

Review

Schiff's Bases and Crown Ethers as Supramolecular Sensing Materials in the Construction of Potentiometric Membrane Sensors

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Abstract: Ionophore incorporated PVC membrane sensors are well-established analytical tools routinely used for the selective and direct measurement of a wide variety of different ions in complex biological and environmental samples. Potentiometric sensors have some outstanding advantages including simple design and operation, wide linear dynamic range, relatively fast response and rational selectivity. The vital component of such plasticized PVC members is the ionophore involved, defining the selectivity of the electrodes' complex formation. Molecular recognition causes the formation of many different supramolecules. Different types of supramolecules, like calixarenes, cyclodextrins and podands, have been used as a sensing material in the construction of ion selective sensors. Schiff's bases and crown ethers, which feature prominently in supramolecular chemistry, can be used as sensing materials in the construction of potentiometric ion selective electrodes. Up to now, more than 200 potentiometric membrane sensors for cations and anions based on Schiff's bases and crown ethers have been reported. In this review cation binding and anion complexes will be described. Liquid membrane sensors based on Schiff's bases and crown ethers will then be discussed.

Keywords: Supramolecule, Potentiometric membrane, Sensor, Ion Selective Electrode, Schiff's Base, Crown Ether

1. Introduction

From a color change in a flask to highly sophisticated biological mechanisms, every action that occurs around us is the result of chemical reactions and physicochemical interactions occurring in various combinations. These reactions and interactions often seem to occur randomly, but this is rarely true. They often occur between selected partners—especially when the reactions and interactions occur in a highly organized system such as those found in biological settings—as the molecule recognizes the best (or better) partner. This mechanism is called "molecular recognition".

Supramolecular chemistry, which is defined as the chemistry of molecular systems beyond individual molecules and which is highly dependant on the phenomenon of molecular recognition due to a host-guest relationship, was first established more than one hundred years ago. Alfred Werner was the first to introduce the concept of coordination chemistry [1]. The so-called "lock and key" concept in the study of the enzyme interactions, coined by Emil Fischer, can be regarded as a major concept associated with molecular recognition [2,3]. Molecular assembly and host–guest chemistries were later integrated into the individual concept of supramolecular chemistry by Lehn. This has helped elaborate the close relationship between this field and the complex supermolecular species, which are formed due to the effect of intermolecular forces on more than one chemical species, holding them together. It should be stated that the functionality of a supermolecule is beyond a simple summation of those of its individual components [3]. Many new novel compounds with high selectivities for ion or molecule separation, transport and catalytic purposes have been developed by scientists who have been active in different branches of chemistry.

2. Principle of Potentiometric Membrane Sensors

Since the 1930s, potentiometric membrane sensors have found great practical applicability in different fields. The response mechanism of these sensors is based on the measurement of a potential under a zero current regime or a under a low electrical current flow. Potentiometric membrane sensors, which have been designed based on molecular recognition, contain a molecule that selectively recognizes another target species through various molecular interactions. As it is widely known, potentiometric electrodes possess as advantages the direct, simple, rapid, inexpensive and selective detection of ionic activities. The selectivity of these sensors stems from the highly selective interactions between the membrane material and the target species [4].

The most prominent ingredient of a potentiometric ion-selective electrode (ISE) is, by definition, its selective membrane. Once an ion can pass through the boundary between the organic phase of the membrane and the internal and the sample solution, an electrochemical equilibrium will be established, under which it is probable that different potentials are developed in the two aqueous phases. So, in case the ionophore can exchange only one certain target ion, the potential difference between the phases will reflect the activities of the target ion in the two solution and the membrane phases.

If a membrane separates two solutions of different ionic activities a_1 and a_2 , the so-called Nernst equation is known to govern the potential difference (E) across the membrane:

$$E = \frac{RT}{zF} \ln\left(\frac{a_2}{a_1}\right) \quad (1)$$

If a_1 is constant, only $a_2=a_x$ can be related to the measured potential (E). Under ideal conditions, it is only the activity of the target ion in the phases that affects the potential. The Nernst equation describes the relation between the activity and the electrochemical potential:

$$E = \frac{RT}{z_x F} \ln\left(\frac{a_x}{a_1}\right) \cong E = Const. + S \cdot \log(a_x) \quad (2)$$

where z_x is the charge of the target ion and S equals $59.16/z_x$ [mV] at 298 K.

Using two identical reference electrodes in the solutions on both sides of the sensing element, “E or the electromotive force (EMF)” can be easily measured. In practice, this parameter is measured between the ISE (already containing an internal reference electrode) and an external reference electrode in the sample solution. One should keep in mind that this is a zero current measurement that is performed under equilibrium conditions in which the transfer rate of ions from the solution to the membrane is equal to that from the membrane to the solution. It is assumed that under ideal conditions, other ions which cannot permeate the membrane will have no considerable effect on the potential difference.

The activity of the target ion governs the potential of such a membrane which is also governed to some extent by the activity of the interfering ions under actual conditions. If the activity of a hypothetical interfering ion, Y, with a charge of z_y , is a_y , and if the selectivity coefficient of the sensor to this ion is K_{xy} , the effect of interfering ion on the measured potential difference is considered by the so-called Nikolski-Eisenman equation:

$$E = Const. + S \cdot \log(a_x) + \frac{z_x}{z_y} \cdot \log(K_{xy} \cdot a_y) \quad (3)$$

2.1. Polymeric membrane

Any polymeric membrane ISE consists of components, the nature and the amounts of which greatly affect the nature and the characteristics of the sensor. These components include the polymeric matrix, the ionophore, the membrane solvent mediator and the ionic additive.

The first polymeric ISE membranes, in which the polymer was considered to provide the required physical properties, like elasticity and mechanical stability, consisted of valinomycin as the ionophore, which was incorporated into silicone rubber [5] or PVC [6], without the addition of lipophilic ionic sites [7-10]. There are other polymers which can be used instead of PVC in the membrane construction. Soft polyurethanes with a low content of crystalline units [11], silicone rubber [5], poly(vinylidene chloride) [12] and polysiloxanes [13] can also be used as the matrix.

Membrane solvents (plasticizers) are used to increase the plasticity of membrane, which is required to give a homogeneous organic phase. This ingredient also affects the selectivity behavior of the ISE membrane. In the case of ligand-free ISE membranes or those based on an ion exchanger, incapable of

specific interactions with a target ion, what governs the selectivities is the difference between the standard free energies of the ions in the aqueous and the organic phases.

Such selectivity trends are always the same as the so-called Hofmeister series, which for some cations and anions agrees with those of the free hydration energies of the ions. A plasticizer change from the polar *o*-NPOE or nitrobenzene (NB) to the apolar dibutyl phthalate (DBP), for example, is reported to reduce the M^{2+} -selectivity of the ISE with the ionophore 2,3,8,9-tetraazacyclododeca-1,3,7,9-tetraene [14]. This is known to be due to the polarity of the plasticizer, which can be estimated from the interaction of the charged species with a continuum of the given dielectric constant (Born model) [15]. More polar solvents prefer divalent over monovalent ions. The nature of the plasticizer also strongly influences the measuring range of the ion-selective sensors, too. Another factor, highly influenced by the membrane solvent, is the formation of the ion-pairs. The amount of ion-pairs formed between the complexed ions and the lipophilic counter ions, which is known to influence the slope of the response curve, is predicted to be negligible in the polar membranes, while this is significant in the case of non-polar membranes. For example, where the M^{2+} cations associate with the X^- anions, so that the MX^+ monovalent species predominantly takes part in the phase transfer equilibrium [16] and/or occurs in the membrane, a characteristic slope for a typical monovalent ion will be expected. Plasticizers which can be potentially used in potentiometric membrane are as follows: Benzyl acetate (BA), bis(2-hydroxyethyl) phthalate (BEHP), bis(1-butylpentyl) adipate (BBPA), bis(2-ethylhexyl) adipate (DOA), bis(2-ethylhexyl) phthalate (dioctyl phthalate) (DOP), bis(2-ethylhexyl) sebacate (BEHS), bis(*n*-octyl) sebacate (DOS), dibenzyl ether (DBE), dibutyl phthalates (DBP), dibutyl sebacate (DBS), didecyl phthalate (DDP), didecyl sebacate (DDS), (R, R)-2,3-dimethoxysuccinic acid bis(1-butylpentyl) ester (DMSNE), ethyldidecyloctadecylammonium nitrate (EDOA), 2-fluorophenyl 2-nitrophenyl ether (FNDPE), 2-nitrophenyl phenyl ether (*o*-NPPE), 2-nitrophenyl octyl ether (*o*-NPOE) and tri-*n*-butyl phosphate (TBP).

The first example of the application of an ionic additive reported was that of a tetraphenyl borate salt. This was added to the membranes of a cation-selective electrode to reduce the anionic interference, observed in the presence of lipophilic anions like thiocyanate [17]. This also leads to a lowering of the electrical resistance of the membrane, which is of special importance in the case of microelectrodes [18]. The ionic additives are also ion exchangers having the ability to induce selective responses in the absence of sufficient ionophore amounts. The concentration of these species must, hence, be adjusted carefully [19].

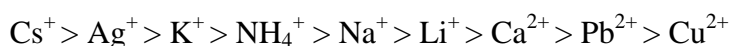
The ionophore or the membrane-active recognition element can be an ion exchanger or a neutral macrocyclic compound, having molecule-sized dimensions and containing cavities or semi-cavity to surround the target ions [20,21]. The ionophore, or the membrane-active recognition element, which is the most important component of the membrane will be discussed later.

3. Cation-Binding Ionophores

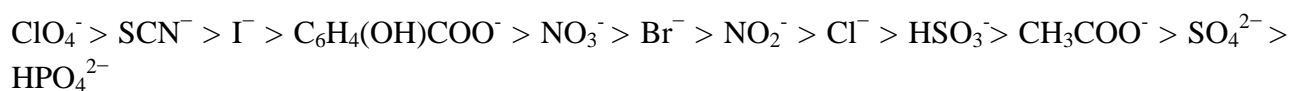
Cation recognition has developed very fast because it was based on a mixture of the well-established coordination geometry of most cationic species and the high binding energies resulting from the ion-dipole interactions. This also led to the development of the supramolecular chemistry,

due to the fact that many of the fundamental concepts of this field are derived from studies on cation recognition.

The selectivity patterns of ISEs can be regarded to be the result of the different binding strengths of ionophores and the tested ions. Phase transfer of aqueous ions in and out of an organic ISE membrane is necessary for the classic behavior of ISEs, during which the interaction of the ions with the ionophore becomes possible. The ion transfer process will be controlled by the lipophilicity of the ions in case the ionophore does not have any selective tendencies for any of the ionic species [22]. This means ions of higher lipophilicity will cause larger response [23,24] which leads to the so called Hofmeister [25] selectivity pattern, merely based on the lipophilicity of the ions, which can be demonstrated for cations and anions as follows:



The equivalent pattern for the anions is:



These patterns are called the Hofmeister series [25]. One should also note that the presence of a selective ionophore in the ISE membrane leads to decreases in the total free energy required for the transfer of the ionophore-ion complex into the organic phase. So, the stronger the binding of the ionophore to an ion is, the more the phase transfer equilibrium of the ions will be affected. If the complexation constant (K_f) of an ionophore with one or more of the ions is strong enough, a meaningful difference between the observed selectivity and that expected according to the Hofmeister regime will be seen [26]. Based on the same hypothesis, the more strongly the ionophore complexes with a certain target ion, the larger the difference will be in the magnitude of the selectivity coefficients versus the series. The ISE based on the calcium-selective ionophore ETH 1001, with a K_f value of 3.5×10^{-2} M for Ca^{2+} ions in the NPOE/PVC membranes, for example, has selectivity coefficients in the order of 10^{-6} for Ca^{2+} over K^+ and Na^+ , which is a vivid distinction from the series [27].

It is clear that there are other requirements beyond the formation of a strong complex with a specific ion to make an ionophore suitable for the construction of an ISE. In short the complexation of the ionophore must also be kinetically fast [28,29]. This quality, which lowers the free energy barrier for the free and complexed states and leads to a facile complexation, the ion-carrier must be preorganized and flexible to some extent [4].

Another factor limiting the applicability of an ionophore is its lipophilicity, which makes the ionophore compatible with the polymer membrane, which substantially diminishes the leaching of the ionophore from the organic membrane into the aqueous phase increasing the sensors life time and the reproducibility of its response. This is usually achieved by substituting long alkyl chains or other bulky organic groups to its binding framework.

The response of the ISE also depends on the type of interactions between the ionophore and the target ion, which can be of chemical or physical natures. The chemical interactions can be summarized

as Lewis acid-base reactions of hard and/or soft types, hydrogen-binding, best-fit mechanisms, complexation, chelate effects, sandwich complex formation and precipitation reactions [30].

3.1. The principle of the complexation reactions

Complex formation is very important, especially in the science of biology. In this process, bonding interactions occur, which are usually weaker than the covalent bonding. The complex formation processes are characterized by the thermodynamic stability and selectivity, which depend on the energy amount (K , ΔG , etc.), and the kinetic stability and selectivity, which depend on the reaction rate.

The interaction between two species can be either attractive or repulsive. The former one results in complex formation. Stability, formation mechanism and formation or dissociation rates are the main parameters in complexation. The complex stoichiometry is another effective factor used to describe a complex. The complexes are divided into the two groups of addition (denoted by $[S, L]$) and inclusion complexes (denoted by $[SCL]$).

Complexation can actually be defined as a simple interaction between a donor (ligand) and an acceptor (substrate). In the case of inclusion complexes, however, there has to be a 2 or 3D cavity in the ligand structure in order to host the substrate $[SCL]$ [31-34].

Once a ligand encounters several substrates (S_1, S_2, S_3, \dots), complex formation may happen according to the three routes of distinctive, selective or specific complexation.

In a distinctive complexation, the ligand (L) tends to form complexes with any of the substrates, which means the thermodynamic and kinetic effects between L and all substrates are identical and hence all K_f values are equal. This is in accordance with selective complexation; the ligand prefers one of the substrates to the others and has a higher tendency to form a complex with it. In the specific complexation, on the other hand, L forms a complex with only one of the substrates.

Molecular recognition is based on selective or specific complexation routes, which lead to static, dynamic (kinetic) or a mixture of both selectivities.

This selective behavior can be very important, as in the case of drug consumption in the body, where the drug selectivity and its selective interaction are vital. The static selectivity considers the formation constant, the association energy, dissociation energy and the free energy (ΔG , K_f) since they help define the stability of complexes. Dynamic selectivity, on the other hand, considers the formation rate, the rate constant, the transition state, the activation energy as well as the rate of the forward and reverse reactions.

The characteristics of the ligand as well as the substrates are crucial in molecular recognition, because the selective bonding between the ligand and the substrate originates from this information. This information is literally stored in the ligand and is read out by the substrate. This characteristic information helps define the stability, selectivity, reactivity and transport of the complexes.

As stated before, the information stored in the ligand must be readout by the substrate and the association and dissociation rates control the readout.

Ion-molecule complexes are usually stronger than the molecule-molecule complexes, because of the strong interaction between ions and the molecule; however, there are some exceptions to this and some

molecule-molecule complexes are strong. These exceptions are the result of hydrogen and hydrophilic bonding or strong acceptor-donor interaction.

3.2. Factors effective in complexation

Many inorganic cations are monomolecular and spherical in shape. As a result, it is the structure of the ionophores and their geometric factors that play important roles in determining the ion-selectivities. There are basic factors, which can effectively change the selectivity of the ligand or the ionophore including: the ligand topology which can be sub-classified into the ligand dimensionality, its connectivities, shape, size, conformation, chirality and also its cavity or ring size. The degree of flexibility of the ligand holding of the donor atoms by the host backbone, which makes their positions suitable to match the shape of the coordination sphere of the target species, is another factor. Finally, the presence of lariats (functional groups, arms or chains added to the ionophores to change selectivity) has a great effect on binding.

Another very important factor that affects the complexation properties of the ligand binding sites which depends on the nature and number of the binding sites, is their shape, size, arrangement and reactivity.

The planarity of the ligand is also important in its complexation properties. Some factors, related to the cation and influencing the selectivity behavior, include the geometric shape of the ion, its charge density and its size (the ionic radius). The last factor seems to have a large influence on the selectivity. For instance, 12-crown-4 is selective toward the Li^+ ion, the radius of which is 0.68 Å, while another crown ether, 18-crown-6, interacts selectively with K^+ which has a radius of 1.33 Å.

