Improved Thiocyanate-Selective Electrode Based on Tetra(trimethylphenyl)-porphyrinato Manganese(III) Chloride: The Electronic and pH Effects

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The thiocyanate-selective PVC membrane electrodes based on 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)-porphyrinatomanganese(III) chloride [Mn(TMP)Cl] and 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinato-manganese(III) chloride [Mn(Cl$_8$TPP)Cl] as ion carriers were investigated. The effect of ionophores, membrane compositions, plasticizers, and solution pHs on the response characteristics were studied. The Mn(TMP)Cl as an ionophore shows the best potentiometric sensitivity with a slope of -58.7 mV/decade and a detection limit of log[SCN⁻] = -6.90, and selectivity for thiocyanate over strong hydrophobic interfering anions such as ClO$_4$⁻ and salicylate. The potentiometric response is affected by the electronic effect of the substituents and solution pHs. The presence of substituents with electron donating and more liphophilic characters around the ligated metal center produces an improved response toward SCN⁻.

Key Words : Ion-selective electrodes, Manganese porphyrins, Potentiometric determination, Polymeric membrane, Thiocyanate ion

Introduction

Ion-selective electrodes (ISEs) as potentiometric sensors are considered as useful analytical devices, and provide some benefits such as portable, rapid, inexpensive, and simple method for the determination of ionic species. The selective detection of many anions has a critical drawback such as the classical Hofmeister series that is correlated with a preference for hydrophobic anions. Therefore, the need for ionophores with improved selectivities and sensitivities in the field of anion-selective electrodes is increased. A very interesting development in the field of ion-selective electrodes (ISEs) is the preparation of electrodes that can chemically recognize specific anions and offer potentiometric responses that differ from the conventional anion-exchanger-based membranes. One of new carriers with anti-Hofmeister that can be used in the development of potentiometrically chemical sensors should be metalligand interactions. Metalloporphyrins,[1-5] metallophthalocyanines,[6] cyclometallic amines,[7] Schiff base complexes.[8-13] and N$_4$-metal complexes[14-17] have been observed to show such specific metalligand interactions. ISEs based on these metalligand interactions have been reported for the determination of thiocyanate anion, and they showed the deviation from the classical Hofmeister series. Among them, metalloporphyrins have been interested owing to their ion-discriminating ability, the diversity of their structures, and the selective axial ligation between the central metal and primary anion.[18-20] It was well known that the substitution at *meso*- or pyrrole-positions of porphyrins was found to cause a change of redox potential and solubility in solvent media.[21-22] It was reported that the potentiometric response of thiocyanate-selective electrodes was affected by the structure of manganese porphyrins and the lipophilic sites of additive.[23-24] In the present study, we want to report the improved potentiometric properties

towards thiocyanate anion for the polymeric electrode based on manganese(III) tetra(trimethylphenyl)porphyrin chloride [Mn(TMP)Cl] due to the electronic effect of substituent at *meso*-position of porphyrin ring. PVC polymeric membranes based on Mn(TMP)Cl and Mn(Cl$_8$TPP)Cl were characterized for the selective determination of thiocyanate anion.

Experimental Section

Reagents. Mn(TMP)Cl (**I**) and Mn(Cl$_8$TPP)Cl (**II**) tested as thiocyanate ionophores are shown in Figure 1. They were synthesized and purified according to the literatures[25,26] in our laboratory. High molecular weight PVC, dioctyl sebacate (DOS), dioctyl phthalate (DOP), dioctyl adipate (DOA), 2-nitrophenyl octyl ether (*o*-NPOE), tridodecylmethylammonium chloride (TDDMACl), and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare PVC membrane electrodes. Analytical grade sodium and potassium salts of tested anions were used. All other chemicals used were analytical grade. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions. The solutions were adjusted to the given pH using 0.05 M H$_3$PO$_4$-NaOH buffer.

