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MINI-REVIEW

Electrochemical Modified Electrodes Based on Metal-Salen Complexes

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Abstract: A general view of the electroanalytical applications of metal-salen complexes is discussed in this review. The family of Schiff bases derived from ethylenediamine and *ortho*-phenolic aldehydes (*N*,*N*′-ethylenebis(salicylideneiminato)—salen) and their complexes of various transition metals, such as Al, Ce, Co, Cu, Cr, Fe, Ga, Hg, Mn, Mo, Ni, and V have been used in many fields of chemical research for a wide range of applications such as catalysts for the oxygenation of organic molecules, epoxidation of alkenes, oxidation of hydrocarbons and many other catalyzed reactions; as electrocatalyst for novel sensors development; and mimicking the catalytic functions of enzymes. A brief history of the synthesis and reactivity of metal-salen complexes will be presented. The potentialities and possibilities of metal-Salen complexes modified electrodes in the development of electrochemical sensors as well as other types of sensors, their construction and methods of fabrication, and the potential application of these modified electrodes will be illustrated and discussed.

Keywords: Metal-salen complexes, electrocatalysis, modified electrodes, PVC membranes

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INTRODUCTION

A Schiff base (or azomethine), named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group—but not hydrogen. Schiff bases are of the general formula $R_1R_2C{=}N\text{-}R_3$, where R_3 is a phenyl or alkyl group that makes the Schiff base a stable imine. Schiff bases can be synthesized from amine and an active carbonyl compound, such as aldehydes or ketones, by nucleophilic addition forming a carbinolamine intermediate, followed by a dehydration to generate an imine, Fig. 1. Schiff base compounds were reported for the first time by Hugo Schiff in 1864 (Hobday and Smith 1973; Holm et al. 1966; Cozzi 2004).

These bases are very efficient as ligands. Many Schiff bases have a second functional group, generally an OH group, near the imine function. This proximity of the functional groups permits the formation of 5 or 6 member chelate rings when coordinated with metal ions. The Schiff base ligands have a diversified structure with the nitrogen- and oxygen-donor systems being the most numerous. However the nitrogen- and sulfur-donor ligand systems and only nitrogen-donor systems have been studied (Holm et al. 1966). Due to the various synthetic procedures, numerous Schiff bases of various structure types have been synthesized. (Fig. 2). Probably the best known Schiff base ligand is *N,N′*-ethylenebis(salicylideneiminato) or Salen, which is a bifunctional and tetradentate (ONNO) ligand. The more general

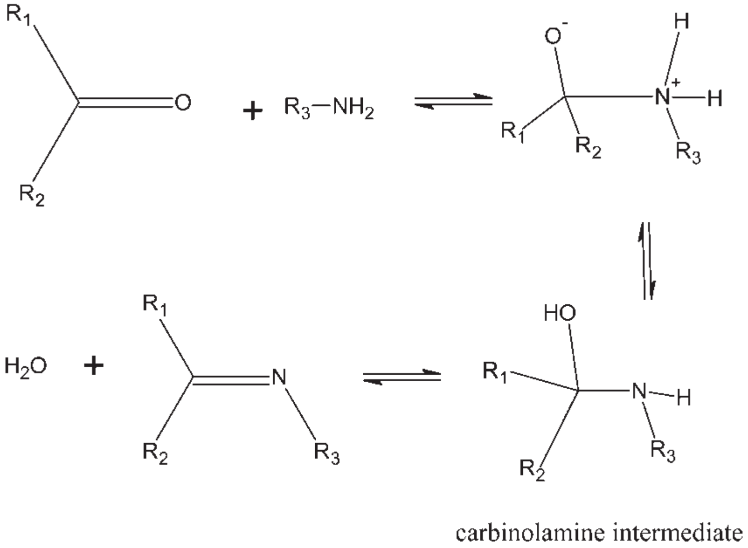


Figure 1. General scheme for the formation of a Schiff base.

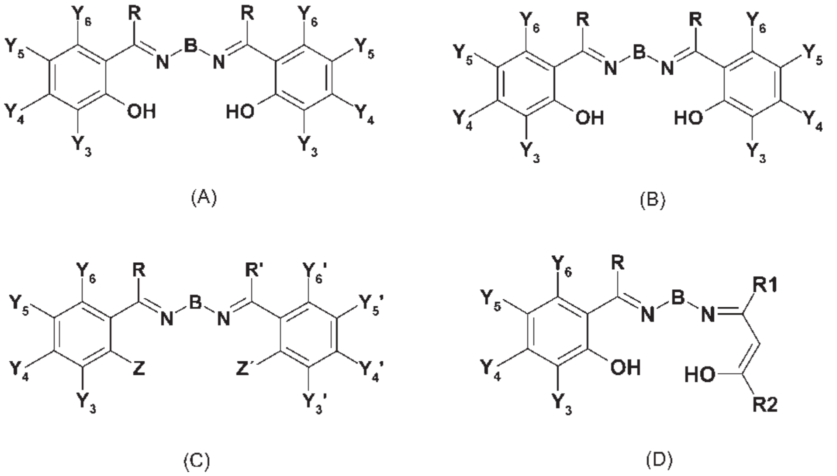


Figure 2. General structures: (A) symmetrical tetradentate salen-type Schiff bases ligands; (B) symmetrical chiral tetradentate salen-type Schiff bases ligands; (C) asymmetric tetradentate ZNNZ-type Schiff base; (D) dissymmetric ONNO-type Schiff base. Where **B** is an alkyl or aryl group, for chiral ligands this group is generally optically active; **R**, **R′**, **R1** and **R2** are alkyl or aryl groups; $\mathbf{Y_N}$ and $\mathbf{Y'_N}$ are substituents on the aromatic ring of the salicylaldehyde derivatives; **Z** and **Z′** are either OH, SH or NH_2. Note that **R**, **R′**, **R1** and **R2** are not necessarily the same in (C) and (D); $\mathbf{Y_N}$ and $\mathbf{Y'_N}$ are not necessarily the same in (C); and **Z** and **Z′** are not necessarily the same in (C).

term Salen-type is used in the literature to describe the class of [O, N, N, O] bis-Schiff base ligands. The properties of the Salen-type ligands can be accomplished by fine-tuning the electronic and steric effects of substituent groups.