In this case, the thickness of the ligand acts as a shield for the substrate lipophilicity. The polarity of the ligand is also influential. It is, as a result, important to distinguish and recognize the polar and nonpolar sides of the ligand. It seems to be necessary to state that another source of the effective information is the medium, which plays a central role in the complexation reaction.

One of these other sources is the nature of the solvent. It is clear that the substrate, the ligand and the complex are solvated. The ability of solvent molecules in solvating the ions, which lets the solvent compete with the ligand in coordinating the ion, has a fundamental role. Due to the necessity of cation and macrocycle dissolution before formation of the complex, the solvation processes of these species are expected to have a huge influence on the stability of the resulting complex in solution.

Another effective parameter includes the effect of the counter ion, which is of value in the case of the charged complexes. The neutralization of the charged complex is necessary to the transportation of the charged complex, which is normally done by the counter ion. The nature of the counter ion has a major effect on ion pair formation. For instance, a good ion pairing is not observed in the case of Cl^- , while MnO_4^- creates strong ion pairs.

4. Anion-Binding Ionophores

For many reasons the number of anion selective electrodes, which constitute an important group of ISEs, is lower than that of the cationic sensors. One reason is that the size of anions is relatively larger than that of cations. Another reason is the various shapes and high hydration energy of anions. Finally,

anions can have different forms based on the pH of the medium. However, the number of sensors for anions has been considerable [35].

Usually an ion-selective membrane, which can be either an inorganic salt or an organic polymeric matrix containing a metal complex as the ionophore, plays the role of the selector element of the potentiometric indicator electrode. In the case of the latter, a strong interaction between the ionophore and the anion is required, thus a complex shows a selective tendency which can be used in the construction of anion selective sensors. The potentiometric response, in the case of anion ISEs, is considered to be the result of the axial coordination of the target ion to the metal center [37-39].

Conventional ionophores (like quaternary ammonium salts) have been used in the construction of anion selective sensors with the selectivity order of $\text{ClO}_4^- > \text{SCN}^- > \text{salicylate}^- > \text{NO}_3^- > \text{Br}^- > \text{NO}_2^- = \text{Cl}^- > \text{HCO}_3^- > \text{H}_2\text{PO}_4^- = \text{F}^- = \text{SO}_4^{2-}$, which can be regarded to be merely based on the lipophilicity of the ions (i.e. Hofmeister selectivity). As in the case of cation ISEs, anion carriers with different selectivity sequences have been sought.

It was found that the use of metal complexes as the ionophore results in potentiometric anion selectivity patterns that are very different from the Hofmeister sequence which is believed to stem from the selective axial ligation of the anion with the metal ion centers in the complexes. These so-called anti-Hofmeister sequences can vary depending on the nature of the central metal [40], as is observed in the case of Schiff's base complexes of different metal ions. To explain such an effect we will review these interactions.

4.1. Metal center-anion interaction

The application of metal centers as anion binding receptors with anti-Hofmeister behavior has been very common. The metal centers can be either ionic (complexed in an organic ligand) or they can have organometallic natures. The latter, e. g. metalloporphyrins, metallophthalocyanines and Schiff bases have been more promising. The mentioned metal–ligand interactions induce an anion-selectivity in the membrane that significantly differs from those observed in the case of conventional anion ionophores containing lipophilic quaternary ammonium or phosphonium salts, which lead to lipophilicity based selectivity patterns. Such electrodes largely depend on the nature of the metal center of ionophore and the stability of the complex [41].

The application of both charged and neutral metal centers, depending on the organic ligand and the metal center, has been reported, which necessitates slight changes to the membrane composition.

As in the case of the cationic counterparts, it is necessary to add some lipophilic anionic sites to the membrane, so that the sensor selectivity is optimized. This is absolutely vital in the case of the neutral receptors.

4.2. Anionic sensors with hydrogen bonding

Hydrogen bonding, although weaker than the common electrostatic interactions resulting from axial coordination, can also play a crucial role in the recognition process. This mechanism is only possible through the proper orientation of the interacting functional groups which justifies the absence of hydrogen bonding during recognition in many cases.

4.3. Anionic sensors with quaternary ammonium or guanidinium sites

As mentioned before, the Hofmeister pattern is observed in the case of the sensors with polymeric ion exchange membranes, containing cationic sites with no special tendencies. According to this selectivity pattern, the more hydrophilic anions (like H_2PO_4^- and Cl^-) are less favorable than the more lipophilic ones (like ClO_4^- and NO_3^-).

4.4. Anionic sensors with trifluoroacetophenone receptors

In contrast to the receptors described in the previous sections, the selectivities of which resulted from non-covalent interactions with the anion, the trifluoroacetophenone derivatives form a covalent bond with the target anion.

5. Study of Complexation

In practice, the selectivity behavior of an ionophore is evaluated after its incorporation into the sensor. For example membrane-based techniques have been used to evaluate the binding properties of the ionophore according to which the ISE response is studied with the membrane containing two ionophores. Also, in other methods, the ionophore-based membranes are sandwiched with an ionophore-free membrane then the responses at different interfaces are compared. Other methods have been developed to examine the selectivity and the potential of a would-be ionophore outside the membrane phase. For instance, the strength of the ion–ionophore interactions is studied in solution phases via NMR [4].

5.1. Complexation study by conductometric method

Conductivity measurements can be useful tools to investigate complexation. The measurements can be conducted with a Metrohm 660 conductivity meter and a dip-type conductivity cell, made of platinum black with a cell constant of 0.83 cm^{-1} . In all measurements, the cell should be thermostated at the temperature of $25.0 \text{ }^\circ\text{C}$, using a Phywe immersion thermostat. In typical experiments, 25 mL of an ion solution ($1.0 \times 10^{-4} \text{ M}$) are placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, it should be noted that both the starting solution and the titrant have the same ion concentration. Then, a known amount of an ionophore or a ligand ($1.0 \times 10^{-2} \text{ M}$) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved.

The 1:1 binding of the cations with the ionophore can be expressed by the following equilibrium:



The corresponding equilibrium constant, K_f , is given by

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{(ML^{n+})}}{f_{(M^{n+})}f_{(L)}} \quad (5)$$

Here, $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represent the equilibrium molar concentration of the complexes, the free cation, the free ionophore and the activity coefficient of the indicated species, respectively. Under the diluted conditions, the activity coefficient of the unchanged ligand $f_{(L)}$ can be reasonably assumed to be unity [42]. The use of the Debye–Hückel limiting law of the 1:1 electrolytes [43] leads to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in Eq. (5) is canceled out.

Therefore, the complex formation constant in terms of the molar conductance can be expressed as [44]:

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(A_M - A_{obs})}{(A_{obs} - A_{ML})[L]} \quad (6)$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \quad (7)$$

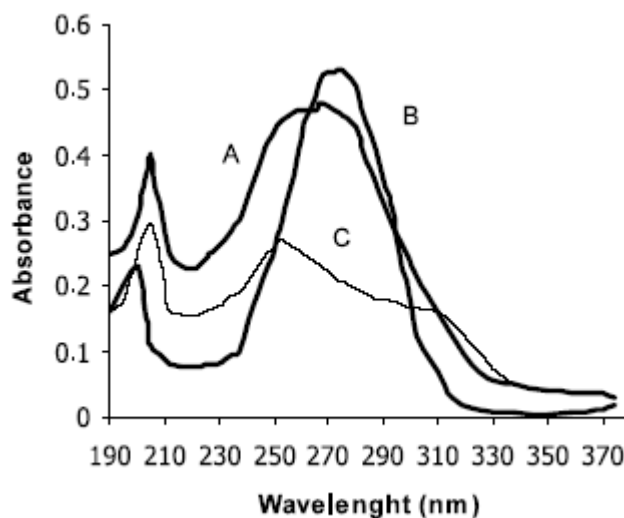
Here, A_M is the molar conductance of the cation before the addition of the ionophore; A_{ML} is the molar conductance of the complexes, A_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the added ionophore and C_M the analytical concentration of the cation salt. The complex formation constant, K_f , and the molar conductance of the complex, A_{ML} , were obtained by computer fitting the Eqs. (5) and (6) to the molar conductance-mole ratio data, using the nonlinear least-squares program KINFIT [45-53].

5.2. Complexation study by spectroscopic methods

5.2.1. UV-VIS study

The ligand coordination with the ion can be investigated by spectroscopy, for example. From the UV/Vis spectra, as illustrated in Figure 1, it is possible to distinguish the interactions between the ligand and the ion. The substantial decrease in the absorbance at a certain wavelength of the ligand solution, after adding the ion solution stepwise, may give a new adsorption peak at another wavelength, which is related to complex formation. At the same time, the effects of the other ions on the spectrum of the carrier should be investigated. The detectable changes in the UV/Vis spectra should be considered [54-56].

Figure 1. An example of an UV-Vis. spectrum for complexation study. A: ligand spectrum; B: the complex spectrum; C: metal ion spectrum.



When a metal ion, M , reacts with a ligand, L , to form a 1:1 complex, the formation constant is given as:

$$K_f = \frac{[ML]}{[M][L]} \quad (8)$$

The mass balance equations and the observed absorbance given by:

$$C_M = [M] + [ML] \quad (9)$$

$$C_L = [L] + [ML] \quad (10)$$

$$\Lambda_{obs} = \varepsilon_L[L] + \varepsilon_{ML}[ML] = \Lambda_o / C_L [L] + \varepsilon_{ML}[ML] \quad (11)$$

where C and e values are the analytical concentration and molar absorptivities of the species indicated and A is the absorbance of the ligand in the absence of metal ion. The mass balance equations can be solved in order to obtain an equation for the free ligand concentration, $[L]$, as:

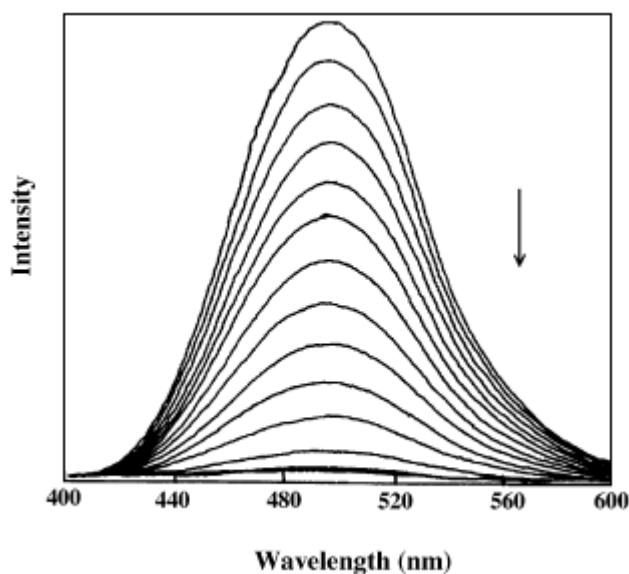
$$K_f[L]^2 + (1 + K_f(C_M - C_L))[L] - C_L = 0 \quad (12)$$

For the evaluation of the formation constant from absorbance-mole ratio data, the non-linear least-squares curve fitting program KINFIT was used.

5.2.2. Fluorescence study

The ligand complexation with the ion can be studied by the fluorescence method. The existence of sharp isobestic points in the resulting fluorescence spectra further support the formation of the complex between the ionophore and the ion [57].

Figure 2. An example of fluorescence spectrum for complexation study. The ligand fluorescence intensity is quenched in the presence of increasing concentration of metal ion.



The ion concentrations were changed sequentially at a constant ligand concentration and the enhancement in the emission intensities is compared to that of the corresponding ligand.

The 1:1 complexation constant can be calculated from the emission intensity and the concentration of the metal ion, [M], as follows [58,59]:

$$\frac{I - I_0}{I_\infty - I} = K \left\{ [M]_t - [L]_t \left(\frac{I - I_0}{I_\infty - I_0} \right) \right\} \quad (13)$$

where I is the emission response of the ligand at a certain ion concentration, I_0 is the emission response of the ligand in the absence of the ion, I_∞ is the emission response when no further change occurred while continue adding ion, $[L]_t$ is the total concentration of the ligand molecule and $[M]_t$ represents the total ion concentration. The complexation constants were calculated using a non-linear curve-fitting method [60].

5.2.3. NMR study

Multinuclear NMR is a very powerful (although not ideal) technique to study alkali metal complexes with macrocyclic ligands, particularly in non-aqueous solutions. For instance, the use of ^{23}Na NMR for the study of the sodium ion complexes with five crown ethers, namely 15-crown-5 (15C5), benzo-15-crown-5 (B15C5), 18-crown-6 (18C6), dicyclohexyl-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6), in binary acetonitrile (AN)-dimethylformamide (DMF) mixtures can be considered. The ^{23}Na chemical shifts were determined as a function of the [crown]/ $[\text{Na}^+]$ mole ratio at 25.0 ± 0.5 °C in various AN-DMF solvent mixtures for different crown ethers used [61].

The formation constants of the corresponding 1:1 complexes were calculated from the variation of the ^{23}Na chemical shift with the crown/ Na^+ mole ratio.

$$\delta_{obs} = \left\{ [K_f C_M - K_f C_L - 1] + (K_f^2 C_L^2 + K_f^2 C_M^2 - 2K_f^2 C_L C_M + 2K_f C_L + 2K_f C_M + 1)^{1/2} \times (\delta_M - \delta_{ML}) / 2K_f C_M \right\} + \delta_{ML} \quad (14)$$

where K_f is the concentration formation constant for the 1:1 complex, C_L and C_M are the analytical concentrations of the crown ether and Na^+ ion, respectively, and δ_M and δ_{ML} are the corresponding chemical shifts of the free and complexed sodium ion. The non-linear least-squares curve fitting program KINFIT [45] was used to evaluate the K_f and δ_{ML} values for the 1:1 complexes. The formation constants of all the 1:1 complexes were evaluated by computer fitting of the chemical shift–mole ratio data from equation 14.

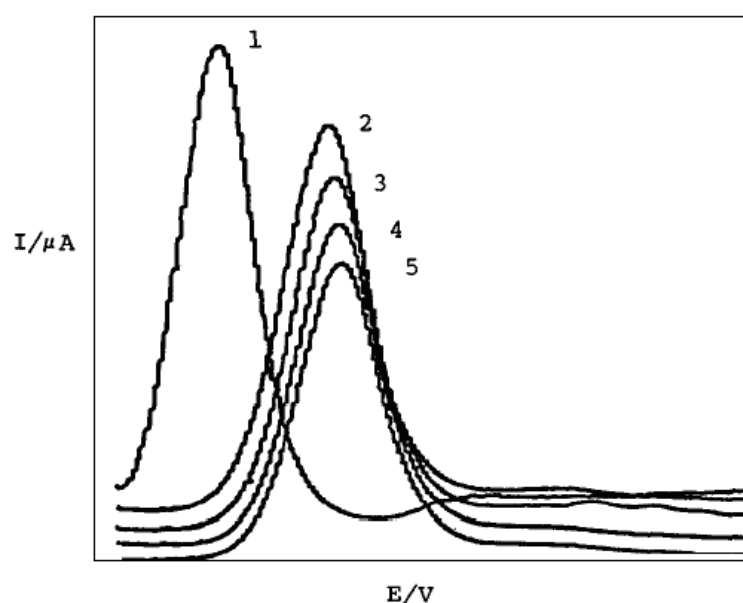
5.3. Complexation study by electrochemical methods

5.3.1. Polarographic study

Among a variety of physicochemical methods used for the study of cation-macrocycle interactions, polarographic methods have shown their ability as very useful means of studying the electrochemical behaviour of macrocyclic compounds and the stability and selectivity of their complexes with various cations in both aqueous and non-aqueous media.

In the polarographic investigation of metal ion complexes, the difference between the half-wave potentials of the free and complexed metal ions is a measure of the complex stability [62]. The determination of the formation constants of the metal ion-macrocyclic complexes, studied in different solvent mixtures, is based on measurements of the shifts in $E_{1/2}$ or E_p brought about by the addition of an increasing amount of the ligands.

Figure 3. An example of polarographic study for complexation. Differential pulse polarogram of a metal ion in the absence (1) and in the presence of the increasing ligand concentration (from 2 to 5).