Preparation of polymeric thiocyanate-selective electrodes. Membrane solutions were prepared by dissolving varying amounts of the manganese porphyrins, together with appropriate amounts of plasticizers, and PVC in about 1 mL of THF and mechanically stirred. TDDMACl as membrane additive was also incorporated in some of the membranes. Several blank membranes were also prepared by incorporating the additive into plasticized PVC in the absence of the porphyrins. The typical compositions of PVC-based thiocyanate-selective electrodes were summarized in Table 1. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes.
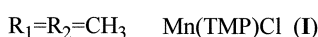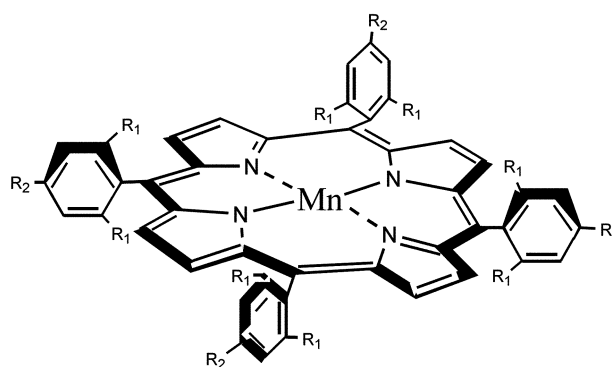
$R_1 = R_2 = CH_3$ Mn(TMP)Cl **(I)**

$R_1 = Cl$ $R_2 = H$ Mn(Cl$_8$TPP)Cl **(II)**

Figure 1. Macromolecular structures of substituted manganese(III) porphyrins (**I** and **II**) used in this study.

Solvent from PVC membrane was allowed to evaporate for a day at room temperature. The thickness of the polymeric membrane was about 0.3 mm.

Potentiometric measurements. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl was used as an internal filling solution. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-02). The potentiometric responses of the thiocyanate-selective electrodes were measured in the conventional configuration. The electrodes were equilibrated for 24 h in 0.01 M potassium thiocyanate solution. The potential measurements were carried out at 25 ± 1 °C with Kosentech 16-channel potentiometer (KST101-1) coupled to a computer by setting up the following cell assembly:

Ag/AgCl, KCl (sat'd) | sample solution PVC membrane.

The dynamic response curves were produced by adding standard solutions of anions to magnetically stirred buffer solution. The pH of sample solutions was monitored simultaneously with a conventional glass pH electrode. Calibration curves were constructed by plotting the potential (EMF) versus logarithm of the concentration of thiocyanate at constant pH.

The selectivity coefficients ($\log K^{pot}_{SCN^-, j}$) were determined by separate solution method (SSM) using salts of the anions involved. The slope was obtained by plotting the calibration curve in the concentration range of 10^{-6} to 10^{-1} M. Activity coefficients were assumed to be constant for all of the primary ions, and no correction was made for slight changes in the liquid junction potential of the reference electrode. At least three-time measurements were performed, and the data were determined from the plot. Before each set of measurements, the electrodes were soaked in doubly distilled water.

Results and Discussion

The potentiometric response. Among metalloporphyrins, the derivatives of manganese porphyrin as an ionophores

exhibit high thiocyanate sensitivity and selectivity in the polymeric membranes. Manganese porphyrins having strong electron donating groups at *meso*-positions of porphyrin shift to cathodic direction in redox potentials. An effect of PVC membrane composition on the potentiometric response and selectivity of the ionophore-based membranes were extensively studied. The composition of these membranes is presented in Table 1. Typical results for the thiocyanate selective electrodes m-1 and m-8 based on Mn(TMP)Cl and Mn(Cl$_8$TPP)Cl as ionophores, respectively, are shown in Figure 2. The potentiometric results for SCN⁻ anion were summarized in Tables 1 and 2. The polymeric membrane based on Mn(TMP)Cl exhibits a linear stable response over a concentration range (1.5×10^{-7}-1.0×10^{-1} M) with a slope of 58.7 mV/decade and a detection limit of log[SCN⁻] = -6.90, and this Nernstian is for a monovalent anion response. When compared with Mn(TMP)Cl having an electron donating groups, the membrane based on Mn(Cl$_8$TPP)Cl that has an electron withdrawing groups shows a slightly higher detection limit of log[SCN⁻] = -6.61. This result agrees with the previous literature that reported a detection

