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Review

A Review of the Potentiometric Samarium Ion-Selective Sensors

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Abstract- The key role of developing new and effective analytical tools and techniques for various species need not be discussed. Furthermore, reviewing the trends dominating the development of such tools and techniques can be of great importance to those active in the research and development areas. In designing an electrochemical sensor, finding a suitable selectophore is very important. In potentiometric ion-selective sensors, ionophores play a significant role in the selective response of the sensor. Besides the ionophore, other components of the electrode can improve the response. This review article tends to focus on the development of samarium ion electrodes over the past decades to provide researchers in the area of selective electrochemical analysis with a better insight into one of the various areas of electrochemical sensor development. Accordingly, the history of the development of potentiometric ion-selective sensors for samarium ions, with details on the ionophores, compositions, and electrochemical properties thereof has been provided.

Keywords- Potentiometry; Sm^{3+}; Ionophore; Electrode; Plasticizer; Ionic additive

1. INTRODUCTION

Developing tools and techniques to precisely analyze low quantities of metallic ions in environmental samples is a persistent need in different laboratories, especially given the focus on environmental analyses as a key tool for various research on environmental applications [1]. Application of rare-earth salts in different industries has been recorded to increase at an average of 5–15% per year, in technological fields ranging from lasers, phosphors, and magnetic bubble memory films to refractive index lenses, fiber optics, and superconductors. The materials are also used in gasoline cracking catalysts, polishing agents, as well as in removing sulfur electronegative elements in iron and steel industries [2]. Although the elements are known to possess low toxicity according to the Hodge-Sterner classification, inhalation of their dust or vapor accounts for higher risks, given their accumulation and gradual absorption in the body [3]. Lanthanides are also known to cause damage to cell membranes, of seaborne creatures and leave negative effects on their reproduction and nervous systems [4].

A shiny silver rare-earth metal, samarium is valued for its strong magnetic properties, which have turned it into an essential ingredient in permanent magnets. Tet, the element is no exception from what was said above and, can cause workplace hazards, if the dusts of its salts are inhaled, which can lead to lung embolisms if experienced persistently. High concentrations of the ionic forms of the element can damage the liver too [5,6].

The conventional technique used for the determination of traces of rare-earth ions in a range from mass spectrophotometry [7], ICP-MS and ICP-AES [8,9], isotope dilution mass spectrometry [10], neutron activation analysis [11], and XRF spectrometry [12]. An alternative for these costly and cumbersome techniques is the application of low-cost potentiometric sensors, which offer a set of advantages including ease of use, considerable sensitivity, and selectivity. Various ion-carriers (ionophores) have been developed and used for various metal ions [13-27].

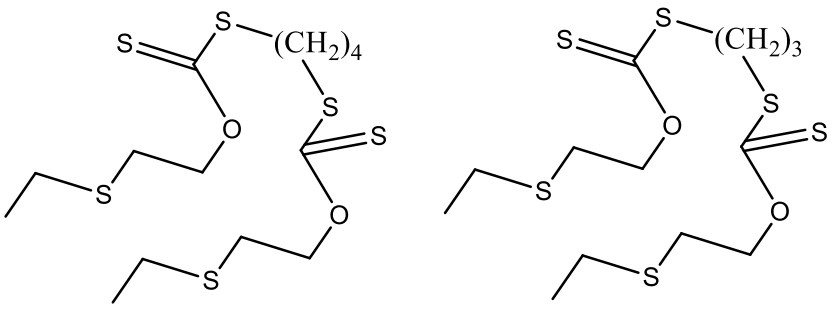
Although ion-selective electrodes have proven to be robust and versatile analytical tools, during the mid-1990s there were a very limited number of electrodes for the determination of rare earth elements [28-48], which were either solid-state sensors based on rare-earth oxide [44,45] or membranes electrodes composed of di-nonyl naphthalene sulfonic acid [46], bis(2-ethylhexyl)phosphoric acid [48], and tributyl phosphate [45].

2. ION-SELECTIVE ELECTRODES FOR SAMARIUM

Various studies were conducted on the design and synthesis of ionophores for lanthanides, and the initial was reported to be used for the development of samarium selective electrodes [17-19] which was followed by the development of different ionophore-based sensors for various lanthanides [43,48].