Recent interest in the design, synthesis and characterization of unsymmetrical Schiff base ligands from ethylenediamine for transition metal ion complexes has come from the realization that coordinated ligands around central metal ions in natural systems are unsymmetrical (Atkins et al. 1985). Although unsymmetrical ligands can clearly offer many advantages over their symmetrical counterparts in the elucidation of the composition and geometry of metal ion binding sites in metalloproteins, and in the development leading to the duplication of enzymatic efficiency and selectivity of natural systems with synthetic materials, the difficulty of preparing such ligands has hampered progress because simple condensation methodology with three components is no longer applied.

One important feature of the complexes formed from such unsymmetrical ligands is expected to be unique structural properties, which may sterically and electronically differ from those of conventional (symmetrical) ligands.

Fine-tuning of the electronic properties of the complexes simply by changing substituents on the aromatic ring should be possible since the other side is constant (Bu et al. 1997).

Since the success of the Jacobsen–Katsuki asymmetric epoxidation of unfunctionalized olefins using chiral salen-type manganese(III) Schiff base catalysts in the early 1990s (Zhang et al. 1990), there has been a resurgence of interest in chiral salen-type ligands for asymmetric catalysis (Jacobsen 1993). It is well-known in homogeneous asymmetric catalysis that stereochemical communication between the ligand environment of the catalyst and the substrate is essential for obtaining high enantioselectivities (Walsh 1979). Although steric effects play a major role in the asymmetric induction mechanism, electronic effects have also been shown to be quite important (Jacobsen et al. 1991; Palucki et al. 1998).

Of the many effective chiral ligands, usually based on (1R,2R)-1,2-diaminocyclohexane and (1S,2S)-1,2-diaminocyclohexane, only a few are synthetically or structurally well-suited to electronic tuning. Therefore the ability to easily synthesize a series of structurally similar ligands with subtle variations in steric and electronic configuration is essential to optimize and fully understand a catalyst system. As a class, salen-type ligands consist of a flexible and kinetically nonlabile ligand template wherein both steric and electronic properties of the metal center may be tuned in a synthetically straightforward manner (Jacobsen et al. 1991). Despite the wide range of synthetic and mechanistic possibilities with salen-type ligands, electronic tuning has been almost exclusively limited to symmetrical cases (Jacobsen et al. 1991).

The facile synthesis of a series of structurally similar ligands, which incorporate subtle variations in their steric and electronic configuration, is highly desirable. The use of unsymmetrical chiral salen Schiff base ligands in asymmetric catalysis is on the increase.

Preparation of Schiff Bases

Schiff bases are prepared by the condensation between an active carbonyl compound and a primary amine. The active carbonyl compounds can be aldehydes or ketones and the primary amine can be aliphatic or aromatic. Tetradentate Schiff base ligands are prepared by the condensation of a diamine and two active carbonyl compounds, usually substituted salicylaldehydes or β-diketones, such as acetylacetone. If the diamine is chiral then the resulting Schiff base is also chiral.

The reaction to prepare Schiff bases is reversible, progressing through a carbinolamine intermediate, Fig. 1, and requires the removal of water, often by azeotropic distillation with benzene or toluene, to achieve high yields. The reaction is acid-catalyzed but catalysts are not generally required when aliphatic amines are involved. Ethanol and methanol, at room temperature or in refluxing conditions, have been successfully used (Aranha et al. 2007; de

Azevedo-Marques et al. 2007). Schiff base ligands are usually purified by recrystallization from ethanol or methanol. If the Schiff bases are insoluble in pentanes or hexane, they can be purified by stirring the crude reaction mixture in these solvents. In these cases it is sometimes necessary to add a small portion of diethyl ether or dichloromethane to eliminate impurities. This simple procedure is generally used to prepare symmetrical tetradentate Schiff base ligands.

Simple and often one pot condensation of two components, ethylenediamine either with salicylaldehydes or with acetylacetones, can easily lead to the formation of tetradentate Schiff base ligands, which can incorporate a variety of metal ions for different purposes. Several approaches have been developed in the preparation of unsymmetrical Schiff base ligands derived from ethylenediamine, salicylaldehyde and acetylacetone (Kwiatkowski and Kwiatkowski 1984; Kuska et al. 1972; Bu et al. 1997) to explore the properties of their metal complexes. One important feature of the complexes formed from such unsymmetrical ligands is expected to be unique structural properties, which may sterically and electronically differ from those of conventional (symmetrical) ligands due to a unique combination of aromatic donors (salicylaldehyde portion) and nonaromatic donors (acetylacetone portion) bridged by ethylenediamine units.

While the synthesis of these symmetrical catalysts is generally highly efficient and straightforward, the unsymmetrical Schiff-base ligands are much less accessible. Accordingly, reports of the chiral unsymmetrical salen ligands have been scarce up to now (Sasaki et al. 1987; Campbell and Nguyen 2001; Pietikäinen and Haikarainen 2002; Ambroziak and Szypa 2007). The published methods involve a stepwise synthesis of non-C_2-symmetric salen ligands containing two different donor units via mono-imines. However, these syntheses are generally unreliable and the mono-imines prepared from salicylaldehyde and 1,2-diamine is always contaminated with various amounts of the C_2-symmetric bis-imine even after attempted purification (Sasaki et al. 1987; Campbell and Nguyen 2001). Unsymmetrical salen ligands, however, have been successfully synthesized only via mono-protection of the diamine (Campbell and Nguyen 2001; Kaik and Gawroński 2003). The preparation of unsymmetrical chiral Schiff base ligands have been especially successful when the active carbonyl group in the first step is 2-hydroxynaphthaldehyde (Ambroziak and Szypa 2007) or an (2-hydroxyphenyl)ketone (Pietikäinen and Haikarainen 2002).

Coordination Chemistry

Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. In the area of bioinorganic chemistry interest in Schiff base complexes has centered on the role such complexes may have in providing synthetic models for the metal containing sites in metallo-proteins and -enzymes.

Metal ion complexes of Schiff bases have been prepared and studied since the nineteenth century. In 1840, Ettling and co-workers (Holm et al. 1966; Hobday and Smith 1973) isolated a dark green solid from the reaction of copper(II) acetate and salicylaldehyde in an aqueous ammonia solution. Schiff discovered the experimental technique of preparing metal-imine complexes by the reaction of a preformed metal salicylaldehyde compound with a primary amine. In 1869, Schiff prepared several complexes using phenyl and aryl primary amines and salicylaldehyde and established a 2:1 ligand to metal ratio for the products (Holm et al. 1966; Hobday and Smith 1973). This technique may be viewed as an ancestor of the 'metal-template' approach that has evolved as an efficient route for the synthesis of macrocyclic ligands and complexes. Delépine in 1899 prepared similar complexes by the reaction of a metal acetate salt, salicylaldehyde with methylamine or benzyl amine in alcohol and determined the metal-ligand ratio as 1:2 (Holm et al. 1966; Hobday and Smith 1973).

