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Review

A Review on Neodymium Selective Electrochemical Sensors

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Abstract- The analysis of neodymium and its compounds in various samples is very important, and the application of varied instrumental techniques for this purpose has hence been reported. Accordingly, different electrochemical electrodes have been developed for the analysis of Nd^{3+} over varied concentration ranges in different matrices. This text tends to offer an overview of these potentiometric instruments with a focus on the structure of the ionophores, as well as the nature and amount of the components used to develop the sensing parts of these electrodes.

Keywords- Neodymium Ion selective electrode; Potentiometry; Sensor; Ionophore; Selectophore

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1. INTRODUCTION

The first application of Nd was in forming colored glass namely Alexandrite, which is a reddish-purple to yellow glass under sunlight. Alexandrite has a blue color when radiated with white fluorescent, and turns green in trichromatic light [1]. The phenomena have been associated with the distinct absorption bands of Nd [2]. Given these properties, Nd-doping is used in astronomical applications, and lowering the green touch of glass. Nd is used together with praseodymium, to form didymium glass for use in welders' goggles, color-enhancing filters, incandescent light bulbs, or rear-view mirrors of cars Magnetic Nd compounds are also used in wind turbines, or electric motors Magnetic Resonance Imaging applications.

Metallic Nd and its salts are toxic, especially when ingested. Inhaling Nd dust can lead to lung embolisms, and the inhaled species can accumulate in and damage the liver [3].

Solutions containing traces of Nd ions are commonly determined through mass spectrometry (MS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), isotope dilution MS, neutron activation analysis, and X-ray fluorescence spectrometry [4-9].

As an alternative ion-selective electrodes (ISEs) based on ion carriers offer various advantages in terms of cost and ease of application. These instruments have proven to be applicable for the analysis of various cations and anions with good sensitivity and selectivity profiles. As opposed to advanced electrochemical techniques, ISEs offer comparatively reliable responses over wide concentration windows [10-27]. ISEs can be classified into PVC membrane electrodes (PMEs), microelectrodes, coated wire electrodes (CWEs), and carbon paste electrodes (CPEs).

A chronological overview of the various reports on Nd ion selective electrodes is presented below with a focus on the structure of the ion carriers used in the construction of the sensing element, the other components of the sensors, and their response profiles.

2. NEODYMIUM SENSORS

The first reports on neodymium potentiometric ion-selective sensors date back to the works of Agarwal and Gupta et al [28] in 2004. The report was on Nd^{3+} membrane sensors based on 75% PVC and 25% ion-exchange resin [i.e. tetracycline-sorbed zirconium(IV) tungstophosphate (TC-ZWP)]. The electrode was reported to have a linear Nernstian response in the concentration window of 1×10^{-1}-5×10^{-5} M, and a detection limit (DL) of around 25 sec. The electrode produced stable responses for at least 45 days. The developed membrane had good selectivity and its response was independent from pH from 3-7 [28].

In 2005 Shamsipur et al reported the application of 5-pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane (Figure 1) to construct an Nd^{3+} selective membrane sensor [29]. To this end they used spectrofluorometric to evaluate the tendency of the ionophore to interact with lanthanum, samarium, gadolinium, ytterbium and neodymium ions and determined the stability of the resulting complexes to be maximum for Nd^{3+} and minimum for La^{3+}.

The optimal membrane composition was reported to be 30% of PVC, 50% of o-NPOE 50%, 4% of the ion-carrier and 16% of oleic acid as an iononic additive. Membranes with this composition were reported to have Nernstian responses of 19.6±0.3 mV/decade of concentration, in the concentration window of 1.0×10^{-6}-1.0×10^{-2} M, with a detection limit of 7.9×10^{-7} M. Short response times of less than 5 s and the long applicability period of 9 weeks were further advantages of the sensor. Some interference was reported to come from from Yb^{3+} (pK_{SSM}=1.1/pK_{FIM}=1.2), Ce3+ (pK_{SSM}=1.3/pK_{FIM}=1.3), and Gd3+ (pK_{SSM}=1.4/pK_{FIM}=1.3).

