Review

Developments in the Field of Conducting and Non-conducting Polymer Based Potentiometric Membrane Sensors for Ions Over the Past Decade

Farnoush Faridbod 1, Mohammad Reza Ganjali 1,*, Rassoul Dinarvand 2 and Parviz Norouzi 1

1 Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran
2 Medical Nanotechnology Research Centre, Medical Sciences/University of Tehran, Tehran, P.O. Box 14155-6451, Iran

* Author to whom correspondence should be addressed; E-mail: ganjali@khayam.ut.ac.ir; Tel: +98-21-61112788

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Abstract: Many research studies have been conducted on the use of conjugated polymers in the construction of chemical sensors including potentiometric, conductometric and amperometric sensors or biosensors over the last decade. The induction of conductivity on conjugated polymers by treating them with suitable oxidizing agents won Heeger, MacDiarmid and Shirakawa the 2000 Nobel Prize in Chemistry. Common conjugated polymers are poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, poly(terthiophene)s, poly(aniline)s, poly(fluorine)s, poly(3-alkylthiophene)s, polytetraphiafulvalenes, polynapthalenes, poly(p-phenylene sulfide), poly(p-phenylenevinylene)s, poly(3,4-ethylene-dioxythiophene), polyparaphenylene, polyazulene, polyparaphenylene sulfide, polycarbazole and polydiaminonaphthalene. More than 60 sensors for inorganic cations and anions with different characteristics based on conducting polymers have been reported. There have also been reports on the application of non-conducting polymers (nCPs), i.e. PVC, in the construction of potentiometric membrane sensors for determination of more than 60 inorganic cations and anions. However, the leakage of ionophores from the membranes based on these polymers leads to relatively lower life times. In this article, we try to give an overview of Solid-Contact ISE (SCISE), Single-Piece ISE (SPISE), Conducting Polymer (CP)-Based, and also non-conducting polymer PVC-based ISEs for various ions which their difference is in the way of the polymer used with selective
membrane. In SCISEs and SPISEs, the plasticized PVC containing the ionophore and ionic additives govern the selectivity behavior of the electrode and the conducting polymer is responsible of ion-to-electron transducer. However, in CPISEs, the conducting polymer layer is doped with a suitable ionophore which enhances the ion selectivity of the CP while its redox response has to be suppressed.

**Keywords:** Conducting polymer, sensor, ion selective electrodes, non-conducting polymer, potentiometric membrane sensor

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1. Introduction

Potentiometric measurements are based on monitoring potential values under a zero current flow regime, in order to determine the analytical concentration desired components in an analyte. In these methods the potential difference between an indicator electrode (i.e. ion-selective electrode, redox electrode, metal-metal oxide electrode) and the reference electrode is measured as the analytical potential. The potential of an electrochemical cell is due to the changes in the free energy that occurs if
the chemical phenomena reach an equilibrium; which is a concept that is typically applied in quantitative analysis in relation to electrochemical cells, in which case, the difference between the cathodic and the anodic potentials is the potential of the electrochemical cell and is calculated using the so-called Nernst equation. Another source of potential may be physical phenomena not involving explicit redox reactions but having non-zero free energy initial conditions. For instance ion concentration gradients across a semi-permeable membrane can is one of such phenomena. This can also be potentiometric phenomena, and is the basis of measurements that use ion-selective electrodes, according to which the below equation is used to determine the concentration of the analyte:

$$E_{\text{mem}} = \text{Constant} - \frac{RT}{z_i} F \ln a_i$$

(1)

where $z_i$ and $a_i$ represent the charges and the activity of the ion of interest respectively. Potentiometric ion sensors represent well-established analytical tools. The ISE illustrated in Figure 1 is a typical electrode in which the transduction between the ion and electron takes place at the internal reference electrode (Ag/AgCl) immersed in the inner filling solution (KCl), as follows:

$$\text{AgCl} + e^- \leftrightarrow \text{Ag} + \text{Cl}^-$$

(2)

The identical reaction (2) occurs at the external reference electrode (RE), illustrating the reversible and stable connection between the ionic ($\text{Cl}^-$) and electronic ($e^-$) signals. The selectivity is the result of incorporation of specific ionophores in the ion-selective membrane. Potentiometric ion sensors (ISEs) are very attractive, especially due to their small-size and portability, and low cost. Neutral or charged carrier based ISEs, which are available for about 60 different analytes, have found widespread applications in routine uses like clinical analysis [1-7]. On the other hand, to fully use the potentials of this technique, more durable and maintenance-free ISEs that are easily miniaturized are needed.

The works showing that the detection limit of conventional ISEs has the potentials to be lowered towards the sub-nanomolar concentration level [8], making them suitable for trace analyses has attracted more interest to these devices [2]. The development of new and applicable membranes such as plasticizer-free membranes [9], covalently attached ionophores [10], stable carborane anions [11], and monolithic capillary based ISEs [12], can be regarded as a sign of the great interest in these analytical tools.
Fabrication of all-solid-state ISEs that do not require internal filling solutions is another common approach, which necessitates careful design of the solid contact between the ion-selective membrane and the electronic conductor [9-11, 13]. The introduction of the so-called coated-wire electrodes (Figure 2b) about three decades ago, can be regarded as an important step towards solid-state ISEs [14]. These devices, however, suffered from the ill-defined transduction of the ionically conducting ion-selective membrane and the electronic conductor, which made them rather instable. Scientists overcame this by simply using a hydrogel based electrolyte instead of the liquid internal electrolyte of the classical ISE (Figure 2a and 2c) [15]. Hydrogel-contact ISEs suffer, however, from shortcomings originating from the water uptake/release and the resulting volume changes of the hydrogel layer which is a function of the salt concentration of the hydrogel. Another approach to solid-state ISEs is based on the modification of the coated-wire electrodes (Figure 2b), through the application of an intermediate layer of suitable redox and ion-exchange properties at the wire membrane interface [13], in which case, even the application of a monolayer of redox-active compound allows a well-defined pathway for ion-to-electron transduction [16]. Monolayers, however, suffer an inherently low frequency redox capacitance to provide stability condition which depends on the low frequency redox capacitance of the conducting polymer. The low-frequency impedance response of conducting polymers is similar to ideal capacitance resulting from reversible oxidation of the polymer bulk connected with ion transport. The small current that passes through the electrode during potentiometric measurements inevitably results in oxidation/reduction of the conducting polymer, i.e. charging/discharging of the bulk capacitance [17].

**Figure 2.** Structure of ion selective electrode electrodes; a) conventional ISE with an internal reference electrode and internal filling solution; b) coated wire or graphite coated ISE; c) ISE with a hydrogel contact.

The above mentioned may be one of the reasons behind the increasing interest in the application of conducting polymers as ion-to-electron transducers in this group of ISEs [9-11]. The ion-to-electron transduction process in this case is quite identical with the mechanism of this process at the internal reference electrode of the conventional or hydrogel-contact ISE and can be summarized as:

\[
M^+ A^- + e \leftrightarrow M + A^- \quad (3)
\]
where $M^+$ is metal ion (e.g. Ag$^+$) or oxidized conducting polymer unit, $e^-$ is electron, $M$ is metal (e.g. Ag) or neutral conducting polymer unit, and $A^-$ is anion (e.g. Cl$^-$).

Because of the priceless electrical and electrochemical characteristics of conducting polymers, they have found many applications since their discovery. One of them is their wide use in the fabrication of electrochemical sensors such as potentiometric, amperometric and conductometric sensors [10, 18]. They can be used to convert chemical information such as concentration or activity into electrical signals in the solid state. Combination of the properties of the conjugated polymer transducers with those leading to selective molecular recognition is a very important step in the way of obtaining durable chemical sensors. This wide application and great interest is mostly due to the their potential to exhibit improved response properties and also their high sensitivity to small perturbations which are great advantages in comparison to the inert polymers which were used only to enhance the mechanical strength of the membranes. Apart from their unique conductivity and ion transport properties leading to the mentioned advantages, conducting polymers also enjoy the benefits of being compatible with biological molecules in neutral aqueous solutions or even they can be used to bind biomolecules to a biosensor [18-22].

2. Conducting Polymer Based Sensors

Detailed classifications divide “conducting polymers” into several types, including doped conjugated and redox polymers, polymer composites and polymer electrolytes. These compounds have shown to be very promising for the purpose of building different chemical sensors [23-25]. There are several reasons behind their being suitable as transducers in solid-state ISEs. First, they are able to form an ohmic contact to materials of high work functions, like carbon, gold and platinum. Second, due to the solubility of several CPs, they can be deposited from solutions. Third, they have ability to be electroactive materials of mixed electronic and ionic conductivity, which gives them the unique potential to transduce ionic signals into electronic ones.

Figure 3 illustrates some CP monomers and CPs commonly used as ion-to-electron transducers in construction of all solid state potentiometric sensors. Conducting polymers have been used in the construction of ISEs according to general approaches, which have led to the development of solid contact ion selective electrodes (SCISEs), and single-piece ion selective electrodes (SPISEs) and conducting polymer based ion selective electrodes (CPISEs). In SCISEs, the conducting polymer is electro polymerized on the surface of the electronic conductor and then, coated with the ion-selective membrane. The selective membrane determines the selectivity, and the conducting polymer only acts as an ion-to-electron transducer of the sensor. This way, both the ion-exchange and redox characteristics of the conducting polymers are successfully combined with the selectivity of the ionophore-based ion-selective membranes. In SPISEs, the selective membrane contains conducting polymer due to the solubility and the consequent dispersability of conjugated polymers in an organic solvent. In both the above mentioned ISEs, the plasticized PVC containing the ionophore and ionic additives govern the selectivity behavior of the electrode and the conducting polymer is responsible of ion-to-electron transducer. In CPISEs, the conducting polymer layer is doped with a suitable ionophore which enhances the ion selectivity of the CP while its redox response has to be suppressed. Thus, the
redox sensitivity limits the use of CPISEs in direct measurements. The further explanation about these different types of ISEs will be discussed below.

**Figure 3.** Common used CP monomers and CPs as ion-to-electron transducers in construction of all solid state potentiometric sensors.
2.1. Solid-contact ion selective electrode (SCISE)

To construct an SCISE (Figure 4) the CP can be electropolymerized on an electronic conductor and then coated with the ion-selective membrane. In the case of the electrodes prepared in this way, the PVC ion selective coating determines the ion selectivity, while the CP film acts as the ion-to-electron transducer. Bobacka et al. have recently used a number of CPs, like polypyrrole (PPy), poly(3-octylthiophene, POT), and poly(3,4-ethylenedioxythiophene, PEDOT) for the construction of SCISEs [9-11]. Due the special nature and design of the SCISEs, these devices have also been miniaturized to yield solid state ion-selective microelectrodes [26].

Figure 4. different types of conducting polymeric based ISE; a) electronic conductor; b) electronic conductor with a high work function (the work function is the minimum energy needed to remove an electron from a solid to a point close to the solid on the macroscopic scale outside the solid surface); c) conducting polymer; d) ion selective membrane; e) ion selective membrane containing conducting polymer; f) conducting polymer doped with ionophores.

2.2. Single-piece ISE (SPISE)

This approach uses the solubility, and the consequent dispersability, of conjugated polymers in organic solvents such as tetrahydrofuran (THF), which is a commonly used as the solvent to dissolve the membrane components during the preparation of plasticized PVC-based ISEs. So, in case the CP is also dissolved as an additional membrane component it can be physically integrated within the ion-selective membrane, resulting in the so-called single-piece electrode (SPISE) [27]. The presence of the CP in the membrane composition, however, definitely influences the electrode selectivity which changes the role of the CP from SCISE where they have a mere physical role, to SPISEs (Figure 4) where the CP also has a role as a membrane composition, which necessitates the careful optimization of this species in the later approach. It should be noted that, no matter which of the two above-mentioned approaches is used, it is still the plasticized PVC containing the ionophore and ionic additives that governs the selectivity behavior of the electrode.

On the other hand, since the life time of the plasticized PVC membranes is affected by leaching of the membrane components from the membrane into the sample solution, many efforts have been made
to achieve plasticizer-free membranes and covalently bound ion recognition sites, in which case CPs also offer unique possibilities.

2.3. Conducting polymer-based ISE(CPISE)

Conducting polymers (e.g. PPY) are known to possess mixed ionic/redox responses, which introduces some considerations, in case one tends to develop ISEs with a CP polymeric matrix or in other words a conducting polymer-based ISE (CPISE), including the fact that the ion selectivity of the CP should be enhanced while its redox response has to be suppressed. This can be achieved through doping the CP with metal-complexing ligands, the ion selectivity of which depends on the metal-complexing ligand used [28]. Although the redox sensitivity limits the use of CPISEs in direct measurements, such ISEs have been successfully used as potentiometric indicator electrodes in non-classical titrations [29]. For instance in the case of the PPY electrodes, the applicability of the CPISE in titrations was demonstrated by determination of Ca\(^{2+}\) in mineral water [30].

