorporating $\text{Mn(III)}_2\text{-BSAPDCA}$ decreased with increasing KI concentration, whereas that of carrier-free membrane remained almost constant. This phenomenon was related to the transfer of I^- across the solvent membrane, resulting from the interaction between I^- and $\text{Mn(III)}_2\text{-BSAPDCA}$. The Warburg impedance at low frequencies indicated that the transfer process of I^- across the solvent membrane was diffusion-controlled.^{32,33}

Preliminary application

An electrode incorporating $\text{Mn(III)}_2\text{-BSAPDCA}$ was successfully applied to the determination of inorganic total iodine in iodized table salt. Iodate in the salt sample was reduced by arsenious acid(III) in an acidic medium to produce iodide, and was analyzed by a calibration-curve method with a $\text{Mn(III)}_2\text{-BSAPDCA}$ based electrode. The inorganic total iodine obtained was 32.95×10^{-4} (w/w) ($n = 5$), which was in fair

agreement with the result given by the titration method (33.27×10^{-4} (w/w) ($n = 5$)).³⁴

Conclusion

In this paper, we have described a new highly selective iodide electrode incorporating a binuclear manganese(III) complex, bis(salicylaldehydeaminopropanol)dichloroacetic-dimanganese(III) ($\text{Mn(III)}_2\text{-BSAPDCA}$), as a neutral carrier. This electrode exhibits a variety of good performance characteristics, including easy preparation and procedures, high selectivity and sensitivity, good stability and reproducibility, fast response and low cost. The electrode can be applied to the determination of iodide in actual samples.

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