The earliest work on the development of a Sm^{3+} sensor dates back to the work of Ogata et al. [49]. They coated carbon rod electrodes with a polymeric membrane containing 10.2 wt.%

of 1,4-bis(3-thiapentylxanthato) butane (Figure 1a) as the ion carrier. The ion carrier which contains several O and S donor atoms was used together with, 28.7 wt.% of PVC, 60.4 wt.% of o-nitrophenyl octyl ether (NPOE), and 0.7 wt.% of potassium tetrakis(4-chlorophenyl)borate (KTCPB). The resulting electrodes were reported to produce a Nernstian response of 19.7 mV per decade of concentration change in the analysis of Sm^{3+} with a limit of detection as low as 5×10^{-7} M. A second ionophore, namely 1,4-bis(3-thiapentylxanthato) propane (Figure 1b) was also evaluated but the results were found to be less favorable.



a b

Figure 1. a) structure of 1,4-bis(3-thiapentylxanthato) butane; b) 1,4-bis(3-thiapentylxanthato) propane

The sensor based on 1,4-bis(3-thiapentylxanthato) propane was reported to have a linear response in the range of 5×10^{-3}-2×10^{-3}, a response time of 12 seconds, a detection limit of 1×10^{-6} and a response slope of 19.2 mV per decade (decade of concentration), while these qualities were improved in the case of 1,4-bis(3-thiapentylxanthato) butane and were reported to be 5×10^{-3}-1×10^{-3}, a response time of 5 seconds, a detection limit of 5×10^{-7} and a response slope of 20.0 mV per decade. This was attributed to the better semi-cavity size of the latter in comparison to 1,4-bis(3-thiapentylxanthato) propane. Major interferences in the response were reported to be caused by Cu^{2+}, $Fe^{3+,}$ and Pb^{2+}, as well as soft cations such as Pd^{2+} and Au^{3+} [49].

The same team further reported a membrane ion selective electrode for Sm^{3+} using the identical optimal ionophore [35] and reported a linear range of 1×10^{-1} - 1×10^{-5}, a response time of 5 seconds with a sensitivity of 20.0 ± 0.3 mV per decade. They compared the results with those obtained with a set of similar ion carriers namely bis(3-thiapentylxanthato) propane (XI), bis(2-methylpropyl-xanthato) methane (I), bis(2-methylpropyl-xanthato) ethane (II), bis(2-methylpropyl-xanthato) propane (19.4 ± 0.6 mV/ decade), and bis(2-methylpropyl-xanthato) butane (19.2 ± 0.3 mV/ decade), bis(2-butylpropyl-xanthato) propane (18.0 ± 0.3 mV/ decade), bis(2-butylpropyl-xanthato) butane (19.2±0.3 mV/ decade), bis(5-methyl, 3-thiahexylxanthato) propane (19.4±0.5 mV/ decade) and, bis(5-methyl, 3-thiahexylxanthato)butane (19.1 ± 0.2 mV/ decade), bis(3-thiahepthylxanthato)propane (16.9 ±

0.7 mV/ decade), and bis(3-thiahepthylxanthato)butane (19.2±0.4 mV/decade) but the best results were observed in the case of the optimal ion carrier of the previous report.

The membrane composition was reported to be 10.2 wt.% of the ion carrier, 60.4 wt.% of o-NPOE, 28.7 wt.% of PVC, 0.7 wt.% of KTCPB. The senor showed an optimal response in the pH range of 4.5-6.7 and had good selectivity against interfering lanthanide ions [50].

In 2003, Shamsipur et al reported developing PVC membrane and coated graphite sensors using 4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione (Et 4todit) as the ion carrier (Figure 2) [51].

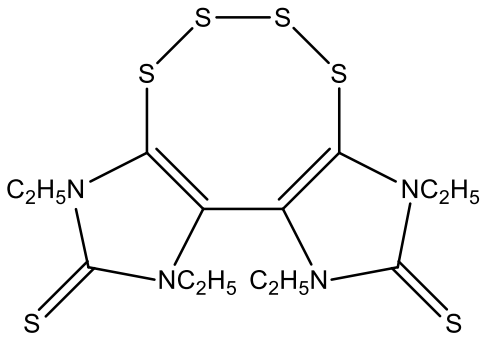


Figure 2. Structure of 4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione

Given the data on the binding behavior of the ion carrier with a range of cations, they observed that the ions formed 1:1 complex with Sm ions. Therefore, they used the ionophore in the construction of a selective polymeric membrane electrode (PME) and a selective coated graphite electrode (CGE) for Sm^{3+}. Both electrodes comprised polymeric membranes with a composition of 30% wt. of PVC powder, 65% wt. of o-NPOE, 2% wt. of NaTPB, and 3% wt. of the ion carrier.