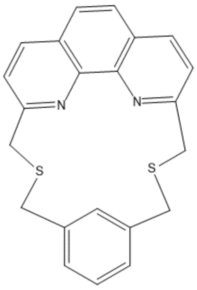


Figure 1. Structure of 5-pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane

Ganjali et al [30] reported another PVC-based ISE for Nd3+ using on 2-{[(6-aminopyridin-2-yl)imino]methyl}phenol (Figure 2). The optimal sensor had a composition of 30% wt. of PVC, 62% wt. of benzyl acetate (BA), 6% wt. of the ionophore and 2% wt of sodium tetraphenyl borate (NaTPB) and it produced a response slope of 19.6±0.3 mV per decade over the concentration from 1.0×10^{-5}-1.0×10^{-2} M and a detection limit of 2.0×10^{-6} M. The maximum matched potential (MPM) selectivity coefficient was 2.7×10^{-2} which was recorded in the cases of Sm^{3+} and Ce^{3+}, while La^{3+} and Gd^{3+} were the next most interfering species with selectivity coefficients of 2.5×10^{-2} and 1.5×10^{-2}, respectively.

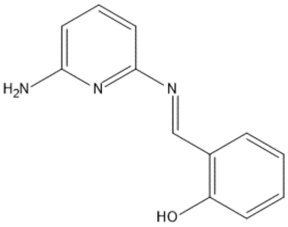


Figure 2. Structure of 2-{[(6-am-inopyridin-2-yl)imino]methyl}phenol

Norouzi et al [31] reported a next sensor for neodimium ions. They reported an om using a membrane composed of 6% wt. of N-(2-furylmethylene) pyridine-2,6-diamine (Figure 3), 33% wt. of PVC powder, 59% wt. of nitro benzene (NB), and 2% wt. of KTpClPB 2%.

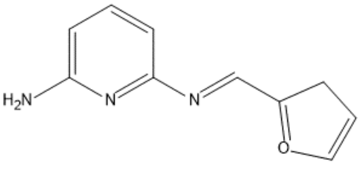


Figure 3. Structure of N-(2-furylmethylene) pyridine-2,6-diamine

The response of the optimal sensor was reported to be linear from 1.0×10^{-5} to 1.0×10^{-2} M, with a slope of 19.6±0.3 mV/decade of concentration, and its lower detection limit reached as low as 7.0×10^{-6}, and its response was independent from pH in the range of $4.0<pH<8.0$. Sm^{3+}, La^{3+}, and Gd^{3+} had the highest interfering effects on the sensor response with log K^{MPM} values of -1.5, -1.6, -1.8.

In a later work [32], membranes based on benzyl bisthiosemicarbazone (Figure 4) were used to construct Nd^{3+} sensors which had a linear response of 19.7±0.4 mV/decade of the concentration. In the range of 1.0×10^{-6} and 1×10^{-6} M, with a detection limit of 6.2×10^{-7} M. The sensor was reported to be applicable in the pH range of 3.7-8.3. The optimal membrane sensor had a composition of 2 61% wt. ortho nitrophenyl octyl ether (*o*-NPOE), 30% PVC, 6% wt. of the ion carrier, and 3% wt. of NaTPB. The highest interference was reported for Dy^{3+}, $La^{3+,}$ and Hg^{2+} with MPM selectivity coefficients of 7.8×10^{-3}, 7.8×10^{-3} and 7.8×10^{-3}.

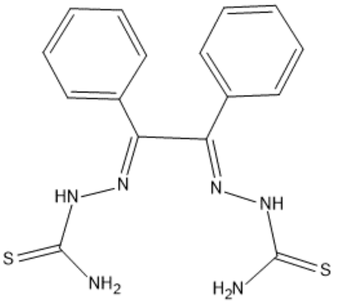


Figure 4. Structure of benzyl bis thiosemicarbazone

In another report 9% wt. of 11, 13-diaza-4, 7, 12-trioxo-2(3), 8(9)-dibenzoyl-cyclotetridecane-1, 11-diene (Figure 5) was used in a composition further containing 29% wt. of PVC powder, 59% wt. of dibutylphthalate (DBP) and 3% wt. of sodiumtetrakis (*p*-chlorophenyl) borate (NaTpClPB) to form a PVC-based ISE for neodymium ions. The sensor had a Nernstian response of 19.4±0.3mV per decade of concentration in a rather wide range of 1.0×10^{-8} to 1.0×10^{-1} M and had a detection limit of 8.0×10^{-7} M. The highest iterferences were recorded to be from Sm^{3+}, La^{3+}, Pr^{3+} and Gd^{3+} with respective log K_{MPM} values of -1.4, -1.7,-1.8 and -1.9

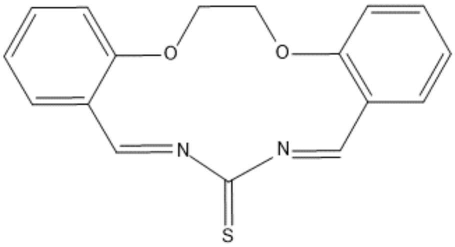


Figure 5. Structure of 11, 13-diaza-4, 7, 12-trioxo-2(3), 8(9)-dibenzoyl-cyclotetridecane-1, 11-diene

In 2009, two ionophores namely N, N_-bis((1H-pyrrol-2-yl) methylene) cyclohexane-1,2-diamine (Figure 6) and 3,3-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene) bis(methan-1-yl-1-ylidene) bis(5-hydroxymethyl) pyridine-2-ol) (Figure 7) were used for the construction of Nd^{3+} sensors [34].

