The potentiometric behavior of polymer supported metalloporphyrins as anion-selective electrodes

Kum-Chul Oh a, Seon Mook Lim a, Insook R. Paeng b,*, Ki-Jung Paeng a, *

a Department of Chemistry, Yonsei University, Wonju 220-710, South Korea
b Department of Chemistry, Seoul Women’s University, Seoul 139-774, South Korea

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Abstract

The potentiometric behavior of polystyrene pyridine copolymer supported manganese (III) and tin (IV) protoporphyrin IX (MnPPIX-PSP4 and SnPPIX-PSP4) was investigated. As expected, both MnPPIX-PSP4 and SnPPIX-PSP4-based membrane electrodes showed size exclusion effects on salicylate, these may be caused by a cross-linked polymer matrix which can act as an asymmetric cellulose membrane to exclude the bigger sized lipophilic anions such as salicylate. Pyridine attached to the polymer chain can influence the selectivity pattern of the aforementioned membrane electrodes as the axial ligand to the central metal of the porphyrins. The lifetimes of the polymer supported ionophore-based membrane electrodes are significantly enhanced from those of porphyrin-based electrodes and the super-Nernstian phenomenon found on Sn porphyrin-based membrane electrodes also disappeared. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer supported metalloporphyrin; Anion-selective electrode

1. Introduction

The development of polymeric and solid state ion selective sensors directly monitoring anions based on metalloporphyrins in complex biological fluids forms a rapidly growing field of research [1–3]. These electrodes (solid state forms) are now routinely used as flow through detectors in several automated clinical analyzers [4]. Generally, the potentiometric response of many of the anion selective polymer membrane electrodes follow a dissociated ion exchange mechanism in which selectivity is based on the classical Hofmeister sequence (ClO₄⁻ > I⁻ > salicylate (Sal⁻) > NO₃⁻ > Br⁻ > Cl⁻ > OAc⁻ > SO₄²⁻) [5]. Because the electrode selectivities of potentiometric sensors based on various metalloporphyrins are governed by specific chemical interactions between the metalloporphyrins and anions in the sample solution such as complex formation or coordination, it is well known that such sensors exhibit a non-Hofmeister sequence.

However, these anion selective membranes exhibit some shortcomings such as a limited lifetime due to leaching of the ionophore to the contacted solution, a super-Nernstian response to target anions by the membrane electrodes based on certain metalloporphyrins due to the formation of dimers and a huge response to lipophilic anions such as salicylate over target anions. If more hydrophobic porphyrins are employed, the leaching problems can be reduced. However, the detection limits and linearity of sensors have to be sacrificed because hydrophobicity of ionophores may interfere with the contact with hydrophilic anions. Using ionophores chemically bonded to polymer matrices may overcome this problem. For instance, chemically bonded ionophores cannot be extracted, and restricted movement of the ionophore may remove the super-Nernstian response by prohibiting the formation of dimers. A cross-linked polymer matrix can act as an asymmetric cellulose membrane to exclude the larger sized lipophilic anions such as salicylate [6,7].

Recently, our group reported an anion-selective electrode based on polystyrene pyridine copolymer supported manganese (III) protoporphyrin IX structures (MnPPIX-PSP4) [8]. The membrane based on MnP-
PIX-PSP4 exhibited excellent selectivity to iodide ion compared to other anions examined, but no response to salicylate. We concluded that this effect is caused by the size exclusion effect. This is the first work in which it can be claimed that addition of only 1% of a polymer attached ionophore into a plasticized PVC membrane leads to this size exclusion effect.

However, the response to salicylate was dramatically enhanced with addition of a cationic lipophilic additive to the membrane and the selectivity pattern found at the aforementioned membrane was somewhat similar to the Hofmeister sequence [5,8]. This is a totally different selectivity pattern compared to that of the membranes based on manganese porphyrins. The selectivity of membranes containing metalloporphyrins reverts to the classical Hofmeister sequence when one side of the metal center of the porphyrin is totally blocked with an intramolecularly bound neutral axial ligand [9]. Since both Mn(III) and Sn(IV) porphyrins are known to function as charged carriers, it has been demonstrated that the electrode performance and selectivity of such species are enhanced by the addition of lipophilic anionic sites [10–13]. Furthermore, selectivity and dimer formation of some charged carrier type anion ionophores are affected by the presence of endogenous cationic sites of polymer matrices in the absence of exogenous anionic sites [14,15]. Thus, further studies are needed to find a correlation between the membrane electrodes based on polymer supported metalloporphyrins and their selectivity patterns.