Depending on the reversibility of the systems studied and the relative stability of the resulting complexes, one of the following three different polarographic methods is used for the determination of the stability constants [63]:

Method 1. In the case of the reversible amalgam-forming reduction of labile complexes of relatively high stability, the shift in half-wave (or peak) potential to more negative values upon addition of an excess amount of ligand was found to be in accordance with the Lingane equation:

$$\Delta E_{1/2} = (E_{1/2})_M - (E_{1/2})_C = (RT/nF)(\ln K_f + \rho \ln[L]_t) \quad (15)$$

where $(E_{1/2})_M$ and $(E_{1/2})_C$ are the half-wave potentials of the free and complexed metal ion, n is the number of electrons transferred, K_f is the complex formation constant, $[L]_t$ is the analytical concentration of the ligand and ρ is the stoichiometry of the complex. The values of ρ and $\log K_f$ can be obtained from the slopes and intercepts of the linear plots of $\Delta E_{1/2}/(RT/nF)$ vs. $\log [L]_t$, respectively.

Method 2. Measurement of the half-wave potential of the anodic polarographic signals resulting from the oxidation of mercury to its bivalent state in the presence of the ligands. The complex formation constants can be obtained from the following equation [64]:

$$\Delta E_{1/2} = (E^\circ_{cell}) = (RT/2F)(\ln K_f + \ln[L]_t^{\rho-1}) \quad (16)$$

where E°_{cell} is the formal potential of the Hg/Hg(II) half-cell vs. SCE.

Method 3. Measurement of the positive shift in the reversible cathodic half-wave potential of Hg^{2+} complexes (as indicator) with increasing concentration of another M^{2+} cation which can compete with Hg^{2+} for the ligand. The formation constants for M^{2+} complexes were obtained from the equation [65]:

$$\Delta E_{1/2} = (E_{1/2})_{HgML} - (E_{1/2})_{HgL} = (RT/2F)(\ln K_f + \rho \ln[M^{2+}]_t) \quad (17)$$

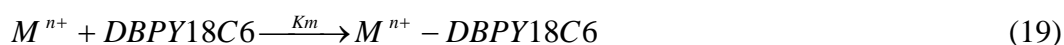
where $(E_{1/2})_{HgML}$ and $(E_{1/2})_{HgL}$ are the cathodic half-wave potentials of the $Hg^{2+}L/Hg$ system in the presence and absence of M^{2+} ion, respectively, and $[M^{2+}]_t$ is the analytical concentration of the M^{2+} ion.

5.3.2. Potentiometric study

The stability constant of the M^{n+} -Ligand complex (equation 18) at various temperatures, K_f , can be determined by a competitive potentiometric method using a Ag^+/Ag electrode as a probe. Simple potentiometric titration of the Ag^+ ions with a solution of the ligand can be used in case of Ag^+ . For example, calculation of $K_f Ag^+$ with dibenzopyridino-18-crown-6 (DBPY18C6) is shown as follows [66]:

$$[Ag^+]_{tot} = [Ag^+] + [Ag^+ - DBPY18C6] \quad (18)$$

For a solution containing Ag^+ and DBPY18C6, the total concentrations can be written as:





The stability constants of the M^{n+} ion complexes, K_M , with DBPY18C6 (equation 20) at various temperatures can be determined by the double decomposition reaction of M^{n+} with the corresponding Ag^+ complex (Equation 19) by monitoring the equilibrium concentration of the silver ions in the presence of the M^{n+} ions using the equilibrium constant $K_E = K_M/K_{Ag}$ for reaction 20 together with the stability constant K_{Ag} obtained from the direct titration of the Ag^+ ions with the ligand.

$$[M^{n+}]_{tot} = [M^{n+}] + [M^{n+} - DBPY18C6] \quad (21)$$

In this case, the total concentrations of M^{n+} and DBPY18C6 are written as:

$$[DBPY18C6]_{tot} = [DBPY18C6] + [Ag^+ - DBPY18C6] + [M^{n+} - DBPY18C6] \quad (22)$$

A MINQUAD program was used to compute the formation constants K_{Ag} and K_M from the resulting potential concentration data [67].

5.4. Complexation study by theoretical calculation

In order to obtain a clue about the tendency of the ionophore to the ions, some ab-initio quantum-mechanical calculations can be carried out. The pairwise interaction energy, $\Delta E(A-B)$, between two molecules (A and B) is estimated as the difference between the energy of the $E(A-B)$ complex and the energies of the isolated partners:

$$\Delta E(A-B) = E(A-B) - E(A) - E(B) \quad (23)$$

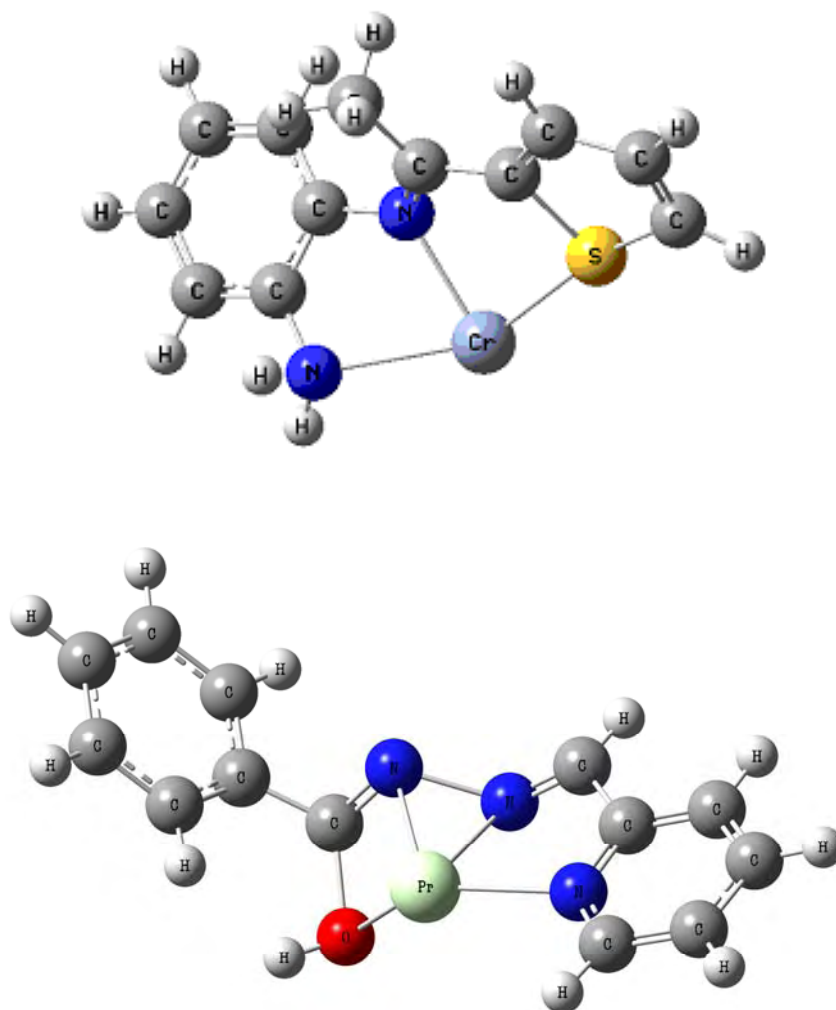
The calculations were performed with the second-order Møller-Plesset (MP2) perturbation theory [68,69], which includes the electron correlation energy in addition to the Hartree-Fock (HF) energy. The use of such a calculation level is fully justified by the fact that the description of the base stacking requires calculations with the explicit inclusion of the electron correlation [70]. The interaction energy at a given order of the Møller-Plesset (MP) perturbation expansion is calculated as:

$$\Delta E_{MPn} = \Delta E_{HF} + \sum_{i=2}^n \Delta E_{Corr}(MPi) \quad (24)$$

where ΔE_{HF} is the HF energy and $\Delta E_{Corr}(MPi)$ is the i^{th} order perturbative correction to the correlation energy. Only the valence electrons were explicitly correlated in our computations, which correspond to the usual frozen core approximation. The perturbation expansion (24) to the second order, which is expected to take into account the major contributions of the van der Waals energies (electrostatic, polarization, dispersion, electron transfer and exchange contributions) also is limited [71].

For most of the atoms, the lanl2mb basis set is used (due to the difference in atom properties) for the optimization of the molecules. All the calculations were performed using the Gaussian 98 package [72]. The interaction energies for the ionophore and some metal ions can be calculated from the equation (23).

Figure 4. Some examples of theoretical calculation for complexation study. Optimal conformation of the ionophore complexation with ions is shown in these figures.



6. Schiff's Bases as Supramolecular Sensing Materials in the Construction of Potentiometric Membrane Sensors

A very good example of supramolecular studies is the design and synthesis of molecules or metal complexes that can be used for the construction of sensing membranes that selectively respond to a particular analyte, because of the incorporation of the designed species. In such a case, it is necessary to match the size and binding properties of the species to make it or its derivative as selective towards the desired analyte as possible.

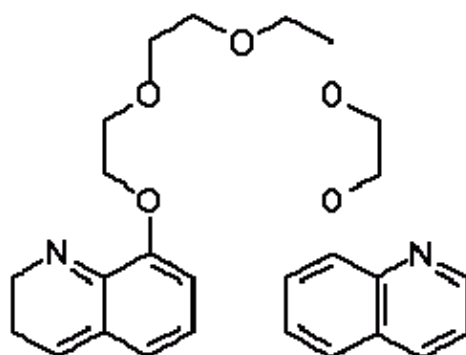
Supramolecular ionophores can be cation or anion selective. These sensing materials can be classified as ring-shaped or cyclic ionophores, cylindrical ionophores, hemispherical ionophores (also called molecular baskets or cages) and acyclic or linear compounds.

Cyclic ionophores are often cyclic antibiotics or peptides, such as the K^+ -selective ionophore valinomycin or crown ethers like 14-crown-4 or 12-crown-4 derivatives, which demonstrate tendencies toward Li^+ .

Cylindrical ionophores include as most important representative calixarenes, which have a cyclic scaffold that includes a derivative of phenol such as a sodium selective calix[4]arene. Hemispherical ionophores are structurally similar to crown compounds with the difference of having a bridge. They look like bowls with different cavity sizes.

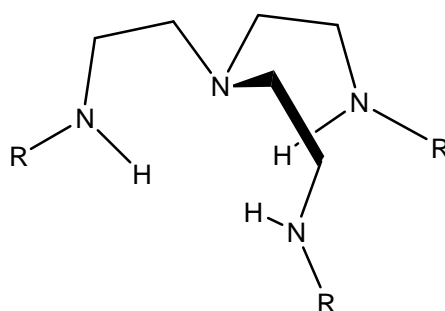
On the contrary to having shown good ion selectivities in some cases, linear compounds are not as important as macrocycles. The most important member of this family are podands, which have more sites gathered around a rigid core by a flexible linkage and that resemble the arms of the molecule. Due to the selectivity of this group, chelate effects can be observed, which increases the selectivity compared to rigid ionophores. Although the structure of these compounds cannot be geometrically preorganized, they can easily bind cations in an optimized conformation with less energy. The Mg^{2+} -selective bi-podand is an example of this group [4].

Figure 5. Structure of a podand.



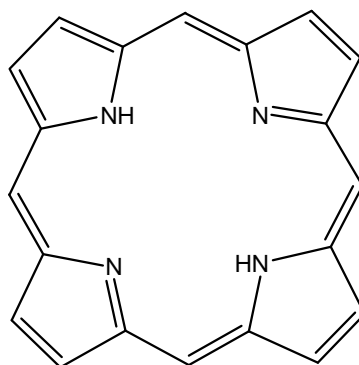
Supramolecular ionophores can be classified as podands (Figure 5), with a crown-ether like structure which only has a linear part that can form a wrap around metal ions complexes. Another group is the Schiff's bases and crown ethers which will be described later. Tripod ligand molecules (Figure 6) constitute another group of such compounds. The tripods can be either symmetrical or non-symmetrical [73,74].

Figure 6. A symmetric tripod ligand.



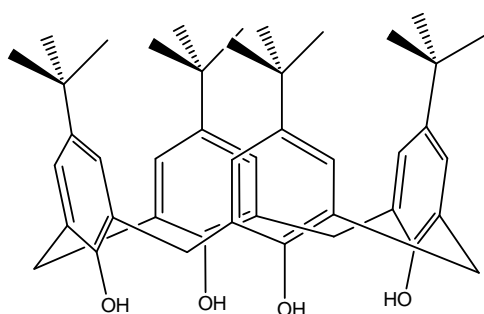
Planar macrocycles like porphyrin (Figure 7) or tetralactam are well-known supramolecular ionophores. Catananes and rotaxanes constitute another group of the supramolecular ionophores, in addition to cyclodextrines that are water soluble compounds.

Figure 7. Structure of a porphyrin.



Calixarenes (Fig. 8) and their different derivatives are also supramolecular ionophores [74], the structures of which allow them to interact with cations, anions, neutral species and their various combinations.

Figure 8. Structure of a calix[4]arene.



We will try to focus on the Schiff's base and crown ethers as supramolecular sensing material due to their widespread applications.

6.1. Structure of Schiff's bases

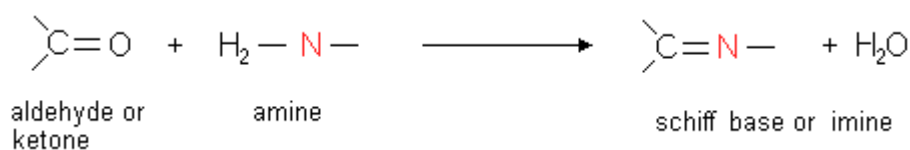
Schiff's bases (also called azomethines or imines) are named after Hugo Schiff. These compounds are functional groups with the general formula $R_1R_2C=N-R_3$. They contain carbon-nitrogen double bonds in which nitrogen atoms are connected to an aryl or alkyl group. The role of the R_3 group is to stabilize the iminic Schiff's base

These compounds are synthesized from an aromatic amine and a carbonyl compound (e.g. aldehydes, ketones, Scheme 1) through a nucleophilic addition, which leads to the formation of a

hemi-aminal, and the consequent dehydration to generate an imine. The reaction of 4,4'-diaminodiphenyl ether with *o*-vanillin can be regarded a typical reaction [75].

Application of aldehydes will lead to the formation of imines of $R_1HC=N-R_2$ type. This is while the result of the same reaction with ketones are $R_1R_2C=N-R_3$ type amines (it should be noted that the reaction of ketones occurs more slowly than that of aldehydes. The overall mechanism of forming Schiff's bases is according to the multi-step reaction below:

Scheme 1. Schiff's base formation from aldehyde or ketone.



An imine (Schiff base), such as that formed from *o*-vanillin, forms complexes with metal ions via N and O donor atoms. The steric and electronic effects around the metal core can be finely tuned through the appropriate selection of electron withdrawing or electron donating substituents in the Schiff's bases. These N and O atoms induce two opposite electronic effects: the phenolate oxygen is regarded a hard donor, which stabilizes the higher oxidation states while the imine nitrogen is a softer donor and will hence stabilize the lower oxidation states of the metal ion [76].

6.2. Application of Schiff's bases and their complexes

Schiff's bases are considered "privileged ligands" which are active and well-designed. These ligands have been extensively studied in coordination chemistry, and are found to be stable under a variety of oxidative and reductive conditions [77]. Schiff's bases are actually able to stabilize many different metals in various oxidation states, controlling the performance of metals in a large variety of useful catalytic transformations [78,79].

Transition metal complexes of these compounds have been used in the catalysis of diverse processes, such as oxygen and atom transfer, enantioselective epoxidation and aziridination, mediating organic redox reactions and as mediators in other oxidation processes. However, very little is known about their complex formation equilibria in the solution [80] and also about the use of salens and their complexes as carriers in the ion-selective electrodes [81].

Schiff's bases have the potentials to be used in different areas such as electrochemistry, bioinorganic, catalysis, metallic deactivators, separation processes and environmental chemistry [79] and they are becoming increasingly important in the pharmaceutical, dye and plastic industries as well as in the field of liquid-crystal technology [76].

6.3. Different types of Schiff's bases:

There are about 135 articles on the potentiometric membranes based on Schiff's bases and their metal complexes as sensing materials. This family can be divided to the two groups of symmetric and

asymmetric Schiff's base. Salens and salophen can be symmetric or asymmetric but hydrazones are the members of the asymmetric Schiff's bases.

6.3.1. Schiff's bases and their complexes

Many potentiometric sensors use symmetric Schiff's bases as the ion recognition element. Symmetric Schiff's bases can act as tetra or hexa dentate ligands and can form a strong and weak complex with metal ions. As mentioned earlier the nature and number of the N, O, S donor atoms and the semicavity size of the ligand are important in the formation of the stable selective complexes. Schiff's base complexes have also proved to be good ion carriers for the anion selective sensors. Table 1 gives a summary of a number of reported membrane sensors based on symmetric and asymmetric Schiff's bases and their complexes.

