

Development of anion selective polymer membrane electrodes based on lutetium(III) porphyrins

Matthew S. Messick, Sandeep K. Krishnan, Matthew K. Hulvey, Erich D. Steinle*

Department of Chemistry, Southwest Missouri State University, 901 S National Avenue, Springfield, MO 65804, USA

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Abstract

Liquid polymer membrane electrodes based on lutetium(III) porphyrins are examined as anion-selective electrodes. The lanthanide metal ion, incorporated into tetraphenylporphyrin or octaethylporphyrin, is added to a plasticized poly(vinyl chloride) membrane. The selectivity coefficients of the resulting membrane electrodes differ from the traditional Hofmeister series, with a preference towards the salicylate anion, while discriminating thiocyanate and iodide. Through separate incorporation of lipophilic ionic additives, the lutetium(III) porphyrin-based electrodes were determined to function via a neutral carrier mechanism. As a result, the addition of cationic (quaternary ammonium) salts to the membrane enhances the response characteristics of the electrodes. An initial study to determine the feasibility of utilizing these electrodes in clinical determinations of salicylate is also demonstrated. Membrane composition and sample pH are varied to optimize salicylate response in the clinical range of salicylate concentrations.

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1. Introduction

Due to several new advances, the field of ion-selective electrode (ISE) sensing has expanded in recent years. The detection limits of ISEs, traditionally derided as poor as compared to other analytical techniques, have improved by several orders of magnitude to reach the sub-nanomolar concentration range [1,2]. While the majority of the ISE community utilizes polyvinylchloride (PVC) as the membrane matrix in ISEs, many non-traditional electrode materials such as plasticizer-free polymers, sol–gels, and liquid crystals have been used [3,4]. Recent review articles document these advances [5,6].

Indeed, even with the emphasis on improving detection limits and examining new membrane materials, one of the crucial components of the ISE is still the ionophore, or membrane active component. ISEs require ionophores that provide high selectivity and reversibility towards

the target ion of choice. While many practical cation-selective ISEs have been available for decades, the field of anion-selective electrodes has lagged behind [7,8]. The conventional anion-exchanger membrane, which depends solely on anion lipophilicity as the method of discriminating anions, results in the classical Hofmeister selectivity series ($\text{ClO}_4^- > \text{SCN}^- > \text{salicylate}^- > \text{I}^- > \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$) [7,9]. However, within the last 20 years, researchers have discovered that many metal-based complexes, when properly incorporated into ISE membranes, demonstrate significant anion-selective ionophore capabilities that result in non-Hofmeister selectivity patterns [10,11]. Ionophores containing a wide variety of metal ions have been examined: aluminum(III) [12], titanium(IV) [13], vanadium(IV) [14], chromium(III) [15], manganese(III) [16], zirconium(IV) [13,17], molybdenum(V) [14,18], tin(IV) [12,19], hafnium(IV) [13], and mercury(II) [20]. The vast majority of metal complex-based ISEs involve metal ions from the transitional area (3d and 4d) of the periodic table, with additional metal ions of main groups IIIA, IVA and VA.

* Corresponding author. Tel.: +1 4178365319; fax: +1 4178365507.

E-mail address: eds323f@smsu.edu (E.D. Steinle).

In contrast, metals from the lanthanide series have not, to date, received much attention. The most documented example in which a lanthanide metal has been utilized as an ionophore is the classical fluoride selective electrode that was developed in 1966 by Frant and Ross that utilizes a single crystal of lanthanum fluoride (LaF_3) [21]. A few recently published experiments have focused on ISEs containing metals in the lanthanide series (terbium, dysprosium, and lutetium) [22,23]. Zhang et al. noted that ISEs based on terbium(III) and dysprosium(III) porphyrins were responsive towards ethacrynic acid and thiocyanate [22]. Leyzerovich et al. demonstrated that dysprosium(III) and lutetium(III) phthalocyanine-based ISEs exhibited sub-Nernstian (-41 mV/decade) slopes towards the anion salicylate with Hofmeister selectivity patterns [23].

Several different types of lanthanide complexes have already been synthesized and studied for other applications, including nuclear magnetic resonance (NMR) and magnetic resonance imaging (MRI) probes, luminescent sensors, and as catalysts [24,25]. In general, these lanthanide complexes have demonstrated preferences towards molecules containing nitrogen and oxygen atoms. There are also documented stability constants between lanthanide metals and many anions [26].