In this report, we examined the potentiometric behavior of the membranes based on polymer-attached metalloporphyrins as anion-selective electrodes at various compositions in order to answer some questions arising from our previous work [8].

2. Experimental

2.1. Reagents

Poly(vinyl chloride), o-nitrophenyl octyl ether (NPOE), tridodecymethylammonium chloride (TD-MACl) and potassium tetrakis (p-chlorophenyl) borate (KTpClPB) were purchased from Fluka (Ronkonkoma, NY). Protoporphyrin IX (PPIX), 4-vinylpyridine, styrene and α,α′-azobisisobutyronitrile (AIBN) were purchased from Aldrich Chemical Co (Milwaukee, USA). The styrene was washed with aqueous NaOH to remove inhibitors, then with water, dried with MgSO4 and distilled under reduced pressure, and passed through a neutral alumina column before use. AIBN was crystallized from acetone and dried under a vacuum at room temperature. All other chemicals, including sodium salts of the anions investigated were analytical reagent grade and used without further purification. Standard solutions and buffers were prepared with the use of deionized water.

2.2. Syntheses of polymer supports

The polymer support, poly(4-vinylpyridine-co-styrene) (PSP4), was prepared using a known method [16]. A typical procedure for PSP4 is described as follows: 3.47 ml (0.03 mol) of freshly distilled styrene, 7.86 ml (0.07 mol) of 4-vinylpyridine and 0.3 g (2 mmol) of AIBN were placed in a Schlenk tube and dissolved in 20 ml of benzene. The mixture was degassed via five freeze–pump–thaw cycles in a vacuum line, and reacted at 60°C for 24 h under a nitrogen atmosphere and cooled to room temperature. The reaction mixture was then poured into petroleum ether and the precipitated polymer was filtered, recrystallized from chloroform + petroleum ether, then dried in vacuo to yield the yellowish polymer.

2.3. Syntheses of polymer-supported MnPPIXs

(MnPPIX-PSP4): 50 mg of MnPPIX (7.7 × 10⁻⁵ mol) and 2 ml of thionyl chloride (SOCl₂, 2.7 × 10⁻² mol) were combined in a 250 ml round bottom flask. When gas evolution subsided, 50 ml of 1,1,2,2-tetra-chloroethane and 3 g of polymer (2.9 × 10⁻² mol of repeating polymer units) were added. The mixture was heated to 130°C while stirring to drive off excessive SOCl₂. After cooling to 10°C, 2 g of AlCl₃ was added, and the mixture was stirred without further cooling, for 24 h. The solid was filtered and thoroughly washed with tetrachloroethane and recrystallized in methanol. The final product was identified using an infrared spectrophotometer (Midac). The amount of attached metalloporphyrin was determined by analyzing extracted manganese by atomic absorption spectroscopic methods (Perkin–Elmer). The structure of the final product is given in Fig. 1.

2.4. Preparation and evaluation of polymer membranes and electrodes

PVC matrix membranes were prepared according to the method reported previously [17]. The composition of the PVC-based anion-selective membrane was 1 wt% ionophore, 33 wt% PVC and 66 wt% plasticizer with a total mass of 200 mg. The detailed compositions of the membranes used in this experiment are listed in Table 1. The polymer with more than 10% (wt/wt%) of metalloporphyrin was chosen as an ionophore. The membranes were prepared by dissolving the mixture in 5 ml of THF. In each case, after curing, small disks (5.5 mm) were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei, Möller, Zürich, Switzerland).
3. Results and discussion