In another attempt to construct a CPISE valinomycin and a lipophilic anion were incorporated in undoped POT to build K\(^{+}\) selective ISEs by dissolving the ingredients in chloroform, and casting the CPISE membrane [31], resulting semi-conducting organic polymer with a reduced redox response (compared to PPY) due to the low electronic conductivity of the undoped POT and the high K\(^{+}\)-selectivity of valinomycin. This is an indication that the selectivity of CP-based membranes can be greatly enhanced by addition of suitable ionophores and ionic sites [31]. POT has also been used, in a similar way, to prepare Cl\(^{-}\) sensors using tridodecylmethylammonium chloride (TDMACl) [32]. Ca\(^{2+}\)-selective CPISEs have also been constructed through the direct addition of a neutral ionophore (ETH 1001) to the soluble PANI [33] or by simply using the Ca\(^{2+}\)-selectivity of the phosphoric acid dopants, incorporated into the membrane [34,35]. In the case of the phosphoric acid dopants either bis(2-ethylhexyl)phosphoric acid [34] or bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphoric acid (DTMBP-PO\(_4\)H) [35] were used as the protonating acid. Some of conducting polymer can be made soluble by treating them with functionalized organic acids, e.g. sulfonic acids and organophosphates [35], which make them at the same time electrically conducting and soluble. Table 1 shows the characterizations of the most reported conducting polymer based ion selective electrodes.

| Ions  | Conducting Polymer | Dynamic Linear Range (M) | Detection Limit (M) | Slope (mV decade \(^{-1}\)) | Ref |
|-------|--------------------|--------------------------|---------------------|-----------------------------|-----|
| H\(^{+}\)-1 | electrochemical polymerization of ortho-methoxyaniline and ortho-methylaniline | pH 2-11 | N.M | 63.8 | 36 |
| H\(^{+}\)-2 | poly(1-aminoanthracene) film | pH 1-12 | 1.0×10\(^{-12}\) | 52.5 | 37 |
| H\(^{+}\)-3 | cobaltabis(dicarbollide) \([3,3’-Co(1,2-C_2B_9H_{11})]^+\)-doped polypyrrole (PPy) | pH 3-12 | 1.0×10\(^{-12}\) | 50 | 38 |
| H\(^{+}\)-4 | polyaniline and its substituted derivatives | pH 2-9 | 1×10\(^{-9}\) | 62.4 ±0.9 | 39 |
Table 1. Cont.

| Ions | Conducting Polymer | Dynamic Linear Range (M) | Detection Limit (M) | Slope (mV decade⁻¹) | Ref |
|------|--------------------|--------------------------|--------------------|---------------------|-----|
| H⁺⁻⁵ | polyaniline (PANI) | pH 2-9                  | 1×10⁻⁶          | 52.7                | 40  |
| H⁺⁻⁶ | polypyrrrole with the dopant anion cobalt bis(dicarbollide) [3,3’-Co(1,2-C₂B₉H₁₁)₂]⁺ | pH 2-9 | 1×10⁻⁹ | 59.8 | 41  |
| H⁺⁻⁷ | polypyrrrole (P-Py) | 10⁻⁶-3                 | N.M               | 45.5                | 42  |
| H⁺⁻⁸ | polypyrrrole       | N.M                    | N.M               | 58                  | 43  |
| H⁺⁻⁹ | poly(aniline) ultrathin films | pH 3-9 | 1.0×10⁻⁹ | 55-59 | 44  |
| Na⁺  | polypyrrrole (PPy), doped with NaBF₄ | 10⁻³-10⁻¹ | 3.0×10⁻⁵ | 59.2 | 45  |
| K⁺⁻¹ | polypyrrrole       | 10⁻⁷-10⁻¹              | 10⁻⁷.⁴           | 65.9                | 46  |
| K⁺⁻² | poly(3-octylthiophene) and valinomycin | 10⁻⁵-10⁻¹ | 5×10⁻⁷ | 49 | 47  |
| K⁺⁻³ | polypyrrrole       | 10⁻⁵ – 10⁻¹            | 1.0×10⁻⁵         | 53.5                | 48  |
| K⁺⁻⁴ | polyaniline (PANI) | 10⁻⁶-10⁻¹              | N.M               | 58.2                | 49  |
| K⁺⁻⁵ | poly(3,4-ethylenedioxythiophene) | 10⁻⁶-10⁻¹ | N.M | - | 50  |
| K⁺⁻⁶ | poly(3,4-ethylenedioxythiophene) | 10⁻⁴-10⁻¹ | 10⁻⁵ | 56.4 | 51  |
| K⁺⁻⁷ | hexacyanoferrate(II)/(II) doped polypyrrrole | 10⁻⁵-10⁻¹ | 10⁻⁵ | 24.3 | 52  |
| K⁺⁻⁸ | polypyrrrole doped with di(2-ethylhexyl)sulfosuccinate | 10⁻⁶-10⁻¹.⁵ | 1.0×10⁻⁶ | - | 53  |
| K⁺ and Cu | poly(3-octylthiophene) | 10⁻⁶-10⁻¹ and 10⁻⁷-10⁻¹ | 5.8×10⁻⁵ and 6.8×10⁻⁵ | 58 and 54 | 54  |
| Mg²⁺ and Ca²⁺ | poly(3,4-ethylenedioxythiophene) | 10⁻⁵-10⁻¹ | 1.0×10⁻⁵ | 29.1 and 28.6 | 55  |
| Ca²⁻⁻¹ | polyaniline functionalized with bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-phosphonate | 10⁻¹ to 10⁻⁴ | 8×10⁻⁷ | 27.8 ± 0.2 | 56  |
| Ca²⁻⁻² | polyaniline and di(2-ethylhexyl)phosphate | 10⁻¹-10⁻³ | 10⁻⁴ | 27.0 ± 0.4 | 57  |
| Ca²⁻⁻³ | polypyrrrole based | 0.1-10⁻¹⁰ | 10⁻⁵ | 27.3 | 58  |
| Ca²⁻⁻⁴ | polyaniline and di(2-ethylhexyl)phosphate | 10⁻³-10⁻¹ | 5×10⁻⁵ | 28.6 ± 1.1 | 59  |
| Li⁺, Ca²⁺ and Cl⁻ | poly(3-octylthiophene) | 10⁻⁴-10⁻¹⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻.substrate) | 3×10⁻⁴⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻::-¹⁻⁻⁻⁻⁻.substrate) | 6×10⁻⁷⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁺⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻(667,131),(970,139)(712,133),(970,139)(712,137),(970,139)(712,131),(970,139)(712,133),(970,139)(712,137),(970,139)(712,131),(970,139)(712,133),(970,139)(712,137),(970,139)(712,131),(970,139)(712,133),(970,139)(712,137),(970,139)(712,131),(970,139)(712,133),(970,139)(712,137),(970,139)(712,131),(970,139) and K⁺ | polyaniline functionalized with bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-phosphonate | 10⁻⁹-10⁻¹⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻.substrate) | 5×10⁻⁹and 4.4×10⁻⁷ | 48.8 | 61  |
| Sr²⁺ | polyaniline/polycarbonate | 1×10⁻¹⁰ to 1×10⁻⁹ | N.M | - | 62  |
| Pb²⁺ or Ca²⁺ | poly(3,4-ethylenedioxythiophene) | 10⁻⁵-10⁻¹ and 10⁻⁴-10⁻¹ | 5.0×10⁻⁵ and 5.0×10⁻⁴ | 29.9 and 27.3 | 63  |
| Pb²⁻⁻¹ | polypyrrrole | 10⁻⁴⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻substrate) | 10⁻⁹ | 58.2 | 64  |
| Cu²⁻⁻¹ | poly(3,4-ethylenedioxythiophene) films doped by hexacyanoferrate anions | 10⁻⁶-10⁻² | 10⁻⁶ | 30 | 65  |
Table 1. Cont.

| Ions | Conducting Polymer | Dynamic Linear Range (M) | Detection Limit (M) | Slope (mV decade⁻¹) | Ref |
|------|--------------------|--------------------------|---------------------|---------------------|-----|
| Cu²⁺-2 | poly(3,4-ethylenedioxythiophene) (PEDOT) doped with 2-(o-arsenophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic sodium salt (Arsenazo-1) | N.M | N.M | 59 | 66 |
| Ag⁺⁻¹ | poly(3,4-ethylenedioxythiophene) (PEDOT) | 10⁻²⁻¹ | 5×10⁻⁵ | 56 | 67 |
| Ag⁺⁻² | poly(3-octylthiophene) (POT) | 10⁻²⁻¹ | 10⁻⁵⁻⁵ | 49 | 68 |
| Ag⁺⁻³ | poly(3,4-ethylenedioxythiophene) | 10⁻³⁻¹ | 5×10⁻⁵ | 60.7 | 69 |
| Ag⁺⁻⁴ | poly(3,4-ethylenedioxythiophene) doped with silver hexabromocarborane | 10⁻³⁻¹ | 1.0×10⁻⁵ | 40.5±1.6 | 70 |
| Ag⁺⁻⁵ | poly(3,4-ethylenedioxythiophene) and polypyrrole doped with sulfonated calixarenes | 10⁻³⁻¹ | 10⁻⁵⁻¹ | 55.7 | 71 |
| Zn²⁺ and K⁺ | tetraphenylborate (TPB) ion doped polypyrrole | 10⁻⁰⁻⁵⁻¹ | 10⁻⁶ | 58 | 72 |
| Hg²⁺ | polypyrrole/polyantimonic acid | 10⁻²⁻¹ | 5.0×10⁻⁵ | 29.6 | 73 |
| CO₃²⁻ | [poly(1-hexyl-3,4-dimethyl-2,5-pyrrolylene)] | 1×10⁻⁴ to 1×10⁻¹ | 2.6×10⁻⁴ | -29.5 | 74 |
| NO₃⁻⁻¹ | doping of polypyrrole | 5.0×10⁻⁵-0.50 | 2×10⁻⁵ | -56 ±1 | 75 |
| S²⁻ | poly(3-methylthiophene) and poly-(dibenzo-18-crown-6) | 5.0×10⁻⁵⁻¹ to 1×10⁻³ | 2.0×10⁻⁹ | -35.7 | 76 |
| F⁻, H₂PO₄⁻ | polyaniline modification | 10⁻³⁻¹ | N.M | -45 and -39 | 77 |
| Cl⁻⁻¹ | poly(3-octylthiophene) and tridodecylmethanium chloride | 10⁻²⁻¹ | 5.0×10⁻⁵ | -58 | 78 |
| Cl⁻⁻² | poly(3-octylthiophene) (POT) | 10⁻²⁻¹ | 5.0×10⁻⁴ | -55.1 | 79 |
| Cl⁻⁻³ | poly(pyrrole) layers doped with chloride (PPyCl) | 2×10⁻³⁻²×10⁻³ and 10⁻³⁻²×10⁻³ | N.M | -58.1 and -33.1 | 80 |
| Cl⁻⁻⁴ | polypyrrole | 10⁻²⁻¹ | 4×10⁻⁷ | -55.9 | 81 |
| Cl⁻⁻⁵ | polypyrrole | 10⁻²⁻¹ | 1.4×10⁻⁴ | -49.8 | 82 |
| Cl⁻⁻⁶ | poly(3,4-ethylenedioxythiophene) (PEDOT) | 10⁻²⁻¹ | 7×10⁻⁷ | -44.4 | 83 |
| Br⁻ | poly(methylthiophene-methylpyrrole) copolymer | 10⁻²⁻¹ | 6×10⁻⁵ | -50 | 84 |
| I⁻⁻¹ | poly(3-methylthiophene) conducting polymer | 1×10⁻⁻₂⁻⁵×10⁻¹ | 1×10⁻⁶ | - | 85 |
| dodecyl sulfate | dodecylsulfate-doped polypyrrole | 10⁻²⁻⁷×10⁻¹ | 5×10⁻⁶ | -57.5 | 86 |

A brief description of potentiometric sensors assimilating conducting polymers is presented. There are several reports of ion-selective sensors based on conducting polymers including about nine reports
about H⁺ sensors including different conducting polymers often doped with different agents [36-44]. Hutchins and colleagues reported in 1993 a pH sensor with a linear dynamic range of 10⁻¹¹ to 10⁻² M concentration of H⁺. A Li⁺ assay was reported by Bobacka et al. in 1994 using a potentiometric sensor that included a conducting poly (3-octylthiophene) polymer, which was also investigated with Ca²⁺ and Cl⁻ [60]. There is a single report of Na⁺ sensor by Cadogan et al. in 1992, where the detection limit for sodium ions was reported to be 3×10⁻⁵ M [45]. Eight K⁺ selective sensors were developed during 1999-2007, among which the best detection limit was 10⁻⁷.₄ M, reported by Pawlowski et al. in 2006 [46-53]. In the same year Paczosa-Bator et al. obtained a slope of 29.1 for the calibration curve for a Mg sensitive conducting polymer doped with ATP [55]. Over a three year period (2003-2006) seven Ca²⁺ ion sensors based on different conducting polymers were reported [56-62]. MMA/DMA copolymer was incorporated as a conducting polymer in a Ca²⁺ sensitive sensor by Sutter et al. in 2004. The detection limit was determined to be 10⁻⁹.₃ M. A sensor for strontium ions which included polymers of polyaniline with polycarbonate was fabricated in 2002 [64]. In 2006 and 2007 two Cu²⁺ electrochemical sensors based on a common conducting polymer were reported while the doping agents were not the same [65, 66]. Poly(3,4-ethylenedioxythiophene) films doped by hexacyanoferrate anions was one combination used as a conducting polymer for Cu(II) selective sensor. Five papers on Ag⁺ sensors based on conducting polymers were published [67-70]; three of them were in 1995, in which Vazques and coworkers made a sensor detecting 10⁻⁵.₃ M of Ag⁺. Khan et al. in 2004 developed a novel ion selective membrane electrode for assay of Hg(II) reaching a detection limit of 5×10⁻⁵ M. A polypyrrole/polyantimonic acid combination was used as conducting polymer [73]. Pandey et al. in 2002 developed a polypyrrole based sensor for Zinc capable of determining Zn ions in the linear range of 10⁻¹ to 10⁻⁵.₆ [72]. Lead ions were determined in one case in 2007, in which Kissiel et al. reported a linear dynamic range of 10⁻² to 10⁻⁵ M for a calibration curve with a slope of 29.9 for Pb ions [63].

Some anions also have been under investigation by conducting polymer based electrochemical sensors during the last decade. The first halogen (F⁻) was determined together with H₂PO₄ with a modified polyaniline sensor by Shiskanove et al. in 2005 [77]. Six publications have probed chloride ion sensors during 1999 to 2004 [78-83]. The best detection limit was achieved by Michalska et al. in 2003. They obtained a detection limit of 4×10⁻⁷ M utilizing a polypyrrole as conducting polymer. Another halogen (Br⁻) was investigated once in 1997 by Wang et al. achieving a detection limit of 6×10⁻⁵ M for Br⁻ [84]. In 1994 Galal et al. reported an iodide selective sensor and there was another report on an iodide sensor in 1999 by Wolf et al. in which I⁻ was determined down to 5×10⁻⁴ M [85,86]. A potentiometric sulfide selective electrode based on two different conducting polymers with a fine performance was developed by Atta et al. The detection limit of their proposed electrode was 8×10⁻⁷ M of sulfide ions [76]. Hutchins et al. also investigated a NO₃⁻ selective electrode in 1995 [75]. The linear dynamic range of the latter report was 8.0×10⁻⁵ to 2.5×10⁻² M of NO₃⁻. In 2002 Song et al. reported a CO₂²⁻ sensor incorporating poly(1-hexyl-3,4-dimethyl-2,5-pyrrolylene) as conducting polymer [74]. Another organic compound, dodecylsuphate (DDS), was determined by a conducting polymer based sensor in which the detection limit was investigated to be down to 5×10⁻⁶ M of DDS [86].
3. Non-conducting Polymer PVC-Based ISEs

The electrodes with mobile charged sites, illustrating ionophores (organic or inorganic) compounds which bind to cations and anions, are broadly used in complex biological and environmental samples [6]. Nowadays, the response mechanism of these electrodes has been extensively investigated [7], revealing that the scientific interest should be principally concentrated on the research and the design of new ionophores [3].