The direct incorporation of lipophilic ionic additives into polymer membranes has become a fairly standard practice for anion-selective ISEs [27–31]. These additives are utilized primarily to enhance the selectivity of the given ISEs towards the target anion and to improve response slopes. The charge of the proper additive is tied directly to the response mechanism of the chosen ionophore. In cases in which a charged carrier mechanism (the ionophore is initially positively charged and becomes neutral upon subsequent ligation of an anion) is prevalent, anionic (typically tetraphenylborate derivatives) sites are added to the polymer membrane. However, when a neutral carrier mechanism (when the ionophore is initially neutral and becomes negatively charged when bound to a sample anion) is dominant, cationic (typically quaternary ammonium salts) sites are introduced. The theory describing the neutral carrier mechanism for anion-selective electrodes [27] expresses that the incorporation of cationic additives is crucial as the positive sites serve as counterions to the product of the fully ligated and negatively charged ionophore.

When examining the possible response mechanisms of metalloporphyrin-based ISEs, it is important to consider the nature of the metalloporphyrin. Six-coordinate metal ions have four positions occupied with the pyrrolic nitrogens in the porphyrin ring, leaving two axial ligand positions (fifth and sixth) free to bind ligands. A metal ion with a trivalent cationic oxidation state (M^{3+}) and a divalent negatively charged porphyrin ring (TPP^{2-}) combine for a metalloporphyrin with a single positive charge (i.e., M(III)[TPP]^+). In several published cases, such as ISEs containing indium(III) and gallium(III) porphyrins, the positively charged metalloporphyrin is the active ionophore and operates via a charged carrier mechanism [27,28]. However, there are published examples when the presence of an anionic ligand in the fifth

axial position (for example, Co(III)[TPP]Cl) does not prevent anion coordination at the sixth axial position, resulting in ISEs with neutral carrier characteristics and non-Hofmeister anion selectivity patterns [27,31].

In this work, lutetium(III) complexes of tetraphenylporphyrin and octaethylporphyrin are examined as anion-selective ionophores. ISEs based on these compounds exhibit a slight preference for the anion salicylate over other highly lipophilic species such as iodide and thiocyanate. Through the separate incorporation of cationic and anionic additives to these polymer membranes, a neutral carrier response mechanism for these ISEs was determined. Preliminary experiments with a view to adapting these ISEs towards clinical determinations of salicylate are also demonstrated. Membrane composition was varied in order to enhance the selectivity and dynamic range of salicylate measurements.

2. Experimental

2.1. Reagents

The ionophores hydroxo(5,10,15,20-tetraphenylporphyrinato)lutetium(III) (Lu(III)[TPP]OH) and hydroxo(2,3,7,8,12,13,17,18-octaethylporphyrinato)lutetium(III) (Lu(III)[OEP]OH) were purchased from Frontier Scientific (Logan, UT). Membrane components tridodecylmethylammonium chloride (TDMAC), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), poly(vinyl chloride) (PVC), and *o*-nitrophenyl octyl ether (*o*-NPOE) were used as received from Fluka (Ronkonkoma, NY). 2-(*N*-morpholino)ethanesulfonic acid (MES) and 3-(*N*-morpholino)propanesulfonic acid (MOPS) buffers were purchased from Sigma (St. Louis, MO). The sample solutions for potentiometric measurements consisted of sodium salts of the given anions in buffer solutions. The buffers used in this work were 0.05 M MES (at pH 5.5 or 6.5) and 0.05 M MOPS (at pH 7.5).

2.2. ISE membrane formulation and EMF measurements

The membranes that were employed in the ISEs consisted of 1 wt.% ionophore, varying amounts of lipophilic ionic additives (TDMA^+ and TFPB^-), 66 wt.% *o*-NPOE and 33 wt.% PVC. When the weight percent of the ionophore increased to 2.5 and 5.0 wt.%, the ionic additive concentration increased accordingly, while maintaining a 2:1 ratio of *o*-NPOE to PVC. To construct the membranes, the components were dissolved in tetrahydrofuran (THF), which was then allowed to evaporate overnight, producing a flexible polymeric membrane. Disks (7 mm o.d.) were then cut from the parent membrane and mounted into electrode bodies (ISE-561, Glasbläserei Möller, Zürich, Switzerland). A 0.01 M NaCl solution was used as both the filling solution and the outer conditioning solution. A double-junction reference electrode (Mettler Toledo, Columbus, OH) was filled with 0.1 M KNO_3 bridge electrolyte.

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