In 1931, Pfeiffer and co-workers began a systemic study of the synthesis of Schiff base complexes. The large number of complexes with Schiff bases derived from salicylaldehyde, substituted salicylaldehydes, *ortho*-aminosalicylaldehyde and pyrrole-2-carboxaldehyde (Holm et al. 1966; Hobday and Smith 1973). At this time experiments revealed that transition metal ions react with substituted salicylaldehyde Schiff bases to form colored products. Dubsky and Sokol, also in 1931, isolated the *N,N′*-ethylenebis(salicylideneiminato) complexes of copper(II) and nickel(II) (Holm et al. 1966). In 1938 Tsumaki discovered the oxygen-carrying property of Co(Salen) in the crystalline state (Tsumaki 2003).

Catalysis

Salen-type complexes are a fundamental class of compounds in coordination chemistry, known since 1933 (Holm et al. 1966; Hobday and Smith 1973). They have been extensively studied and more than 2500 have been synthesized (Dalton et al. 1998). Interest in salen-type complexes intensified in 1990 when the groups of Jacobsen (Zhang et al. 1990) and Katsuki (Irie et al. 1990) discovered the enantioselective epoxidation of unfunctionalised alkenes using chiral Mn(salen)complexes as catalysts. Over the last 15 years, salen ligands have been widely used in asymmetric catalysis (Jacobsen 1993; Canali and Sherrinton 1999; Jacobsen and Wu 1999; Cozzi 2004). The various types of reactions include oxidation of hydrocarbons (Lee et al. 1998), the enantioselective cyclopropanation of styrenes (Ambroziak and Szypa 2007), the asymmetric aziridination of olefins (Ambroziak and Szypa 2007), asymmetric Diels–Alder cycloaddition reactions (Ambroziak and Szypa 2007), the asymmetric epoxide ring-opening reactions (Ambroziak and Szypa 2007), the hydrolytic kinetic resolution of epoxides (Shin et al. 2004), the alkylation of aldehydes (Maeda et al. 2004), the oxidation of sulfides to sulfoxides (de Azevedo-Marques et al. 2007), in the oxidation of alcohols (Aranha et al. 2007), the asymmetric addition of organometallic reagents to aldehydes (Aranha et al. 2007) and in the asymmetric synthesis of α-methyl α-amino acids (Achard et al. 2004).

ELECTROCHEMICAL MODIFIED ELECTRODES BASED ON METAL-SALEN COMPLEXES

Potentiometric Electrodes Based on Metal-Salen Complexes

Potentiometric electrodes or so-called ion-selective electrodes (ISEs) work through the measurement of an equilibrium potential, i.e. the potential at zero current of the ISE vs. a suitable reference electrode. These potentials are a function of the activity of the analyte in solution, not of their concentrations. The Debye-Huckel equation relates concentrations to activities and can often be employed (Brett and Oliveira-Brett 1998). The potentiometric electrodes based on metal-Salen complexes contain a selective membrane or film of a Salen-complex as recognition element since some selective chemistry takes place at the surface of the electrode producing an interfacial potential. An ion-selective electrode in conjunction with a reference electrode is an ISE cell (galvanic cell). Conventional notation of the cell is:

outer ref.|test solution|internal ref. or
outer ref.|test solution|ion-selective electrode

and the measured cell emf, E (right electrode potential minus left electrode potential) is described by the Nicolsky-Eisemann equation:

$$E = \text{constant} \pm 2.303\,\mathrm{RT}/\mathrm{Z_A F}\,\log[a_A + K_{A,B^{pot}}\, a_B^{ZA/ZB} + \ldots] \qquad (1)$$

where E is the experimentally determined galvanic potential difference of ISE cell (in V); R the gas constant equal to 8.314510 J K^{-1} mol^{-1}; T the absolute temperature in K; F the Faraday constant, 9.6485309×10^4 C mol^{-1}, a_A the activity of A (analyte); a_B the activity of interfering specie B, $K_{A,B^{pot}}$ the potentiometric selectivity coefficient for specie B with respect to the primary specie (analyte), Z_A the charge number—an integer with sign and magnitude corresponding to the charge of the principal ion, A and Z_B the charge number corresponding to the charge of interfering ion B (Umezawa et al. 2000).

It can be seen from Equation (1) that the membrane is more selective for the analyte A with the lower value of $K_{A,B^{pot}}$.

The potentiometric ISE provides a highly selectivity and sensitive method for the determination of a given analyte. Advantages of such potentiometric electrodes are simplicity of instrumentation (only a pH meter is needed), relatively fast response, reasonable selectivity, wide linear range, low cost, and easy production. As presented, potentiometric ISE generate an electric potential proportional to the logarithm of analyte activity (Nernstian behavior) in the sample to be analyzed.

According to the nature of the binding sites, the membranes can be divided into those containing fixed ionic sites, mobile ion-exchanger, or neutral ionophores. It is well known that the sensitivity and selectivity of an ISE depend not only on the nature of binding sites used, but also on the membrane composition and the properties of solvent mediators and additives used (Janata 1989; Cattrall 1997; Ganjali 2005; Badr 2006), which control the internal dielectric constant, lipophilicity, transport, and other mechanical and electrical properties of the membrane.

Table 1 summarizes some potentiometric ion-selective electrodes based on metal Salen-complexes. As can be seen in this table, several metal-Salen complexes were used as active ionophores within plasticized poly(vinyl chloride) (PVC) membranes. Many efforts during recent years have focused on both the development of membrane ion selective electrodes (ISE) for various analytes and the synthesis of new and more selective ionophores. Salen-complexes of several metal ions have been shown to possess high selectivity metal-ligand interactions, which induce anion selectivity in membranes that are somewhat different from the classical anion exchangers. Conventional anion-selective electrodes based on quaternary ammonium or phosphonium salts, have low selectivity once the selectivity is determined by the hydration energy and the relative solubilities of the individual anions in the solvent mediator, and the electrodes usually show the so-called Hofmeister selectivity sequence (lipophilic organic anions $> ClO_4^- > IO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^- > HCO_3^- > F^- \geq H_2PO_4^-$), which is governed by ion lipophilicity. The more lipophilic anions are preferred and anion-exchanger based membrane electrodes lack selectivity for hydrophilic anions. Furthermore, anion-exchanger based membrane electrodes do not satisfy the require selectivity for the analysis of hydrophobic anions in many practical applications (Badr 2006).