In this way, the fabrication highly ion-selective electrodes (ISEs) become feasible [4,5]. The recent publication of several review studies [3-7] with reference to ISEs delineates their great significance. This relatively modern field has been subject to extensive research in the period of 1999-2007 when more than 100 ISEs just employing Schiff bases as ionophore [5].

3.1. ISE membrane components

Each polymeric membrane ISE comprises four basic components:

1. The polymeric matrix
2. The ionophore (membrane–active recognition)
3. The membrane solvent (plasticizer)
4. Ionic additives

The ISE nature and characteristics are considerably influenced by the nature and the amount of each component. As far as the polymeric membrane is concerned, it separates the test solution from the inner compartment, containing the target ion solution [4].

3.1.1. The polymeric matrix

Initially, to construct the liquid ISE membrane porous materials were soaked in a solution of a water-immiscible, nonvolatile, viscous organic liquid containing the dissolved ionophore. Recently, polymers have been utilized as homogeneous membrane matrices. For the preparation of a sensing membrane, a typical composition is as follows: 33% (w/w) PVC as the polymeric matrix, 66% plasticizer for the matrix homogenization and 1% ionophore. Regarding the first polymeric ISE membranes, their manufacture involved valinomycin as the neutral ion carrier in silicone rubber or PVC without the addition of lipophilic ionic sites. In such polymeric membranes, the polymer could provide the required physical properties (e.g. elasticity and mechanical stability). It should be stressed that these ISEs exhibited a Nernstian response, owing to the possible ionic impurity presence in the used PVC as well as in the presence of the other membrane components. Moreover, membranes with no ionic sites did not respond to the target ion concentration, as they incorporate almost completely pure membrane ingredients [7].

Aside from PVC, other polymers can be also employed in membrane fabrication. The suitability of the polymer to be employed in a sensing membrane (when the required solubility is displayed) is defined by the glass transition temperature (Tg) of the polymer (Tg is the temperature at which an amorphous solid, such as glass or a polymer, becomes brittle on cooling, or soft on heating). The Tg
value should be below the room temperature. As a consequence, the designed membranes are fluid enough under the ambient conditions, they allow the diffusion of the membrane components, they present reasonable ionic conductivities and they illustrate the proper mechanical properties to be handled for routine processes. If the polymers are characterized by high $T_g$ values (e.g. the $T_g$ value of the high molecular weight PVC is 80 °C), the use of plasticizers will be necessary. On the contrary, if the polymers are characterized by low $T_g$ values, such as soft polyurethanes with a low content of crystalline units, silicone rubber, poly(vinylidene chloride) and polysiloxanes, the use of plasticizers is not obligatory. In this way, the risk of the plasticizer leaching is avoided. Nevertheless, when no plasticizer is incorporated in the membrane, the ion selectivity modification by varying the plasticizer is no longer an alternative.

Different polymer types have been examined to be applied to membrane preparation. The majority of the examinations focused on the PVC derivatives with 1.8 % carboxylate groups. The respective sensing devices, based on several neutral carriers, presented similar characteristics to those of the PVC matrices. The reason is that the COOH groups remain principally undissociated. The aminated PVC or the related polymers are at least partly protonated upon contact with the aqueous samples, having been used to fabricate the so-called ionophore-free H$^+$-selective liquid membrane electrodes. The neutral-carrier-based Na$^+$-selective ISEs with a vinyl chloride-vinyl alcohol copolymer (OH-PVC) matrix illustrated reduced protein-induced asymmetry effects.

The ISE membrane biocompatibility is of vital importance with regard to the clinical applications. For the in-vitro measurements, the protein deposition on the membrane surfaces causes membrane asymmetries and instabilities [6]. Then, frequent recalibration and skilled personnel are required. In contrast, in the in-vivo measurements, attention should be paid to the components leaching as they may have inflammatory, toxic and/or thrombogenic properties. Polyurethanes can decrease the inflammatory response and display excellent adhesive properties. A way to improve their biocompatibility is to covalently bond hydrophilic poly(ethylene oxide) to the surface of the polyurethane membranes. With respect to the blood compatibility, its improvement is possible by covalently attaching heparin to the membrane surface. Photocurable polymer matrices are usually used for the development of miniaturized electrodes by standard photolithography, as applied to the microelectronics technology. Such matrices, tested for the ISE membrane suitability, are the acrylates and the methacrylates, the methacrylated siloxane resins, the epoxyacrylates, polystyrene and the acrylates of urethane oligomers. Concerning the miniaturized electrodes, it is recommended to covalently attach all the membrane components, including the ionophore. To the polymer matrix, not only charged but also uncharged ionophores have been covalently bonded, seemingly with no essential loss in the electrode performance [7].

3.1.2. The ionophore (membrane–active recognition)

The ionophore or the ion carrier is the most vital component in a polymeric membrane sensor in terms of selectivity and selectivity. The ionophore or the membrane–active recognition can be an ion exchanger or a neutral macrocyclic compound [3]. It has molecule-sized dimensions and it contains cavities or semi-cavity to surround the target ions. The binding between the ionophore and the target
ion is the molecular-level phenomenon, sensed by the ISE. Therefore, the various ISE selectivities towards the other ions are regarded to derive from the difference in the binding strengths between the selected ionophore, to be used in the sensor, and the different ions. The ISE function involves the phase transfer of the aqueous ions into an organic medium of the ISE, which is typically the plasticized PVC (as it will be discussed later). Actually, the transferred ions interact with the membrane components. In case that the incorporated ionophore is a simple ion-exchanging species, (e.g. a lipophilic ionic additive), the ion transfer process from the aqueous phase into the polymeric membrane of the sensor will be controlled by the lipophilicity of the exchanged ions, such as a phase transfer equilibrium. The selectivity behavior of an ion-exchanger based ISE, where the ionophore does not have any chemical recognition abilities, certainly reflects the relative lipophilicities of the studied ions. In other words, higher ion lipophilicity results in a greater sensor response towards the ion. After a number of studies conducted with ion-exchanging ISEs and liquid–liquid extraction assays, a lipophilicity-dependent selectivity pattern was concluded. This pattern, however, is valid only when the response is a function of the ion lipophilicity. For the cations, the corresponding pattern is:

\[ \text{Cs}^+ > \text{Ag}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{Ca}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} \]

In parallel, the respective pattern for the anions is as follows:

\[ \text{ClO}_4^- > \text{SCN}^- > \Gamma^- > \text{salicylate} > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- > \text{Cl}^- > \text{HSO}_4^- > \text{acetate} > \text{SO}_4^{2-} > \text{HPO}_4^{2-} \]

These patterns are known as the Hofmeister series [87]. On the other hand, the incorporation of a selectively binding ionophore into the ion-sensing membrane reduces the total free energy for the transfer of the ionophore-bound ions to the organic phase in comparison with that of the simply aqueous ions. When the ionophore binds to an ion strongly, its influence on the ion phase transfer equilibrium is higher. The complex formation constant \( K_f \) of an ionophore and one or more of the ions is sufficiently strong, a difference is expected in the observed/calculated selectivity for the ionophore-based sensor, compared with the lipophilicity series depicted above. Likewise, if the ionophore-ion complexes are stronger, a greater difference is expected in the magnitude of the selectivity coefficients versus the lipophilicity series [4,7].

### 3.1.3. The membrane solvent (Plasticizer)

The additives, which increase the plasticity or fluidity of the material to which they are added, are called plasticizers. Normally, the composition of the solvent polymeric membranes, used in the ion-selective devices, is about 30-33% (w/w) PVC and 60-66% of a membrane solvent. Such a composition exhibits optimal physical properties, ensuring relatively high mobilities for their constituents. The membrane solvent has to be physically compatible with the polymer (i.e. have plasticizer properties), so as to give a homogeneous organic phase. Additionally, it may affect the selectivity behavior. In contrast, the selectivities of the carrier-based ISEs are significantly influenced by the membrane solvent. For example, a plasticizer change from the polar \( o\text{-NPOE} \) or nitrobenzene (NB) to the apolar dibutyl phthalate (DBP) reduced the \( M^{2+} \)-selectivity of the ISE with the ionophore 2,3,8,9-tetraazacyclododeca-1,3,7,9-tetraene. This influence can be attributed to the plasticizer polarity,
which can be estimated from the interaction of the charged species with a continuum of the given dielectric constant (Born model) [7].

Nonetheless, the plasticizer selection is performed in line with its compatibility with the ionophore (solubility reasons) as well as the final ISE application. The names/abbreviations of the most common plasticizers employed in the ISE fabrication are as follows: benzyl acetate (BA) [88], bis-(1-butylpentyl)adipate (BBPA) [89], bis(2-ethylhexyl) adipate (DOA) [90], bis(2-ethylhexyl) phthalate (dioctyl phthalate, DOP) [91], bis(2-ethylhexyl) sebacate (BEHS) [92], bis(n-octyl)sebacate (DOS) [93], dibenzyl ether (DBE) [94], dibutyl phthalates (DBP) [95], dibutyl sebacate (DBS) [93], didecyl phthalate (DDP) [96], 2-nitrophenyl phenyl ether (o-NPPE) [98], o-nitrophenyl octyl ether (o-NPOE) [99,100] and tri-n-butyl phosphate (TBP) [101].

3.1.4. Plasticizer-Free Polymer Membrane ISEs

PVC has been utilized as a polymer matrix for more than 30 years [7], despite the fact that there are many drawbacks related with its usage. Plasticizer leakage is one them. Diminished sensor lifetimes, unstable responses and sample perturbation are caused by the plasticizer exudation from the sensing membranes. Furthermore, the decreased plasticizer content can reduce the ionophore solubility and the ion exchanger within the membrane, leading to a considerable sensitivity and selectivity reduction. A usual disadvantage of the plasticized-PVC observed in the ion-selective field effect transistors (ISFETs) is its poor adhesion to the gate oxide surfaces, which results in a shortened lifetime of the sensing device [7].

3.1.5. Ionic additives

The permselectivity of the ISE membranes is a prerequisite in order to attain a theoretical response. The permselectivity ensures that no significant amount of the counter ions may enter the membrane phase. To achieve this so-called Donnan exclusion with the electrically neutral carriers, the counter ions (ionic sites) confined to the membrane must be present. Despite the fact that the neutral-carrier-based ISE membranes could function properly, even when they contain only a very small amount of ionic sites, the addition of a lipophilic ion salt is advantageous for various other reasons. The anionic interference decrease, observed in the presence of lipophilic anions (e.g. thiocyanate) is the basic reason for the addition of a tetraphenyl borate salt to the membrane of a cation-selective electrode. Simultaneously, the electrical resistance of the membrane is diminished, which is especially important in microelectrodes. The ionic additives are ion exchangers, which themselves induce a selective response if no or only an insufficient ionophore amount is present. It becomes pretty obvious that their concentration must be carefully adjusted [7].

The most important salts used as lipophilic additives are potassium tetrakis(p-chlorophenyl) borate (KTPClPB) [102,103], sodium tetrakis-[3,5-bis(1,1,3,3-hexafluoro-2-methoxy-2-propyl)phenyl]borate (NaHFPB) [104], sodium tetraphenyl borate (NaTPB) [105], tetrakis(4-fluorophenyl)borate (cesibor) [106], tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB) [98] as cationic additive and
hexadecylpyridinium bromide (HDPB) [107], hexadecyltrimethylammonium bromide (HTAB) [107],
triocetyltrimethylammonium chloride (TOMACl) [108] as anionic additive.

A variety of tetraphenyl borate derivatives were recently employed as anionic additives. Their
disadvantage is that their chemical stability is limited, especially in the presence of acids, oxidants and
light. The decomposition of these compounds is attributed to the H\(^+\) ions attack on the phenyl
substituents. The introduction of electron withdrawing substituents may increase the stability. The best
available anionic additives are sodium oleic acid (OA) [95] and potassium tetrakis[p-chlorophenyl]-
borate (KTpClPB) [103], on account of their chemical stability and lipophilicity. Ganjali et al. reported
the use of the first fatty acid (e.g. oleic acid), as an appropriate lipophilic additive, for inducing
permselectivity to some PVC membrane selective electrodes. Suitable cationic additives are considered
to be the lipophilic tetraalkylammonium salts, like the hexadecyltrimethylammonium bromide (HTAB)
[107]. The hydrophilic counter ions of these lipophilic additives are exchanged with the primary ion as
soon as the ISE is conditioned in the respective solutions.

To avoid the ionic sites leakage, their covalent bonding to the polymer matrix can be of interest (e.g.
in sulfonated PVC). It should be nonetheless mentioned that the polymer could display a modified
selectivity behavior, owing to the direct interaction of the sulfonate group with the cations [4,7].

3.2. Non-conducting Polymer Membrane Sensors for the Hydrogen Ion and the First Main
Group Cations

The macrocyclic ligands can form selective and stable complexes with the metal ions of compatible
dimensions [94] and can potentially be applied to their separation and determination [110-112]. For
these reasons, continuous interest has been focused on the design and synthesis of new functionalized
macrocycles for specific applications. Polymeric carrier-based ion-selective electrodes (ISEs), which
are selective towards the alkali and the alkaline earth metal ions such as sodium, potassium and
lithium, have been the focus of numerous studies [7].

Potentiometric detectors based on ISEs are also considered suitable for this determination, since
they offer advantages such as high selectivity, sensitivity, good precision, simplicity, portability, non-
destructive analysis, ability to monitor the ion activity without extensive sample preparation and low
cost. Because of the importance of developing new ionophores in the construction of liquid membrane
ISEs, many cyclic and acyclic macromolecules have been introduced as ionophores.

A large number of H\(^+\)-ISEs, based on different ionophores, have been introduced, during the past
decade. They also exhibit excellent selectivities, which are absolutely comparable with, or in some
cases, are even better than those of the glass electrodes. The names of some of the ionophores that were
used in these sensors are 4,5-dibromofluorescein octadecylester (ETH 7075) [113], alkyl dibenzylamline
[114], porphyrin [115], 1,1(-bis(11-mercaptopoundecyl) ferrocene [116], tertiary amine containing
different alkyl chains [117], \(N,N,N,N\)-tetra benzylethenediamine \([118]\), \(p\)-tert-butylcalix[4]arene-oxa-
crown-4 \([119]\), \(N,N\)-dialkylbenzylethylenediamine \([120]\), tridecylamine (TDDA) \([121,122]\,
alkyl dibenzyl amines \([123]\), and tribenzylamine \([124]\).