The optimal membrane composition in the case of N, N-bis((1H-pyrrol-2-yl) methylene) cyclohexane-1,2-diamine was prepared using 150 mg of PVC powder, 300 mg of o-NPOE, 5 mg of the ligand and 5 mg of NaTPB, which led to a Nernstian response of 19.8±0.3mVdecade^{-1} in the concentration range of 5.0×10^{-7} to 1.0×10^{-2} M and a detection limit of 1.0×10^{-7}M.

3,3-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene) bis(methan-1-yl-1-ylidene) bis(5-hydroxymethyl) pyridine-2-ol) was used in an identical composition and the resulting membrane led to a lower response slope of 19.3 ± 0.1 3mVdecade^{-1} from 3.1×10^{-6} to 1.0×10^{-2}.

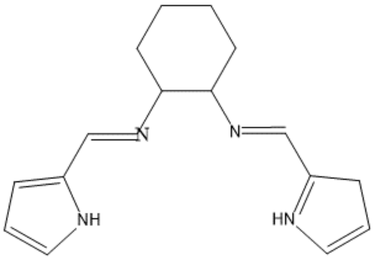


Figure 6. Structure of N, N_-bis((1H-pyrrol-2-yl) methylene) cyclohexane-1,2-diamine

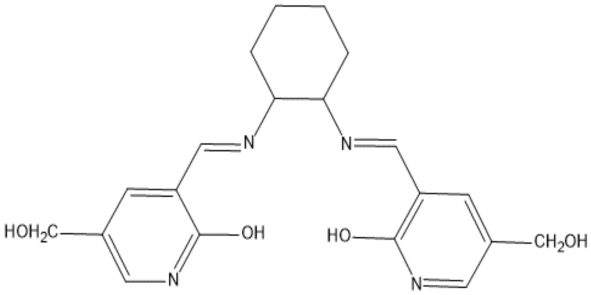


Figure 7. Structure of 3,3-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl)pyridine-2-ol)

Selectivity evaluations indicated that although both membranes had good selectivity behaviors, the membranes based on N, N-bis((1H-pyrrol-2-yl) methylene) cyclohexane-1,2-diamine had a better selectivity profile. In more detail, both electrodes had similar electivity behaviors with the maximum interference from Ni^{2+} and Ag^{+} (pK_{sel}:1.25, 1.62 (ligand 1), and pK_{sel}: 1.00, 1.3, (ligand 2), respectively). Also, in the case of the second membrane Ca^{2+} and K^{+} (pK_{sel}:1.3, 1.9) also caused relatively considerable interference.

In 2010, the results of a similar comparative study were reported [35]. In this report 1,5-di(cyanoethane)-2,4:7,8:13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2,7,13-triene

(Figure 8), and 1,5-di(cyanoethane)-2,3,4-pyridine-7,8:13,14-dibenzo-1,3,5-triaza-9,12-dioxa cyclopentadeca-2,7,13-triene (Figure 9) were used as the ionophores.

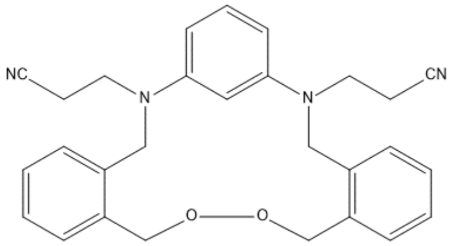


Figure 8. Structure of 1,5-di(cyanoethane)-2,4:7,8:13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2,7,13-triene

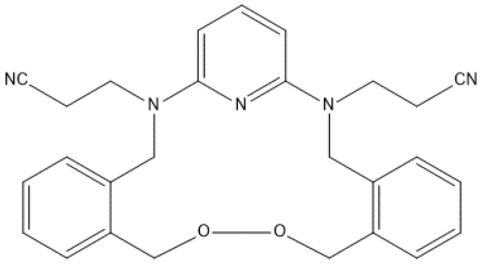


Figure 9. Structure of 1,5-di(cyanoethane)-2,3,4-pyridine-7,8:13,14-dibenzo-1,3,5-triaza-9,12-dioxa cyclopentadeca-2,7,13-triene