Recently, electrodes using PVC membranes incorporating metal-Salen complexes is believed to be based on the coordination of analyte anions as axial ligands to the metallic center of the ionophore, showing an anti-Hofmeister pattern (Ganjali et al. 2001; Ganjali et al. 2002; Ganjali et al. 2003; Ganjali et al. 2005; Xu et al. 2005; Badr 2006). As an example of such behavior, a cobalt(II)-Salen was used as suitable ionophore for the preparation of a polymeric nitrite-selective electrode (Ganjali et al. 2003). The electrode presented a Nernstian behavior over a very wide NO_2^- ion

Table 1. Configuration and some characteristics of potentiometric sensors modified with salen-complexes

Analyte	Application	Modifier	Immobilization	Linear range (mol L^{-1})	Limit of detection (mol L^{-1})	Lifetime	Ref.
Bromide	Potentiometric titration of bromide	Fe-Salen	PVC-membrane	7.0×10^{-6} – 1.0×10^{-1}	6.0×10^{-6}	9 weeks	Ganjali et al. 2004
Copper(II)	Brass and urine samples	*o*-MeSalen (I) *m*-MeSalen (II) *p*-MeSalen (III)	PVC-membrane	1.0×10^{-5} – 1.0×10^{-1}	3.6×10^{-6} (I) 3.1×10^{-6} (II) 6.3×10^{-6} (III)	—	Fakhari et al. 2005
Fluoride	—	Co-Salen	PVC-membrane	—	—	—	Badr 2006
Fluoride	Drinking water	Ga-Salen	PVC-membrane	—	6.0×10^{-5}	—	Meyerhoff et al. 2005
Iodide	Potentiometric titration of Ag^{+} ions	Ce-Salen	PVC-membrane	8.0×10^{-6} – 5.0×10^{-2}	6.0×10^{-6}	>8 weeks	Ganjali et al. 2002
Iodide	Titration of iodide ion	Mn-Salen	Carbon paste	3.4×10^{-5} – 1.0×10^{-1}	—	—	Shamsipur et al. 2000
Iodide	Drug preparations	Co-Salen	PVC-membrane	2.0×10^{-6} – 6.0×10^{-2}	7.0×10^{-7}	—	Yuan et al. 1993
Monohydrogen phosphate	Fertilizer and waste water samples	MoO_2-MeSalen	PVC-membrane	1.0×10^{-6} – 1.0×10^{-1}	2.0×10^{-7}	>8 weeks	Ganjali et al. 2006
Monohydrogen phosphate	Fertilizers samples	VO-Salen	PVC-membrane	5.0×10^{-6} – 1.0×10^{-1}	3.0×10^{-6}	2 months	Ganjali et al. 2003a

(*continued*)

Table 1. Continued

Analyte	Application	Modifier	Immobilization	Linear range (mol L^{-1})	Limit of detection (mol L^{-1})	Lifetime	Ref.
Nickel(II)	Biological and environmental samples	Ni-Salen	PVC-membrane	3.2×10^{-6} – 5.0×10^{-2}	—	4 months	Jain et al. 2005
Nitrate	Freshwater sediments and biofilms	Co-Salen	PVC-membrane	—	6.3×10^{-6}	—	Verschuren et al. 1999
Nitrite and thiocyanate	—	Co-Salen	PVC-membrane	—	—	—	Badr et al. 2006
Nitrite	Sausage and milk samples	Co-Salen	PVC-membrane	1.0×10^{-6} – 1.0×10^{-1}	5.0×10^{-7}	>2 months	Ganjali et al. 2003b
Thiocyanate	—	Cr-Salen	PVC-membrane	—	—	—	Badr et al. 2006
Thiocyanate	Milk sample	Cd-Salen	PVC-membrane	1.0×10^{-6} – 1.0×10^{-1}	7.0×10^{-7}	>2 months	Ganjali et al. 2001
Triiodide	Titration of triiodide ion	Hg-Salen	PVC-membrane	5.0×10^{-8} – 1.0×10^{-1}	2.0×10^{-8}	9 weeks	Ganjali et al. 2005

concentration from 1.0×10^{-6} to 1.0×10^{-1} mol L^{-1} and a very low detection limit of 5.0×10^{-7} mol L^{-1}. The electrode shows a very good selectivity and was successfully applied to the determination of nitrite ion concentration in sausage and milk samples. The selectivity sequence for a series of anions shown by the nitrite ISE is as follow: $NO_2^- >> ClO_4^- > SCN^- > I^- > \text{Citrate}^- > NO_3^- > SO_4^{2-} > Br^- > Cl^- = HPO_4^{2-} > I_3^- = CO_3^{2-} > CH_3COO^- > \text{Salicylate}^- > F^-$, an anti-Hofmeister response pattern.

Metallo-Salen of cobalt(II) (Co-Salen), chromium(III) (Cr-Salen) and Aluminium(III)-Salen (Al-Salen) were used as the active ionophores within plasticized PVC membranes by Badr (Badr 2006). It is shown that central metal-ion plays a critical role in directing the ionophore selectivity. Optimized membrane electrodes based on Co-Salen exhibit enhanced responses toward nitrite/thiocyanate over a wide range of other anions including the more lipophilic anions (e.g., perchlorate and iodide), and environmentally relevant anions such as nitrate, sulfate and chloride. Optimum nitrite selectivity of Co-Salen was obtained using 30 mol% lipophilic anionic sites to the membrane, while addition of cationic sites results in Hofmeister selectivity pattern, suggesting that Co-Salen works via the charged-carrier mechanism within the polymeric film. This mechanism was explained based on the oxidation of Co(II) metal-ion center during the conditioning period. Electron spin resonance was utilized to support this oxidation process. The results presented in this study also demonstrate the effect of changing the central metal-ion on potentiometric selectivity of metal-Salen based polymeric membrane electrodes. While Co-Salen serves as a charged carrier for NO_2^- and/or SCN^-, Cr-Salen show improved responses toward SCN^- and Al-Sal based membrane electrodes a very good selectivity for fluoride ion.