Table 1. The membrane compositions for thiocyanate-selective electrodes

Membrane	Ionophore (mg)	PVC^a	DOP^a	DOS^a	o-NPOE^a	DOA^a	TDD-MACl^b
m-1	I(1)	33	66				
m-2	I(3)	33	66				
m-3	I(5)	33	66				
m-4	I(1)	33		66			
m-5	I(1)	33			66		
m-6	I(1)	33				66	
m-7	I(1)	33	66				50
m-8	II(1)	33	66				
m-9	II(1)	33		66			
m-10	II(1)	33			66		
m-11	II(1)	33				66	

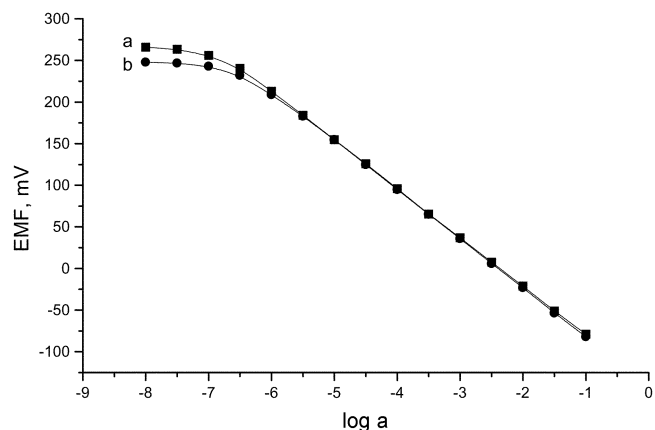^{a}In mg. ^{b}mol% relative to the ionophore.

Figure 2. The potentiometric responses of the membranes (a) m-1 of ionophore **I** and (b) m-8 of ionophore **II** towards thiocyanate anion in pH 3.0 buffer solutions.
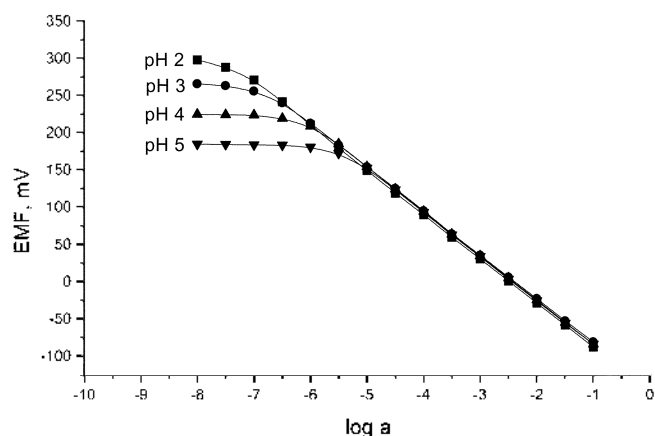
Figure 3. The thiocyanate responses of the membrane m-1 of ionophore I in different pH buffer solutions.

Figure 4. The thiocyanate responses as a function of the capacity of ionophore I in pH 3.0 buffer solutions. (a) 1 mg. (b) 3 mg. (c) 5 mg.

limit of $log[SCN^-] = -6.49$ for the membrane based on (octabromotetraphenylporphyrinato)manganese(III) chloride indicating an electron withdrawing effect [4].