The PME had a rather narrow linear response range of 1.0×10^{-5}-1.0×10^{-1} M, while that of the CGE was wider (1.0×10^{-7}-1.0×10^{-1} M) as theoretically anticipated, and the respective lower detection limits were as low as 8.0×10^{-6} M and 1.6×10^{-8} M for CGE.

The potentiometric responses of the electrodes were independent of the pH of the test solution in the range of 4.0<pH<6.5. The selectivity of the GCE was far better than the PME, and although the highest interference was from Pb^{2+} and Hg^{2+} with respective selectivity coefficients of 9.2×10^{-2} and 8.9×10^{-2}; the maximum interference was from Hg^{2+} and Pb^{2+} with respective selectivity coefficients values of 6.1×10^{-3} and 6.2×10^{-3}.

Almost at the same time, Shamsipur et al reported another set of novel PME and CGE for Sm^{3+} using isopropyl 2-[(isopropoxycarbothioyl) disulfanyl] ethanethioate (Figure 3) as the ion carrier [52]. The response of the PME and GCE were linear in the respective concentration windows of 1.0×10^{-5} to 1.0×10^{-1}, and 1.0×10^{-6} to 1.0×10^{-1} M, with detection limits of 3.1×10^{-6} and 5.0×10^{-7} M. Both electrodes showed no interference from proton ions in the pH window

4.0-7.0. The optimal membrane composition used in the electrodes was 30% wt. of PVC powder, 57% wt. of benzyl acetate (BA), 3% wt. of the ion carrier, and 10% wt. of oleic acid as an ionic additive. Once again, the CGE proved to have better selectivity than the PME for all interfering ions tested. The maximum interference in the case of the PME was from Cd^{2+} (K_{Sel}^{MPM}= 9.0 × 10^{-2}), Co^{2+} (K_{Sel}^{MPM}= 8.3 × 10^{-2}), Gd^{3+} (K_{Sel}^{MPM}= 7.9 × 10^{-2}); while with the GCE the maximum interference was from Cd^{2+} (K_{Sel}^{MPM}= 9.2 × 10^{-3}) and Pb^{2+} (K_{Sel}^{MPM}= 3.2 × 10^{-3}).

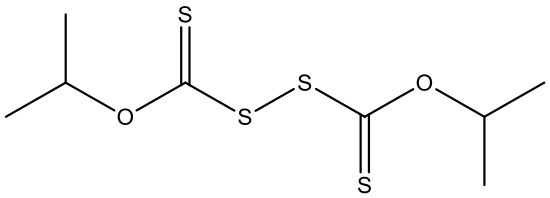


Figure 3. isopropyl 2-[(isopropoxycarbothioyl) disulfanyl] ethanethioate

In 2003, Ganjali et. al reported an Sm^{3+} membrane sensor based on N-[2-[4-[[[(cyclohexyl amino)carbonyl]amino]sulfonyl]phenyl]ethyl]-5-methyl pyrazine carboxamide (Figure 4) [53]. The best electrode performance was observed at a membrane composition of 30 wt.% of PVC, 53 wt.% of benzyl acetate, 11 wt.% of glipzid, and 6 wt.% of sodium tetraphenyl borate (NaTPB). The optimal composition led to a linear response of 19.8 mV/ decade in the range of 1×10^{-6}-1×10^{-1} M. The electrode response was pH independent in the window of 4.0-8.0 and it had a short response time of less than 10 seconds.

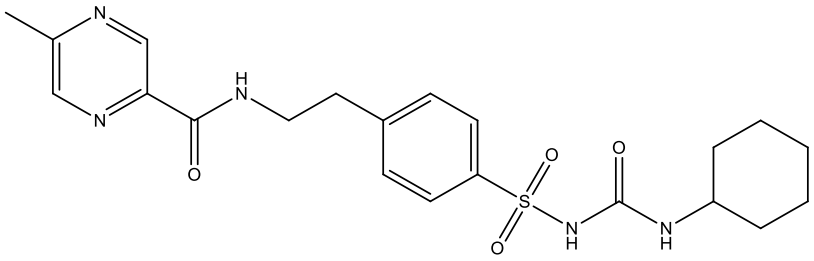


Figure 4. Chemical structure of glipizide

The maximum interference was reported for Pb^{2}, Ag^{+}, and Ce^{3+}, which indicates the considerable selectivity of the electrode to the target ion, even in the presence of these ions.