Table 1. A number of reported potentiometric membrane sensors based on Schiff's bases and their complexes.

Cation	Ionophore	Slope (mV decade ⁻¹)	Linear Range (M)	Most Important Interfering ions (log K _{sel} > -2)	Ref.
Al ³⁺ -1	bis(5-phenyl azo salicylaldehyde)-2,3-naphthalene diimine (5PHAZOSALNPHN)	19.3	5.0 × 10 ⁻⁶ -1.0 × 10 ⁻²	Li ⁺ , NH ₄ ⁺ , Ag ⁺	82
Sn ²⁺ -1	6-(4-nitrophenyl)-2,4-diphenyl-3,5-diazabicyclo-[3.1.0]-hex-2-ene (NDDBH)	28.8 ± 1.1	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻¹	Tl ⁺ , Mn ²⁺ , Ba ²⁺ , Cs ⁺	83
Pb ²⁺ -1	bis(acetylacetonate)- <i>p</i> -phenylene-diamine-lead(II) [LPb(NO ₃) ₂]H ₂ O complex ionophore	30.0 ± 0.2	1 × 10 ⁻⁵ -1 × 10 ⁻¹	-	84
Pb ²⁺ -2	<i>N,N'</i> -bis(5-methylsalicylidene)- <i>p</i> -diphenylmethane diamine	29.4	5.0 × 10 ⁻⁶ -0.10	Zn ²⁺ , Fe ³⁺ , K ⁺ , NH ₄ ⁺	85
Pb ²⁺ -3	<i>N,N'</i> -bis(3-methylsalicylidene)- <i>p</i> -phenylmethane diamine	30.3 ± 0.6	2.0 × 10 ⁻⁵ -0.10	Na ⁺ , K ⁺ , NH ₄ ⁺	86
Pb ²⁺ -4	Schiff base as a neutral carrier	29.4 ± 0.5	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻¹	Na ⁺ , K ⁺ , Cu ²⁺	87
Pb ²⁺ -5	<i>N,N'</i> -bis-thiophene-2-yl-methyleneethane-1,2-diamine	29.79	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻¹	-	88
Pb ²⁺ -6	<i>N,N'</i> -bis(salicylidene)-2,6-pyridinediamine	29.4	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	K ⁺ , Ag ⁺	89
Pb ²⁺ -7	<i>N,N'</i> -dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (I)	30.0 ± 0.1	8.2 × 10 ⁻⁶ -1.0 × 10 ⁻¹	Cd ²⁺ , Zn ²⁺ , Ag ⁺	90
Y ³⁺ -1	A new Schiff's base with sulfur and nitrogen donor atoms (2-((<i>E</i>)1,2-diphenyl-2-[(2-2-sulfanylphenyl)imino]ethylidene)amino)-1-benzenethiol	19.2	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻²	Sc ³⁺	91

Table 1. Cont.

La ³⁺ -1	bis(2-mercaptoanil) diacetyl (BMDA)	19.7	10 ⁻⁵ -10 ⁻¹ and 10 ⁻⁶ -10 ⁻¹	Ce ³⁺ , Gd ³⁺	92
La ³⁺ -2	bis(thiophenal)phenylen-1,3-diamine (TPD)	19.6	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻¹	Sm ³⁺ , Ce ³⁺	93
Ce ³⁺ -1	<i>N,N</i> -bis[2-(salicylidene-amino)ethyl]ethane-1,2-diamine	20	1.41 × 10 ⁻⁷ - 1.0 × 10 ⁻²	La ³⁺	94
Gd ³⁺ -1	<i>S-N</i> Schiff s base (2-[{3-[(2-sulfanylphenyl)imino]- 1-methylbutylidene } amino]phenyl hydrosulfide (SMPH)	19.8 ± 0.3	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁵	Tb ³⁺ , Dy ³⁺ , Eu ³⁺	95
Gd ³⁺ -2	bis(thiophenal) pyridine-2,6-diamine (BPD)	19.4 ± 0.4	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	La ³⁺ , Mg ²⁺ , Hg ²⁺	96
Tb ³⁺ -1	<i>N,N</i> -bis(pyrrolidene) benzene-1,2-diamine	19.8	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻¹	La ³⁺ , Yb ³⁺ , Dy ³⁺	97
Dy ³⁺ -1	<i>N,N</i> -bis(pyrrolidene) benzene-1,2-diamine	20.6 ± 0.2	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻¹	Ce ³⁺ , La ³⁺	98
Dy ³⁺ -2	a new asymmetrical Schiff's base [(<i>E</i>)- <i>N</i> -(2-hydroxybenzylidene)-benzohydraide] or BBH	20.1 ± 0.8	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶	Yb ³⁺ , Tm ³⁺ , Na ⁺	99
Ho ³⁺ -1	<i>N</i> -(1-thien-2-yl-methylene)-1,3-benzothiazol-2-amine	19.7	10 ⁻⁵ -10 ⁻²	Lu ³⁺ , Dy ³⁺ , Gd ³⁺	100
Lu ³⁺ -1	a new asymmetrically <i>S-N</i> Schiff's base, <i>N</i> -(thien-2-ylmethylene)-pyridine-2,6-diamine (TPD)	20.5 ± 0.4	1.0 × 10 ⁻² -1.0 × 10 ⁻⁶	Nd ³⁺ , Dy ³⁺ , Gd ³⁺	101
UO ₂ ²⁺ -1	2,2'-[1,2-ethanediy] bis (nitrilo-ethylidene)]bis(1-naphthalene)	28.5 ± 0.8	10 ⁻¹ -10 ⁻⁷	Mg ²⁺ , Cu ²⁺	102
Cr ³⁺ -1	a new tridentate <i>S,N,O</i> Schiff's base 4-hydroxysalicylade-2-mercaptoanil (TSNO)	20.2	3.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	Na ⁺ , La ³⁺ , Pb ²⁺	103
Cr ³⁺ -2	2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene (TTCT)	19.5	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	Ag ⁺	104
Cr ³⁺ -3	2-hydroxybenzaldehyde-O,O'-(1,2-dioxetane-1,2-diyl) oxime	19.6 and 19.2	1.5 × 10 ⁻⁶ – 8.0 × 10 ⁻³ M for PME and 4.0 × 10 ⁻⁷ – 3.0 × 10 ⁻³ M for CGCE	Ce ³⁺ , Cu ²⁺	105
Cr ³⁺ -4	<i>N</i> -(1-thien-2-ylethylidene)-benzene-1,2-diamine (SNS)	19.9 ± 0.3	1.0 × 10 ⁻⁶ - 1.0 × 10 ⁻¹	Fe ³⁺ , Eu ³⁺ , Mg ²⁺	106
Cr ³⁺ -5	Schiff bases, <i>N</i> -(acetoacetanilide)-1,2-diaminoethane (L-1) and <i>N,N'</i> -bis (acetoacetanilide)-triethylene-tetrammine (L-2)	19.8	8.9 × 10 ⁻⁸ -1.0 × 10 ⁻¹	-	107
Mn ²⁺ -1	<i>N,N',N'',N'''</i> -1,5,8,12-tetraza-dodecane-bis(salicylaldiminato) (H ₂ L)	30	5.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	Cd ²⁺ , Fe ³⁺ , Ni ²⁺	108

Table 1. Cont.

Fe ³⁺ -1	2-[(2-hydroxy-1-propenyl-buta-1,3-dienylimino)-methyl]-4- <i>p</i> -tolylazo-phen ol [HPDTP]	28.5± 0.5	3.5× 10 ⁻⁶ -4.0 × 10 ⁻²	Fe ²⁺ , Cr ³⁺	109
Co ²⁺ -1	5-((4-nitrophenyl)azo)- <i>N</i> -(2',4'-dimethoxyphenyl)salicylaldimine	29	9.0×10 ⁻⁷ -1.0×10 ⁻²	K ⁺ , Ag ⁺	110
Ni ²⁺ -1	thiophene-derivative Schiff base	29.5± 1.0	5.0×10 ⁻⁶ -1.0×10 ⁻¹	-	111
Ni ²⁺ -2	<i>N,N'</i> -bis-(4-dimethylamino-benzylidene)-benzene-1,2-diamine	30	1.0× 10 ⁻² -2.0× 10 ⁻⁷	Tl ⁺ , Ag ⁺	112
Ni ²⁺ -3	Schiff bases, <i>N</i> -(2-hydroxy-benzyl)- <i>N'</i> -(2-hydroxy-benzylidene)-ethylenediamine and <i>N</i> -(2-hydroxybenzylidene)-Al'-(2-picoly)ethylenediatmine (II)	30 and 29	6.3×10 ⁻⁶ to 5.0 × 10 ⁻¹ and 3.2×10 ⁻⁶ to 5.0 × 10 ⁻¹	Ag ⁺ , Co ²⁺ , Hg ²⁺	113
Ni ²⁺ -4	<i>N',N''</i> -bis((naphthalen-1-ymethylene)ethane-1,2-diamine	29.9	1.0 × 10 ⁻¹ -5.0 × 10 ⁻⁶	Na ⁺ , K ⁺ , Ba ²⁺ , Co ²⁺ , Ag ⁺ , Zn ²⁺	114
Cu ² , Ni ²⁺ -1	two Schiff base ligands: <i>N</i> -[2-thienylmethylidene]-2-propanolamine (TNAIP) and <i>N</i> -[2-thienylmethylidene]amino-propane (TNAP)	29	1.0×10 ⁻⁶ -1.0×10 ⁻²	Cd ²⁺ , Fe ³⁺	115
Cu ² , Ni ²⁺ -2	Electrodes 1 and 2 are based on mixed complexes of Cu(II) and Ni(II) with <i>N</i> -[2-thienyl-methylidene]-2-aminopyridine as ligand and electrodes 3 and 4 are based on the mixed complexes with <i>N,N'</i> -[2,2'-bis-thienyl-methylidene]tolylene	29	1.0×10 ⁻⁵ -1.0×10 ⁻²	Co ²⁺ , Fe ³⁺	116
Cu ² , Ni ²⁺ -3	<i>N</i> -[2-thienylmethilidene]-2-aminoethanol (TNAHE)	29 and 29	10 ⁻⁶ -10 ⁻¹ and 10 ⁻⁵ -10 ⁻¹	-	117
Cu ²⁺ -1	naphthol-derivative Schiff's base	29± 1	5.0×10 ⁻⁶ -5.0×10 ⁻²	Na ⁺ , Hg ²⁺ , Ni ²⁺	118
Cu ²⁺ -2	bis-2-thiophenal propanediamine (TPDA)	29.1	1.0×10 ⁻¹ - 6.0×10 ⁻⁸	Ag ⁺	119
Cu ²⁺ -3	new thiophene-derivative Schiffs base	29.3± 0.7	6.0×10 ⁻⁸ - 1.0×10 ⁻¹	Zn ²⁺ , Hg ²⁺	120
Cu ²⁺ -4	diphenylisocyanate bis(acetyl-acetone) ethylenedinnine (DIBAE)	29.8	1.0×10 ⁻¹ -1.0 × 10 ⁻⁶	-	121
Cu ²⁺ -5	2,2'-[4,4'diphenyl-methanebis-(nitrilomethylidyne)]-bisphenol	29	8.0× 10 ⁻⁶ -1.0× 10 ⁻¹	Hg ²⁺	122
Cu ²⁺ -6	2,2-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] <i>m</i> -cresol-(I), 2,2-[1,2-ethandiyl-bis(nitrilomethylidene)-bis] <i>p</i> -cresol(II) and 2,2'-[1,2-ethandiyl-bis(nitritomethylidene)-bis]ortho cresole(III)	29.2± 0.3, 29.7 ± 0.3 and 28.2 ± 0.3	1.0×10 ⁻⁵ -1.0 × 10 ⁻¹	Ni ²⁺ , Co ²⁺ , Pb ²⁺	123

Table 1. Cont.

Cu ²⁺ -7	<i>N,N'</i> -bis-pyridin-2-ylmethylene-naphthalene-1,8-diamine	29.6	10 ⁻⁶ - 10 ⁻²	Cu ²⁺	124
Cu ²⁺ -8	Bis(2-hydroxyacetophenone)-butane-2,3-dihydrazone (BHAB)	29.6	5.0×10 ⁻⁸ -1.0×10 ⁻²	-	125
Cu ²⁺ -9	Copper (II) complex of 2,4-dimethyl-1,5,9,12-tetraaza-cyclopentadeca-1,4-diene	29.9	1.1×10 ⁻⁶ -1.0×10 ⁻¹	Co ²⁺ , Mn ²⁺ , Ni ²⁺	126
Cu ²⁺ -10	2-(1'-(4'-(1"-hydroxy-2"-naphthyl)-methyleneamino)butyl imino-methyl)-1-naphthol (BHNB) as a novel Schiff base	29	10 ⁻⁶ -10 ⁻¹	Tl ⁺	127
Cu ²⁺ -11	Schiff Base complexes, derived from 2,3-diaminopyridine and omicron-vanilin	29.6	5.0×10 ⁻⁶ to 1.0×10 ⁻¹	Hg ²⁺ , Ag ⁺	128
Cu ²⁺ -12 (micro)	a symmetrical hexadentate Schiffs base 2-{1-(<i>E</i>)-2-((<i>Z</i>)-2-[(<i>E</i>)-2-[(<i>Z</i>)-1-(2-hydroxyphenyl)ethylidene]hydrazono)-1-methylpropylidene)-hydrazono]ethyl)phenol (HDNOS)	25.9 ± 0.3	1.0×10 ⁻¹¹ -1.0×10 ⁻⁵	Ni ²⁺ , Pb ²⁺ , Cd ²⁺	129
Cu ²⁺ -13	copper(II) salicylaniline Schiffs base	30	10 ⁻⁶ -10 ⁻²	Li ⁺ ,Na ⁺ ,Cs ⁺ ,k ⁺	130
Cu ²⁺ -14	naphthol-derivative Schiff's base	29.5	5.0×10 ⁻⁶ -5.0×10 ⁻²	Hg ²⁺ ,Ni ²⁺ ,Na ⁺	131
Zn ²⁺ -1	<i>N,N'</i> -bis(acetylacetone)ethylene-diimine	30.0	1.0× 10 ⁻⁶ -1.0×10 ⁻¹	Cu ²⁺ , Al ³⁺ , Cd ²⁺	132
Ag ⁺ -1	Schiff base- <i>p-tert</i> -butyl-calix[4]arene	59.7	1.0×10 ⁻⁵ -.0×10 ⁻¹	Hg ²⁺	133
Ag ⁺ -2	a dioxime-type Schiff base, <i>N,N'</i> -bis(2'-hydroxyimino-1'-phenyl-propylidene)-1,3-propanediamine, PHO3, derived from α -isonitroso-propiofenone and 1,3-diamino-propane	59	10 ^{-6.3} -10 ^{-1.1}	Hg ²⁺	134
Ag ⁺ -3	Schiff base <i>p-tert</i> -butyl calix-[4]arene derivatives containing <i>N</i> and <i>O</i> as binding sites	59	1.0×10 ⁻⁵ -.0×10 ⁻¹	Hg ²⁺	135
Ag ⁺ -4	calix[4]arene compound of 5,11,17,23-tetra- <i>tert</i> -butyl-25,27-dihydroxy-calix[4]arene-thia-crown-4	53.8 ± 1.6	1.0×10 ⁻⁶ -1.0×10 ⁻²	Hg ²⁺	136
Ag ⁺ -5	calix[4] arene derivative	58.9	1.0×10 ⁻⁵ -1.0× 10 ⁻¹	K ⁺ , NH ₄ ⁺ , Na ⁺	137
Ag ⁺ -6	[bis 5-(4-nitrophenyl azo)salisylaldimine] 1,8-diamino, 3,6-dioxooctane (BNSAO)	56.2 and 58.4	1.9 × 10 ⁻⁶ – 2.7 × 10 ⁻² and 9.0 × 10 ⁻⁷ – 3.1 × 10 ⁻²	K ⁺ , NH ₄ ⁺	138

Table 1. Cont.