The ligands were used to coat graphite electrodes. To this end, a membrane composed of 5% wt. of ligand 1, 3% wt. of NaTPB, 57% wt. of o-NPOE, and 35% wt. of PVC was prepared using ligand 1. The membrane had a response slope of 19.8±0.4 mV/decade of concentration in the concentration window of 8.4×10^{-8}-1.0×10^{-2} M and a detection limit of 3.8×10^{-8} M. With ligand 2 the optimal composition was reported to be 5% wt. of the ion carrier, 3% wt. of NaTPB, 53% wt. of o-NPOE and 39% wt. of PVC powder. In this case, the response was 19.7±0.5 mV/decade from 4.6×10^{-8} to 5.0×10^{-2} M and the limit of detection was as low as 1.6×10^{-8} M. In light of the information and the fact that the selectivity profiles of the two electrodes were also comparable with maximum interference from La^{3+}(pK_{sel}:1.6 (L1), and pK_{sel}:2.0 for (L_2)), Yb^{3+} (pK_{sel}:1.7 (L1), pK_{sel}:1.9 (L2)), Co^{2+} (pK_{sel}:1.1(L1), pK_{sel}:1.2 (L2)), both coated glass electrodes were introduced as proper tools for the analysis of Nd3+ ions in solutions.

5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole (Figure 10) has also been reported as a Nd^{3+} selective ionophore [36]. Electrodes based on this ligand had a composition of 2% wt. of the ionophore, 66% wt. of NB, 2% wt. of NaTPB, and 30% wt. of PVC powder and had a potential response of 19.8 ± 0.4 mV/decade of concentration from 1.0×10^{-6}-1.0×10^{-2} M with a limit of detection of 5.9×10^{-7} M. The most interfering species were reported to be Cr^{3+} and Cd^{2+} with respective K_{sel} values of 5.8×10^{-3} and 5.4×10^{-3}.

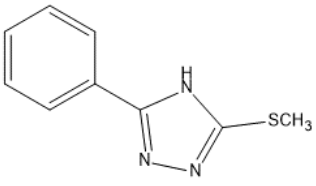


Figure 10. Structure of 5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole

The same ion carrier was also used, in an identical composition, in developing a coated wire electrode (CWE) with a linear response in the same concentration widow as the PVC membrane sensor with a rather higher sensitivity of 20.2±0.2 mV/decade of concentration [40].

In later research, 2-{[(6-aminopyridin-2-yl) imino] methyl}-phenol (Figure 2) was used in a composition further containing modified multi-walled carbon nanotube (MWCNT-NH_2), nanosilica (NS), graphite, and 1-n-butyl-3-methylimidazolium tetrafluoroborate [bmim]BF4 at respective amounts of 5% wt., 2% wt., 20% wt., and 53% wt. The resulting electrode produced a response of 19.8±0.12 mV/decade of concentration from 1.0×10^{-6}-1.0×10^{-2} M and the detection limit was determined to be 8.0×10^{-7} M.

The selectivity of the electrode was evaluated in the presence of Gd^{3+}, Yb^{3+}, Tb^{3+}, La^{3+}, Sm^{3+}, Dy^{3+}, Pr^{3+}, Lu^{3+}, Ce^{3+}, Eu^{3+}, Tm^{3+}, Zn^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Ho^{3+}, Nd^{3+}, K^{+}, and the maximum interference were reported to be caused by Sm^{3+}, La^{3+}, and Ce^{3+} with selectivity coefficients of 2.7×10^{-2}, 2.3×10^{-2}, 2.1×10^{-2}.

Raj Kumar et al reported using epoxy resin to bind tin (IV) antimonotungstate (SnSbW) and zirconium (IV) antimonotungstate (ZrSbW) as electro-active materials to produce Nd^{3+} ISEs [38]. Based on their report SnSbW, produced the best results when used in a 50:50 weight composition with the resin, leading to a linear response from 10^{-4} M to 10^{-1} M with a super-Nernstian slope of 40.0 mV/decade of Nd^{3+} concentration. ZrSbW also produced an acceptable response when used with 60% wt. of the resin and produced in a near-Nernstian 25.0 mV/decade of concentration-response over a relatively wider concentration range of 10^{-5} to 10^{-1} M. The respective electivity coefficients were determined to be 0.015, 0.019, 0.006, 0.025, 0.250, 0.062, 0.079, 0.039, 0.012, 0.004 for La^{3+}, Sm^{3+}, Gd^{3+}, Eu^{3+}, Pr^{3+}, Ce^{3+}, Dy^{3+}, Y^{3+}, Fe^{3+}, Ce^{3+} in the case of the SnSbW electrodes. I the case of the ZrSbW the reported respective selectivity coefficients were 0.0190, 0.0125, 0.0060, 0.0150, 0.0120, 0.0125, 0.0390, 0.0310, 0.0015, 0.0010, 0.0005 for La^{3+}, Sm^{3+}, Gd^{3+}, Eu^{3+}, Pr^{3+}, Ce^{3+},Tb^{3+}, Al^{3+}, Pb^{2+}, Cu^{2+}, and Na^{+}.