Because the polymeric membranes based on transition metal complexes as ionophores can show significant pH sensitivity, the potentiometric responses of the membranes were measured at different pH solutions with the concentrations of target thiocyanate anion. Figure 3 shows the pH dependence of potentiometric responses of PVC membrane electrode (m-1) prepared from Mn(TMP)Cl with DOP as a plasticizer. As it can be seen in Figure 3, the response of the membrane is hardly affected by pH changes in the high concentrations above 10^{-5} M thiocyanate, but depends on the solution pHs in the low concentrations below 10^{-6} M thiocyanate. In order to convince these results, the separate experiments were carried out. When pH dependence of potentiometric response for the membrane (m-1) was measured in 10^{-3} M thiocyanate solution between pH 2 and 10, the membrane potentials were constant with the solution pHs employed. Similar results were obtained from the membranes based on other compositions. However, the membrane potentials were decreased with the increase of the solution pHs in 10^{-7} M thiocyanate solution. These results indicate that the metal center of manganese porphyrins is crucial for the pH dependence of the membranes. OH⁻ and SCN⁻ ions can coordinate competitively to the axial position of the metal center. The potentiometric response in the region of low concentrations of SCN⁻ ion is reduced due to the interference of OH⁻ at high pHs which exist higher concentration of OH⁻, but it in the region of high concentrations of SCN⁻ ion is hardly affected by OH⁻. Therefore, a pH of 3 was chosen for further experiments in order to minimize the effect of OH⁻ and to consider solution acidity.

The capacity of ionophore contained in the membranes is optimized by preparing membranes with 66 mg DOP, 33 mg PVC, and differing capacities of the ionophore I, ranging from 0.0 to 5.0 mg. Several thiocyanate calibrations are performed using each membrane. The thiocyanate responses as a function of the capacity of ionophore in 0.05 M H_3PO_4-
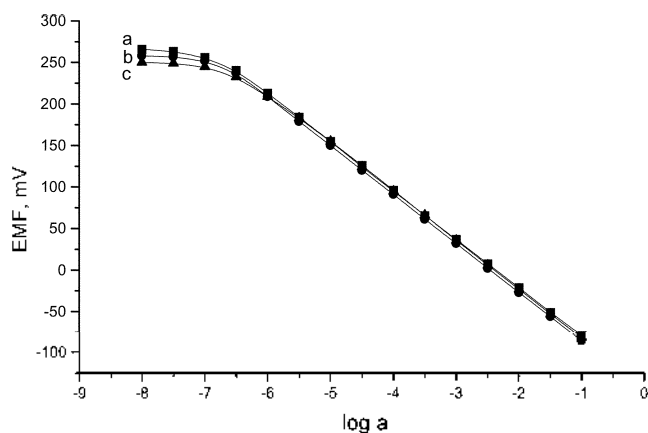
NaOH of pH 3.0 buffer solutions are shown in Figure 4. Based on the detection limit and the slope, the optimal capacity of ionophore Mn(TMP)Cl is 1 mg in the PVC membrane. Above 1 mg the responses of the ISE in terms of detection limit of the calibration curve fall off a little. This result is different with one obtained from coated-graphite electrodes using manganese porphyrins,[2] and indicates that the polymeric membranes are more effective than coated electrodes in small quantity of ionophore. Therefore, membranes with 1% ionophore were used for all experiments.

The effect of plasticizers used was investigated in PVC polymeric membranes containing 1 mg ionophore Mn(TMP)Cl, 33 mg PVC, and 66 mg plasticizers. Figure 5 illustrates the thiocyanate calibration curves for their electrodes in 0.05 M H_3PO_4-NaOH buffer solutions of pH 3.0. Membranes fabricated by DOP showed the best detection limit, the best linear range, and most Nernstian slopes for SCN⁻ anion. DOP was chosen as a proper plasticizer in the SCN⁻-ISE membranes.

The effect of the lipophilic cationic additive (TDDMACl) on the response characteristics of the membranes was investigated by incorporation of 50 and 100 mol% of this
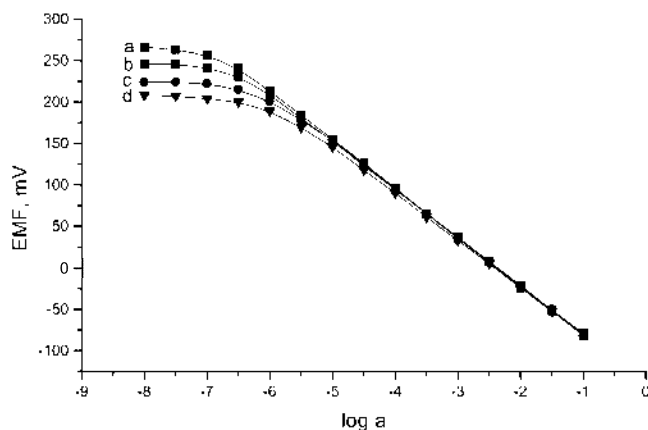
Figure 5. The thiocyanate responses of the membranes prepared from different plasticizer with ionophore I in pH 3 buffer solutions. (a) DOP. (b) DOS. (c) DOA. (d) o-NPOE.