In a parallel work the same team used N-[2-[4-[[[(Cyclohexylamino) carbonyl] amino] sulfonyl] phenyl] ethyl]-5-methyl pyrazine carboxamide (Figure 4) to develop a CGE using a liquid membrane composed of 30% wt. of PVC, 53% wt. of benzyl acetate, 11% wt. of the ionophore and 6% NaTPB [54]. The GCE had a Nernstian response from 1.0×10^{-5} to 1.0×10^{-10} M, and its limit of detection was as low as 8.0×10^{-11} M [54]. The selectivity of the electrode was found to be very high with the highest MPM selectivity coefficients of 8.5×10^{-5}

for K^+; 7.9×10^{-5} for Pb^{2+}; and 7.3×10^{-5} for Cu^{2+}. The response of the electrode was pH-independent from 3.0 to 10.5.

Later Sm^{3+} membranes were reported based on tin (IV) boratophosphate in PVC by Mittal et al [55]. They used polystyrene and epoxy resin as binders, and reported a membrane composed of 40% wt. of tin (IV) boratophosphate and 60% wt. of epoxy resin to ha a super-Nernstian slope of 40 mV/ decade from 1×10^{-5} M to 1×10^{-1} M. The sper-Nernstian sensitivity of the sensor was attributed to the poor permeability and incomplete perm-selectivity of the membrane matrix for target ions, or the possible permeability of the membrane for anions or the possible differences of target ion activity in the bulk as opposed to the phase boundary.

The electrode had a fast response in less than 10 and good selectivity against alkali, alkaline earth elements, as well as some transition and rare earth ions. Its response was not influenced by pH from 4.0 to 10.0. Using the fixed interference method (FID) the maximum interface to the electrode response was determined to be from Na^+ and Pr^{3+} ions at a target ion concentration of 10^{-4} M, while at 10^{-3} M, Ca^{2+} also showed a considerable interference.

Another report on the application of a boratophosphate for the construction of an Sm^{3+} selective potentiometric sensor was made by the same group [56] who optimally used 10% wt. of 90% wt. of zirconium boratophosphate in a PVC membrane and as an electro-active material. The best membrane had a Nernstian slope of 20.2 mV/ decade in the concentration window of 1×10^{-5} to 1×10^{-1} M. The FID selectivity coefficients were determined and at a 10^{-4} M target ion solution, the maximum interferences were from La^{3+}, Nd^{3+}, and Al^{3+}, while at 10^{-3} M, Na^+, and Pr^{3+} showed maximum interference, and Eu^{3+}, Dy^{3+}, and Ca^{2+} also caused considerable interference. Further, the electrode response was not influenced by pH from 6.0 to 10.0.

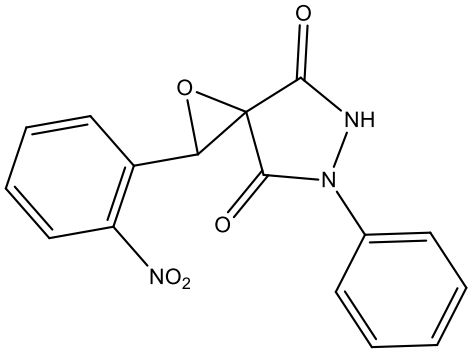


Figure 5. [1-phenyl-3′(2-nitrophenyl) spiro[Oxirane-2.4-Pyrazoline]-3,5-dione]

1-phenyl-3′(2-nitrophenyl) spiro[Oxirane-2.4-Pyrazoline]-3,5-dione (Figure 5) was used as an Sm^{3+} ionophore in a PVC/o-NPOE/KTClPB membrane and the resulting membrane had a Nernstian response of 19.3±0.2 mV/ decade from 10^{-6} to 10^{-1} M. The limit of detection for the electrode was determined to be 6.1×10^{-7} M. The quick response time of less than 5 minutes,

and the applicable pH of the electrode from 4.0 to 8.2 were among other properties of the electrode [57]. The selectivity profile of the sensor was determined through the separate solution method (SSM) and matched potential method (MPM). Based on the former, the maximum interference to the sensor response was NH_4^+ ($Log K_{Sel}^{MPM}$=-1.15), Nd^{3+} ($Log K_{Sel}^{MPM}$= -1.35), K^+ ($Log K_{Sel}^{MPM}$=-1.40) and Fe^{3+}($Log K_{Sel}^{MPM}$=-1.42); while the MPM method selectivity studies showed the highest interference to be caused by NH_4^+ ($Log K_{Sel}^{MPM}$=-0.98), Cs^+ ($Log K_{Sel}^{MPM}$=-1.14), K^+ ($Log K_{Sel}^{MPM}$=-1.22), Nd^{3+}($Log K_{Sel}^{MPM}$=-1.23) and Fe^{3+}($Log K_{Sel}^{MPM}$= -1.35).