Another Nd^{3+} sensor was reported using N,N′-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene (Figure 11). The slope of the calibration plot obtained using the optimal membrane sensor was 19.5±0.4 mV/decade of concentration from 5.0×10^{-6} to 1.0×10^{-2} M (limit of detection: 4.8×10^{-6} M). The optimal membrane composition was reported to be 3% wt. of the ionophore, 65% wt. of DBP, 2% wt. of NaTPB and 30% wt. of PVC powder. None of the tested interfering ions namely Tm^{3+}, Lu^{3+}, Dy^{3+}, Sm^{3+}, Eu^{3+}, Ho^{3+}, Yb^{3+}, Er^{3+}, Tb^{3+}, Na^{+}, K^{+}, Ca^{2+}, Cd^{2+}, Ni^{2+}, Pb^{2+} could cause more interference than Sm^{3+} and Pb^{2+} with respective selectivity coefficients of 8.4×10^{-3} and 8.2×10^{-3}, reflecting the excellent selectivity of the developed sensor [39].

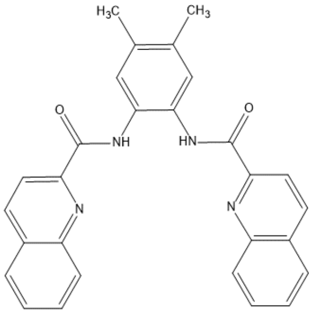


Figure 11. Structure of N,N′-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene

In a later work Pourjavid et al reported using a membrane with a composition of 4% wt. of N-(furfuralidene)-N -isonicotinoylhydrazine (Figure 12) as an ionophore together with 63% wt. of o-NPOE, 3% wt. of NaTPB and 30% wt. of PVC as a selective Nd3+ sensor [40]. Other plasticizers namely acetophenone and benzyl acetate were also evaluated, but the best response was observed with o-NPOE. Also, it was reported that NaTPB produced better results in terms of the calibration plot slope as opposed to oleic acid (OA). The best response was observed in the range of 1.0×10^{-7} to 5.0×10^{-1} M (detection limit: 8.6×10^{-8} M) and the response slope was 20.1±0.3 mV/decade of concentration. The electrode proved to be highly selective and the selectivity coefficients of the most disruptive species namely Pr^{3+}, Sm^{3+}, and Ce^{3+} did not exceed 2.4×10^{-3}, 1.7×10^{-3}, 1.2×10^{-3}.

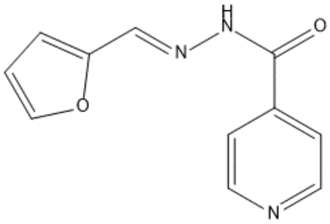


Figure 12. Structure of N-(furfuralidene)-N -isonicotinoylhydrazine

2% wt. of N-benzoylethylidene-2-aminobenzylamine (Figure 13) as an ion carrier together with 30% wt. of PVC, 58% wt. nitro benzene and 10% wt. of oleic acid as an ionic additive was reported [42] to be used in an ion selective electrode for Nd^{3+} ions with a response slope of 21.2 ± 0.2 mV/ decade of concentration from 1.0×10^{-6} to 1.0×10^{-2} M and a detection limit of 6.3×10^{-7} M. The maximum interference was reported for Sm3+ with a selectivity coefficient of 7.2×10^{-3}.