Copper(II) selective electrodes have been fabricated from PVC matrix membranes containing several Salen ionophores (Fakhari et al. 2005). Of those ionophores employed by the authors the 2,2′-[1,2-ethanndiyl-bis(nitrilomethyllidine)-bis]meta cresol presented the best potentiometric response to Cu(II) ion. The electrode gives a linear potentiometric response in the Cu^{2+} ion concentration range from 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 29.2 ± 0.3 mV decade^{-1} and limit of detection of 3.6×10^{-6} mol L^{-1}. The Cu(II) selective electrode shows a very good selectivity with respect to alkali, alkali earth and some transition metal ions. Jain et al. (2005) prepared ten ion-selective electrodes for Ni(II) using two ionophores. The best performance was obtained with the electrode having membrane of N-(-2-hydroxybenzylidene)-N′-(2-picolyl) ethylenediamine Ni(II) with composition m/m%: ionophore (1%), PVC (33%), chloronaphtalene (65.5%) and sodium tetraphenylborate (0.5%). This electrode exhibits Nernstian response in the concentration range from 3.2×10^{-6} to 5.0×10^{-2} mol L^{-1} of Ni(II) with a slope of 29.0 mV decade^{-1}.

Amperometric/Voltammetric Electrodes Based on Metal-Salen Complexes

Chemically modified electrode (CMEs) comprise a relatively modern approach to electrode system that finds utility in (1) a wide spectrum of basic electrochemical investigations, including the relationship of heterogeneous electron transfer and chemical reactivity to electrode surface chemistry, electrostatic phenomena at electrode surfaces, and electron and ionic transport phenomena in polymers, and (2) the design of electrochemical devices and systems for applications in chemical sensing, energy conversion and storage, molecular electronics, electrochromic displays, corrosion protection, and electro-organic syntheses (Umezawa et al. 2000). The essential distinction between modified electrodes and directed coverage with membranes is that surface modification involves more than just creating a physical barrier–it either changes the surface layers of the electrode itself or creates a layer with some form of chemical as well as physical selectivity. Some electrode processes are enhanced while others are inhibited (Brett and Oliveira-Brett 1998). These electrodes prepared by the modification of a conductive substrate to produce an electrode suited to a particular function, whose properties are different from those of the unmodified substrate. In many cases, the modifying layer is electroactive, acting as a mediator between solution and the electrode substrate in electron transfer. For electroanalytical purposes, such manipulation of molecular composition of the electrode aims at improving sensitivity, selectivity and/or stability allowing for tailoring its response in order to meet analytical needs.

The electrocatalysis at CMEs is used to amplify the detection signal. It consists in acceleration of heterogeneous electron transfer of the target analyte, which is slow at the same potential at a bare electrode, induced by an immobilized charge mediator, i.e., metal-Salen catalyst. The acceleration of such reaction by the immobilized mediator permits the quantification of the analyte at less extreme potentials, because catalyzed electrode reactions usually occur near the formal potential of the mediator (Umezawa et al. 2000). By applying less extreme potentials, both detectability and selectivity can be improved significantly, as compared with those obtained at non-modified electrodes.

Several examples of amperometric/voltammetric electrodes based on metal-Salen complexes are shown in Table 2.

Carbon paste electrodes modified with VO-Salen complex were evaluated for several pharmaceutical compounds (Teixeira et al. 2003; Teixeira et al. 2004a; Teixeira et al. 2004b; Teixeira et al. 2005; Teixeira et al. 2007; Bergamini et al. 2006). In these works, the voltammetric response of the modified electrode is based on two reactions. One electrochemical related to the oxidation of the metallic center of the VO-Salen and the other involving the chemical redox process involving the oxidized form of the complex and the reduced form of the analyte. The major advantage of this

Table 2. Configuration and some characteristics of amperometric and voltammetric sensors modified with salen-complexes

Analyte	Application	Modifier	Immobilization	Linear range (mol L^{-1})	Limit of detection (mol L^{-1})	Lifetime	Ref.
Amoxicillin	Pharmaceutical samples	VO-Salen	Carbon paste	1.9×10^{-5} – 9.2×10^{-5}	8.5×10^{-6}	—	Bergamini et al. 2006
Ascorbic acid	Fruit juices	Co-Salen	Electropolymerized film	1.0×10^{-6} – 1.0×10^{-3}	—	—	Liu et al. 2000
Cysteine	Pharmaceutical samples	VO-Salen	Carbon paste	2.4×10^{-4} – 2.3×10^{-3}	1.7×10^{-4}	—	Teixeira et al. 2005
Dipyrone	Pharmaceutical samples	VO-Salen	Carbon paste	9.9×10^{-6} – 2.8×10^{-3}	7.2×10^{-6}	—	Teixeira et al. 2004
Glucose (I) Uric acid (II)	—	Fe-Salen	Thin film	1.0×10^{-6} – 1.0×10^{-2} (I) 5.0×10^{-6} – 3.0×10^{-5} (II)	1.0×10^{-6} (I) 1.0×10^{-7} (II)	—	Liou et al. 2000
Imino compounds	—	Cu-Salen	Electropolymerized film	—	—	—‘	Azzem et al. 1995
L-dopa	Pharmaceutical samples	VO-Salen	Thin film	1.0×10^{-6} – 1.0×10^{-4}	8.0×10^{-7}	—	Teixeira et al. 2007
Nitric oxide	Biological samples	Co-Salen (I) Fe-Salen (II)	Electropolymerized film	2.0×10^{-8} – 2.8×10^{-6} (I) 2.0×10^{-8} – 1.1×10^{-6} (II)	1.2×10^{-9} (I) 1.0×10^{-9} (II)	$>$5 days	Mao et al. 2000

(*continued*)

Table 2. Continued

Analyte	Application	Modifier	Immobilization	Linear range (mol L^{-1})	Limit of detection (mol L^{-1})	Lifetime	Ref.
		Cu-Salen (III)		2.3×10^{-8} – 2.1×10^{-6} (III)	2.0×10^{-9} (III)		
		Mn-Salen (IV)		4.0×10^{-8} – 1.5×10^{-6} (IV)	2.0×10^{-9} (IV)		
Nitric oxide	Biological samples	Ni-Salen	Electropolymerized film	1.0×10^{-8} – 4.0×10^{-6}	5.0×10^{-9}	>1 month	Mao et al. 1998
Organohalides	—	Co-Salen	Electropolymerized film	—	0.06 ppm	—	Ordaz et al. 2000
Pyridine	—	Ni-Salen	Thin film	2.48×10^{-2} – 1.48×10^{-1}	—	—	Sukwattanasinitt et al. 2003
Pyridoxine	Pharmaceutical samples	VO-Salen	Carbon paste	4.5×10^{-4} – 3.3×10^{-3}	3.7×10^{-5}	—	Teixeira et al. 2004

electrode is the decrease in the over-potential of these analytes and/or the increase in the current magnitude improving the sensibility and selectivity of the technique for the quantification of these compounds.