During the past decade, there were four reports on Li\(^+\) ion selective electrodes based on NASICON-
type ceramics, 16-crown-4 derivatives, and 1,10-phenanthroline derivatives [125-128], four reports on
Na\(^+\) based on calix[4]arene triesters, cetylpyridinium-nitroprusside ion pair, dibenzopyridino-18-crown-6 and silacrown ether [129-132], more than 13 reports on K\(^+\) based on rifamycin, benzo-15-crown-5, gamma-cyclodextrin, benzo-15-crown-5 fluoroionophore, dibenzo-18-crown-6, 5-dicarboxylic acid, decyl-18-crown-6, 4-acryloylamidobenzo-15-crown-5, bis(15-crown-5 ether) derived from xanthene-4,5-dicarboxylic acid, 2,2-(bis[3,4-(15-crown-5)-2-nitrophenylcarbamoxymethyl]tetradecane, styrene/4(-vinylbenzo-24-crown-8) copolymer, valinomycin, bis(crown ether) ionophore containing two benzo-15-crown-5 moieties and cis-and trans-bis(crown ether)s [133-145], for Rb\(^+\) there was one report which is based on crown ethers incorporating anthraquinone, benzoquinone, and 1,4-dimethoxybezene [146] and 11 reports on Cs\(^+\) ion selective electrodes based on upper-rim calix[4]crown, calix[4]arene dibenzocrown ether, lipophilic calix[6]arene tetraester derivatives, pyrone compound, quadruply-bridged calix[6]arenas, biscalix[4]arene-25,25',27,27'-bis(1,3-dioxypropane)-bis(5,11,17,23-p-tert-tetrabutylcalix[4]arene-26,28-diol), calix[4]arene derivative [25-(3-bromopropoxy)-5,11,-17,23-tetra-kis(tert-butyl)-26,27,28-tris(1-propyloxy)calix[4]arene], poly(tetrafluoroethylene-co-ethylene-co-vinyl acetate), 1,3-alternate thiacalix[4]bicrown-6,6, Cs-12-molybdo-phosphate, sodium tetrakis-[3,5-bis(trifluoromethyl)phenyl] borate [147-157].

**Figure 5.** The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for alkali cations.

The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for alkali cations is shown in Figure 5.

Table 2 shows the characterization of the best reported alkali cation selective sensors based on non-conducting polymer.
Table 2. Characterization of a number of reported ion selective sensors based on non-conducting polymers for alkali cations.

| Cation | Ionophore                                                                 | Slope (mV decade⁻¹) | Linear Range (M) | Most Important Interfering ions (log K_{sel} > -2) | Ref. |
|--------|---------------------------------------------------------------------------|---------------------|------------------|---------------------------------------------------|------|
| Li⁺-1  | lipophilic crown-4 derivatives 1,10-Phenanthroline Derivatives             | 58                  | 10⁻²⁻¹0⁻¹        | Na⁺, K⁺,NH₄⁺                                        | 125  |
| Li⁺-2  | 1,10-Phenanthroline Derivatives                                           | 58.7                | 10⁻⁴⁻¹0⁻¹        | Na⁺, K⁺                                            | 128  |
| Na⁺    | 1-methyl-1-vinyl-14-crown-5                                               | 55.0                | 3.16×10⁻⁶ - 1.0×10⁻¹ | K⁺                                                 | 132  |
| K⁺     | styrene/4(-vinyl-benzo-24-crown-8) copolymer                             | 58                  | 1.0×10⁻⁶ - 1.0×10⁻¹ | -                                                  | 140  |
| Rb⁺    | crown ethers incorporating anthraquinone, benzoquinone, and 1,4-dimethoxybezene | 54.7                | 1.0×10⁻² - 1.0×10⁻¹ | Na⁺, K⁺, Mg²⁺, NH₄⁺, Li⁺                            | 145  |
| Cs⁺    | calix[4]arene derivative [25-(3-bromo-proploxy)-5,11,-17,23-tetrakis(tert-butyl)-26,27,28-tris(1-propyloxy) calix[4]arene] | 58                  | 1.0×10⁻⁴ - 1.0×10⁻¹ | -                                                  | 153  |

Some of the above ionophores used in construction of non-conducting polymer ISEs for first main group cations are shown in Figure 6.

Figure 6. Structures of some ionophores used in construction of ion selective membrane sensors for some of first main group cations
3.3. Non-conducting Molymer Membrane Sensors for the Second Main Group Cations

During the past decade, there were nine reports on Be\(^{2+}\) ion selective electrodes, mostly based on benzo-9-crown-3 and its derivatives [102, 158-165], three reports on Mg\(^{2+}\) based on the synthetic neutral carrier ETHT 5504, araldite zirconium(IV) selenomolybdate and benzo-15-crown-5 [166-168], more than eight reports on Ca\(^{2+}\) based on polyaniline functionalized with bis[4-(1,1,3,3-tetramethylbutyl)phenyl]phosphate, bilirubin (1,3,6,7-tetramethyl-4,5-dicarboxyethyl-2,8-divinyl-[b13]-dihydrobilenone, dibenzo-18-crown-6, 2-(2-hydroxyphenyl)iminio]1,2-diphenylethanone, ETH 1001 and ETH 129, dimethyl 1-(4-nitrobenzoyl)-8-oxo-2,8-dihydro-1H-pyrazolo[5,1-a]isoxindole-2,3-dicarboxylate, x-furyl dioxime [99, 169-175], For Sr\(^{2+}\) there were eight reports based on lipophilic diamides containing pyridine rings, dibenzo-24-crown-8 and 4-tert-butylcalix[8]arene, 5,11,17,23, 29,35-hexakis-(1,1,3,3-tetramethylbutyl)-37,38,39,40,41,42-hexakis(carboxymethoxy)-calix[6]arene, 5,7,12,14-di-benzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane, 1,10-diaza-5,6-benzo-4,7-dioxacyclohexa-decane-2,9-dione [174-181] and three reports on Ba\(^{2+}\) ion selective electrodes [182-184]. The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for alkaline cations is shown in Figure 7.

**Figure 7.** The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for alkaline earth cations

Table 3, shows the characterization and properties of the reported alkaline cation membrane sensors.
Table 3. Characterization of a number of reported ion selective sensors based on non-conducting polymers for alkaline earth cations.

| Cation  | Ionophore                                                                 | Slope (mV decade⁻¹) | Linear Range (M)                  | Most Important Interfering ions (log $K_{sel} > -2$) | Ref. |
|---------|---------------------------------------------------------------------------|----------------------|----------------------------------|------------------------------------------------------|------|
| Be⁴⁺-1  | 2,3,5,6,8,9-hexahydro-1,4,7,10-benzoetra oxacyclodecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hydride 2,6-diphenyl-4-benzo-9-crown-3-pyridine | 29.9                 | 1.0×10⁻⁷-1.0×10⁻¹                 | Na⁺, Ca²⁺, Li¹⁺                                      | 151  |
| Be²⁺-2  | synthetic neutral carrier ETHT 5504 araldite zirconium(IV) selenomolybdate | 28.6                 | 1.0×10⁻⁵-1.0×10⁻¹                 | Mg²⁺, Ca²⁺, K⁺, Na⁺                                  | 152  |
| Mg²⁺-1  | [2-(2-hydroxyphenyl)iminol]-1,2-diphenylethanone dimethyl [1-(4-nitrobenzoyl)-8-oxo-2,8-dihydro-1H-pyrazolo[5,1-a]isoindole-2,3-dicarboxylate] | 28.5                 | 1.0×10⁻⁶-8.0×10⁻⁷                 | -                                                   | 166  |
| Mg²⁺-2  | Ca²⁺-1 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane 1,10-diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione | 29.0                 | 3.98×10⁻⁶-1.0×10⁻¹                 | Ca²⁺                                                | 173  |
| Ca²⁺-2  | Sr²⁺-1 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane 1,10-diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione | 30.0                 | 1.6×10⁻⁶-3.0×10⁻¹                 | -                                                   | 179  |
| Ba⁴⁺-1  | Ca²⁺-2 5,7,12,14-dibenzo-2,3,9,10-tetraoxa-1,4,8,11-tetraazacyclotetradecane 1,10-diaza-5,6-benzo-4,7-dioxacyclohexadecane-2,9-dione | 29.7                 | 1.0×10⁻⁶-1.0×10⁻¹                 | -                                                   | 180  |

Chemical structures of some of the above ionophores used in construction of non-conducting polymer ISEs for second main group cations are shown in Figure 8.

Figure 8. Structures of suitable ionophores used in construction of ion selective membrane sensors for some of second main group cations.
3.4. Non-Conducting Polymer Membrane Sensors for the Third Main Group Cations

The development of ISEs for trivalent cations is difficult, owing to the high hydration energy and their existence as free $M^3+$ in narrow pH ranges. Due to the many industrial applications of these elements, their potentiometric monitoring is of great interest. A limited number of selective membrane sensors were developed for the cations of the IIIA Group.

During the past decade, there were five reports on $\text{Al}^3+$ ion selective electrodes based on furyl (ethanedione, di-(2-furyl)), bis(5-phenylazalicylaldehyde)-2,3-naphthalene diimine, hydroxythioxanthones, xanthone derivative, and $N,N$-bis(salicylidene)-1,2-phenylenediamine (salophen) [185-189], two reports on $\text{Ga}^3+$ sensors based on clorogallium(III), 2,9-dimethyl-4,11-diphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetraene (DDTCT) [190, 191], two reports on $\text{In}^3+$ ISEs based on 1-benzyl-3-methyl-4-benzoyl-5-pyrazolone, 15-crown-5-dicyclohexano-18-crown-6 [192, 193], and seven reports on $\text{Tl}^3+$ ion selective electrodes based on quinoline-carbonitrile calix[6]arene or calix[5]arene derivatives, 1,21,23,25-tetramethyl-2,20:3,19-dimetheno-[H,2]H,23H,25H-bis-[1,3]dioxocino[5,4-i:5', 4'-i]benzo[1,2d:5,4-d']bis[1,3]benzodioxocin, 2'-amino-1,3,5'-trioxospiro[indane-2,4'(5'H)-3'-cyano indeno(1.2-b)]pyran, dibenzyldiaza-18-crown-6, tetrachloothyallate(III)-2,3,5-triphenyl-2-H-tetrazolium ion pair, and $N'$-dioctylethlenediamine-$N'$-disuccinic acid [194-200]. The statistical diagram of the reported potentiometric membrane sensors based on non-conducting polymer for third main group cations is shown in Figure 9. According to the literature survey, there are no reports on potentiometric sensors based on conducting polymers for third main group.

**Figure 9.** The statistical diagram of the reported potentiometric membrane sensors based on non-conducting polymer for third main group cation.

Table 4, shows the characterization and properties of the reported third main group cation membrane sensors.
Table 4. Characterization of a number of reported ion selective sensors based on non-conducting polymers for third main group cations.

| Cation   | Ionophore                                | Slope (mV decade\(^{-1}\)) | Linear Range (M) | Most Important Interfering ions (log \(K_{sel} > -2\)) | Ref. |
|----------|------------------------------------------|----------------------------|------------------|------------------------------------------------------|------|
| Al\(^{3+}\) | xanthone derivative                       | 20.0                       | 1.0 \times 10^{-6} - 1.6 \times 10^{-1} | Hg\(^{2+}\), Ba\(^{2+}\)                              | 188  |
| Ga\(^{3+}\) | chlorogallium(III)                        | 30                         | 10^{-6} - 10^{-2} | -                                                   | 190  |
| In\(^{3+}\) | 1-benzyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) | 18.7                       | 3.2 \times 10^{-5} - 1.0 \times 10^{-1} | Ga\(^{3+}\)                                           | 192  |
| Tl\(^{3+}\)-1 | 2'-amino-1,3,5'-trioxo-spiro[indane-2,4'\(5'H\)-3'-cyano-indeno(1.2-b)]pyran | 59                         | 0.1-1.0 \times 10^{-6} | Rb\(^+\), Cs\(^+\)                                   | 197  |
| Tl\(^{3+}\)-2 | \(N'\)-dioctylethylene-diamine-\(N'\)-disuccinic acid | 56                         | 6.4 \times 10^{-7} - 10^{-2} | Rb\(^+\)                                              | 200  |

Chemical structures of some above ionophores which are used in construction of non-conducting polymer ISEs for third main group cations are shown in Figure 10.

**Figure 10.** The structures of the suitable ionophores used in construction of third main group cation membrane sensors

![Chemical structures](image-url)
3.5. Non-conducting Polymer Membrane Sensors for the Fourth Main Group Cations

Tin and lead ions are the only cations of this group which have the reported membrane sensors. During the past decade, there were two reports on Sn\(^{2+}\) ion selective electrodes based on dibenzo-18-crown-6 and 6-(4-nitrophenyl)-2,4-diphenyl-3,5-diaza-bicyclo[3.1.0]hex-2-ene [201,202], and more than 40 reports on Pb\(^{2+}\) ion selective electrodes based on quinaldic acid derivatives, capric acid, piroxicam, 2,2'-dithiodibenzonic acid, anthraquinone derivatives, 4-tert-butylcalix[6]arene, meso-tetrakis(2-hydroxy-1-naphthyl)porphyrin, atropisomers, dibenzodiaza-15-crown-4,4,5-diaza-9-(4-methyl-phenyl)imino fluorine, 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo) phenylhydrazone, oximino-phenyl-2-ketomethyl quinoline, 1-furoyl-3-(2hydroxyethyl)thiourea, dibenzyl phosphate, tetrabenzyl pyrophosphate and diphenylphosphinic anhydride, tetraphenylporphyrin, 1-furoyl-3-phenylthiourea, 4,7,13,16-tetraethenoyl-1,10-dioxa-4,7,13,16-tetraazacyclooctadecane, 4'-vinylbenzo-15-crown-5-1,5-bis[2-(N,N-dialkylcarbamoylmethoxy)phenoxo]3-oxa-pentanes, 1,4,1,5-bis[2-(N,N-dialkylcarbamoyl-pentadeacyloxy)phenoxo]-3-oxapentanes, dithiophenediazacrown ether derivatives, N, N'-bis-thiophene-2-ylmetheneethane-1,2-diamine, calix[4]arene amide derivatives, 1,8-dihydroxy-2,7-bis(prop-2'-enyl)-9,10, 5,5'-dithiobis-(2-nitrobenzoic acid), bis[(1-hydroxy-9,10-anthraquinone)-2-methyl]sulfide, 1-furoyl-3,3-diethylthiourea, bis(acetylacetone)-p-phenylenediamine lead(II) complex, N,N'-bis(5-methylsalicylidene)-p-diphenylenemethane diamine, N,N'-bis(3-methyl-salicylidine)-p-phenylmethane diamine, 1,10-dibenzyl-1,10-diaza-18-crown-6, N,N'-bis-thiophene-2-ylmetheneethane-1,2-diamine, N,N'-bis(salicylidene)-2,6-pyridinediamine Schiff's base as a neutral carrier, N,N'-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclocotadecane [203-239]. The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for fourth main group cations is shown in Figure 11.