Ag ⁺ -7	5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-calix[4]arene-thia-crown-4	53.8 ± 1.6	1.0×10 ⁻⁶ -1.0×10 ⁻²	Hg ²⁺	139
Ag ⁺ -8	7,8: 16,17-dibenzo- 6,9,15,18-tetraoxo- 1,5,10,14-tetrathia-cyclooctadeca-7,16- diene [Bz(2)Oxo(4)(18) dieneS(4)]	58.4	1.26×10 ⁻⁶ -1.0×10 ⁻¹	Tl ⁺ , Hg ²⁺ , Pb ²⁺	140
Cd ²⁺ -1	5-[[[(4-Methyl phenyl) azo)-N-(6-amino-2-pyridin) salicylaldimine] (S-1), and 5-[[[(4-methyl phenyl) azo)-N-(2-diamino-2-cyano-1-ethyl cyanide) salicylaldehyde] (S-2)]	28 and 22	1.5×10 ⁻¹ -7.5×10 ⁻⁷ and 2.0×10 ⁻¹ -4.0×10 ⁻⁷	Pb ²⁺ , Ni ²⁺	141
Cd ²⁺ -2	N,N'-[bis(pyridm-2-yl)-formylidene] butane- 1,4-diamine (SI) and N-(2-pyridinyl-methylene)-1,2-benzenediamine (S-2)	29.5	7.9 × 10 ⁻⁸ -1.0 × 10 ⁻¹	Cu ²⁺ NH ⁴⁺ Cr ³⁺	142
Hg ²⁺ ,Cu ²⁺ -1	Tetraethylthiuram disulfide was chosen as a chemical modifier	79.4 and 43.1	10 ⁻⁷ -10 ⁻³ and 10 ^{-7.18} - 10 ^{-3.67}	Mg ²⁺ , Al ³⁺	143
Hg ²⁺ -1	sulfur Schiff's base 1-(2-hydroxy-1,2-diphenylethylidene)thio-semicarbazide (HDPET)	29	1.0×10 ⁻⁶ -2.0×10 ⁻²	Ag ⁺	144
Hg ²⁺ -2	bis[5-((4-nitrophenyl)azo salicylaldehyde)] (BNAS)	30	5.0 × 10 ⁻² -7.0× 10 ⁻⁷	-	145
Hg ²⁺ -3	ethylenediamine bithiophene-carboxaldehyde (EDBT)	30.0 ± 0.4	10 ⁻⁷ -10 ⁻²	Ag ⁺	146
Hg ²⁺ -4	Ethyl-2-(benzoylamino)-3-(2-hydroxy-4-methoxyphenyl)-2-propenoate (EBHMP)	48.5 ± 1.0	3.0 × 10 ⁻⁷ -3.1× 10 ⁻²	Cu ²⁺ ,Cd ²⁺ , Pb ²⁺	147
Hg ²⁺ -5	bis(2-hydroxybenzophenone) butane-2,3-dihydrazone (HBBD)	29.7	1.0 × 10 ⁻⁶ -1.0× 10 ⁻¹	Fe ³⁺ ,Cd ²⁺ , La ³⁺	148
SCN ⁻ -1	tricoordinate Schiff base copper(II) complex	-57.6	2.6×10 ⁻⁶ -1.0×10 ⁻¹	-	149
SCN ⁻ -2	two zinc(II) ions and two molecules of the bis-N,O-bidentate Schiff base 2,2'-[methylenebis(4,1-phenylenenitrilomethylidyne)]bis-phenol	-57.5	10 ^{-3.5} - 10 ⁻²	N ³⁻ , NO ₂ ⁻	150
SCN ⁻ -3	cadmium-Schiff's base complex	-57	1.0×10 ⁻⁵ - 1.0×10 ⁻¹	-	151
SCN ⁻ -4	(N,N'-bis-salicylidene-1,2-ethylenediamine)	-59.1	10 ⁻⁶ -10 ⁻¹	MnO ₄ ⁻ , I ⁻	152
SCN ⁻ -5	2,2-[(1,3-dimethyl-1,3-propanediylidene)dinitrilo]bis-benzenethiolato cadmium(II)	-58.9	10 ⁻⁶ -10 ⁻¹	MnO ₄ ⁻ , ClO ₄ ⁻ , Br ⁻	153

SCN ⁻ -6	butane-2,3-dione bis(salicylhydrazonato) zinc(II)	-56.5	10 ⁻⁶ -10 ⁻¹	ClO ₄ ⁻	154
SO ₄ ²⁻ -1	Schiff base complex of Zn(II)	-29.7 and - 29.3	5.0×10 ⁻⁵ -10 ⁻¹	SCN ⁻ , ClO ₄ ⁻	155
SO ₄ ²⁻ -2	strontium Schiff's base complex (SS)	-29.2	10 ⁻² -10 ⁻⁶	SO ₃ ²⁻ , CO ₃ ²⁻ , Cl ⁻	156
SO ₄ ²⁻ -3	zinc-Schiff base	-29.2	10 ⁻² -10 ⁻⁶	-	157
SO ₄ ²⁻ -4	<i>N,N'</i> -ethylenebis(5-hydroxy- salicylideneiminato) chromium(III) Chloride	-28.9	1.5 × 10 ⁻⁶ -4.8 × 10 ⁻²	I ⁻ , HPO ₄ ⁻	158
F ⁻ -1	Gallium(III)-Schiff base	-61.1	1.0×10 ⁻⁵ -1.0×10 ⁻¹	SCN ⁻	159
Cl ⁻ -1	ruthenium(III) Schiff's base	-54.5	1.0×10 ⁻¹ -3.0×10 ⁻⁶	-	160
Cl ⁻ -2	Schiff base complex of cobalt(II)	-59	2.5×10 ⁻⁵ -0.5×10 ⁻¹	Br ⁻	161
I ⁻ -1	Schiff base complex of Fe(III)	-71.0	1.0×10 ⁻⁶ -5.0 × 10 ⁻¹	SCN ⁻ , F ⁻ , NO ₂ ⁻	162
I ⁻ -2	[5,10,15,20-tetrakis(4- <i>N,N</i> - dimethylaminobenzene)por- phyrinato]Mn(III) acetate	-59.4	1.0 × 10 ⁻² -7.5 × 10 ⁻⁶	Salicylate, SCN ⁻ , ClO ₄ ⁻	163
I ₃ ⁻ -1	bis (salicylaldehyde) ethylene- diamine mercury(II) complex MS)	-59.0	5.0 × 10 ⁻⁸ -10 × 10 ⁻²	-	164
I ₃ ⁻ -2	<i>N,N'</i> -1,2-propylene-bis-(5-methyl salicylidene iminato) copper(H)	-61.4	4.0 × 10 ⁻⁵ -0.7 × 10 ⁻¹	I ⁻ , SCN ⁻ , ClO ₄ ⁻	165
I ₃ ⁻ -3	a Charge-Transfer Complex of (1,3-diphenyldihydro-1H- Imidazole-4,5-dione dioxide with Iodide	-59.3	10 ⁻⁷ -10 ⁻¹	-	166
I ₃ ⁻ -4	2-(((2(((<i>E</i>)-1-(2-hydroxyphenyl) methylidene)amino)phenyl) imino) methyl)phenol with iodine (CTC)	-59	5.0 × 10 ⁻⁸ -1.0 × 10 ⁻²	-	167
I ₃ ⁻ -5	Schiff base 2,2'[4,4'-diphenyl- methane bis (nitromethylidyne)] bisphenol, L, with copper (II) and schiff base 2,2'[4,4'-diphenyl- methane bis (nitromethylidyne)] bisphenol, L, with iron (III)	-60	6.0×10 ⁻⁶ - 8.0×10 ⁻¹ and 5.0×10 ⁻⁵ -1.0×10 ⁻¹	SCN ⁻ , Salicylate	168
I ₃ ⁻ -6	bis- <i>N,O</i> -bidentate Schiff base	-61.4	4.0×10 ⁻⁵ - 0.7×10 ⁻¹	I ⁻	169
Salicylate	Schiff base complexes of Co(III)	-57.2	1.6 × 10 ⁻⁶ -1.0 × 10 ⁻¹	SCN ⁻	170
Salicylate	the complex <i>N,N'</i> -1,4-butylene bis(3-methyl salicylidene iminato) copper(II)	-59.1	1.0 × 10 ⁻⁶ -1	-	171
Cysteine	<i>N,N'</i> -bis(salicylidene)-1,2- phenylenediaminocobalt(II)	-59	2.0 × 10 ⁻⁶ -1.0 × 10 ⁻²	-	172

Structures of some of the above ionophores are depicted in Figures 9 –15.

Figure 9. Structure of bis(5-phenyl azo salicylaldehyde) 2,3-naphthalene diimine (5PHAZOSALNPHN) (Al^{3+} -1).

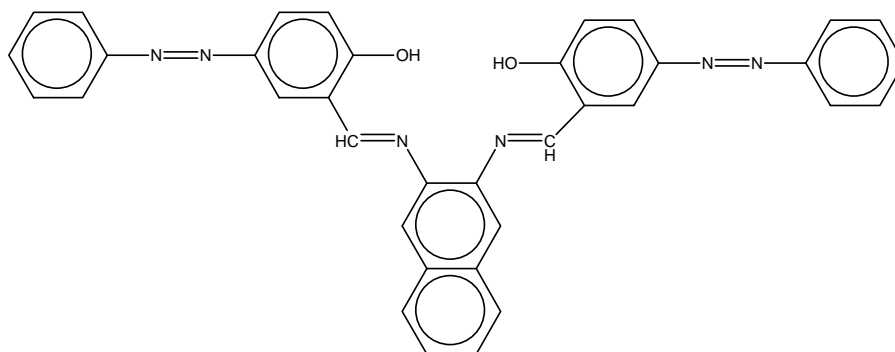


Figure 10. Structures of two suitable ionophores used in construction of the Pb^{2+} selective membrane sensors.

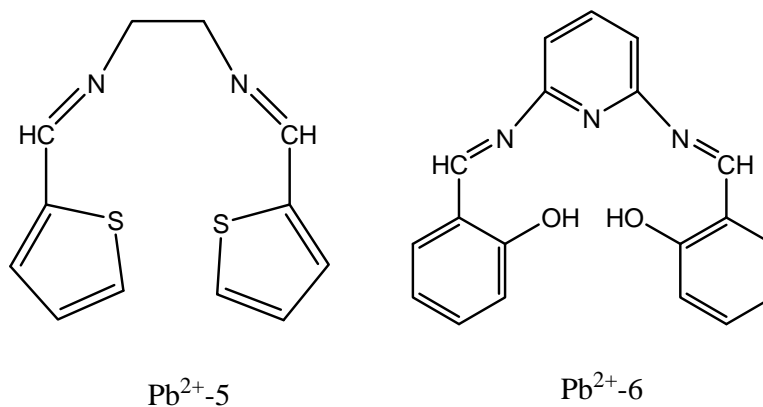


Figure 11. Structures of some ionophores used in construction of the lanthanide selective membrane sensors.

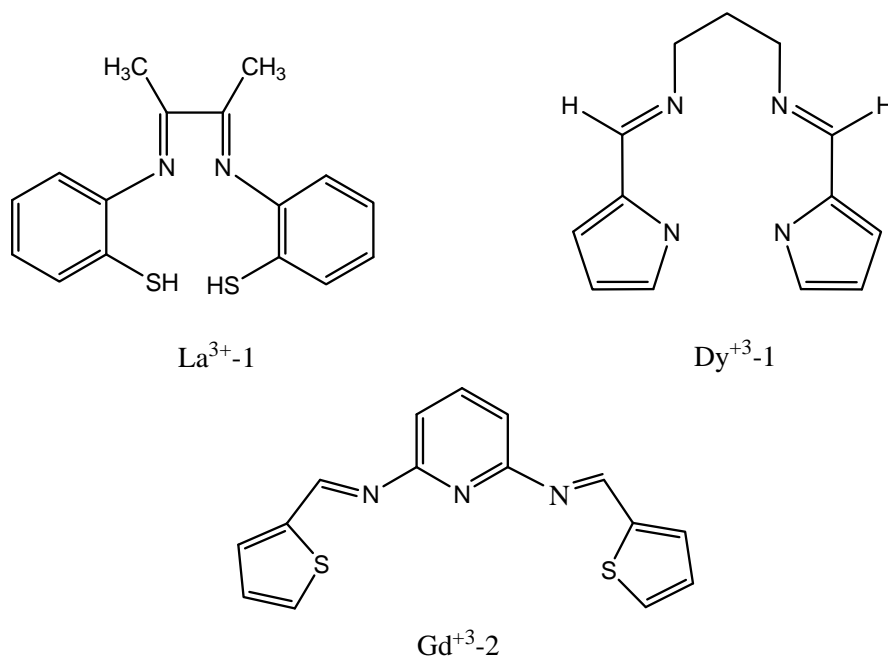


Figure 12. Structures of two suitable ionophores used in construction of the Cr^{3+} selective membrane sensors.

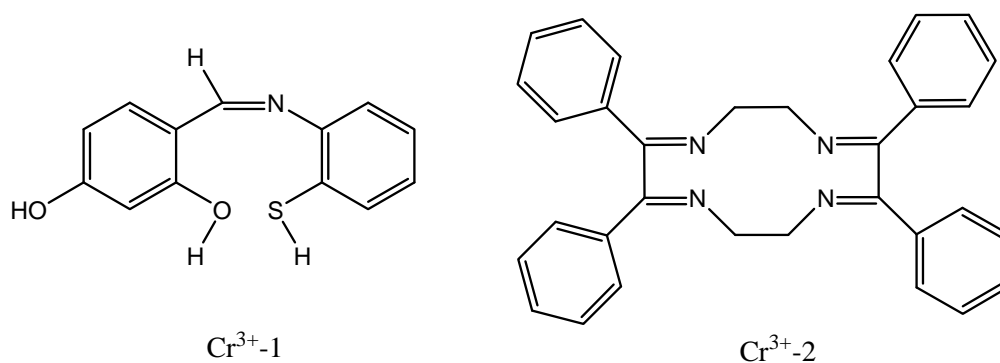


Figure 13. Structures of some symmetric Schiff's base ionophores used in construction of the Cu^{2+} selective membrane sensors.

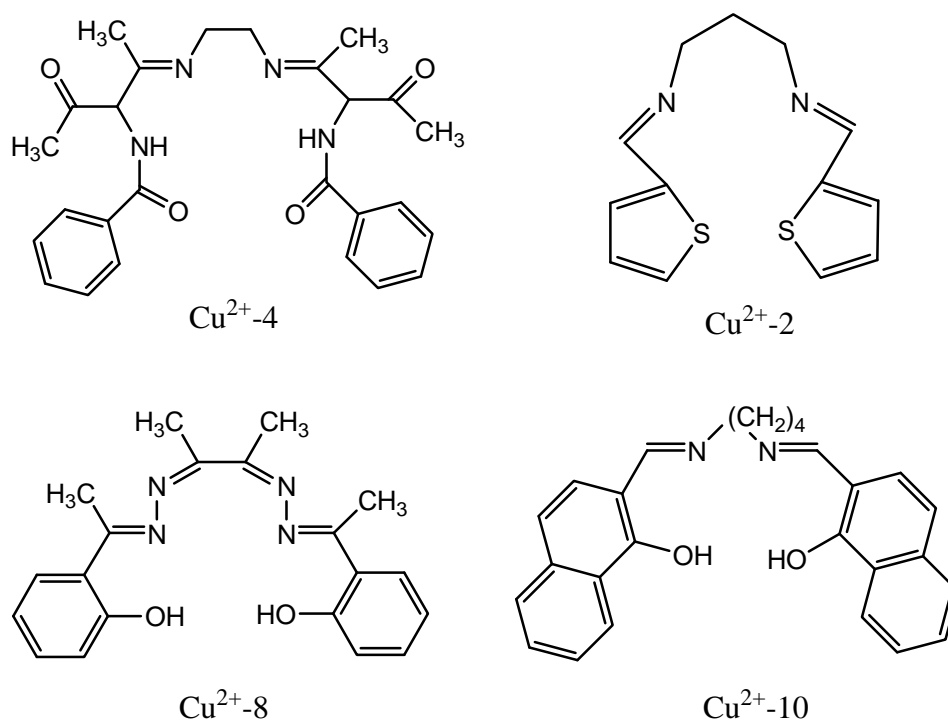


Figure 14. Structures of ionophores used in construction of the Ag^+ , Cd^{2+} and Hg^{2+} selective membrane sensors.