In 2007 Zamani, et al [58] developed an Sm^{3+} selective PVC membrane sensor using 3-{[2-oxo-1(2H)- acenaphthylenyliden] amino}-2-thioxo-1,3- thiazolidin-4-one (Figure 6).

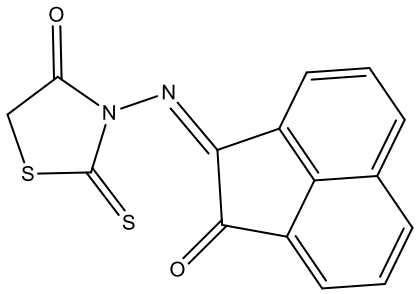


Figure 6. 3-{[2-oxo-1(2H)- acenaphthylenyliden] amino}-2-thioxo-1,3- thiazolidin-4-one

The optimal membrane electrodes containing 30% wt.; of PVC, 63.5% wt. of o-NPOE;1.5% wt. of NaTPB; and 5% wt. of the ion carrier had a linear response of 19.3 ± 0.6 mV/ decade in the concentration window of 1.0×10^{-6}-1.0×10^{-1}, had a pH independent response in the range of 3.5<pH< 7.5, a response time of about 10 seconds and a rather long lifetime. The highest interreferences were reported to be caused by Yb^{3+} ($K_{MPM}=5.5\times10^{-3}$), Gd^{3+} ($K_{MPM}=5.0\times10^{-3}$), Tb^{3+}($K_{MPM}=3.5\times10^{-3}$), and Al^{3+} ($K_{MPM}=3.0\times10^{-3}$).

Ganjali et al [59] developed an asymmetric potentiometric Sm(III) micro-sensor through depositing a layer of a film containing 2-((2-thioxothiazolidin-4- one)methyl)phenol (Figure 7) on the tip of a microwire. They reported the optimal membrane composition to be 20% wt. of PVC powder, 73% wt. of dibutyl phthalate (DBP), 2% wt. of NaTPB, and 5% wt. of the ion carrier. The asymmetric structure and miniature dimensions of the solid-state microsensor were expected to improve its detection limit, which was achieved as reflected by its respective linear response of 18.27 ± 0.3 mV/ decade over the concentration range of 1.0×10^{-9}-1.0×10^{-4} M (limit of detection=8.0×10^{-10} M). The asymmetric microelectrode proved to be very selective too, since none the evaluated interfering species (i.e., Na^+, K^+, Mg^{2+}, Ca^{+2}, Co^{2+}, Pb^{+2}, Fe^{3+}, La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Ho^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}, Lu^{3+}) had $logK_{Sel}^{MPM}$ values higher than -3.1 (for Gd^{3+} and Ce^{3+}).

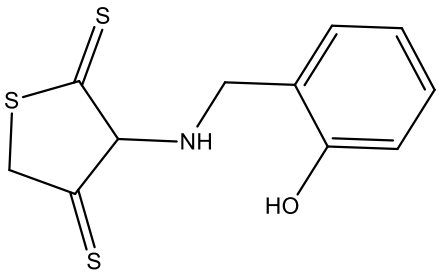


Figure 7. 2-((2-thioxothiazolidin-4- one)methyl)phenol

Zamani et al [60] also reported using 2.0% wt. of 2-[(E)-1-(1H-pyrrol-2-yl)methylidene]-1-hydrazinecarbothioamide (Figure 8), in a PVC membrane further containing 66% wt. of nitrobenzene and 2% wt. of NaTPB. This way they developed an Sm^{3+} selective sensor with a Nernstian response of 19.8 ± 0.3 mV/ decade from 10^{-2} to 10^{-6} M, with a detection limit of 5.2 $\times 10^{-7}$ M. The electrode was applicable in the pH range of 4.2-8.5 without interference from proton ions. The maximum interference was caused by Cu^{2+} with MPM $logK_{Sel}^{MPM}$ of -2.35, and the rest of the potential interfering species (i.e., Cr^{3+}, La^{3+}, Yb^{3+}, Gd^{3+}, Tb^{3+}, Ce^{3+}, Pr^{3+}, Er^{3+}, Nd^{3+}, Eu^{3+}, Ho^{3+}, Dy^{3+}, Lu^{3+}, Na^{+}, K^{+}, Mg^{2+}, Ca^{2+}, $Ni2^{+}$, Co^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+}, Ag^{+}) caused lower interference.