**Figure 11.** The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for fourth main group cation

Table 5, shows the characterization and properties of the reported fourth main group cation membrane sensors.
Table 5. Characterization of a number of reported ion selective sensors based on non-conducting polymers for fourth main group cations.

| Cation | Ionophore                                                                 | Slope (mV decade⁻¹) | Linear Range (M)   | Most Important Interfering ions (log K_{sel} > -2) | Ref.  |
|--------|---------------------------------------------------------------------------|----------------------|---------------------|---------------------------------------------------|-------|
| Sn²⁺ -1| dibenzo-18-crown-6(DB18C6)                                                | 27.5                 | 1.0 × 10⁻⁶ - 1.0 × 10⁻² | -                                                 | 201   |
| Sn²⁺ -2| 6-(4-nitrophenyl)-2,4-diphenyl-3,5-diazabicyclo[3.1.0] hex-2-ene           | 28.8                 | 1.0 × 10⁻⁵ - 1.0 × 10⁻¹ | -                                                 | 202   |
| Pb²⁺ -1| anthraquinone derivative                                                  | 29.5                 | 1.0 × 10⁻⁷ - 1.0 × 10⁻² | -                                                 | 207   |
| Pb²⁺ -2| 1-phenyl-2-(2-quinolyl)-1,2-dioxo-2-(4-bromo)phenylhydrazone              | 28.7                 | 1.0 × 10⁻⁶ - 1 × 10⁻¹  | -                                                 | 222   |
| Pb²⁺ -3| diporphyrin xanthene(ADPX)                                                | 28.2                 | 2.6 × 10⁻⁶ - 1.0 × 10⁻¹ | -                                                 | 229   |
| Pb²⁺ -4| N,N'-bis(salicylidene)-2,6-pyridinediamine                                | 29.4                 | 1.0 × 10⁻⁶-1.0 × 10⁻¹  | K⁺, Ag⁺                                           | 234   |

Chemical structures of some of the above ionophores used in the construction of non-conducting polymer ISEs for fourth main group cations are shown in Figure 12.

Figure 12. Some structures of the suitable ionophores used in construction of lead and tin ion membrane sensors.
3.6. Non-conducting Polymer Membrane Sensors for the Transition Metal Cations

Among the 29 transition metals, liquid membrane sensors have been reported only 14 of them. Construction and application of ion selective electrode as a potentiometric sensor for determination of the ions in the real samples, offers interesting advantages such as simplicity, speed, relatively fast response, low cost, wide linear dynamic range and ease of preparation and procedures.

A literature survey reveals that during the past decade, more than 170 ion selective membrane sensors for transition metal cations have been reported. One report for Y$^{3+}$ based on $S\cdot N$ Schiff's base [240], one report for Zr$^{4+}$ based on bis(diphenylphosphino) ferrocene [241], one report for vanadyl ion based on $N,N'$-bis-(salicylidene)-2,2-dimethylpropane-1,3-diamine [242], 12 reports on Cr$^{3+}$ ion selective electrodes based on 2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene, a new tridentate $S,N,O$ Schiff's base 4-hydroxysalicylade-2-mercaptoanil, 2-hydroxybenzaldehyde-$O\cdot O'$-(1,2-dioxetane-1,2-diyl) oxime, $N$-(1-thien-2-ylethyliden)benzene-1,2-diamine, 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and calix[6]arene, tri-$o$-thymotide, oxalic acid bis(cyclohexylidene hydrazide), ion-pair [Cr(oxalate)$_3$]$^{3+}$ anion and tricaprylmethylammonium cation, tetraazacyclotetradecane, tetratosyltetraaza 12C4, tritosyltriaza 9C3, 4-dimethylaminoazobenzene, 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one, and 1,5-diphenylcarbazide [100, 243-254], two reports on Mn$^{2+}$ PVC membrane sensors based on $N,N',N''\cdot N'''$-1,5,8,12-tetraazadodecane-bis(salicylaldiminato) 14,16-dimethyl-1,4,7,10,13-pentaazacyclohexadeca-13,16-diene [255,256], 11 reports on Fe$^{3+}$ ion membrane sensors based on 2-[(2-hydroxy-1-propenylbuta-1,3-dienylimino)-methyl]-4-$p$-tolylazophenol, a mu-bis(tridentate) ligand 2-phenyl-1,3-bis[3'$\cdot$aza-4'$\cdot$(2'$\cdot$-hydroxyphenyl)-prop-4-en-1'$\cdot$yl]-1,3-imidazolidine, benzo-18-crown-6 crown ether, ion-pair between [Fe(oxalate)$_3$]$^{3+}$ anion and tricaprylmethylammonium cation, formylsalicylic acid derivatives, 1,4,8,11-tetraazacyclotetradecane, 5,10,15,20-tetakis(pentafluorophenyl)-21H, 23H-porphyrin, 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) [257-267].

Ten reports on Co$^{2+}$ ion selective electrodes based on 5-((4-nitrophenyl)azo)-$N$-$N'$-bis(salicylidene)-3,4-diaminotoluene, benzo-substituted macrocyclic diamide, 2,3,4-pyridine-1,3,5,8,11,14-hexaazacyclohexadeca-2-ene, dibenzopyridino-substituted macrocyclic diamide, oxime of 1-(2-oxocyclohexyl)-1,2-cyclohexanediol, OXCCD, (2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate, dibenzopyridino-substituted macrocyclic diamide, 1-phenyl-3-methyl-4-benzoyl-5-benzoxypyrazole, benzo-substituted macrocyclic diamide (18-membered macrocyclic diamide) [268-279].

Fourteen reports on Ni$^{2+}$ ion selective electrodes based on 5,10,15,20-tetraphenylporphyrin, 2,5-thiophenyl bis(5-tert-butyl-1,3-benzoxazole), 5,11,17,23,29,35-hexakis-$r$-octyl-37,38,39,40,41,42-hexakis($N$-phenylthiocarbamoylmethoxy) calix[6]arene, $N,N'$-bis-(4-dimethylaminobenzylidene)-benzene-1,2-diamine $[\text{Ni}(\text{Me}_4\text{Bzo}_2[14]\text{aneN}_4)]$Cl$^2$-, benzylbis(thiosemicarbazone), 1,3,7,9,13,15,19,21-octaazapentacyclooctacosane (pentacyclooctaaza), 3,4;11,12-dienbenzo-2,5,10,13-tetraoxo-1,6,9,14-tetraazacyclohexadecane, dibenzodiaza-15-crown-4, Schiff's bases, $N$-(2-hydroxybenzyl)-$N'$-(2-hydroxybenzylidene)ethylenediamine and $N$-(2-hydroxybenzylidene)-Al$^-$-(2-picolyl)ethylenediatmine, thiophene-derivative Schiff's base, $N'^2,N'^2$-bis((naphthalen-1-ymethylene)ethane-1,2-diamine [280-293].
More than 30 reports on Cu$^{2+}$ ion selective sensors based on \(N\)-[2-thienylmethylidene]-2-propanolamine, mixed complexes of Cu$^{2+}$ and Ni$^{2+}$ with \(N\)-[2-thienylmethylidene]-2-aminopyridine, naphthol-derivative Schiff's base, bis-2-thiophenal propanediamine, thiopene-derivative Schiff's base, diphenylisocyanate bis(acetylacetone) ethylenedinnine, \(2,2'\)-[\(4,4'\)diphenyl-methanebis(nitrilomethylidine)]-bisphenol, \(2-(1'-(4'-(1''-hydroxy-2''-naphthyl)methyleneamino)butyliminomethyl)-1\)-naphthol, derived from 2,3-diaminopyridine and omicron-vanilin \(2,2'\)-[\(1,2\)-ethandiyl-bis(nitrilomethylidine)-bis]metacresole(1), \(2,2'\)-[\(1,2\)-ethandiyl-bis(nitrilomethylidine)-bis] \(-p\)-cresol(II) and \(2,2'\)-[\(1,2\)-ethandiyl-bis(nitrilomethylidine)-bis]-\(\alpha\)-cresol(III), \(2-(1\)-(\(E\))-(2-\(\alpha\)-(\(E\))-(2-\(\alpha\)-(\(E\))-(2-\(\alpha\)-(\(E\))-2-hydroxyphenyl)ethylenidene]hydratono)-1-methylpropyldiene]hydratono]ethyl)phenol, \(N,N'\)-bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine, copper(II) complex of 2,4-dimethyl-1,5,9,12-tetraaza-cyclopentadeca-1,4-diene, 1,2,5,6,8,11-hexaaza-cyclo-dodeca-7,12-dione-2,4,8,10-tetraene, Cu-II-cyclo-hexaneone thiosemicarbazone complex, 6,7,8,9,10-hexahydro-2H-1,13,4,7,10-benzodioxatiazacylclopentadecine-3,11(4H,12H)-dione, dithi/macrocyle (4-phenyl-11-decan-1-y-1,7-dithia-11-1-aza-cyclotetradecane-4-sulfide), \(2-(1'-(4'-(1''-hydroxy-2''-naphthyl)methyleneamino)butyliminomethyl)-1\)-naphthol, aza-thioether crowns containing a 1,10-phenanthroline sub-unit, \(2,2'\)-[\(1,9\)-nonane-diylbis(nitrilomethylidyne)]-bis-(1-naphthol6-methyl-4-(1-phenylmethylidene)amino-3-thioxo-1,2,4-triazin-5-one, bis(acetylcetone)propylenediimine, 4-amino-6-methyl-1,2,4-triazin-5-one-3-thione, 2-mercaptobenzoxazole, 9,10-anthraquinoline derivative, synthesized macrocyclic diamide, copper(II) salicylaniline Schiff's base, naphthol-derivative Schiff's base, synthesized macrocyclic diamide, copper(II) complex of ethambutol, diphenylisocyanate bis(acetylcetone) ethylenedinnine, 2-quinolyl-2-phenylglyoxal-2-oxime (phenylglyoxal-alpha-monoxime), 1,10-phenanthroline sub-unit, bis-2-thiophenal propanediamine, 2,2'-dithiodianiline and dibutyl phthalate, cephaloridine [294-332].

Thirty nine reports on silver selective electrodes based on Schiff's base-\(p\)-tert-butylcalix[4]arene, a dioxime-type Schiff's base, \(N,N'\)-bis(2'-(hydroxyimino-1'-phenyl-propylidene)-1,3-propanediamine, \(PHO_3\), derived from alpha-isonitrosopropiophenone and 1,3-diaminopropane, calix[4]arene derivative, Schiff base \(p\)-tert-butylcalix[4]arene derivatives containing N and O as binding sites, [bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxoocotane, 2,3-butanedionio-thiosemicarbazide, bis(dialkyldithiocarbamates), 2-aminothiophenal based dipodal, calix[4]arene compound of 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4, calix[4]arenes in the partial cone conformation, 7,8:16,17-dibenzo-6,9,15,18-tetraoxo-1,5,10,14-tetrathiaacyclooctadeca-7,16- diene \([B_2OxoxC_{18}dieneS_4]\) tethathia macrocyclic carrier, calix[4]arene derivatives with four imine units, silver ethylmercurythiosalicylate (silver thimerosal), diaza-18-crown-6, containing two oxime donor groups, hexaithia-18-crown-6, diphenyl selenide, benzyl phenyl selenide and dibenzyl selenide, 2,2'-dithiobis(benzothiazole), meso-tetraphenylporphine \([H_2T(4-OCH_3)PP]\), 3-(2-pyridylethylimino)-2-butanoneoxime, 25,27-dihydroxy-26,28-bis-[5-(4-methyl-6-hydroxypurimidine)thiaamlyoxy] calix[4]arene, \(N,N'\)-bis(2-thienylmethylene)-1,2-diaminobenzene, methyl-2-pyridyl ketone oxime (MPKO), phenyl-2-pyridyl ketone oxime and bis(2-(o-carboxyphenoxy)methyl)-4-bromo-1-methoxybenzene, octahydroxycalix[4]arene derivative, macrocycle, Me-6(14) diene-2HClO_4, aza-thioether crowns containing a 1,10-phenanthroline sub-unit 2-mercaptobenzenimidaazole, octaacyl-resor[4]arene, calix[2]furan[2]pyrrole, exocyclic sulfur and selenium ligands based on calix[4]arenes and crown ethers, \(O,O,O\)-tris(2-ethylhexyl) phosphorothioate and \(O,O,O\)-tributyl phosphorothioate with a thiophosphoryl
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(P=S) group, cyclam (1,4,8,11-tetraazacyclotetradecane) nitrogen containing calixarene derivatives, bis-pyridine tetramide macrocycle, calixarene derivative containing nitrogen atom, bis(dialkyl-dithiophosphates) [333-372].

Ten reports on Zn$^{2+}$ selective sensors based on N,N'-bis(acetylacetone)ethylenediamine, 5,6-benzoxa-4,7,13,16,21,24-hexaaza-1,10-diazabicyclo[8,8,8]hexacos-5-ene, C2(B)22 cryptand, benzo-substituted macrocyclic diamide, dibenzo-24-crown-8, bis(2-nitrophenyl)disulfide, hematoporphyrin IX, sulipride drug N-[ethyl-1 pyrrolidinyl-2)methyl]methoxy-2 sulfamoyl-5 benzamide, 5,6,14,15-dibenzo-1,4-dioxoa-8,12-diazacyclopentadecane-5,14-diene [373-382].