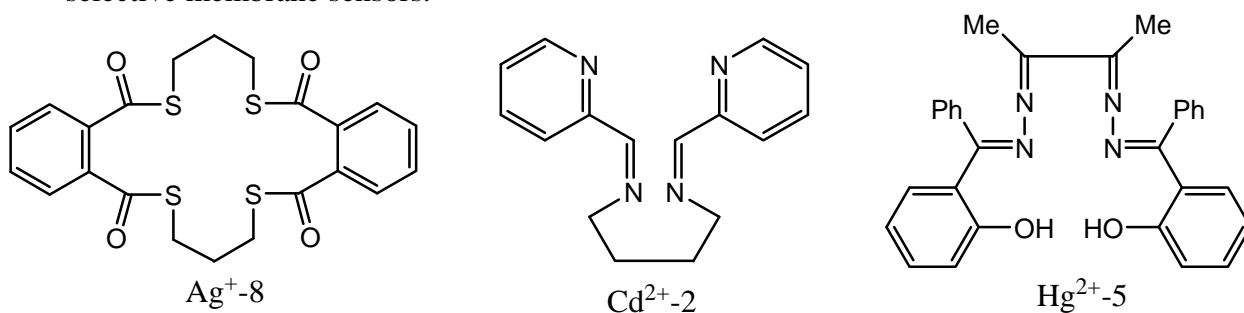
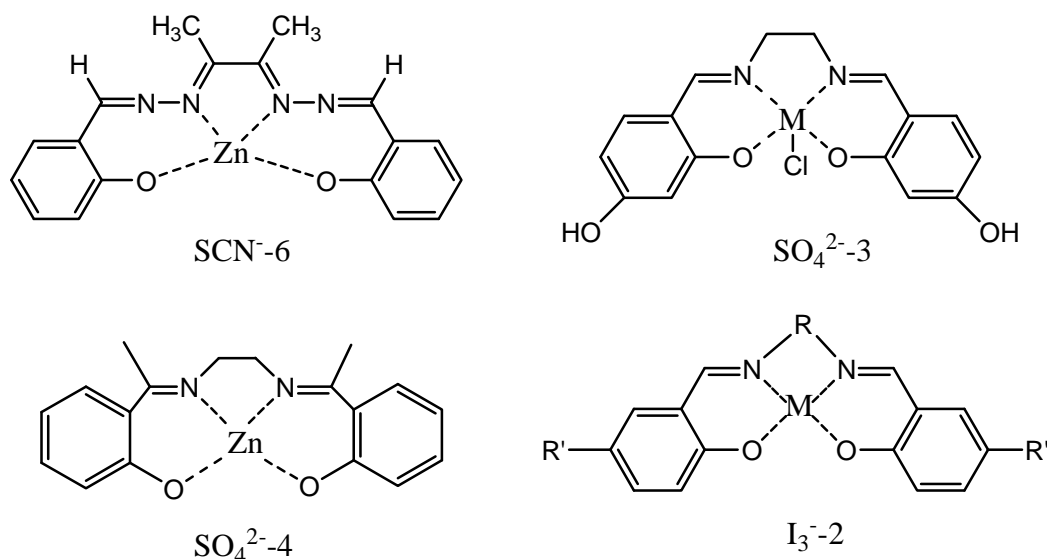


Figure 15. Structures of some suitable Schiff's base complexes used in construction of some anion selective membrane sensors.



6.3.2. Salens

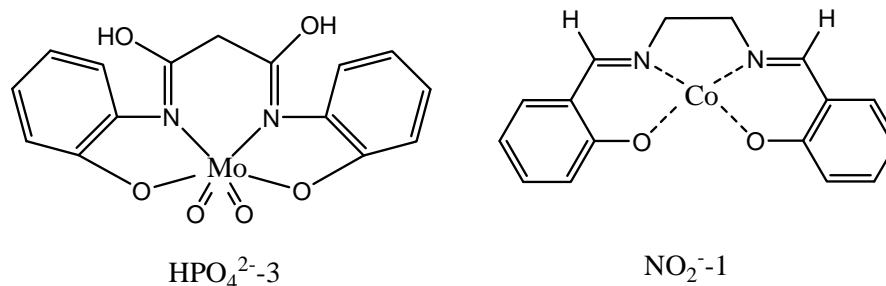
The term "salen" is the abbreviation of the name of a popular chelating ligand used in coordination chemistry and homogeneous catalysis, i. e. salicylic aldehyde and ethylenediamine.

SalenH₂ forms complexes with most transition metals, where in most cases the metal takes a square pyramidal or octahedral coordination, M(salen)L and M(salen)L₂. Examples include VO(salen) and Co(salen)Cl(pyridine).

Numerous salen-derivatives are known, e.g. the ligand abbreviated "Salph" is derived from the condensation of 1,2-phenylenediamine and salicylaldehyde [173]. Table 2 shows a number of reported membrane sensors based on salens and their complexes. Chemical structures of some salens are shown in Fig. 16.

Table 2. A number of reported potentiometric membrane sensors based on salen.

Cation	Ionophore	Slope (mV decade ⁻¹)	Linear Range (M)	Most Important Interfering ions (log K _{sel} > -2)	Ref.
NO ₂ ⁻ -1	Co(II)-Salen	-58.2	10 ⁻⁶ -10 ⁻¹	-	174
HPO ₄ ²⁻ -1	Vanadyl salen	-28.8	1.0×10 ⁻¹ -5.0×10 ⁻⁶	-	175
HPO ₄ ²⁻ -2	oxo-molybdenum methyl-salen	-28.6	1.0×10 ⁻¹ - 4.0×10 ⁻⁷	-	176
HPO ₄ ²⁻ -3	oxo-molybdenum methyl-salen (MS)	-28.6	1.0×10 ⁻¹ -4.0×10 ⁻⁷	-	177
Br ⁻ -1	iron(III)-salen (IS)	-59.0	7.0×10 ⁻⁶ -1.0×10 ⁻¹	SCN ⁻ , I ⁻ , Cl ⁻	178
I ⁻ -1	salen-Mn(II)	-59.0	1.0×10 ⁻⁵ -3.4 ×10 ⁻¹	CN ⁻	179
I ⁻ -2	Cerium-salen	-57.5	5.0×10 ⁻² -8.0×10 ⁻⁶	SCN ⁻	180
I ₃ ⁻ -1	Mercury-salen	-59.0±0.5	5.0×10 ⁻⁸ -1.0×10 ⁻²	-	181

Figure 16. Structures of two salens used in construction of some anion selective membrane sensors.

6.3.3. Salophen

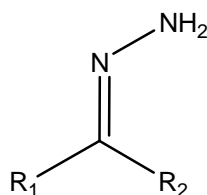
Salophen or acetylparamidophenyl salicylate is a Schiff's base with non-toxic properties, which is an effective substitute for salicylic acid. Table 3 shows a number of reported membrane sensors based on salophens and their complexes.

Table 3. A number of reported potentiometric membrane sensors based on salophen.

Cation	Ionophore	Slope (mV decade ⁻¹)	Linear Range (M)	Most Important Interfering ions (log $K_{\text{set}} > -2$)	Ref.
$\text{Al}^{+3} - 1$	NM-bis(salicylidene)-1,2-phenylenediamine (salophen)	20.1	$8.0 \times 10^{-7} - 3.0 \times 10^{-2}$	Cu^{2+} , Cr^{3+}	182
$\text{NO}_2^- - 1$	Co(II)-salophen	-59.8	$10^{-6} - 10^{-1}$	-	183
$\text{NO}_2^- - 2$	Uranyl salophen	56.2	$10^{-3} - 10^{-1}$	-	184
$\text{H}_2\text{PO}_4^- - 1$	Uranyl salophenes	-59	$10^{-4} - 10^{-1}$	-	185
$\text{HPO}_4^{2-} - 2$	vanadyl salophen	-24.3	$10^{-1} - 10^{-6}$	-	186
$\text{F}^- - 1$	uranyl salophen derivatives	-56	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	-	187
$\text{I}^- - 1$	cobalt-salophen	- 58.9	$5.0 \times 10^{-7} - 1.0 \times 10^{-1}$	-	188

6.3.4. Hydrazones

Hydrazones are a class of organic compounds with the general structure of $\text{R}_2\text{C}=\text{NNR}_2$ (Figure 17) which are related to ketones and aldehydes by the replacement of the oxygen with the NNR_2 functional group. These compounds are commonly formed through the reaction of hydrazine on ketones or aldehydes. Table 4 shows a number of reported membrane sensors based on hydrazone derivatives.

Figure 17. The basic structure of a hydrazone.**Table 4.** A number of reported potentiometric membrane sensors based on hydrazone derivatives.

Cation	Ionophore	Slope (mV decade ⁻¹)	Linear Range (M)	Most Interfering ions (log K _{sel} > -2)	Important ions	Ref.
La ³⁺ -1	<i>N,N'</i> -adipylbis(5-phenyl-azosalicylaldehyde hydrazone)	19.4	10 ⁻⁶ -10 ⁻²	Yb ³⁺		189
La ³⁺ -2	Bis(2-methylbenzaldehyde)-butane-2,3-dihydrazone (TDSB)	19.8	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻¹	Cu ²⁺ , Ce ³⁺ , Pr ³⁺		190
La ³⁺ -3	<i>N</i> -[hexahydrocyclopentapyrol-2((1H)yl)amino]-carbonyl]-4-methylbenzene sulfonamide	20.1	10 ⁻⁶ -10 ⁻¹	Sm ³⁺ , Ce ³⁺		191
La ³⁺ -4	3-hydroxy- <i>N'</i> -(pyridin-2-ylmethylene)-2-naphthohydrazide (HPMN)	19.2	10 ⁻⁷ -10 ⁻²	Yb ³⁺ , Ce ³⁺		192
La ³⁺ -5	8-amino- <i>N</i> -(2-hydroxybenzylidene)naphthylamine (AIP)	20.3 ± 0.3	1.0 × 10 ⁻⁷ -1.0 × 10 ⁻¹	Pr ³⁺		193
La ³⁺ -6	<i>N'</i> -(1-pyridin-2-ylmethylene)-2-furohydrazide (NPYFH)	19.2 ± 0.6	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	Sm ³⁺ , Nd ³⁺		194
Pr ³⁺ -1	<i>N</i> -(pyridin-2-ylmethylene)benzohydrazide	21.1	10 ⁻² -10 ⁻⁶	Sm ³⁺ , Er ³⁺		195
Nd ³⁺ -1	<i>N</i> -(2-furylmethylene)pyridine-2,6-diamine	19.6	10 ⁻⁵ -10 ⁻²	La ³⁺ , Gd ³⁺ , Sm ³⁺		196
Nd ³⁺ -2	2-[(6-aminopyridin-2-yl)imino]methyl}phenol	19.6	10 ⁻⁵ -10 ⁻²	La ³⁺ , Sm ³⁺		197
Sm ³⁺ -1	3-[[2-oxo-1(2 <i>H</i>)-acenaphthylenyliden]amino]-2-thioxo-1,3-thiazolidin-4-one	19.3	10 ⁻⁶ -10 ⁻¹	-		198
Eu ³⁺ -1	bis(thiophenol)butane2,3-dihydrazone	19.8	1.0 × 10 ⁻⁵ -1.0 × 10 ⁻²	La ³⁺ , Gd ³⁺ , Sm ³⁺		199
Er ³⁺ -1	Pyridine-2-carbaldehyde-2-(4-methyl-1,3-benzothiazol-2-yl)hydrazone	21.8	10 ⁻⁵ -10 ⁻²	Sm ³⁺ , Tm ³⁺ , Gd ³⁺		200

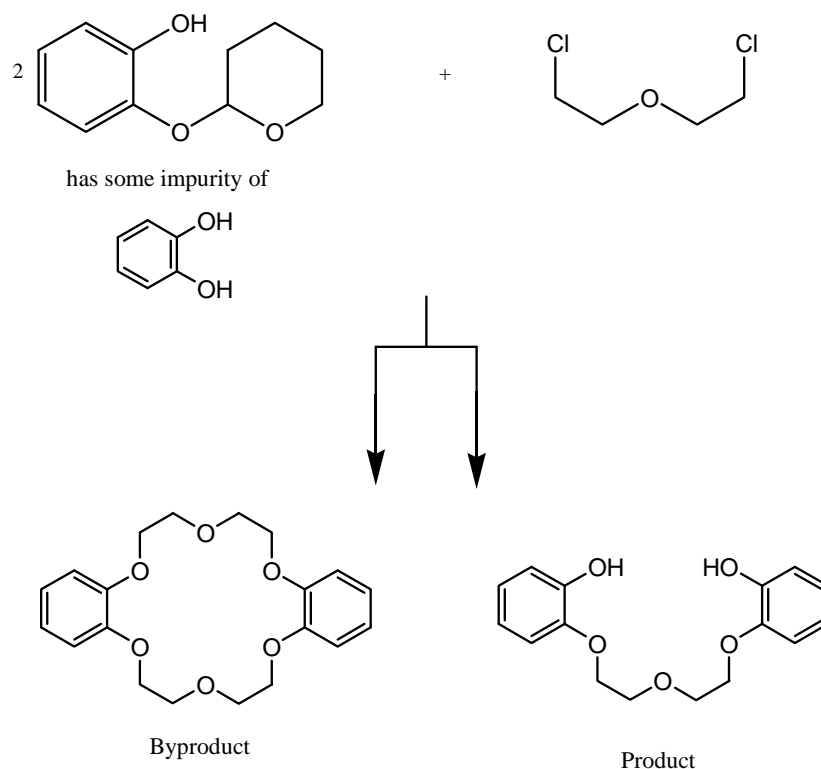
Table 4. Cont.

Er ⁺³ -2	<i>N'</i> -(2-Hydroxy-1,2-diphenyl-ethylidene) benzohydrazide (HDEBH)	21.0	10 ⁻⁷ -10 ⁻²	Ho ³⁺	201
Er ⁺³ -3	<i>N'</i> -(2-Hydroxy-1,2-diphenyl-ethylidene) benzohydrazide (HDEBH)	17.5 (microelectrode)	1.0×10 ⁻³ -3.0×10 ⁻¹⁰	-	202
Tm ⁺³ -1	thiophene-2-carbaldehyde-(7-methyl-1,3-benzothiazol-2-yl)hydrazone	19.5	10 ⁻⁵ -10 ⁻²	Er ³⁺	203
Yb ⁺³ -1	3-hydroxy- <i>N'</i> [(2-hydroxy-phenyl)methylene]-2-naphthohydrazide	19.2	10 ⁻⁷ -10 ⁻²	Nd ³⁺ , Pb ²⁺ , Gd ³⁺	204
Hg ²⁺ -1	bis(2-hydroxy-benzophenone) butane-2,3-dihydrazone (HBBD)	29.7	1.0 × 10 ⁻⁶ -1.0 × 10 ⁻¹	Fe ³⁺ , Cd ²⁺ , La ³⁺	205
I ₃ ⁻ -1	complex of iodine and bis(2-hydroxyacetophenone)-butane-2,3-dihydrazone."	-58.99 ± 0.3	1.0×10 ⁻² - 5.0×10 ⁻⁷	-	206
I ₃ ⁻ -2	bis(2,4-dimethoxy-benzaldehyde)butane-2,3-dihydrazone with iodine	-60.6	10 ⁻⁷ -10 ⁻²	-	207
I ₃ ⁻ -3	bis(2-hydroxy-acetophenone)butane-2,3-dihydrazone.	-58.99	1.0×10 ⁻² - 5.0×10 ⁻⁷	-	208

7. Crown Ethers as Supramolecular Sensing Materials in Construction of Membrane Sensors.

Crown ethers are macrocyclic compounds containing symmetrically distributed ether linkages in a large ring. The first crown ether, a cyclic hexaether, was accidentally discovered during the synthesis of bisphenols (Scheme 2). This compound was found to increase the dissolution of potassium permanganate in benzene and chloroform [3].

Crown ethers selectively complex metal or ammonium salts, depending on their size, number and type of heteroatom. 12-Crown-4, for example, tends to complex with Li⁺, while 18-crown-6 prefers K⁺. The resulting metal complexes, in which crown ether acts as the host and the metal cation is the guest, fall into the class of host-guest chemistry.

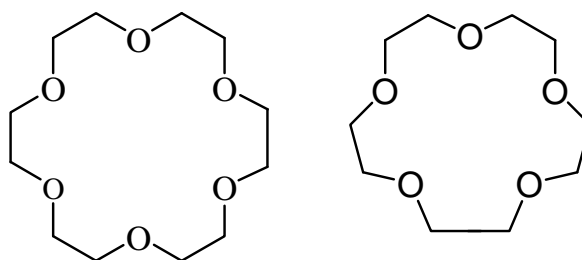
Scheme 2. Synthesis method of the first crown ether.