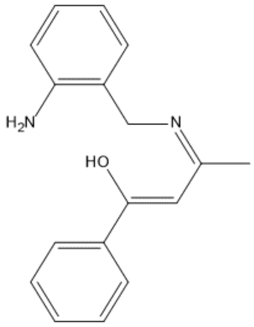


Figure 13. Structure of N-benzoylethylidene-2-aminobenzylamine

K. R. Bandi et al [43] used two multidentate Schiff bases namely 5-((1-(3-(3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)-1H-indol-1-yl)propyl)-1H-indol-3-yl) methyle neamino) -1,3,4-thiadiazole-2-thiol (Figure 14-a/L1) and N-((1-(3-(3-((thiazol-2-ylimino) methyl)-1H-indol-1-yl)propyl)-1H-indol-3-yl)methylene)thiazol-2-amine (Figure 14-b/L2) to prepare Nd^{3+} coated glass electrodes (CGEs) and polymeric membrane electrodes (PMEs). The optimal membrane composition for in the case of L1 was 2% wt. of KTpClPB; 58% wt. of o-NPOE; 36% wt. of PVC and 4% wt. of L1. The PMEs and CGEs were compared and the latter was proven to be better in terms of the detection limit (1.1×10^{-8} M), applicable concentration window (3.1×10^{-8}–1.0×10^{-1} M) and slope 19.8 ± 0.3 mV/decade of activity. In the case of L2 the best composition was 6% wt. of the ligand, 2% wt. of KTpClPB, 55% wt. of o-NPOE and 37% wt. of PVC powder, yet the applicable concentration range was narrower than the electrodes based on L1 (3.1×10^{-6}-1.0×10^{-1} and the electrode was rather lass sensitive (19.5 ± 0.4 mV/decade of activity). The maximum interferences were caused by Gd^{3+} with respective selectivity coefficients of 8.9×10^{-3} for the PME and 1.5×10^{-4} for GCE, as well as, Sm^{3+} with respective selectivity coefficients of 8.7×10^{-3} for PME and 1.3×10^{-4} for GCE.

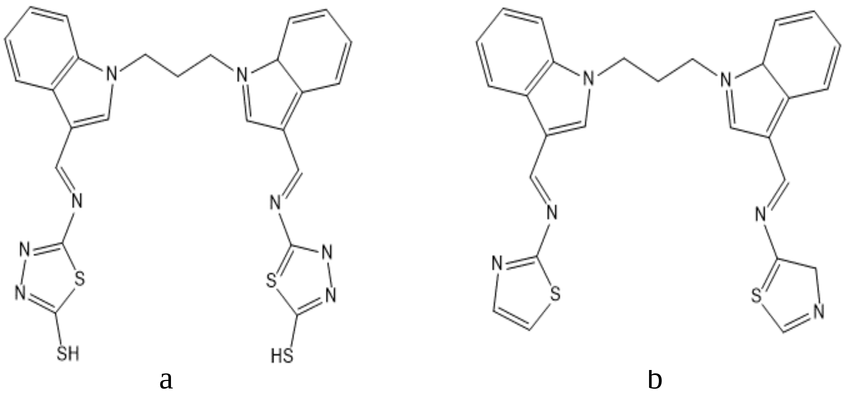


Figure 14. Structures of a) 5-((1-(3-(3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)-1H-indol-1-yl)propyl)-1H-indol-3-yl)methyleneamino)-1,3,4-thiadiazole-2-thiol (L1) and b) N-((1-(3-(3-((thiazol-2-ylimino)methyl)-1H-indol-1-yl)propyl)-1H-indol-3-yl) methylene) thiazol-2-amine (L2)

In another work, 1,2-dimaleimidobenzene (Figure 15) was used together with DBP, PVC powder, and a mixture of “NaTPB+oleic acid” as ionic additives at a ratio of 2:61:30:2+5 to construct a polymeric membrane electrode [44]. The slope of the calibration curve of the electrode was 20.7±0.3 mV/decade of activity in the range of 1.0×10^{-6} to 1.0×10^{-2} M and had a detection limit of 5.8×10^{-7} M. The highest selectivity coefficients were determined to be 6.2×10^{-3} and 4.4×10^{-3}, 3.4×10^{-3} for Cr^{3+}, Cd^{2+} and Ni^{2+}.

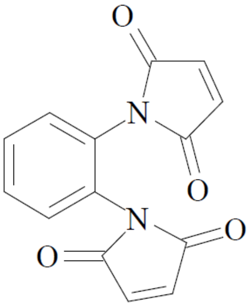


Figure 15. Structure of 1,2-dimaleimidobenzene

Another Nd^{3+} selective sensor was reported based on modifying a carbon paste electrode using N1,N2-bis(salicylidine)butane-1,4-diamine (Figure 16). The electrode composition was reported to be 90% wt. of graphite and 10 % wt. of the ionophore and it produced a linear response in the concentration window of 1.0×10^{-6} to 1.0×10^{-2} M with a slope of 19.5 ± 0.3 mV/decade of concentration. [45].