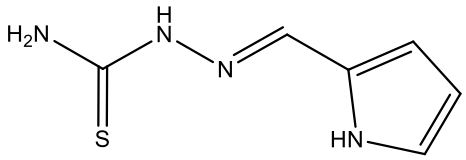


Figure 8. 2-[(E)-1-(1H-pyrrol-2-yl)methylidene]-1-hydrazinecarbothioamide

Another report on a samarium ion selective electrode is that of S.K. Agrahari and A.K. Srivastava [61] who used 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Figure 9) together with 2% wt. of NaTPB, 2% wt. of multi-wall carbon nanotube, 33% wt. of PVC powder and 60.5% wt. of nitrobenzene as the plasticizer to prepare a membrane mixture to be deposited on a graphite element. This could be described as the first application of a closed ring ionophore with hard O or medium N donating atoms for the preparation of an Sm^{3+} ion sensor, which has had a history with other lanthanide ions [62-68]. The coated graphite electrode revealed a Nernstian slope of 20.2 mV/ decade over a range of concentrations from 1.0×10^{-8} –1×10^{-2} M of Sm^{3+}, independent from pH from 2.5 to 8.5. The use carbon nanotubes, was meant to improve the electron transfer between the electroactive species.

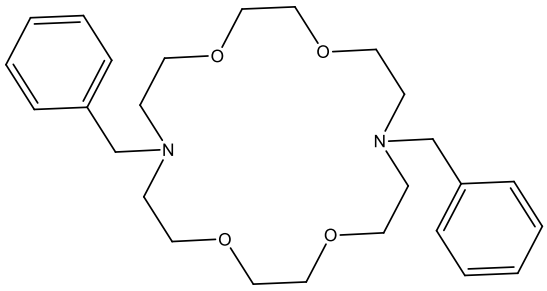


Figure 9. 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane

B. Rezaei et al [69] used 1,3-di(thiophene imino)benzoic acid (Figure 10) together with 31% wt. of PVC powder, 62% wt. tributylphosphate, and 3.2% wt. of NaTPB to build a samarium sensor after PM6/SPARKLE semi-empirical evaluations using the MOPAC program. Computational modeling results can be predicted behavior of Sm-DTBA interactions which was used as an ionophore for the construction of a samarium-selective potentiometric membrane sensor.

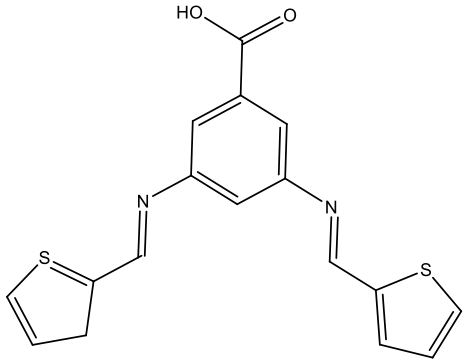


Figure 10. 1,3-di(thiophene imino)benzoic acid

This sensor response was reported to be 19.6 mV/ decade from 1.0×10^{-1}-5.0×10^{-6} M, and it had a detection limit of 3.1×10^{-6} M and a response time of 5 seconds. The sensor response had no interference from H^+ ions in the pH range of 4.5-8.5. The highest matched potential (MPM) selectivity coefficient was determined to be 1.6×10^{-2} for Fe^{3+} and all other potential interfering ions evaluated (Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cr^{3+}, Y^{3+}, Gd^{3+}, Dy^{3+}) caused lower interference.