7.1. Classes of Crown Ethers

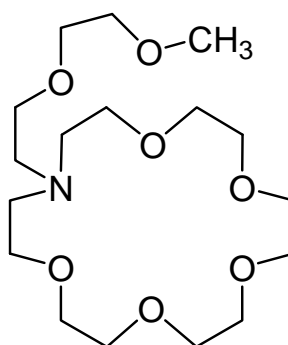
The selectivity of the complexes of crown ethers is based on the size of the substrate and the ring size and distribution of the donor atoms in the crown. It is obvious that crown ethers of larger inner cores tend to bind larger ions. It should be noted that the relative flexibility of the crown rings leads to some degree of structural freedom during complexation. This is undesired with respect to selective binding and hence there have been efforts to improve the crown ether structures (Figure 18). Table 5 summarizes the cavity sizes of some simple crown ethers and cryptands [3].

Table 5. Cavity size of some simple crown ethers and cryptands [209,210].

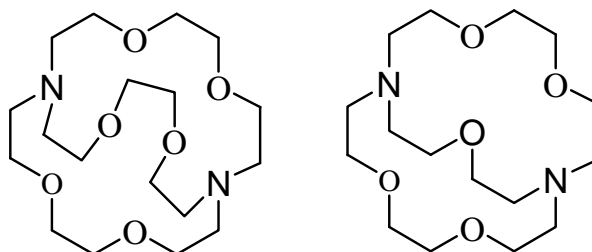
Compound	Size of the Cavity (Å)
15-crown-5	1.7-2.2
18-crown-6	2.6-3.2
21-crown-7	3.4-4.3
Cryptand 111	1.0
Cryptand 211	1.6
Cryptand 221	2.2
Cryptand 222	2.8
Cryptand 322	3.6
Cryptand 332	4.2
Cryptand 333	4.8

Figure 18. Structures of some crown ethers and cryptands.

Crown ether



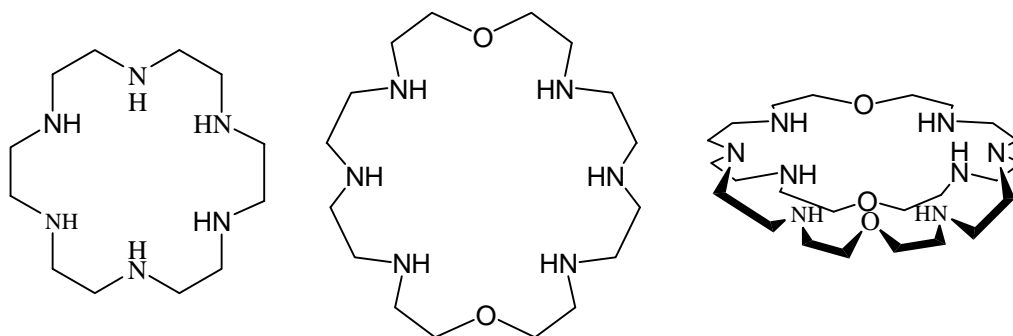
Lariat crown ether



Cryptand

Cryptands have a rigid structure which does not allow the flexible structural changes observed in the case of podands and crown ethers, hence their central cavities are much more constrained, resulting in higher binding selectivities.

The selectivity of the crowns can be increased through a similar mechanism, which is the substitution of podand arms to 2D crown ether, converting them to hosts with a 3D cavity. Because the host structure, in this case, looks like a lariat (a lasso), such hosts are called lariat ethers. The spherands comprise another family incorporating a rigid cycle with a binding site pointing to the cavity inside [3].

Figure 19. Structures of some aza crown ethers and cryptands.

Another class of host compounds is prepared by replacing the O atoms of the crown ethers by nitrogen. This group is called macrocyclic polyamines. Protonated amine hosts are also capable of binding anions (Figure 19). Due to the fact that some of these compounds have elliptic shapes, they can be used for the recognition of linear anions such as the azide anion (N_3^-).

Macrocyclic polyamines, having hydrophobic alkyl chains, can be fixed on an electrode surface to create an anion-sensing device. Macrocyclic polyamines are also known for their tendency to multivalent phosphates.

Another group of these compounds are crown ethers with sulfur atoms, which are called as thia-crowns. These groups together with the macrocyclic polyamines tend to complex soft ions such as transition metal ions, on the contrary to crown ethers which prefer hard species like alkali metal ions.

7.2. Controlling the recognition ability of a crown ethers

If the recognition ability of crown ethers can be controlled, novel kinds of hosts can be designed. Fig. 20 shows a biological example, in which the host consists of oligoethylene glycol with bipyridyl units at both ends, wherein the bipyridine unit and the oligoethylene glycol have different complexation tendencies. Two bipyridine units sandwich a copper ion, inducing a change in the oligoethylene chain from a linear to a pseudo-cyclic (podand) form. As a result, an alkali ion can be complexed by the oligoethylene loop. This means that the binding properties of a binding site of the host are adjusted by the bonding of the other to a copper ion. But it would be more convenient to control the complexation behavior through physical stimuli such as light and electricity, which have no interfering chemical roles on the system [3].

As another method of control, the electron-driven recognition has been suggested. The binding ability of the hosts in Figure 21 changes as a result of redox reactions between thiol and disulfide groups [3].

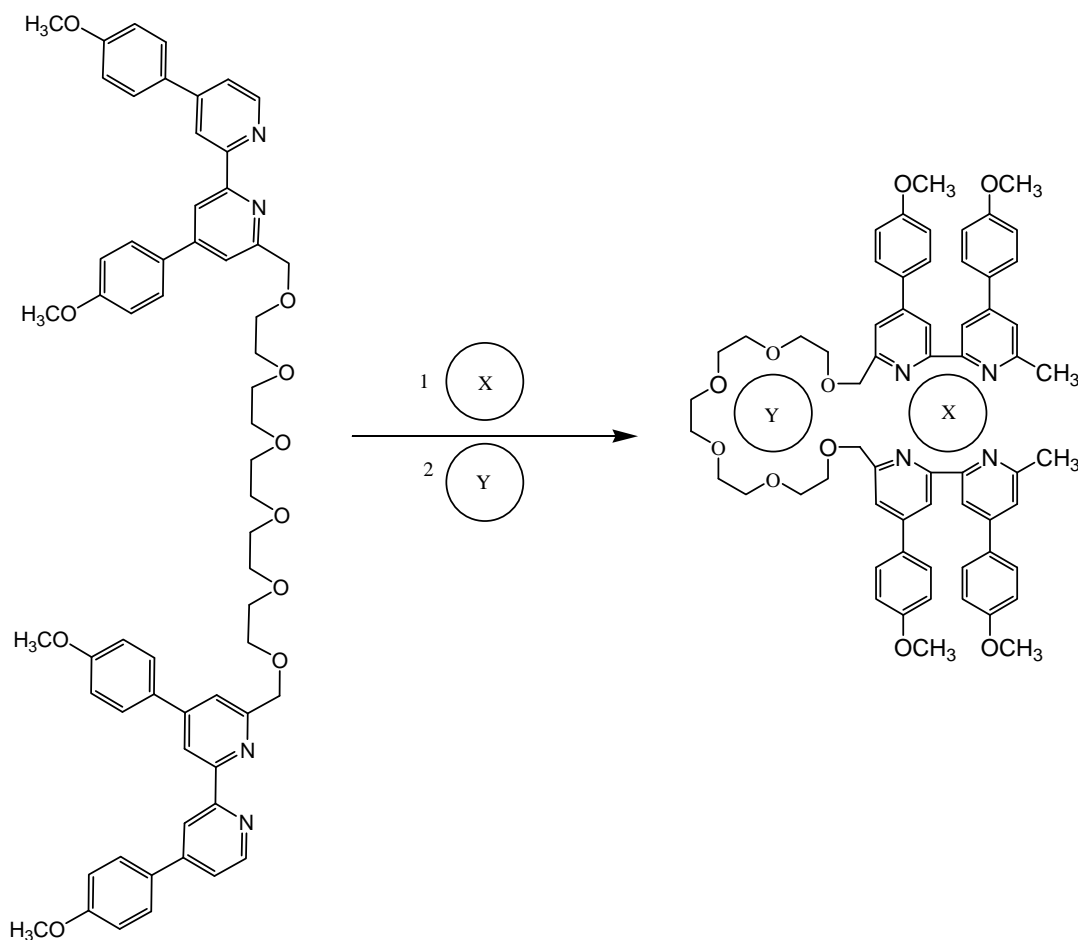
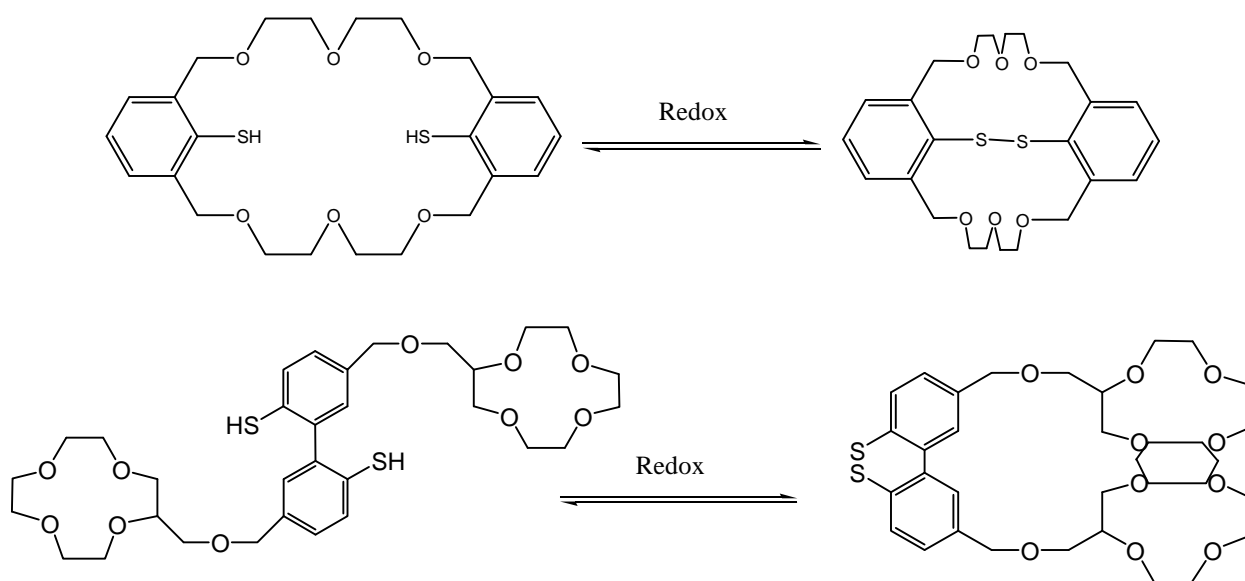
Figure 20. Controlling the recognition ability of crown ethers through an external stimulus [3].**Figure 21.** Loss of binding ability through redox reactions between thiol and disulfide groups [3].

Table 6 shows a number of potentiometric sensors based on crown ethers as sensing materials.

Table 6. A number of reported potentiometric membrane sensors based on crown ethers.

Cation	Ionophore	Slope (mV decade ⁻¹)	Linear Range (M)	Most Important Interfering ions (log K _{set} > -2)	Ref.
Li ⁺ -1	Decalino-14-Crown-4	58	1×10 ⁻⁶ – 1	Na ⁺	211
Li ⁺ -2	Tnf-Based 16-Crown-4 Derivatives	58.2	1×10 ⁻⁵ -1×10 ⁻¹	Na ⁺ ,NH ₄ ⁺	212
Li ⁺ -3	Lipophilic Crown-4 Derivatives	58	10 ⁻⁴ -10 ⁻¹	Na ⁺ , K ⁺ ,NH ₄ ⁺	213
Li ⁺ -4	16-crown-4 derivatives	59.7	7×10 ⁻⁴ - 1.5×10 ⁻³	-	214
Na ⁺ -1	Bis[(12-crown-4)methyl] methyl(dodecyl)malonate [bis(12-crown-4)] and polyether-amide compounds (ETH 157, ETH 2120)	54	1.0×10 ⁻⁴ -1.0×10 ⁻¹	K ⁺	215
Na ⁺ -2	Bis(10-crown-3)-hexa- methylenebis(3,6,10- trioxacycloundecane)	54	1×10 ⁻⁵ -1	K ⁺	216
Na ⁺ -3	Crown-bridged calix[4]quinones	54	1.0×10 ⁻⁴ -1.0×10 ⁻¹	K ⁺	217
Na ⁺ -4	dibenzopyridino-18- crown-6	51.2	1.0×10 ⁻⁴ -1.0×10 ⁻¹	Pb ²⁺ , NH ₄ ⁺ , Cs ⁺	218
Na ⁺ -5	1-methyl-1-vinyl-14- crown-5	55.0	3.16×10 ⁻⁶ -1.0×10 ⁻¹	K ⁺	219
K ⁺ -1	styrene/4(-vinylbenzo-24- crown-8) copolymer	58	1.0×10 ⁻⁶ 1.0×10 ⁻¹	-	220
K ⁺ -2	Bis(crown ether) ionophore containing two benzo-15-crown-5 moieties	57	5.0×10 ⁻⁶ 1.0×10 ⁻¹	NH ₄ ⁺ , Na ⁺ , Cs ⁺	221
Rb ⁺ -1	crown ethers incorporating anthraquinone, benzo- quinone, and 1,4- dimethoxybenzene	54.7	1.0×10 ⁻⁵ -1.0×10 ⁻¹	Na ⁺ ,K ⁺ ,Mg ²⁺ ,NH ₄ ⁺ ,Li ⁺	222
Rb ⁺ -2	dibenzo-21-crown-7 (DB21C7)	57.8	1.0×10 ⁻⁵ -5.0 ×10 ⁻²	-	223
Cs ⁺ -1	upper-rim calix[4]crown	48	1×10 ⁻⁶ -1×10 ⁻¹	Rb ⁺	224
Cs ⁺ -2	calix[4]arene dibenzocrown ether	58.5	1×10 ⁻⁶ -1 × 10 ⁻¹	Na ⁺ ,K ⁺	225
Cs ⁺ -3	1,3-alternate thiacalix[4]biscrown-6,6	57.6	1.0×10 ⁻⁶ to 3.2×10 ⁻²	K ⁺	226
Be ²⁺ -1	benzo-9-crown-3	28	2.5×10 ⁻⁶ -4.0×10 ⁻³	-	227
Be ²⁺ -2	2,4- dinitrophenylhydrazineben- zo-9-crown-3	29.5	1.0×10 ⁻¹ - 4.0× 10 ⁻⁷	-	228
Be ²⁺ -3	naphto-9-crown-3	29.5	1.0×10 ⁻¹ - 8.0×10 ⁻⁶	-	229

Table 6. Cont.