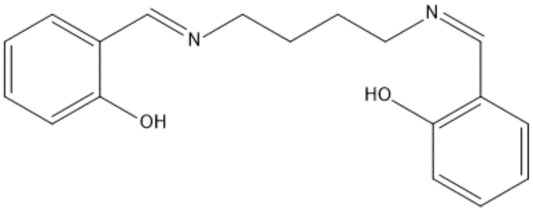


Figure 16. Structure of N1,N2-bis(salicylidine)butane-1,4-diamine

In 2018 a PME was reported for the determination of Nd^{3+} using 3% wt. of 4-hydroxypyrrolidine-2-carboxylic acid (Figure 17) in a composition further containing 2% wt. of NaTPB, 66% wt. of AP, and 30% wt. of PVC. The calibration curve of the sensor was linear from 10^{-6} to 10^{-2} M with a slope of 20.5 ± 0.4 mV per decade of concentration and its detection limit reached as low as of 7.5×10^{-7} M [46]. The values of the MPM selectivity coefficients were Pr^{3+} :2.0×10^{-4}, Yb^{3+}: 1.0×10^{-4}, La^{3+}:3.5×10^{-4}, Mg^{2+}: 2.0×10^{-4}, Tm^{3+}: 2.5×10^{-3}, Pb^{2+}: 0.85×10^{-4}, Lu^{3+}: 2.6×10^{-4}, Na^{+}: 3.0×10^{-4}, Eu^{3+}: 5.3×10^{-4}, K^{+}: 4.0×10^{-4}: Ho^{3+}: 1.0×10^{-4}, Co^{2+}: 5.7×10^{-4}, Gd^{3+}: 10×10^{-4}, Cd^{2+}: 6.5×10^{-4}, Sm^{3+}: 2.5×10^{-4}, Ca^{2+}: 7.0×10^{-4}, Er^{3+}: 2.1×10^{-4},

Fe^{3+}:6.0×10^{-4}, Tb^{3+}: 3.8×10^{-4}, Cr^{3+}: 8.5×10^{-}4, Dy^{3+}: 20: ×10^{-4}, Ni^{2+}: 6.0×10^{-4} indicating that the highest interference was from Tm^{3+}.

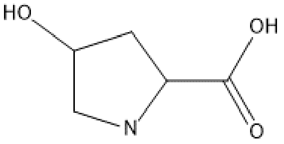


Figure 17. Structure of 4-hydroxypyrrolidine-2-carboxylic acid

Mirzaee1 et al [47] used 1-nitroso-2-naphtol (Figure 18):PVC: nitrobenzene (NB): sodium tetraphenyl borate (NaTPB) at a weight ratio of 1:30:67:2, to obtain an Nd^{3+} sensor with a detection limit of 6.5×10^{-7} M, and a response slope of 19.7±0.4 mV/decade of Nd^{3+} activity over 1.0×10^{-6} to 1.0×10^{-2} M. The MPM selectivity coefficients of the tested interfering ions were below 9.0×10^{-4} which was for the most interfering ion namely Gd^{3+}.

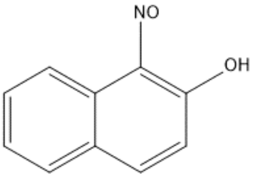


Figure 18. Structure of 1-nitroso-2-naphtol

One of the latest reports on an Nd^{3+} sensor is the work of Sosidi et al [48] who used 4-Sebacoylbis(1-phenyl-3-methyl-5-pyrazolone) (Figure 19) as an ionophore and reported a linear response of 18.5 ± 0.2 mV/decade of Nd^{3+} activity from 10^{-4} to 10^{-1} M. Yet the report does not discuss the composition of the optimal membrane or its selectivity behavior.

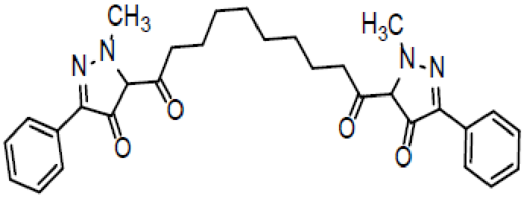
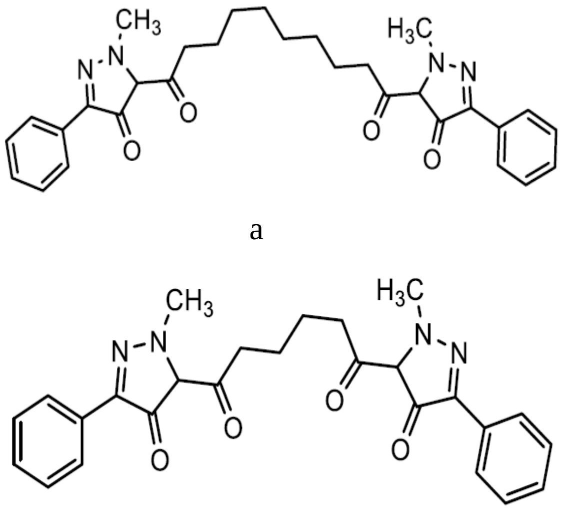