Fifteen reports on Cd$^{2+}$ PVC membrane sensors based on incorporating nitrogen and sulfur containing tridentate dicyclohexano-24-crown-8, [1,1'-bicyclohexyl]-1,1',2,2'-tetrolic acid, 1-furoyl-3-benzyl-3-phenylthiourea, dibenzo-24-crown-8, 5-[(4-methylphenyl)azo]-N-(6-amino-2-pyridinyl)salicylaldimine, 5-[(4-methylphenyl)azo]-N-(2-diamino-2-cyano-1-ethyl cyanide) salicylaldehyde, cetlypyridiniumtetraiodo cadium or cetlypyridinium-tetabrom cadium, dioctyl phthalate and sodium tetraphenyl borate, 3,4:11,12-dibenzo-1,6,9,14-tetraazacyclohexadecane, dicyclohexano-18-crown-6, tetrahtia-12-crown-4, 8-hydroxyquinoline, 8-hydroxyquinoline, monoaza-18-crown-6, N,N'[bis-(pyridin-2-yl)formylidene] butane-1,4-diamine and N-(2-pyridinylmethylen)-1,2-benzenediamine [383-395].

Twenty five reports on Hg$^{2+}$ ion selective sensors based on tetraethylthiuram disulfide were chosen as a chemical modifier, bis[5-((4-nirotephenyl)azo salicylaldehyde)], p-tert-butylcalix[4]crown with imine units, sulfur Schiff’s base 1-(2-hydroxy-1,2-diphenylethylidene)thiosemicarbazide, ethylenediamine bisthiophenecarboxaldehyde, ethyl-2-(benzoylamino)-3-(2-hydroxy-4-methoxy-phenyl)-2-propenoate, bis(2-hydroxybenzophenone) butane-2,3-dihydrazide, dithiosalicylic acid, 4-(4-N,N-dimethylphenyl)-2,6-diphenylpyridyl tetrafluoroborate, 2-amino-6-purinethiol and 5-amino-1,3, 4-thiadiazole-2-thiol, polyaniline Sn(IV) phosphate, 5,5'-dithio-bis(2-nitrobenzoic acid) and tricyclazole, N,N-dimethylformamide-salicylacylhydrazone, tribromomercurate-rhodamine B ion-pair complex, diamine donor ligand, pentathia-15-crown-5, 1-(2-nitro-4-methylphenyl)-6-methyl-6-methoxy-1,4,5,6-tetrahydro-pyrimidine-2-(3H)thione, dibenzodiazathia-18-crown-6-dione, 25,27-dihydroxy-26,28- bis[(1-naphthalene) selenopropoxy] calix[4]arene, 2,3,4,9,10,1,1-dipyrindine-3,10-diaza-1,5,8,12-tetrahtiaacyclotetradeca-2,9-diene, calixarene derivative containing a thiazole azo group, salicylaldehyde thiosemicarbazone, ethyl-2-benzoyl-2-phenylcarbamoyl acetate, 1,3-diphenylthiouria hexathia-18-crown-6-tetraone [396-420]. The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for transition metal cations is shown in Figure 13.
Figure 13. The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for transition metal cation.

Table 6 shows the characterization and properties of the reported transition metal cation membrane sensors.

Table 6. Characterization of a number of reported ion selective sensors based on non-conducting polymers for transition metal cations

| Cation | Ionophore                                                                 | Slope (mV decade$^{-1}$) | Linear Range (M) | Most Important Interfering ions (log K$_{sel}$ > -2) | Ref. |
|--------|---------------------------------------------------------------------------|--------------------------|-------------------|-----------------------------------------------------|------|
| Y$^{3+}$ | A new Schiff's base with sulfur and nitrogen donor atoms (2-((E)1,2-diphenyl-2-(2-2-sulfanylphenyl)iminooethylidene) amino)-1-benzothiol, DSAB) | 19.2                     | 1.0×10$^{-7}$-1.0×10$^{-2}$ | Sc$^{3+}$                                           | 240  |
| Zr$^{4+}$ | bis(diphenylphosphino) ferrocene                                          | 59.7                     | 1.0×10$^{-7}$-1.0×10$^{-1}$ | -                                                   | 241  |
| Vo$^{2+}$ | N,N'-bis-(salicylidene)-2,2-dimethylpropane-1,3-diamine (NNPD)            | 59.7                     | 1.0×10$^{-7}$-1.0×10$^{-1}$ | -                                                   | 242  |
| Cr$^{3+}$-1 | tetraazacyclotetradecane, tetratosyltetraaza 12C4, and tritosyltriaza 9C3 | 20±1                     | 1.0×10$^{-7}$ - 1.0×10$^{-4}$ | Fe$^{3+}$, Ni$^{2+}$                                | 250  |
| Cr$^{3+}$-2 | 1,5-diphenylcarbazide                                                   | 19.52 ± 0.40             | 6.3×10$^{-8}$ - 1.0×10$^{-2}$ | Ag$^{+}$                                           | 253  |
| Mn$^{2+}$-1 | N,N',N''-1,5,8,12-tetraazadodecane-bis(salicyladiminato)(H$_2$L)          | 30                       | 5.0×10$^{-6}$-1.0×10$^{-1}$ | Cd$^{2+}$, Fe$^{3+}$, Ni$^{2+}$                      | 255  |
| Mn$^{2+}$-2 | 14,16-dimethyl-1,4,7,10,13-pentaazacyclohexadeca-13,16-diene              | 29.5                     | 1.25×10$^{-5}$-1.0×10$^{-1}$ | Zn$^{2+}$, La$^{3+}$, Hg$^{2+}$                     | 256  |
### Table 6. Cont.

| Cation | Ionophore | Slope (mV decade\(^{-1}\)) | Linear Range (M) | Most Important Interfering ions (log Ksel > -2) | Ref. |
|--------|-----------|-----------------------------|------------------|-----------------------------------------------|------|
| Fe\(^{3+}\)-1 | benzo-18-crown-6 crown ether | 15.7±1 | 1×10\(^{-6}\).1×10\(^{-5}\) | - | 259 |
| Fe\(^{3+}\)-2 | 2,4,6-tri(2-pyridyl)-1,3,5-triazine (TPTZ) | 30±1 | 5×10\(^{-7}\).1×10\(^{-2}\) | K\(^+\) | 266 |
| Co\(^{2+}\)-1 | N,N'-bis(salicylidene)-3,4-diaminotoluene dibenzopyridino-substituted macrocyclic diamide | 30 ± 0.2 | 7.9×10\(^{-8}\).1.0×10\(^{-1}\) | Cu\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\) | 269 |
| Co\(^{2+}\)-2 | | 27.5 | 7.0×10\(^{-7}\).1.0×10\(^{-2}\) | - | 272 |
| Ni\(^{2+}\)-1 | N,N'-bis-(4-dimethylamino-benzylidene)benzene-1,2-diamine | 30 ± 1 | 2.0×10\(^{-7}\).1.0×10\(^{-2}\) | Ag\(^{+}\),Hg\(^{2+}\) | 285 |
| Ni\(^{2+}\)-2 | benzylbis(thiosemicarbazone) | 29.0±0.5 | 1.0×10\(^{-7}\).1.0×10\(^{-2}\) | - | 287 |
| Ni\(^{2+}\)-3 | 1,3,7,9,13,15,19,21-octazaapentacyclooctacosane (pentacyclooctaaza) | 30.0 | 1×10\(^{-6}\).1×10\(^{-1}\) | Ba\(^{2+}\) | 288 |
| Ni\(^{2+}\)-4 | dibenzodiaza-15-crown-4 | 28.6 | 7.1×10\(^{-7}\).1.2×10\(^{-2}\) | Ag\(^{+}\), Pd\(^{2+}\) | 290 |
| Cu\(^{2+}\)-1 | bis-2-thiophenal propanediamine (TPDA) | 29.1 | 6.0×10\(^{-8}\).1.0×10\(^{-1}\) | Ag\(^{+}\) | 298 |
| Cu\(^{2+}\)-2 | new thiophene-derivative Schiffs base | 29.3±0.7 | 6.0×10\(^{-8}\).1.0×10\(^{-1}\) | Zn\(^{2+}\), Hg\(^{2+}\) | 299 |
| Cu\(^{2+}\)-3 | diphenylisocyanate bis(acetyllactone) ethylenediaminimine (DIBAE) | 29.8 | 1.0×10\(^{-6}\).1.0×10\(^{-1}\) | - | 300 |
| Cu\(^{2+}\)-4 | 1,2,5,6,8,11-hexaazacyclododeca-7,12-dione-2,4,8,10-tetraene | 29.5±0.3 | 2.0×10\(^{-7}\).1×10\(^{-1}\) | - | 308 |
| Cu\(^{2+}\)-5 | Cu-II-cyclohexaneone thiosemicarbazone complex | 29.2 | 1×10\(^{-9}\).1×10\(^{-1}\) | - | 309 |
| Cu\(^{2+}\)-6 | bis-2-thiophenal propanediamine (TPDA) | 29.1±1 | 6.0×10\(^{-8}\).1.0×10\(^{-1}\) | - | 328 |
| Ag\(^{+}\)-1 | 25,27-dihydroxy-26,28-bis[5-(4-methyl-6-hydroxypurimidine)thiaamyloxy]calix[4]arene | 61.4 | 5×10\(^{5}\).1×10\(^{-1}\) | - | 352 |
| Ag\(^{+}\)-2 | 2-mercaptobenzimidazole (MBI) and 2-mercaptopbenzothiazole (MBT) | 60.2 and 57.8 | 1.0×10\(^{-6}\).1.0×10\(^{-1}\) | - | 354 |
| Ag\(^{+}\)-3 | cyclam (1,4,8,11-tetraazacyclotetradecane) | 59±2 | 1.0×10\(^{-7}\).1.0×10\(^{-1}\) | - | 363 |
| Zn\(^{2+}\)-1 | 5,6-benzo-4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacos-5-ene benzo-substituted macrocyclic diamide | 29.1±0.4 | 1.0×10\(^{-6}\).1.0×10\(^{-1}\) | - | 374 |
| Zn\(^{2+}\)-2 | | 28 | 1.0×10\(^{-9}\).1.0×10\(^{-5}\) | Li\(^{+}\),Na\(^{+}\) | 376 |
| Cd\(^{2+}\)-1 | tetrathia-12-crown-4 | 29.0±1.0 | 4×10\(^{-7}\).1.0×10\(^{-1}\) | Cu\(^{2+}\), NH\(^{4+}\), Cr\(^{3+}\) | 383 |
| Cd\(^{2+}\)-2 | N,N'-[bis(pyridin-2-yl)formylidene] butane-1,4-diamine and N-(2-pyridinylmethylene)-1,2-benzenediamine | 29.5 | 7.9×10\(^{-8}\).1.0×10\(^{-1}\) | - | 394 |
| Hg\(^{2+}\)-1 | ethylenediamine bisthiophencarboxaldehyde | 30.0±0.4 | 10\(^{-7}\).10\(^{-2}\) | Ag\(^{+}\) | 400 |
| Hg\(^{2+}\)-2 | diamine donor ligand | 25±0.1 | 1.25×10\(^{-7}\).1.0×10\(^{-1}\) | - | 411 |

Chemical structures of some above ionophores which are used in construction of non-conducting polymer ISEs for transition metal cations are shown in Figure 14.
**Figure 14.** Some structures of the suitable ionophores used in construction of transition metal cation membrane sensors.

3.7. Non-conducting Polymer Membrane Sensors for the Rare Earth Cations

The main problem in the field of ISEs globally was finding a selective sensor for lanthanides. The world researchers tried to construct a selective sensor for the lanthanide ions with the aid of ionophores having cavity like crown ethers but they were not quite successful. The only way to design an ISE for the lanthanide ions is using ionophores having semi cavity, heteroatoms (mostly S and N as donor atoms), and high flexibility. Such an ionophore can easily form a template with reference to the size of the cation. Furthermore, this ionophore is able to form a stronger complex with one of the cations than with the other ones. This phenomenon can be attributed to the type, the number and the site of its donor atoms, its flexibility as well as the size and the charge density of the cation [421].
The literature survey reveals that during the past decade, more than 70 ion selective membrane sensors have been reported for lanthanide ions. Sixteen reports on lanthanide PVC membrane sensors based on 1,3,5-trithiacyclohexane, monoaza-12-crown-4,5,14-N',hydroxyphenyl-4,15-dioxo-1,5,14,18-tetraazahexacosane, \(N\)-hexahydrocyclopentapyrol-2(1H)yl]amino[carbonyl]4-methylbenzene sulfonamide (gliclazide), bis(2-mercaptanil) diacetyl, bis(thiophenol)phenylen-1,3-diamine, dicyclo-hexano-18-crown-6, \(N,N\)-adipylbis(5-phenylazosalicylaldehyde hydrzone), bis(2-methylbenzaldehyde)butane-2,3-dihydrazone, 2,2'-dithiodipyridine, \(N\)-2,4-dimethylphenyl\(N\)-ethylformamidine, \(N\)-hexahydrocyclopentapyrol-2(1H)yl]amino[carbonyl]4-methyl benzene sulfonamide, 3-hydroxy-\(\text{N}'\)-(pyridin-2-ylmethylene)-2-naphthohydrazide, 8-amino-\(N\)-2-hydroxybenzylidine)-naphthylamine, \(\text{N}'\)-(1-pyridin-2-ylmethylene)-2-furohydrazide, \(N\)-(2-pyridyl)-\(\text{N}'\)-(4-methoxyphenyl)-thiourea [91, 422-436].

Nine reports on cerium ion selective sensors based on 1,3,5-trithiane, 1,3,5-trithiane, azomethine of piperonylidine-4-[2.2]para-cycloxyphanylamine, \(N\)-[(Z)-2-chloro-2-(1-hydroxy-1,1,1-triphosphoranyl)-1-ethenyl]-4-ethyl-1-benzene sulfonamide, 2-aminobenzothiazole and oleic acid, \(N,N\)-bis[2-(salicylideneamino)ethyl]ethane-1,2-diamine, 1,4,7-trithiaclononane and oleic acid, [4-(4'-nitrobenzyl)-1-phenyl-3,5-pyrazolidinedi]on], \(\text{N}'\)-(2-hydroxyphenyl)methylidene]-2-furohydrazide [437-445].

Two reports for Pr\(^{3+}\) membrane sensors based on \(N\)-(pyridin-2-ylmethylene)benzohydrazide [446,447]. Four reports for Nd\(^{3+}\) ion selective sensors based on \(N\)-(2-furylmethylene) pyridine-2,6-diamine, 2-\{[(6-aminobenzonitrile-2-yl)imino]methyl\}phenol, 5-pyridino-2,8-dithiophene[9](2,9)-1,10-phenanthroline, benzyl bisthiosemicarbazone [448-451].