Be ²⁺ -4	2,3,5,6,8,9-hexahydro-1,4,7,10-benzotetraoxacyclododecine-12-carbaldehyde-12-(2,4-dinitrophenyl)hy	29.9	1.0×10^{-7} - 1.0×10^{-1}	Na ⁺ , Ca ²⁺ , Li ⁺	230
Be ²⁺ -5	2,6-diphenyl-4-benzo-9-crown-3-pyridine	29.6	1.0×10^{-7} - 1.0×10^{-1}	Mg ²⁺ , Ca ²⁺ , K ⁺ , Na ⁺	231
Be ²⁺ -6	2,3,5,6,8,9-hexahydro-naphtho [2,3-b]- [1,4,7,10] tetraoxacyclododecine	29.8	1.0×10^{-8} - 1.0×10^{-2}	-	232
Be ²⁺ -7	a derivative of benzo-9-crown-3	29.6	1.0×10^{-6} - 1.0×10^{-1}	-	233
Be ²⁺ -8	a derivative of benzo-9-crown-3	29.5	1.0×10^{-7} - 1.0×10^{-1}	-	234
Mg ²⁺ -1	benzo-15-crown-5	31.0	1.0×10^{-5} - 1.0×10^{-1}	K ⁺ , Cd ²⁺ , Mg ²⁺ ,	235
Sr ²⁺ -1	dibenzo-24-crown-8(I) and 4-tert-butylcalix[8]arene	30	1.4×10^{-5} - 1.0×10^{-1}	Na ⁺	236
Sr ²⁺ -2	benzo-substituted macrocyclic diamides	30	3.2×10^{-5} - 1.0×10^{-1}	-	237
In ³⁺ -1	15-crown-5 (15C5), dicyclohexano-18-crown-6 (DCH18C6)	20.1	3.8×10^{-5} - 5.0×10^{-2}	-	238
Tl ³⁺ -1	dibenzylidiaz-18-crown-6	56.9	1.0×10^{-5} - 1.0×10^{-1}	Cd ²⁺ , Hg ²⁺ , Ag ⁺	239
Sn ²⁺ -1	dibenzo-18-crown-6(DB18C6)	27.5	1.0×10^{-6} - 1.0×10^{-2}	-	240
Pb ²⁺ -1	monobenzo-15-crown-5 (MB15C5), MB15C5-phosphotungstic acid (PW) and MB15C5-phosphomolybdic acid (PMo)	30	1×10^{-1} - 1×10^{-5}	Ag ²⁺ , Hg ²⁺	241
Pb ²⁺ -2	dibenzodiaz-15-crown-4	29	5.0×10^{-6} - 1.0×10^{-2}	-	242
Pb ²⁺ -3	4'-vinylbenzo-15-crown-5	59	4.0×10^{-3} - 1.0×10^{-6}	K ⁺	243
Pb ²⁺ -4	dithiophenediazacrown ether derivatives.	29.2	$10^{5.0}$ - $10^{2.7}$	Hg ²⁺	244
Pb ²⁺ -5	1,10-dibenzyl-1,10-diaza-18-crown-6	29.1 and 28.9	5.0×10^{-6} - 10^{-1}	Cd ²⁺ , Cu ²⁺	245
Pb ²⁺ -6	18-membered thiacycrown derivative	29.0	1.0×10^{-6} - 8.0×10^{-3}	-	246
Pb ²⁺ -7	N,N'-dimethylcyanodiaz-18-crown-6	29	10^{-7} - 10^{-2}	-	247
La ³⁺ -1	monoaza-12-crown-4	20.5 ± 1.0	3.16×10^{-5} - 1.0×10^{-1}	Pb ²⁺ , Mg ²⁺ , Ca ²⁺ , Cu ²⁺ , Zn ²⁺ , Cd ²⁺ , Cr ³⁺ , Ce ³⁺ , Eu ³⁺	248
Ce ³⁺ -1	1,3,5-trithiane	19.2	4.7×10^{-4} - 2.5×10^{-8}	La ³⁺	249

Table 6. Cont.

Cr ³⁺ -1	Different ionophoric species, viz.: 18-crown-6 (18C6), dibenzo-18-crown-6 (DB18C6) and calix[6]arene (CAX)	18.5 and 20	1.0×10^{-5} - 1.0×10^{-1}	Pb ²⁺ and Na ⁺	250
Fe ³⁺ -1	benzo-18-crown-6 crown ether	15.7 ± 1	1×10^{-6} - 1.0×10^{-1}	-	251
Co ²⁺ -1	benzo-substituted macrocyclic diamide	29	2.0×10^{-6} - 1.2×10^{-2}	-	252
Co ²⁺ -2	dibenzopyridino-substituted macrocyclic diamide	29	7.0×10^{-7} - 1.0×10^{-2}	-	253
Ni ²⁺ -1	dibenzodiaza-15-crown-4	28.6	7.1×10^{-7} - 1.2×10^{-2}	Ag ⁺ , Pd ²⁺	254
Cu ²⁺ -1	Aza-thioether crowns containing a 1,10-phenanthroline sub-unit	30	1×10^{-5} - 2×10^{-1}	La ⁺³	255
Cu ²⁺ -2	23-member macrocyclic diamide	30	3.2×10^{-5} - 1.0×10^{-1}	-	256
Ag ⁺ -1	Lipophilic pyrrole-based tetraazacrown ether	55	1.0×10^{-5} - 1.0×10^{-1}	Hg ²⁺	257
Ag ⁺ -2	diaza-18-crown-6, containing two oxime donor groups	59.5	1.0×10^{-5} - 1.0×10^{-2}	-	258
Ag ⁺ -3	hexathia-18-crown-6	59	6.0×10^{-6} - 3.2×10^{-3}	-	259
Ag ⁺ -4	Aza-thioether crowns containing a 1,10-phenanthroline sub-unit	59.4 and 59.1	1.0×10^{-5} - 1.0×10^{-1} and 5.0×10^{-8} - 4.0×10^{-2}	Cu ²⁺ , Tl ⁺	260
Ag ⁺ -5	exocyclic sulfur and selenium ligands based on calix[4]arenes and crown ethers	56.0	1.0×10^{-5} - 1.0×10^{-2}	Hg ²⁺	261
Ag ⁺ -6	5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-calix[4]arene-thiacrown-4	53.8 ± 1.6	1.0×10^{-6} - 1.0×10^{-2}	Hg ²⁺	262
Ag ⁺ -7	1,10-phenanthroline sub-unit	56	1.0×10^{-5} - 1.0×10^{-1}	Hg ²⁺	263
Zn ²⁺ -1	cryptand C2(B)22	24	5.0×10^{-5} - 5.0×10^{-2}	Na ⁺	264
Zn ²⁺ -2	dibenzo-24-crown-8	29.0 ± 0.5	9.2×10^{-5} - 1.0×10^{-1}	-	265
Zn ²⁺ -3	benzo-substituted macrocyclic diamide	29.0	9.0×10^{-5} - 1.0×10^{-1}	-	266
Cd ²⁺ -1	dicyclohexano-24-crown-8	30.0 ± 1.0	3.0×10^{-5} - 1.0×10^{-1}	Fe ³⁺ , Cr ³⁺ , Ce ³⁺	267
Cd ²⁺ -2	dicyclohexano-18-crown-6	29.0 ± 1.0	2.5×10^{-5} - 1.0×10^{-1}	-	268
Cd ²⁺ -3	tetrathia-12-crown-4	29.0 ± 1.0	4×10^{-7} - 1.0×10^{-1}	-	269
Cd ²⁺ -4	monoaza-18-crown-6	29	1.0×10^{-5} - 1.0×10^{-1}	Cu ²⁺ , Na ⁺ , Ca ²⁺	270

Table 6. Cont.

Hg ²⁺ -1	p-tert-butyl calix[4]crown with imine units	27.3	5.0×10^{-5} - 1.0×10^{-1}	-	271
Hg ²⁺ -2	Pentathia-15-crown-5	32.1	2.51×10^{-7} - 1.0×10^{-1}	-	272
Hg ²⁺ -3	dibenzodiazathia-18-crown-6-dione	29	8.0×10^{-6} - 1.0×10^{-2}	Cd ²⁺ , Pb ²⁺ , K ⁺	273
Hg ²⁺ -4	hexathia-18-crown-6-tetraone	29.0 ± 0.3	4.0×10^{-6} - 1.0×10^{-3}	-	274
I ₃ ⁻ -1	Two different charge-transfer complexes and amino crown ether	-59	1.0×10^{-5} - 1.0×10^{-1}	-	275
SCN ⁻ -1	Cu(II)-1,8-dimethyl-1,3,6,8,10,13-hexaazacyclotetradecane complex	-57.2	7.0×10^{-6} - 1.0×10^{-1}	ClO ₄ ⁻	276
SCN ⁻ -2	Ni(II)-azamacrocyclic complex	-57.8	1.0×10^{-7} - 1.0×10^{-1}	-	277
SO ₄ ²⁻ -1	2,5-diphenyl-1,2,4,5-tetraaza-bicyclo[2.2.1]heptane	-28.8	9.0×10^{-6} - 1.0×10^{-1}	-	278

Structures of some of the above ionophores are depicted in Figures 22 –26.

Figure 22. Some structures of crown ethers used as supramolecular ionophores in construction of the first group metal cations membrane sensors.

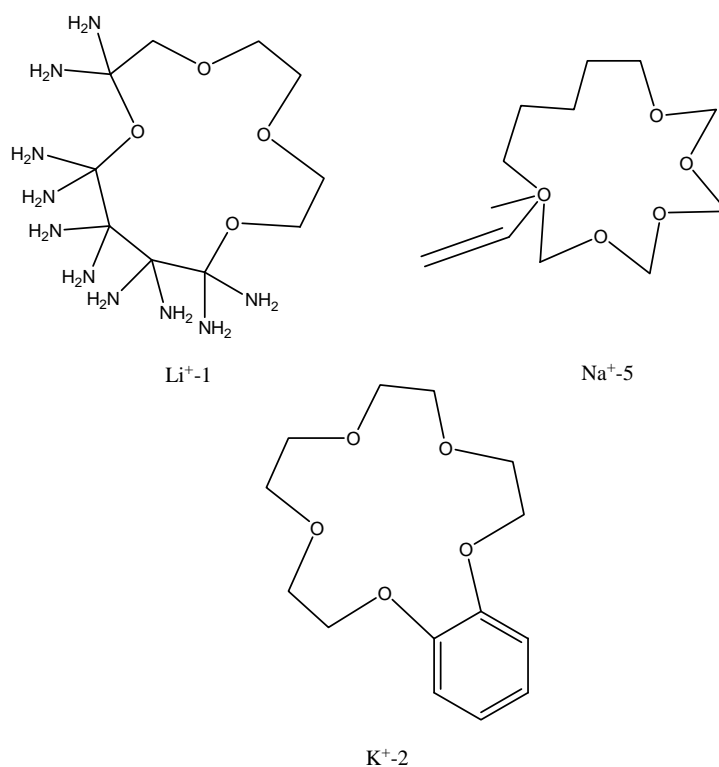


Figure 23. Some structures of crown ethers used as supramolecular ionophores in construction of the Be^{2+} membrane sensors.

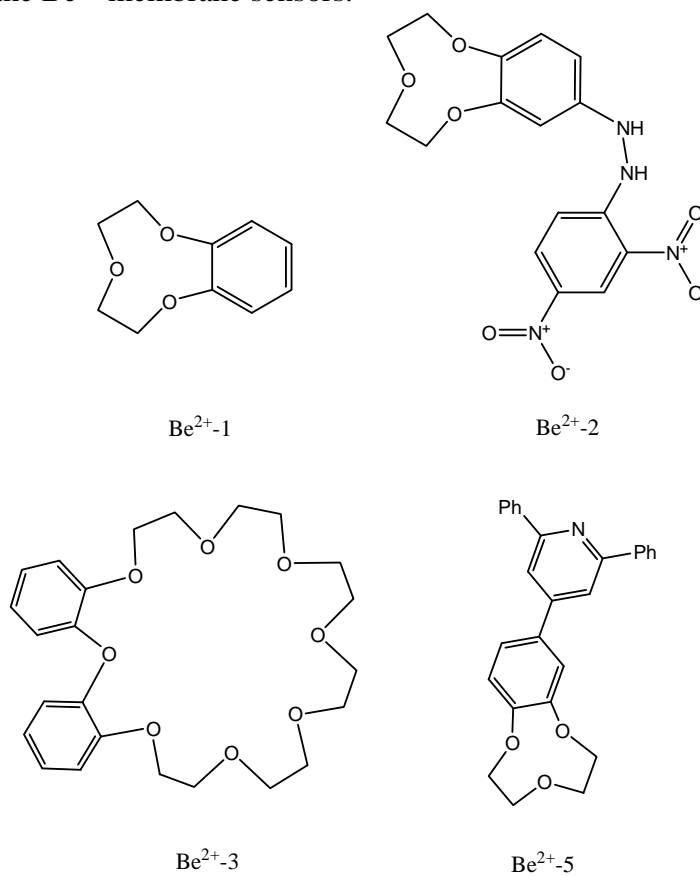


Figure 24. Some structures of crown ethers used as supramolecular ionophores in construction of the Pb^{2+} membrane sensors.

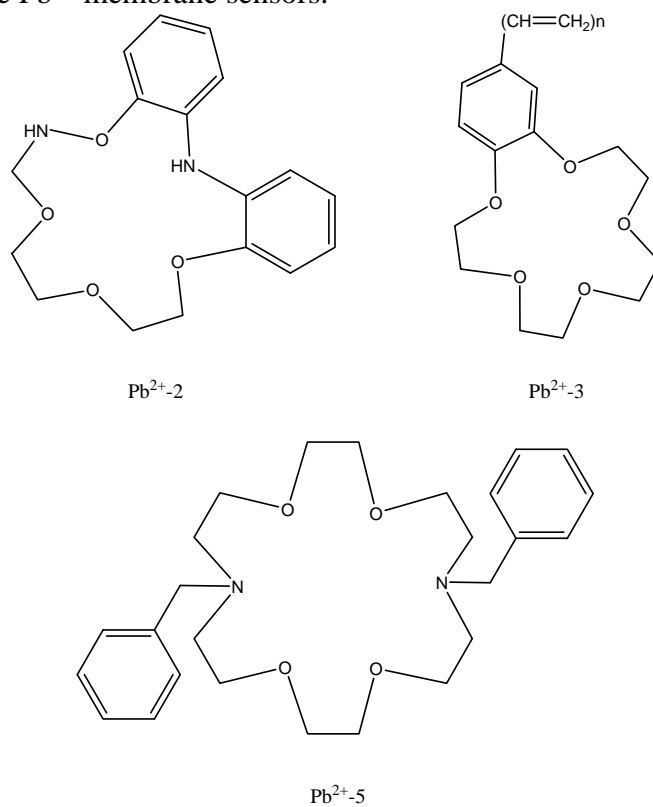


Figure 25. A structure of a crown ether used as supramolecular ionophore in the construction of the Ag^+ membrane sensors.

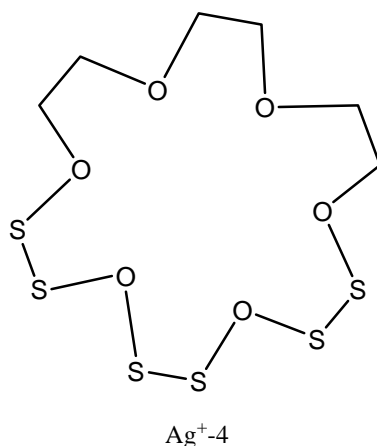
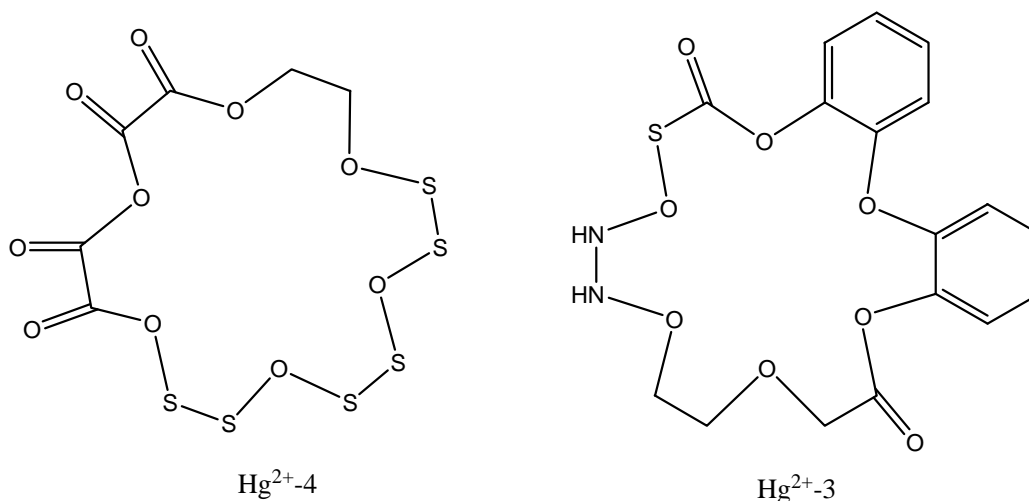


Figure 26. Some structures of crown ethers used as supramolecular ionophore in the construction of the Hg^{2+} membrane sensors.



8. Conclusions

Ionophore incorporated PVC membrane sensors are well-established analytical tools routinely used for the selective and direct measurement of a wide variety of different ions in complex biological and environmental samples. The potentiometric sensors have some outstanding advantages including simple design and operation, wide linear dynamic range, relatively fast response and rational selectivity. The vital component of such plasticized PVC members is the ionophore involved, defining the selectivity of the electrodes complex formation. Molecular recognition causes the formation of many different supramolecules. Different types of supramolecules, like calixarenes, cyclodextrins, podands, have been used as a sensing material in construction of the ion selective sensors. Schiff's bases and crown ethers which feature in supramolecular chemistry can be used as sensing material in the construction of potentiometric ion selective electrodes. Up to now, more than 200 potentiometric membrane sensors based on Schiff's bases and crown ethers have been reported for cations and anions.

In this review cation binding and anion complexes have been described and liquid membrane sensors based on Schiff's bases and crown ethers were discussed.

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