Electrode modified with cobalt-salen polymer has been employed in the application to the electrocatalytic oxidation of ascorbic acid (Liu et al. 2000). During the polymerization, the continuous increase in the current amplitude of Co(III)/Co(II) and Co(II)/Co(I) cathodic peaks indicating the formation of a polymer at the electrode surface. The over-potential of ascorbic acid is reduced more readily, which is favorable for improvement of the analytical characteristic performance of the electrode. Electrodes modified with metal-salen complexes (Co(II)-salen, Ni-salen and Cu-salen) were evaluated in the electrocatalysis of ascorbic acid. For different metal-salen complexes, the oxidation current of ascorbic acid shows the following order Co-salen > Ni-salen > Cu-salen while the oxidation potential has the reversed order. The response of the electrode modified with Co-salen complex for ascorbic acid (AA) may be explained by the Equations (2) and (3):

$$\text{(electrochemical step)}\quad \text{Co(II)-salen}_{(\text{film})} \longrightarrow [\text{Co(III)- salen}]^{+}_{(\text{film})} + e^{-} \tag{2}$$

$$\text{(chemical step)}\quad 2[\text{Co(III)-salen}]^{+}_{(\text{film})} + \text{AA} \longrightarrow \text{Co(II)-salen}_{(\text{film})} + \text{DA} + 2\text{H}^{+} \tag{3}$$

where DA is dehydroascorbic acid.

Metal-salen polymer modified electrodes have been studied by several groups which described the electrochemical response associated to metal containing salen ligand within their structure, and showed the influence of various experimental parameters on their behavior (medium composition, electrode type, electrode configuration) (Dahm and Peters 1994; Bedioui et al. 1991). Such metal-salen polymer-modified electrodes have been shown to be electrocatalysts for amperometric determination of hydrogen peroxide (Miomandre et al. 2001), nitric oxide (Mao et al. 1998; Zhang et al. 2004) and organohalide derivatives (Ordaz et al. 2000).

A modified electrode with a molecular film of Fe(salen)Cl was prepared and characterized for its application in the indirect detection of glucose and uric acid (Liou and Wang 2000). It is shown by the authors that this compound mimics the catalytic functions of peroxidase for determining hydrogen peroxide. Thus, conductive glass (ITO) electrodes modified by coating a $[\text{Fe-salen}]^{+}$ film containing enzyme (glucose oxidase or uricase) were constructed for determining glucose and uric acid, respectively. The amperometric response of the electrode based on the reduction reaction of the $[\text{Fe-salen}]^{+}$ complex by hydrogen peroxide was linear to each substrate concentration ranged from 1.0×10^{-6} to 1.0×10^{-2} mol L^{-1} for glucose and from 5.0×10^{-6} to 4.0×10^{-5} for uric acid at pH 8.5.

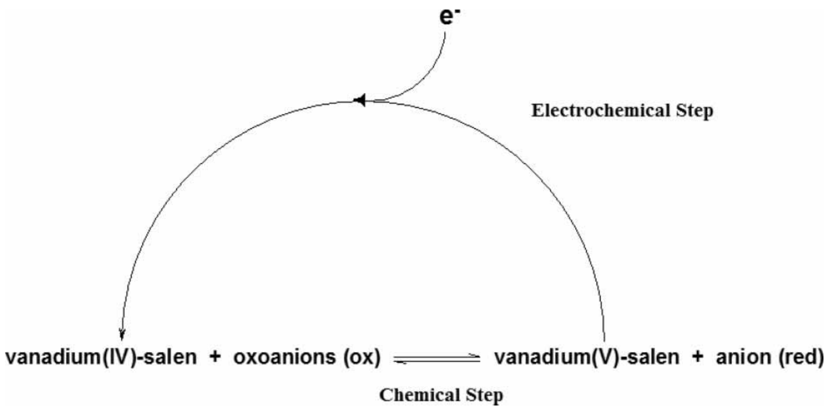
An oxovanadium-salen complex thin film deposited on a graphite–polyurethane electrode was investigated with regard to its potential use for detection of L-dopa in flow injection system (Teixeira et al. 2007). The reaction can be brought about electrochemically where the oxovanadium(IV) complex is first oxidized to oxovanadium(V) complex at the electrode surface. The oxovanadium(V) complex then undergoes a catalytic reduction by the L-dopa in solution back to the oxovanadium(IV) complex, which in turn can be electrochemically reoxidized to produce an enhancement in the oxidation current. The response of the oxovanadium-salen thin film electrode was shown to be more effective than the modified carbon paste electrode (Bergamini et al. 2006). This result indicates that oxovanadium-salen on the surface of the graphite–polyurethane presents higher interaction with the aqueous medium and consequently facilitates the reaction of mediator with the reacting species. Thus the reaction thickness layer for the electrocatalytic process could have a pseudo first-order coupled electrochemical reaction to a chemical reaction.

Salimi et al. (2006) described a glassy carbon electrode modified with multiwall carbon nanotubes (MWCNT) used as a matrix to incorporate a vanadium-Schiff base complex. The immobilization of molecules and biomolecules on MWCNTs has attracted attention due to their significant mechanical strength, high electrical conductivity, high surface area and good chemical stability. The use of MWCNTs affects significantly the electrode reaction for the vanadium(IV)/vanadium(V) oxidation due to the strong interaction of aromatic groups of the Schiff base complex with π-stacking of carbon nanotubes and the possible interaction between vanadium complex and activated carbon nanotubes. In this way, it can be used in electrocatalysis as electron transfer mediator to shuttle electrons between analytes and substrate electrodes. The modified electrodes show excellent electrocatalytic ability for the reduction of iodate, periodate, bromate and nitrite at remarkable positive potential in acidic solutions. The response of the modified electrode for the catalytic reduction is shown in Scheme 1.

APPLICATION

Preparation of a Typical PVC-Membrane Based on Metal-Salen Complexes

To construct the PVC-membrane based metal-Salen Complexes dissolve appropriate amounts of metal-Salen complex (2–8 mg), 50–65 mg of plasticizer (NPOE, NB, DBF, DOP or BA) and appropriate amount of PVC (29–35 mg) in THF (5–10 mL). After complete dissolution of all components and thorough mixing, this cocktail is used to make a membrane (Ganjali et al.



Scheme 1. Response of the Vanadium(IV)-Salen modified electrode for the catalytic reduction of various oxoanions.

2002; Ganjali et al. 2003; Jain et al. 2005; Fakhari et al. 2005) or 5 to 50 μl of cocktail solution is applied directly to a conductive material such as glass carbon electrode, carbon-resin epoxy composite electrode, platinum or copper wire (Cattrall 1997; Fatibello-Filho et al. 2007). The ion-selective electrode is placed in a 0.1 mol L^{-1} buffer or supporting solution containing from 10^{-3} to 10^{-1} mol L^{-1} of analyte for 1–4 h before use and is stored as recommended below.