compound into the membranes. When the additive was contained in the membrane, the slope of the calibration plots was Nernstian value, but the linear ranges were decreased. This additive significantly affected the selectivity of the electrodes as will be discussed in the next section.

An optimum equilibration time was investigated by conditioning membrane electrodes in 10^{-2} M thiocyanate solutions for periods of 12, 24, and 48 h. The optimum time was found to be 24 h for obtaining stable potentials in contact with thiocyanate solution. A response time was tested by measuring the time required to get a steady state potential ($\pm$ 1 mV) after successive additions of thiocyanate ion. The static response times of different electrodes were below 5 seconds, and these novel prepared electrodes do not display any hysteretic effects. The reproducibility and stability of the electrodes were tested by repeated calibrations over periods of 3 months. Repeated monitoring of potentials and calibration, using the same electrode of m-1, gave good slope reproducibility. After 3 months, the electrode was responding at 97% of the initial response. The prolong lifetime of the membrane as the thiocyanate ISE is due to the relatively higher lipophilicity of Mn(TMP)Cl.

Selectivity of the electrodes. The most important characteristic of any ion-sensitive electrode is its relative response for the primary ion over interfering ions present in solution, which is expressed in terms of potentiometric selectivity coefficients. It is interesting to compare the potentiometric selectivity of the membranes containing different ionophores, plasticizers, and additive. Typical results of the logarithmic selectivity coefficients, log $K_{SCN^-,j}$, obtained from the electrode responses of various membranes are given in Table 2. The thiocyanate responses of the membrane to ten interfering anions were tested under the determined optimal conditions. Using an electrode based on a quaternary ammonium salt (TDDMACl), the potentiometric response follows the Hofmeister series, $ClO_4^- >$ $SCN^- >$ salicylate $> I^- > NO_3^- > Br^- \sim N_3^- > NO_3^- > NO_2^- >$ $Cl^- > CH_3COO^- > SO_4^{2-}$. Among the membranes tested, the membrane (m-1) of ionophore I gives the good selectivity. The selectivity series of the membrane containing ionophore I gives the follow as $SCN^- >$ salicylate $> I^- > ClO_4^- > NO_2^- \sim$ $CH_3COO^- \sim HCO_3^- \sim N_3^- > NO_3^- \sim Br^- \sim Cl^-$, and this

series is totally different with Hofmeister series. This ionophore-based ISE exhibited excellent selectivity for SCN^- anion over every anion tested. The membranes containing TDDMACl as an additive, clearly show more tendency for the highly lipophilic anions such as ClO_4^- and salicylate. In fact, the electrode containing TDDMACl/ ionophore is more selective to ClO_4^- than thiocyanate. Such behavior was observed for all ionophores studied in this work. This is consistent with the reports on the use of quaternary ammonium salts for the development of perchlorate-selective electrodes. Since the response of the classical ion-exchangers is based on the lipophilicity of anions, these electrodes are essentially nonselective.