Six reports on Sm\(^{3+}\) PVC membrane sensors based on isopropyl 2-\{[(isopropoxy-carbothioyl]disulfanyl]ethanethioate, Et\(_3\)todit, \(N\)-[2-4-\{[(cyclohexylamino)carbonyl]amino]sulfonyl]-phenyl]ethyl]-5-methylpyrazine carboxamide, \(N\)-[2-4-\{[(cyclohexylamino)carbonyl]amino] sulfonyl]-phenyl]ethyl]-5-methyl pyrazine carboxamide, 3-\{[2-oxo-1(2H)-acenaphthyliden]amino\}-2-thioxo-1,3-thiazolidin-4-one, \{[1-phenyl-3'-(2-nitrophenyl)-spiro[oxirane-2,4-pyrazoline]-3,5-dione\} (PNSOP) [95, 452-455].

Four reports for Eu\(^{3+}\) ion selective sensors based on \(N\),\(N\)-diethyl-\(N\)-(4-hydroxy-6-methylpyridin-2-yl)guanidine, bis(thiophenol)butane-2,3-dihydrazone, 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazi n-5(2H)-one, \(S\)-N hexadentate Schiff’s base, bis(thiophenol)butane-2,3-dihydrazone [456-460].

Four reports for Gd\(^{3+}\) membrane sensors based on \(S\)-N Schiff’s base (2-\{[3-\{[2-(sulfanylphenyl)imino]-1-methylbutyldiene\}amino]phenyl hydrosulfide, antibiotic omeprazole, bis(thiophenal) pyridine-2,6-diamine, and \(N\)-(2-pyridyl)-\(\text{N}'\)-(4-nitrophenyl)thiourea [105, 461-464].

Two reports on Tb\(^{3+}\) ion membrane sensors based on \(N\),\(N\)-bis(pyrrolidene) benzene-1,2-diamine, 4-amino-3-\{[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-yliden]hydrazono\}-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one [465,466].

Four reports on Dy\(^{3+}\) ion membrane sensors based on \(N\),\(N\)-bis(pyrrolidene) benzene-1,2-diamine, a new asymmetrical Schiff’s base [(E)-\(N\)-(2-hydroxybenzylidine)benzohydraide], 6-hydrazino-1,5-diphenyl-6,7-dihydropyrazolo-[3,4-d]pyrimidine-4(5H)-imine [467-470].
Four reports on Ho$^{3+}$ PVC membrane sensors based on $N$-(1-thien-2-ylmethylene)-1,3-benzothiazol-2-amine, $N,N'$-bis(2-pyridinecarboxamide)-1,2-benzene [471-474].

Three reports on Er$^{3+}$ membrane sensors based on $N'$-(2-hydroxy-1,2-diphenylethylidene) benzohydrazide, pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl)hydrazone, and $N$-(2-hydroxy-1,2-diphenylethylidene) benzohydrazide [103, 475-476].

Three reports on Tm$^{3+}$ ion membrane sensors for thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone, 2,2'-dianiline disulfide [477-479].

Five reports on Yb$^{3+}$ ion membrane sensors for 3-hydroxy-$N$-[(2-hydroxyphenyl)methylene]-2-naphthohydrazide, 6-methyl-4-[[1-(1H-pyrrol-2-yl)methylidene]amino]-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one, $N$-(6-picolyl)-$N'$-(4-methoxyphenyl) thiourea, cefixime and $N$-(2-pyridyl)-$N'$-(2-methoxyphenyl)-thiourea [480-484].

Two reports on Lu$^{3+}$ ion membrane sensors based on $N$-(thien-2-ylmethylene)pyridine-2,6-diamine [485,486].

Five reports on Th$^{4+}$ PVC membrane sensors based on 2-(diphenylphosphorothiolyl)$-N',N'$-diphenylacetamide, zirconium phosphoborate, thorium oxinate, Th(C$_9$H$_6$NO)$_4$$\cdot$2H$_2$O, thorium oxinate, Th(C$_9$H$_6$NO)$_4$$\cdot$2H$_2$O, 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis(diphenylphosphinoymethoxy)-calix[4]arene [487-491].

However, there are no reports on lanthanide ion selective sensor based on conducting polymers. The statistical diagram of the reported potentiometric membrane sensors based on non-conducting polymer for lanthanide ions is shown in Figure 15.

**Figure 15.** The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for lanthanide ions.

![Figure 15](image)

Table 7 shows the characterization and properties of the reported lanthanide ions membrane sensors.
Table 7. Characterization of a number of reported ion selective sensors based on non-conducting polymers for lanthanide ions

| Cation | Ionophore                                                                 | Slope (mV decade⁻¹) | Linear Range (M) | Most Important Interfering ions (log K_{sel} > -2) | Ref. |
|--------|---------------------------------------------------------------------------|---------------------|------------------|---------------------------------------------------|------|
| La⁺³⁻¹ | N-2,4-dimethylphenyl-N'-(ethylformamidine (amitraz) 8-amino-N-(2-hydroxy-benzylidene)naphthylamine | 19.8 ± 0.2          | 1.0 × 10⁻⁷-1.0 × 10⁻¹ | -                                                 | 432  |
| La⁺³⁻² |                                                                                        | 20.3 ± 0.3          | 1.0 × 10⁻⁷-1.0 × 10⁻¹ | Pr³⁺                                             | 423  |
| Ce⁺³   | N,N-bis[2-(salicylidene-amino)ethyl]ethane-1,2-diamine                      | 20                  | 1.41×10⁻⁷-1.0 x 10⁻² | La³⁺                                             | 442  |
| Pr⁺³   | N-(pyridin-2-yl-methylene)-benzohydrazide                                   | 21.1                | 10⁻²-10⁻⁶         | Sm³⁺, Er³⁺                                       | 446  |
| Nd⁺³⁻¹ | 5-pyrido-2,8-dithia[9](2,9)-1,10-phenanthrolinephane benzyl bisthiosemicarbazone (BTC) | 20.1                | 10⁻⁵-10⁻²         | Yb³⁺, Gd¹⁺                                       | 449  |
| Nd⁺³⁻² |                                                                                        | 19.7                | 10⁻⁶-10⁻²         | Gd³⁺, Sm³⁺                                       | 450  |
| Sm⁺³⁻¹ | 3-[[2-oxo-1(2H)-acenaphthlenyliden]amino]-2-thioxo-1,3-thiazolidin-4-one     | 19.3                | 10⁻⁶-10⁻¹         | -                                                 | 455  |
| Sm⁺³⁻² | [1-phenyl-3'(2-nitrophenyl) spiro[oxirane-2.4-pyrazoline]-3,5-dione] (PNSOP) | 19.30               | 10⁻⁶-10⁻¹         | Gd¹⁺                                             | 456  |
| Eu⁺³   | 4-(2-hydroxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin n-5(2H)-one (HMTDT) | 19.7 ± 0.4          | 1.0 × 10⁻⁶-1.0 × 10⁻¹ | -                                                 | 457  |
| Gd⁺³   | N-(2-pyridyl)-N'-(4-nitrophenyl)-thioureua                                 | 19.95 ± 0.3         | 3.0 × 10⁻⁷-1.0 × 10⁻¹ | -                                                 | 463  |
| Tb⁺³   | 4-amino-3-[[2-[4-amino-6-methyl-5-oxo-4,5-dihydro-1,2,4-triazin-3(2H)-ylidene] hydrazono]-6-methyl-3,4-dihydro-1,2,4-triazin-5(2H)-one (ATO) | 19.4 ± 0.5          | 1.0×10⁻⁶-1.0× 10⁻¹ | -                                                 | 465  |
| Dy⁺³   | 6-hydrazino-1,5-diphenyl-6,7-dihydropyrazolo-[3,4-d]-pyrimidine-4(5H)-imine | 19.6± 0.3           | 1.0×10⁻¹-1.0×10⁻⁷ | -                                                 | 469  |
| Ho⁺³   | N,N'-Bis(2-pyridine-carboxamide)-1,2-benzene                               | 19.6                | 10⁻³-10⁻²         | Er³⁺, Dy³⁺,Sm³⁺                                  | 472  |
| Er⁺³   | N’-(2-hydroxy-1,2-diphenyl-ethylenidene) benzohydrazide                    | 21                  | 10⁻²-10⁻²         | -                                                 | 475  |
| Tm⁺³   | 2,2’-dianiline disulfide (DADS)                                             | 19.5 ± 0.3          | 1.0×10⁻⁶-1.0×10⁻² | -                                                 | 478  |
Table 7. Cont

| Cation    | Ionophore                                                                 | Slope (mV decade⁻¹) | Linear Range (M)       | Most Important Interfering ions (log Ksel > -2) | Ref. |
|-----------|---------------------------------------------------------------------------|---------------------|------------------------|-----------------------------------------------|------|
| Yb⁺³      | 3-hydroxy-N-[2-hydroxyphenyl]-methylen]-2-naphthohydrazide                | 19.2                | 10⁻² - 10⁻⁶            | Nd³⁺, Pb²⁺, Gd³⁺                               | 480  |
| Lu⁺³      | N-(thien-2-ylmethylene)pyridine-2,6-diamine (TPD)                         | 20.5 ± 0.4          | 1.0 × 10⁻⁶ - 1.0 × 10⁻²| Nd³⁺, Dy³⁺, Gd³⁺                              | 485  |
| Th⁴⁺      | 2-(diphenylphosphorothioyl)-N,N'-diphenylacetamide                         | 15.2                | 10⁻⁶ - 10⁻²            | Mg²⁺, Cu²⁺                                    | 487  |

Chemical structures of some above ionophores which are used in construction of non-conducting polymer ISEs for rare earth cations are shown in Figure 16.

3.8. Non-conducting Polymer Membrane Sensors for Inorganic Anions

The anion selective electrodes, just like the cation selective ones, are an important group of the ion selective electrodes. The number of the anion selective electrodes is lower than that of the cationic sensors, due to reasons like the relative larger size of the anions, their various shapes and their high hydration energy. Nevertheless, a relatively large number of sensors for the anionic species have been published during the past decade.

For an anion-selective electrode, a strong interaction between the ionophore and the anion is required in order to complex the anion in a selective fashion. The potentiometric response of the membranes, doped with these complexes, is believed to be based on the coordination of the analyte anion axial ligand to the metal center of the carrier molecule.

Literature survey reveals that during the past decade more than 70 anion selective membrane sensors have been reported based on non-conducting polymers.

Three reports on bicarbonate PVC membrane sensors based on urea-functionalized calix[4]arenes, 4-(n-hexadecyl)-3-nitro-1-trifluoroacetylbenzene, and long chain S-alkyldiphenylthiocarbazone [492-494].

Four reports on nitrite membrane sensors based on Co(II)-salen, Co(II)-salophen, (tetraphenylporphyrinate) cobalt(III) acetate, and methyl violet [495-498].

Twelve reports on nitrate ion selective sensors based on urea-calixarene, cyclic bis-thiourea, polypyrrole, silver bis(bathophenanthroline) nitrate [Ag(bath)₂NO₃], poly(3-octylthiophene) and poly(aniline) as ion-to-electron transducers, tetradecylammonium nitrate and (npoe) 2-nitrophenyloctyl, tris(2-aminoethyl)amino triamide, tert-octylammonium bromide dissolved in dibutylphthalate, tetradecylammonium nitrate, N,N,N-triallylleucine betaine chloride, doped polypyrrole films, tetradecylammonium bromide [499-510].

Three reports for dihydrogen phosphate based on cobalt rod, uranyl salophenes, and calix[4]arene anion [511-513].
**Figure 16.** Some structures of the suitable ionophores used in construction of lanthanide cation membrane sensors.
Ten reports on monohydrogen phosphate based on vanadyl salen, vanadyl salophen, macrocyclic dithioxamide, molybdenum acetylacetonate, oxo-molybdenum methylsalen, vanadysalen complex (VS), Binuclear organotin, polymeric membrane electrodes, heterocyclic macrocycles, and oxo-molybdenum methyl-salen [107, 514-522].

Three reports on phosphate ion sensors based on bis(pentafluorobenzyl) tin(IV) dibromide, cobalt-wire phosphate ion-selective, and organic tin compounds [523-525].

Two reports on cyanide membrane sensors based on aquacyanocobyrinic acid heptamethyl ester (ACCbs) reagent (orange color) at pH 9.5 to give dicyarrocobester (DCCbs) (violet color) and thin electroplated membranes of silver chalcogenides [526,527].

About 30 reports on thiocyanide PVC membrane sensors based on (N,N'-bis-salicylidene-1,2-ethylenediamine), 2,2'-(1,3-dimethyl-1,3-propanediylidene)dinitrilobis-benzenethiolato cadmium(II), butane-2,3-dione bis(salicylhydrazonato) zinc(II), dinuclear copper complex, N,N'-ethylene-bis(4-methylsalicylidineiminato)nickel(II), zinc-phthalocyanine complex, [Cu(L)][NO3]2 (L=4,7-bis(3-aminopropyl)-1-thia-4,7-diazacyclononane), meso-tetraphenylporphyrin-rhodium(III), linear polyamines, poly(vinyl chloride) membrane electrode based on calix[4]arenes, bis-[[(3-ferrocenyl)-(2-crotonic acid)] copper(II) complex [Cu(II)-BFCA], N,N'-bis-(benzaldehyde)glycine metallic complexes of Cu(II), Ni(II), Zn(II) and Co(II), bis-taurine-salicylic binuclear copper(II) complex, tribenzylltin(IV) dithiocarbamate [Sn(IV)-TBDTB], rhodium(II) phthalocyanine (RhPc), a copper-1,8-dimethyl-1,3,6,8,10,13-azacyclotetradecane complex, (octabromotetraphenylporphyrinato) manganese(III) chloride, nickel and iron phthalocyanines, tricoordinate Schiff's base copper(II) complex, 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinatomanganese(III) chloride [Mn(TMP)Cl] and 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinatomanganese(III) chloride [Mn(C18TPP)Cl], two zinc(II) ions and two molecules of the bis-N,O-bidentate Schiff base, 2,2'-[methylenebis(4,1-phenylene-nitrilomethylidyne)]bisphenol, bisbenzoin-semi-triethylenetetramine binuclear cobalt(II) metallic complex [Co(II)2-BBSTA], N,N'-bis-(furaldehyde)-1,2-phenylenediamine-dipicolyl copper(II) complex [Cu(II)-BFPD], benzaldehyde semicarbazone copper (II) complex [Cu(II)-BASA], bis-benzoin-semi-triethylenetetramine binuclear copper(II) [Cu(II)(2)-BBSTA], manganese(III) tetraphenylporphyrin derivatives, Cu(II)-1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane complex, nickel(II)-azamacrocycle complex, and nickel(II)-1,4-,8,11,15,18,22,25-octatoxyphthalocyanine [528-556].