In 2013 H. Zamani et.al [70] developed another Sm^{3+} sensor based on N,N',N''-tris(4-pyridyl)trimesic amide (Figure 11). The optimal membrane composition is further composed of 30% wt. of PVC powder, 55% wt. of nitrobenzene as the membrane solvent, and a mixture of 2% wt. and 10% wt. of oleic acid as the ionic additive. The best response was reported to be 19.8±0.5 mV/ decade from 1.0×10^{-2} and 1×10^{-6} M (detection limit 4.7×10^{-7} M). The applicable pH range and response time of the electrode were determined to be 3.6-9.2 and below 10 seconds, respectively. The maximum MPM selectivity coefficient was 5.2×10^{-3} in the case of

Cr^{3+}, and the rest of the interfering ions tested (Eu^{3+}, Gd^{3+}, Er^{3+}, Nd^{3+}, Pr^{3+}, Tm^{3+}, Yb^{3+}, Pb^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) had less effects on the response.

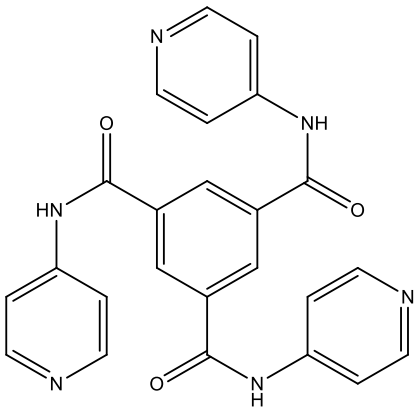


Figure 11. N,N',N''-tris(4-pyridyl)trimesic amide

Zamani et al [71] also reported the application of 2-{[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl}acetic acid (Figure 12) to the same end in a membrane composition of 30% PVC, 2% of the ion carrier, 2% of NaTPB and 66% nitrobenzene. The sensor had a dynamic response range and detection limit of 1.0×10^{-7} to 1.0×10^{-2} M; and 7.4×10^{-8} M. In this range, the sensor response was reported to be 20.8±0.4 mV/ decade and it had a pH independent response from 2.4-8.2 with a response time of around 5.0 s and the highest interference as reported for Tm^{3+} (K_{Sel}^{MPM}= 5.8×10^{-3}).

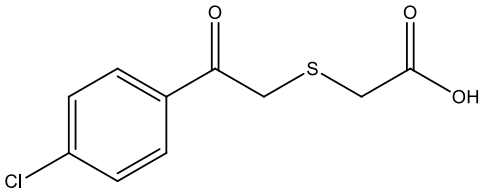


Figure 12. 2-{[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl}acetic acid

3. CONCLUSION

The majority of ionophores used in the construction of Sm^{3+} selective electrodes are acyclic compounds with soft (S) and medium (N) donors and some hard (O) atoms. Based on the data obtained from the references these include 1,4-bis(3-thiapentylxanthato)butane; b) 1,4-bis(3-thiapentylxanthato)propane (Figure 1) [34]; isopropyl 2-[(isopropoxycarbothioyl) disulfanyl] ethanethioate (Figure 3) [52]; N-[2-[4-[[[(cyclohexyl amino)carbonyl]amino]sulfonyl] phenyl] ethyl]-5-methyl pyrazine carboxamide (Figure 4) [53]; [1-phenyl-3′(2-nitrophenyl) spiro[Oxirane-2.4-Pyrazoline]-3,5-dione] (Figure 5) [57]; 3-{[2-oxo-1(2H)-acenaphthylenyliden] amino}-2-thioxo-1,3- thiazolidine (Figure 6) [58]; 2-((2-

thioxothiazolidin-4- one)methyl)phenol (Figure 7) [59]; 2-[(E)-1-(1H-pyrrol-2-yl)methylidene]-1-hydrazinecarbothioamide (Figure 8) [60]; 1,3-di(thiophene imino)benzoic acid (Figure 10) [70]; N,N',N''-tris(4-pyridyl)trimesic amide (Figure 11) [70]; 2-{[2-(4-chlorophenyl)-2-oxoethyl]sulfanyl}acetic acid (Figure 12) [71]. This further supports the formation of stable wrap-around complexes with target species as the main reason for their selectivity to Sm^{3+} ions, as well as other rare earths [62, 72].

Yet the fact 4,5,6,7-tetrathiocino[1,2-b:3,4-b′]diimidazolyl-1,3,8,10-tetraethyl-2,9-dithione (Figure 2); and 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (Figure 9) that are cyclic ligands with rather rigid cyclic reaction/interaction sites (the former with soft S donor atoms and the latter with hard O atoms) still shows that if rigid reaction site have the right size and spatial conformations, such ligands can lead to good selectivity behaviors.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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