3.1. Manganese porphyrin

A previous study showed that MnPPIX-PSP4 exhibited high iodide selectivity against chloride and salicylate ions [8]. In previous reports, a vitamin B12 analogue with an imidazole group coordinated to the metal center gave good selectivity for $I^-$, which is explained by simultaneous interaction of this anion with the metal center and the protonated imidazole ring [20,21]. Manganese(III) tetraphenylporphyrin chloride (MnTPPCl) was used to measure $I_3^-$ as the analyte, [22] and as an iodide optode [23]. Thus, the excellent selectivity toward iodide can be explained by the fact that the MnPPIX-PSP4 has a metal center (manganese) in the porphyrin and pyridine on the polymer chain, which has structure very similar to that of the aforementioned ionophore. However, as shown in Fig. 2, the response to salicylate was dramatically enhanced with addition of a cationic lipophilic additive to the MnPPIX-PSP4 membrane and the selectivity pattern found at this membrane was somewhat similar to the Hofmeister sequence. The response to salicylate increases with the increase of the additive to the membrane to 25 mol%. It is possible that this Hofmeister sequence-like selectivity is caused by the fifth ligand position of the metal in the porphyrin being occupied with a higher electron donating ligands such as imidazole or pyridine. It is well known that strong intramolecular coordination on one side of the metal generally weakens the interactions of ligands at the other axial site. Thus, total ionophores act as charged lipophilic ion-exchanger type species and analyte anions can enter the membrane phase predominately as solvated counter ions with little or no affinity for central Mn(III) atom, if pyridine attached to polymer chains act as ligands coordinated to the fifth ligand position [9].

It is well known that Mn(III) porphyrins are functioning charged carriers and the performance and selectivity of an electrode based on such an ionophore is enhanced by addition of anionic lipophilic additives [13,14]. The performance and selectivity enhancement

Table 1
The composition of anion-selective electrodes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionophore (1 wt%)</td>
<td>MnPPIX-PSP4</td>
<td>MnPPIX-PSP4</td>
<td>MnPPIX-PSP4</td>
<td>MnPPIX-PSP4</td>
<td>SnPPIX-PSP4 b</td>
</tr>
<tr>
<td>Matrix (33 wt%)</td>
<td>PVC</td>
<td>PVC</td>
<td>PVC</td>
<td>PVC</td>
<td>PVC</td>
</tr>
<tr>
<td>Plasticizer (66 wt%)</td>
<td>NPOE</td>
<td>NPOE</td>
<td>NPOE</td>
<td>NPOE</td>
<td>Pyridine (2 mg)</td>
</tr>
<tr>
<td>Additive</td>
<td>None</td>
<td>TDMACl (5 mol%)</td>
<td>TDMACl (25 mol%)</td>
<td>TDMACl (5 mol%)</td>
<td>None</td>
</tr>
</tbody>
</table>

a Polystyrene pyridine copolymer supported manganese(III) protoporphyrin IX structure.
b Polystyrene pyridine copolymer supported tin(IV) protoporphyrin IX structure.
c Poly(vinyl chloride) high molar mass.
d 2-Nitrophenoxy octyl ether.
e Tridodecylmethylammonium chloride.
could be interpreted as being due to the borate additives acting as counter anions against positively charged porphyrins. However, this membrane with an addition of KTpCIPB shows no response to any anions. Thus, polymer supported Mn(III) porphyrins work differently from single porphyrin molecules in the membrane.

We examined the selectivity of the membrane based on MnPPIX-PSP4 with the addition of pyridine which can be coordinated to the fifth ligand position of manganese. The selectivities of the membranes based on MnPPIXs are compared in Fig. 3. According to the previous report [8], the PVC membrane with MnPPIX showed no reasonable potentiometric response to anions, but MnTPPCl is known as a chloride sensing ionophore [24] and is sold for that purpose by a chemical company [3]. The electrode with MnTPPCl exhibits a different selectivity sequence from the Hofmeister series, and this has been explained by a metal–ligand interaction mechanism as either a neutral or charged carrier. According to the previous report, the sequence is $\text{Sal}^- > \text{ClO}_4^- = \Gamma > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^- > \text{SO}_4^{2-}$, and the logarithms of anion selectivity coefficients against $\text{Cl}^-$ ($\log K_{\text{Cl}^-}^{\text{sal}}$) were only 2.4, 1.5, 1.5 and 0.3 for salicylate, $\text{ClO}_4^-$, $\Gamma$ and $\text{Br}^-$, respectively [9]. As is seen in Fig. 3, membrane 1 exhibits the sequence $\text{ClO}_4^- > \Gamma > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^- > \text{SO}_4^{2-}$ and only a marginal response to salicylate, chloride and sulfate at concentrations of less than $10^{-2}$ M. The response of membranes 2 and 3 toward salicylate was significantly enhanced from membrane 1. The membrane 3 showed a near Hofmeister pattern of $\text{ClO}_4^- > \Gamma > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^- > \text{SO}_4^{2-}$. We can interpret this as the first phenomenon (no response to salicylate) attributable to a size exclusion effect and the second (enhanced response to salicylate) being attributable to the fact that lipophilic anion (salicylate) mobility increases with the addition of a cationic lipophilic additive, rather than occupation of the ligand coordinating central metal by a lipophilic additive. This is because the coordination between Mn(III) and the lipophilic cationic site in both ligand positions is unlikely to occur and the response to salicylate and iodide (almost the same) is not an exact Hofmeister pattern. These data suggest that only weak coordination between pyridine attached to the polymer and the metal exists and this has little influence on the selectivity pattern change.
Fig. 4. Potentiometric responses of membrane electrodes prepared with a membrane containing MnPPIX-PSP4 without KTpClPB (membrane 1), with KTpClPB (membrane 2) and with pyridine (membrane 4).