Figure 19. Structure of 4-Sebacoylbis(1-Phenyl-3-Methyl-5-Pyrazolone)

The latest report on Nd^{3+} selective electrodes [49] was based on the application of two ion carriers namely 4-adipoybis (1-phenyl-3-methylpyrazolone-5) (Figure 20-b) and 4-sebacoylbis (1-phenyl-3-methylpirazolone-5) (Figure 20-a). The latter was reported to have a somewhat lower detection limit of 1.91×10^{-5}M and a response slope of 15.9±2.2 mV/decade of Nd^{3+} activity, while those of the former were reported as 2.88×10^{-5} M, and 21.9±1.1 mV/decade of

Nd^{3+} activity. Using the separate solution method, the selectivity profiles of the electrodes were studied for La^{3+}, Ce^{3+}, and Th^{4+} ions, and they were reported to be not selective for La^{3+} and Ce^{3+}, but selective against Th^{4+}.



a

b

Figure 20. Structures of a) 4-sebacoylbis (1-phenyl-3-methylpirazolone-5) and b) 4-adipoybis (1-phenyl-3-methylpyrazolone-5)

4. CONCLUSION

As it has been discussed before [26,50] in the case of other lanthanide ion-selective electrodes suitable ion carriers should constitute flexible semi-cavities, further possessing soft to intermediate donor atoms like S and N in their structure to be able to form wrap-around complexes with target species. This could be the reason why sensors based on rigid ion-carriers namely 5-pyridino-2,8-dithia[9](2,9)-1,10-phenanthrolinephane (Figure 1), 11, 13-diaza-4, 7, 12-trioxo-2(3), 8(9)-dibenzoyl-cyclotetridecane-1, 11-diene (Figure 5), 1,5-di(cyanoethane)-2,4:7,8:13,14-tribenzo-1,5-diaza-9,12-dioxacyclopentadeca-2,7,13-triene (Figure 8),1,5-di(cyanoethane)-2,3,4-pyridine-7,8:13,14-dibenzo-1,3,5-triaza-9,12-dioxa cyclopentadeca-2,7,13-triene (Figure 9), 4-hydroxypyrrolidine-2-carboxylic acid (Figure 17), and 1-nitroso-2-naphtol (Figure 18) showed rather low sensitivity profiles.

Also ion carriers with comparatively smaller chains and bulky groups like N-(2-furylmethylene) pyridine-2,6-diamine (Figure 3) and 5-(methylsulfanyl)-3-phenyl-1H-1,2,4-triazole (Figure 10) gave rise to lower sensitivities, as did the rather rigid ion carriers benzyl bis thiosemicarbazone (Figure 4), N, N_-bis((1H-pyrrol-2-yl) methylene) cyclohexane-1,2-diamine (Figure 6), and 3,3-(cyclohexane-1,2-diylbis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(5-hydroxymethyl)pyridine-2-ol) (Figure 7).

The remaining ionophores, namely 2-{[(6-am-inopyridin-2-yl)imino]methyl}phenol (Figure 21), N,N′-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene (Figure 11), N-(furfuralidene)-N -isonicotinoylhydrazine (Figure 12), N-benzoylethylidene-2-

aminobenzylamine (Figure 13), 5-((1-(3-(3-((5-mercapto-1,3,4-thiadiazol-2-ylimino)methyl)-1H-indol-1-yl)propyl)-1H-indol-3-yl)methyleneamino)-1,3,4-thiadiazole-2-thiol (Figure 14-a) and N-((1-(3-(3-((thiazol-2-ylimino)methyl)-1H-indol-1-yl)propyl)-1H-indol-3-yl) methylene) thiazol-2-amine (Figure 14-b), 1,2-dimaleimidobenzene (Figure 15), N1,N2-bis(salicylidine)butane-1,4-diamine (Figure 16), 4-Sebacoylbis(1-Phenyl-3-Methyl-5-Pyrazolone) (Figure 19), 4-sebacoylbis (1-phenyl-3-methylpirazolone-5) (Figure 20-a) and 4-adipoybis (1-phenyl-3-methylpyrazolone-5) (Figure 20-b), on the other hand, better meet the criteria f suitable ionophores and hence led to very good properties.

Acknowledgments

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