One report on sulfite ion selective sensors based on bis-urea calix[4]diquinones [557]. More than ten reports for sulfate PVC membrane sensors based on Schiff base complex of Zn(II), strontium Schiff's base complex (SS), zinc-Schiff base, N,N'-ethylenebis(5-hydroxysalicylidineiminato) chromium(III) chloride, 1,3,5-triphenylpyrylium perchlorate, alpha,alpha'-bis(N'-phenylthioureylene)-m-xylene, and 2,5-diphenyl-1,2,4,5-tetraazabicyclo[2.2.1]heptane [558-569].

There are four reports on F- ion membrane sensors which are based on gallium(III)-Schiff base, organotin compounds, uranyl salophenes derivatives, Zr(IV)-octaethylporphyrin (OEP) dichloride (Zr(IV)[OEP]Cl-2) [570-573], three reports on Cl- electrodes based on ruthenium(III) Schiff's base, Schiff's base complex of cobalt(II), liquid polymer nano-PEBBLeS [574-576] and 11 reports on ClO3- based on synthesized platinum(II) complexes, 1,4,7,10,13-penta(n-octyl)-1,4,7,10,13-pentaazacyclonadecane, calcium bis [4-(1',1',3',3'-tetramethylbutyl)phenyl]phosphate, phosphadithiamacrocycle, octalammonium chloride, complex of uranyl, phosphorus(V)tetraphenylporphyrin, gold(I) organic
complex, two nickel-hexaazamacrocyclic complexes, some recently synthesized Ni(II)-hexaazacyclotetradecane complexes, and doped poly(3,4-ethylenedioxythiophene) [577-587]; five reports on bromide based on iron(III)-salen (IS), Zn(II) macrocyclic complex, new mercury(II) complex, 

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\text{bis(4-hydroxyphenyl), 1,4-diaza-1,3-butadiene-Hg(II), benzo-derivative xanthenium bromide [588-589]; and 18 reports on iodide membrane sensors based on salen-Mn(II), Schiff's base complex of Fe(III), cerium-salen, [5,10,15,20-tetrakis(4\text{-}N,N\text{-}dimethylaminobenzene)porphyrinato] Mn(III) acetate, cobalt-salophen, silver-tin oxide, halide-selective receptor, urea derivative, porphyrin, titanium, acetylacetone, homogeneous crystalline membrane, thiopyrillum ion derivative, PVC-DZT-Hg(II) compound, triphenyllead chloride, bis(1,3,4-thiadiazole) complexes of Hg(II), copper phthalocyanine, 1,4,8-tri(n-octyl)-1,4,8,11-tetraazacyclotetradecane complexes of a cyclam derivative, and copper(II) complex [593-610] and 23 reports for triiodide membrane sensors based on Schiff's base 2,2'\text{[4,4\text{'}-diphenylmethane bis(nitromethylidyne)] bisphenol, with copper(II) and Schiff's base 2,2'\text{[4,4\text{'}-diphenylmethane bis(nitromethylidyne)] bisphenol, with iron(III), bis(2-hydroxy-acetophenone)butane-2,3-dihydrazone (ICT), bis(salicylaldehyde) ethylendiamine mercury(II) complex MS), N,N'-1,2-propylene-bis-(5-methylsalicylidene iminato) copper(II), a charge-transfer complex, of (1,3-diphenyldihydro-1H-imidazole-4,5-dione dioxide), with iodide, bis(2,4-dimethoxybenzaldehyde)butane-2,3-dihydrazone with iodine, 2\text{-(2(((E)-1-(2-hydroxyphenyl)methylidine)} amino)phenyl)imino)methyl) phenol with iodine, complex of (1,3-diphenyldihydro-1H-imidazole)-4,5-dione dioxide with iodine, complex of bis(2,4-dimethoxybenzaldehyde)butane-2,3-dihydrazone with iodine, bis-N,O-bidentate Schiff's base, bis(2-hydroxyacetophenone)butane-2,3-dihydrazone, 7,16-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, 2,4,6,8-tetraphenyl-2,4,6,8-tetraazabicyclo[3.3.0]octane, 1,6-bis(N,N-diethylthiocarbamoylimino)-1,6-diphenyl-2,5-dithiahexane, mercury-salen, phenothiazine derivatives, tetra(p-chlorophenyl)porphyrinato manganese(III) acetate, tetrachlorophenolphosphorinato manganese(III) acetate, ketoconazole-triiodide, two different charge-transfer complexes and amino crown ether, clotrimazole-triiodide ion, complex of iodine and bis(2-hydroxyacetophenone)butane-2,3-dihydrazone, complex of 2\text{-(2-(E)-1-(2-hydroxyphenyl)methylidine)amino)phenyl)imino)methyl) phenol [88, 611-630]. There is also one report on periodide membrane sensors based on metaperiodate bis(triphenylphosphoranyliden)ammonium [631] and one report for arsenite PVC membrane sensor based on 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinato cobalt(II) [632].

The statistical diagram of the reported potentiometric membrane sensors based on non-conducting polymer for inorganic anions is shown in Figure 17.
**Figure 17.** The statistical diagram of the reported potentiometric membrane sensors based on conducting and non-conducting polymer for inorganic anions.

Table 8 shows the characterization and properties of the reported inorganic anion membrane sensors.

**Table 8.** Characterization of a number of reported ion selective sensors based on non-conducting polymers for inorganic anions.

| Anion     | Ionophore                                                                 | Slope (mV decade\(^{-1}\)) | Linear Range (M)                      | The most interfering ions (log K\(_{\text{int}}\) > -2) | Ref. |
|-----------|----------------------------------------------------------------------------|-----------------------------|----------------------------------------|------------------------------------------------------|------|
| HCO\(_3^-\) | long chain S-alkyldiphenylthiocarbazone.                                   | -54                         | 10\(^{-2}\)-10\(^{-5}\)                | -                                                    | 493  |
| NO\(_2^-\) | (tetraphenylporphyrinato) cobalt(III) acetate                              | -58.4 - 60.8                | 1.0\times10\(^{-6}\)-1.0\times10\(^{-1}\) and 5.0\times10\(^{-8}\)-5.0\times10\(^{-2}\) | F         | 496  |
| NO\(_3^-\) | N,N,N-triallylleucine betaine chloride                                     | -59.1                       | 1\times10\(^{-6}\)-2.25\times10\(^{-2}\) | -                                                    | 507  |
| HPO\(_4^{2-}\) | molybdenum acetylacetonate oxo-molybdenum methylsalen                      | -29.5                       | 1.0\times10\(^{-1}\)-1.0\times10\(^{-7}\) and 1.0\times10\(^{-3}\)-4.0\times10\(^{-7}\) | -          | 516  | 517  |
| HPO\(_4^{3-}\) | molybdenum acetylacetonate oxo-molybdenum methylsalen                      | -28.6                       | 1.0\times10\(^{-1}\)-1.0\times10\(^{-7}\) and 1.0\times10\(^{-3}\)-4.0\times10\(^{-7}\) | -          | 516  | 517  |
| PO\(_4^{3-}\) | bis(pentafluorobenzyl) tin(IV) dibromide                                   | -70.8                       | 10\(^{-5}\)-10\(^{-3}\)                | -                                                    | 523  |
| CN\(^-\)  | thin electroplated membranes of silver chalcogenides                       | -90                         | 10\(^{-6}\)-10\(^{-2}\)                | -                                                    | 527  |
| Anion                  | Ionophore                                                                 | Slope (mV decade⁻¹) | Linear Range (M)                  | The most interfering ions (log K_{sel} > -2) | Ref.  |
|-----------------------|---------------------------------------------------------------------------|---------------------|-----------------------------------|--------------------------------------------|-------|
| SCN⁻¹                 | (octabromotetraphenylporphyrinato)manganese(III) chloride                 | -58.3               | 4.8×10⁻⁷-1.0×10⁻¹                  | -                                          | 544   |
| SCN⁻²                 | manganese(III) tetraphenylporphyrin derivatives                           | -59.5               | 10⁻²-10⁻¹                         | -                                          | 553   |
| SCN⁻³                 | nickel(II)-azamacrocycle complex                                          | -57.8               | 1.0×10⁻⁷-1.0×10⁻¹                  | -                                          | 555   |
| SO₃²⁻                 | bis-urea calix[4]diquinones                                              | -51.5               | 6.0×10⁻²-1.0×10⁻²                  | ClO₄⁻                                    | 557   |
| SO₄²⁻₁                | strontium Schiff's base complex (SS)                                      | -29.2               | 10⁻²-10⁻⁶                         | SO₃²⁻, CO₃²⁻, Cl⁻                           | 559   |
| SO₄²⁻₂                | zinc-Schiff base                                                          | -29.2               | 10⁻²-10⁻⁶                         | -                                          | 560   |
| SO₄²⁻₃                | alpha,alpha'-bis(N'-phenyl-thioureylene)-m-xylene                         | -29.6               | 10⁻⁶ - 10⁻²                       | SCN⁻, Br⁻, NO₂⁻                             | 563   |
| F⁻                   | organotin compounds                                                      | -62.7               | 1.0×10⁻⁶-1.0×10⁻¹                  | -                                          | 571   |
| Cl⁻                   | ruthenium(III) Schiff's base                                              | -54.5               | 1.0×10⁻¹-3.0×10⁻⁶                 | -                                          | 574   |
| ClO₄⁻¹                | complex of uranil                                                        | -60.6 ± 1.0         | 1.0×10⁻⁶-1.0                      | -                                          | 584   |
| ClO₄⁻²                | some recently synthesized Ni(II)-hexaazacyclo-tetradeacene complexes      | -59.3               | 10⁻¹-5.0×10⁻⁷                     | -                                          | 586   |
| Br⁻¹                  | iron(III)-salen (IS)                                                     | -59.0               | 7.0×10⁻⁶-1.0×10⁻¹                  | SCN⁻, I⁻, Cl⁻                              | 588   |
| Br⁻²                  | Zn(II) macrocyclic complex                                               | -59.2               | 2.2×10⁻⁶-1.0×10⁻¹                  | -                                          | 589   |
| I⁻¹                   | cobalt-salophen                                                          | - 58.9              | 5.0 ×10⁻⁷ - 1.0×10⁻¹               | -                                          | 597   |
| I⁻²                   | thiopyrilium ion derivative                                               | -60                 | 8.0×10⁻⁷-1.0×10⁻¹                  | -                                          | 604   |
| I⁻³                   | bis(1,3,4-thiadiazole) complexes of Hg(II)                                | -59.0               | 2.0×10⁻⁶-2.0×10⁻²                  | -                                          | 607   |
| I₃⁻¹                  | (salicylaldehyde) ethylenediamine mercury(II) complex MS                  | -59.0               | 5.0×10⁻⁸-1.0×10⁻²                  | -                                          | 613   |
| I₃⁻²                  | a charge-transfer complex of (1,3-diphenyldihydro-1H-imidazole-4,5-dione) | -59.3               | 10⁻⁷-10⁻¹                         | -                                          | 615   |
| I₃⁻³                  | 2-(((2((E)-1-(2-hydroxyphenyl)methylidene)amino)phenyl)iminomethyl)phenol with iodine (CTC) | -59 | 5.0×10⁻⁸-1.0×10⁻² | - | 615 |
| I₃⁻⁴                  | mercury-salen                                                            | -59.0±0.5           | 5.0×10⁻⁸-1.0×10⁻²                  | -                                          | 623   |
Table 8. Cont.

| Anion         | Ionophore                                                                 | Slope (mV decade$^{-1}$) | Linear Range (M) | The most interfering ions (log $K_{\text{sel}}$ > -2) | Ref. |
|---------------|----------------------------------------------------------------------------|--------------------------|------------------|-----------------------------------------------------|------|
| IO$_4^-$      | metaperiodate bis(triphenylphosphoranylide) ammonium                      | -60.1                    | 8.0×10$^{-3}$-2.7×10$^{-1}$ | -                                                   | 631  |
| Arsenite      | PVC based 5,10,15,20-tetrakis (4-methoxyphenyl) porphyrinato cobalt(II)    | -28.8                    | 7.9×10$^{-3}$-1.0×10$^{-1}$ | -                                                   | 632  |

Chemical structures of some above ionophores which are used in construction of non-conducting polymer ISEs for inorganic anions are shown in Figure 18.

Figure 18. Some structures of the suitable ionophores used in construction of some anion membrane sensors.
4. Conclusions

The main problem with symmetric ion selective PVC membrane electrodes is the leakage of the internal solution to the outer surface of the membrane, causing changes in the surface potential. Therefore, the detection limit of this kind of electrode is about $10^{-6}$ M. Since the lifetime of the plasticized PVC membranes is affected by leaching of the membrane components from the membrane into the sample solution, many efforts have been made to achieve plasticizer-free membranes and covalently bound ion recognition sites, in which case CPs also offer unique possibilities.

Construction of all-solid-state ISEs that do not require internal filling solutions is a common approach, which necessitates careful designs of the solid contact between the ion-selective membrane and the electronic conductor. These devices, however, suffered from the ill-defined transduction of the ionically conducting ion-selective membrane and the electronic conductor, which made them rather instable. Scientists solved overcome this simply by using a conducting polymer instead of the liquid internal electrolyte of the classical ISE. Conducting polymers are able to form an ohmic contact to materials of high work functions, like carbon, gold and platinum. Secondly, due to the solubility of several CPs, they can be deposited from solutions. Thirdly, they have ability to being electroactive materials of mixed electronic and ionic conductivity, which gives them the unique potential to transduce ionic signals into electronic ones.

These kinds of electrodes have lower detection limits, high mechanical resistance and reproducibility rather to the PVC based membrane electrodes. Also, they can be easily miniaturized to yield solid state ion-selective microelectrodes.

However, the diversity of the electrodes having conducting polymer in comparison to the common PVC based membrane electrodes is very low.

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