The response of manganese porphyrins toward the primary anion is related to the ligation to the metal center, and manganese porphyrins act as an ionophore of SCN^- in the membranes. Above results suggest that the ligation ability of SCN^- to the metal center is larger than any interfering anions. The sensitivity and selectivity towards SCN^- for the membranes are affected by the electronic effect of ionophores, and ionophore I having electron donating groups provides the stronger response to SCN^- rather than ionophore II and (octabromotetraphenylporphyrinato)-manganese(III) chloride having electron withdrawing groups [4]. Figure 6 also shows a trace for the response to 100 mL.
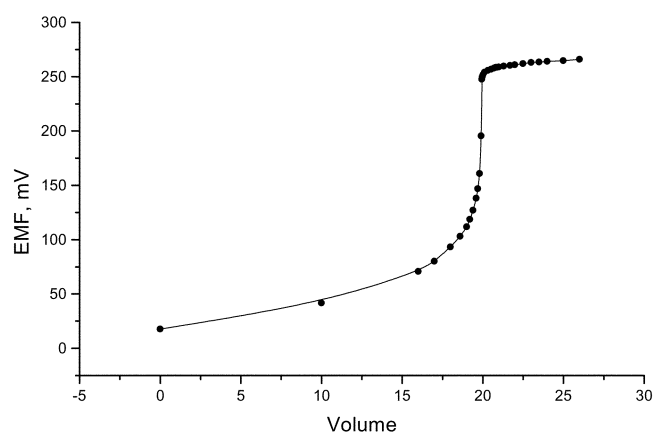

Figure 6. The potentiometric titration curve for 100 mL of 1.0×10^{-3} M NaSCN with 5.0×10^{-3} M silver nitrate in pH 3 buffer solution.

Table 2. Electrochemical properties of PVC-based thiocyanate-selective electrodes

Membrane	Slope (mV/dec.)	Detection limit (log|SCN⁻|)	log$K_{SCN^-,j}^{pot}$									
			ClO_4^-	Sal^-	I^-	NO_3^-	NO_2^-	Cl^-	Br^-	N_3^-	HCO_3^-	CH_3COO^-
m-1	-58.7	-6.90	-3.3	-2.0	-2.4	-4.5	-3.7	-4.7	-4.5	-3.8	-3.8	-3.7
m-2	-58.9	-6.84	-2.0	-1.6	-1.4	-3.4	-3.5	-3.4	-2.7	-3.5	-3.8	-3.5
m-3	-58.0	-6.70	-2.6	-1.8	-1.5	-4.0	-3.3	-3.3	-2.6	-3.5	-3.7	-3.7
m-4	-57.9	-6.25	-2.7	-1.7	-1.5	-3.3	-3.1	-3.2	-2.5	-3.3	-3.7	-3.7
m-6	-58.5	-6.60	-2.4	-1.7	-1.6	-3.2	-3.1	-3.1	-2.8	-3.5	-3.8	-3.7
m-7	-58.0	-6.23	0.3	-0.3	-1.5	-2.2	-2.3	-2.2	-2.7	-3.3	-3.8	-3.6
m-8	-58.7	-6.61	-3.2	-1.5	-1.7	-4.3	-3.6	-3.6	-2.7	-3.7	-3.8	-3.7
m-9	-55.7	-5.30	-3.0	-1.4	-1.1	-3.1	-3.2	-3.0	-2.1	-3.5	-3.7	-3.8
m-11	-54.3	-5.29	-3.2	-1.5	-1.0	-3.4	-3.2	-3.0	-2.3	-3.4	-3.8	-3.8

solution of the 1.0×10^{-3} M NaSCN by the titration with 5.0×10^{-3} M AgNO$_3$ solution. The response through the titration indicates that the amount of SCN$^-$ ion in solution can be accurately determined from the resulting neat titration curve providing a good end point.

Conclusions

The widest linear dynamic range and lowest limit of detection were observed for their electrodes in the absence of any additive, but the addition of additive to the membrane made the deterioration. The substituents on the porphyrin structure were found to cause a significant effect on the sensitivities and selectivities for thiocyanate over several intefering anions. The best results were obtained from the membrane electrodes incorporating Mn(TMP)Cl as a ionophore in the absence of additive. These results imply that the potentiometric response is affected by the electronic effect of the porphyrin substituents and solution pH. It is concluded that the presence of substituents with electron donating and more liphophilic characters around the ligated metal center produces an improved response toward SCN$^-$ over perchlorate and salicylate.

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