Operational Properties of Potentiometric Electrodes Modified with Metal-Salen Complexes

As described, the metal-Salen modified potentiometric electrodes should be preconditioned in a 0.1 mol L^{-1} buffer or supporting solution containing 10^{-3}–10^{-1} mol L^{-1} of analyte for at least 1 h prior to use. It is often convenient to precondition the electrode in a 0.1 mol L^{-1} buffer or supporting solution containing 10^{-3}–10^{-1} mol L^{-1} of analyte overnight. During periods of frequent use, the ISE should be stored in the 0.1 mol L^{-1} buffer or supporting solution containing 10^{-3}–10^{-1} mol L^{-1} of analyte. Prior to each use, the ISE should be soaked *ca* 10–20 min in buffer or supporting solution. In the case of coated wire or rod ISEs they may be stored dry when not in use, but should be preconditioned again prior to reuse.

Table 1 gives a list of some potentiometric electrodes based on metal-salen complexes that have been prepared for analysis of several analytes in biological, environmental, food, and industrial samples. This table also presents the sample matrix, the metal-salen complex used (modifier), membrane, the range of determinable concentration, the limit of detection, the lifetime and/or stability of the ion-selective electrode. Except for one ion-selective electrode, the selective membranes were prepared with the metal-salen complex, plasticizer (NPOE, NB, DBF, DOP or BA) and PVC. As discussed above, the sensitivity and selectivity of an ISE depend not only on the nature of binding sites used, but also on the membrane composition and the properties of solvent mediators and additives used (Janata 1989; Cattrall 1997; Ganjali 2005; Badr 2006), which controls the internal dielectric constant, lipophilicity, transport, and other mechanical and electrical properties of the membrane, thus it is very important to study the effect of membrane composition, nature of solvent mediator and additives used on the potentiometric response of the ion-selective electrode. Several methods for the determination of potentiometric selectivity coefficients are based on the Nicolsky-Eisenman Equation (1). These methods were explained in some detail in the 2000 IUPAC publication (Umezawa et al. 2000) and are comprised of 1) mixed solution methods: (a) fixed interference method (FIM), (b) two solutions method (TSM) and (c) matched potential method (MPM) and 2) separate solution methods: (a) separate solution methods ($a_A = a_B$) (SSM) and (b) separate solution method ($E_A = E$) (SSM ($E_A = E_B$)). The matched potential method (MPM) was used preferentially in those works shown in Table 1 (Ganjali et al. 2001; Ganjali et al. 2002; Ganjali et al. 2003, Ganjali et al. 2004; Fakhari et al. 2005; Ganjali et al. 2005; Jain et al. 2005; Meyerhoff et al. 2005; Ganjali et al. 2006) followed by the separate solution methods ($a_A = a_B$) (SSM) (Jain et al. 2005; Badr 2006). As discussed, the smaller the value of the selectivity coefficient, the more selective is the electrode. The $K_{A,B^{pot}}$ determined ranged from 1.0×10^{-2} to 5.2×10^{-6} indicating that they exhibit sufficient selectivity toward to each analyte over all the potential interfering species studied.

The range of applicability for potentiometric electrodes based on metal-salen complexes shown in Table 1 is from $7.0 \times 10^{-6} - 1.0 \times 10^{-1}$ mol L^{-1} for bromide titration (Ganjali et al. 2004), $1.0 \times 10^{-5} - 1.0 \times 10^{-1}$ mol L^{-1} for copper(II) in brass and urine (Fakhari et al. 2005), $8.0 \times 10^{-6} - 5. \times 10^{-2}$ mol L^{-1} for iodide (PVC membrane) (Ganjali, et al. 2002), $3.4 \times 10^{-5} - 1.0 \times 10^{-1}$ mol L^{-1} for iodide (modified carbon paste) in titration of silver (I) (Shamsipur et al. 2000), $2.0 \times 10^{-6} - 6.0 \times 10^{-2}$ mol L^{-1} for iodide (PVC membrane) in titration of iodide ion (Yuan et al. 1993), $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ mol L^{-1} for monohydrogen phosphate in fertilizer and wastewater samples (Ganjali et al. 2006), $5.0 \times 10^{-5} - 1.0 \times 10^{-1}$ mol L^{-1} for monohydrogen phosphate in fertilizer (Ganjali et al. 2003), $3.2 \times 10^{-6} - 5.0 \times 10^{-2}$ mol L^{-1} for nickel(II) in biological and environmental samples (Jain et al. 2005), $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ mol L^{-1} for nitrite in freshwater, sediments and biofilms (Ganjali et al. 2003), $1.0 \times 10^{-6} - 1.0 \times 10^{-1}$ mol L^{-1} for thiocyanate in milk samples (Badr et al. 2006) and $5.0 \times 10^{-8} - 1.0 \times 10^{-1}$ mol L^{-1} for triiodide in titration of triiodide (Ganjali et al. 2005). The ranges presented depend on the solubility of the analytes in the buffer or supporting solutions and/or physical/chemical characteristics of each PVC membrane used. The limit of detection as determined from the intersection of two extrapolated segments of the calibration graph were situated 3–10 fold below the low concentration of each calibration curve and the RSD ranged from 1.5 to 5.0% in the study of repeatability.

The typical dynamic response time of potentiometric electrode modified with metal-salen complex is measured after successive immersion of the ISE in a series of analyte solutions, each having 10-fold difference in concentrations. The resulting potential-time responses for those electrodes shown in Table 1 ranged form 10 to 50 s, indicating that the time to reach the equilibrium value for each electrode is very short.

Finally, as shown in Table 1, the lifetime of the potentiometric electrodes modified with metal-salen complexes ranged from two to four months (or from 300 to 800 determinations with each polymeric membrane).

Preparation of a Typical Carbon Paste Electrode Based on Metal-Salen Complexes

To prepare the carbon paste electrode, mix 50 − 60% (m/m) of graphite powder and 10–25% (m/m) of metal-salen complex in a mortar for at least 20 min until the modifier is uniformly dispersed through the graphite powder. Then, 15–30% (m/m) of mineral or melted paraffin is added and mixed for at least 20 min to obtain a homogenous paste (Shamsipur et al. 2001). Alternatively, this mixture can be homogenized by mechanically stirring in a beaker containing 5–10 ml of hexane and the final paste is obtained after the evaporation of organic solvent (Teixeira et al. 2004a; Teixeira et al. 2004b; Teixeira et al. 2005).