The membrane 4 shows a near Hofmeister pattern (Fig. 3). Only a few differences from membrane 3 are found. The role of pyridine in the membrane is not known for certain. However, this selectivity change can be explained by the fact that the salicylate selectivity over iodide of membrane 4 means that this membrane exhibits Hofmeister sequence because porphyrins in membrane 4 may lose their ability to coordinate to anions and they only act as dissociated ion exchangers by stronger coordination of pyridine to the fifth ligand position of Mn(III).

Typical calibration curves for iodide obtained by using the aforementioned membranes are shown in Fig. 4. As shown in Fig. 4, the slope of membrane 4 decreased to 45 from 58.5 and 56.0 mV/dec for membrane 1 and membrane 2, respectively. The reduced slopes are found for all other anions examined in this experiment at membrane 4. The membrane containing porphyrin usually shows near-Nernstian behavior for preferred anions (in this case iodide), but these data also suggest that the iodide is not coordinated at the sixth position of Mn(III), and only iodide could enter the membrane phase as a solvated counter ion.

3.2. Tin porphyrin

The selectivity and response characteristics of a SnTPPCl2 based membrane electrode were reported in the early 1990s [25,26]. The selectivity pattern of that membrane was $\text{Sal}^- > \text{SCN}^- > \text{ClO}_4^- > \text{I}^- = \text{Br}^- \approx \text{Cl}^- \approx \text{acetate (Oac}^-\text{)}$. The selectivity coefficients of that membrane toward other anions against salicylate ($\log K_{\text{Sal}^-}^{\text{pot}}$) were $-2.5$, for SCN$^-$ and less than $-3.4$ for ClO$_4^-$ and others. In that report it was also mentioned that radio tracer uptake experiments using $[^{14}\text{C}]$ salicylate showed that the metal center of the metalloporphyrin is critical for selective salicylate transport in the membrane phase. For comparison, typical calibration curves for the various anions obtained by using membranes doped with SnPPIX-PSP4 (membrane 5) are shown in Fig. 5. The anion selectivity coefficients
activity as a porphyrin and acts only as a dissociated ionophore or neutral carrier type membrane electrodes, because porphyrin has two possible sites for ligand exchange [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26]. Unlike manganese diaquo ligated metalloporphyrins within the organic membrane phase of the ISE [26].

Second, a restricted movement of ionophore may result in a 1000 times reduced response for Sal \(^{-}\). Actually, all ionophores cannot be extracted and the lifetime of the membrane may be significantly enhanced. Actually, all the polymer supported metalloporphyrin-based membranes we examined perform for more than two months without losing sensing power to target anions. Second, a restricted movement of ionophore may remove the super-Nernstian response. As mentioned, a previously reported, SnPPIX-PSP4-based membrane electrode exhibits a near-Nernstian response to salicylate. Third, a cross-linked polymer matrix can act as an asymmetric cellulose membrane to exclude the larger sized lipophilic anions such as salicylate. Both MnPPIX-PSP4 and SnPPIX-PSP4-based membrane electrodes showed size exclusion effects on salicylate. Finally, pyridine attached to a polymer chain plays a very important role, not only to enhance the solubility and conductivity of polymer itself, but also in axial ligation to central atoms to change the selectivity pattern.

Acknowledgements

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References