The paste is packed into the tip of a 1 ml of a disposable polyethylene syringe (3 mm i.d.) and a copper wire (piston) is inserted to obtain the external electric contact. To obtain a fresh surface apply a manual pressure to the piston and polish the surface with a white paper.

Preparation of Typical Film Electrodes Based on Metal-Salen Complexes

Characterization of metal salen-based electroactive polymers is an active field of research due to their potential application as electrocatalysts and chemical sensors. The preparation of metal-salen complex based modified electrodes is obtained via oxidative electropolymerization of the monomers (salen) on bare electrodes using cyclic voltammetry or constant-potential electrolysis in weak donor deoxygenated organic solvents (Bedioui et al. 1991; Vilas-Boas et al. 1998; Rodyagina et al. 2005). The incorporation of metal-salen complexes into a polymeric system offers some advantages in certain applications such as: the possibility of thickness control; good membrane-forming properties; the film should permit voltammetric measurements to be carried out in aqueous media and easy preparation of the modified electrodes. However, despite intensive investigation over the past decade, the mechanism of polymerization remains a matter of controversy. Towards the middle of the 1990s, two models for the structure of poly-metal-salen complex emerged (Fig. 3): 1) A model accounting for the generation of the stacked polymer complexes (charge transfer complexes) formed due to the donor–acceptor interaction between the ligand of one monomer fragment and the metal center of another (Dahm et al. 1996; Vilas-Boas at al. 1997; Shagisultanova and Kuznetsova 2003) and 2) A model accounting for the generation of the C-C bonds between the phenyl rings of the ligands of individual polymer chain fragments (Audebert et al. 1991; Tarabek et al. 2004).

The electrochemical behavior is dependent on the supporting electrolyte and on the nature of the central metal, and in this last case the mechanism is more complex (Dahm et al. 1996; Hoferkamp and Goldsby 1989). For example, Goldsby et al. (Goldsby et al. 1989) examined the electrochemical behavior of the nickel(II) *bis*(salicylaldimine) complexes by cyclic voltammetry. These authors observed that the complexes are reversibly oxidized in strong donor solvents and that they are oxidatively polymerized at the electrode surface.

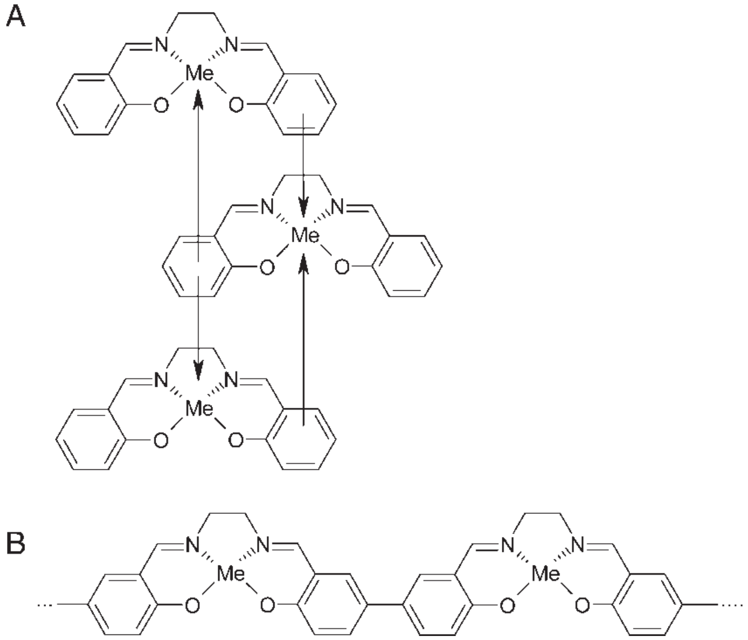


Figure 3. Structure of poly(metal-salen) complexes. A) stack polymer complexes B) polymer chain complexes.

Electropolymerized Film

To obtain an electropolymerized film of metal-salen complex an electrode of different material such as Pt, ITO, glassy carbon or rigid carbon composite is used. In the potential cycling method, the potential is cycled at different scan rates and potential windows for a deoxygenated acetonitrile or DMF solution containing the monomer of metal-salen complex in a supporting electrolyte. To obtain an optimum film thickness the effect of the number of cycles is studied as recommended by Azzem et al. (Azzem et al. 1995). After the electroploymerization, wash the electrode with acetone and distilled water, dry it under an infrared lamp and then coated it with Nafion. Finally, dry it under an infrared lamp for about 1 h before using (Mao et al. 2000; Mao et al. 1998).

Thin Film

Prior to coating, the substrate electrode (Pt, glassy carbon, ITO, graphite composite) should be conditioned following a reported procedure. After the electrode treatment, coating is obtained by the droplet evaporation method. Previously prepare a metal-salen complex solution ($\sim$10 mmol L^{-1} in CH_3CN) to be deposited on the electrode surface, transfer about 100 μL of this solution onto the freshly cleaned surface and wait for total solvent evaporation. Repeat this procedure two more times in order to increase the thickness of the modifier film and thus obtain a more robust sensor (Teixeira et al. 2007). The electrode coated with metal-salen is activated by cyclic voltammetry in KCl solution.

Operational Properties of Amperometric/Voltammetric Metal-Salen Complexes Electrodes

The modification of an electrode surface with metal-salen can be also directed to catalyze an electrochemical reaction, resulting in either a decrease in over-potentials, or an increase in peak currents, or both. Procedures in electroanalysis strongly depend on material aspects such as chemical and physical properties of electrode surfaces, the effects of the applied potential, adsorption, and coatings applied to the electrode surface to enhance detection.

The characteristic properties of carbon paste modified with metal-salen compared to other types of electrodes for electroanalysis are i) a relatively low signal to background current, ii) a wide potential window, iii) easy renewal surface, and iv) easy construction. The principle operational characteristic of these electrodes is the electrocatalytic effect of the metal-salen resulting in the oxidation or reduction of analyte in solution and consequently a decrease in over-potentials. Such cases are typified in the analysis of thiols (Amini et al. 2003; Shahrokhian et al. 2005;

Teixeira et al. 2005), ascorbic acid (Jamasbi et al. 2007), pyridoxine (Teixeira et al. 2005), where Co-salophen (Shahrokhian et al. 2004) and VO-salen complexes (Teixeira et al. 2004; Teixeira et al. 2004) are routinely used to improve the electrode performance. The basic mechanism through which these systems operate is detailed in Fig. 4. The distribution of the metal-salen throughout the electrode material is particularly advantageous in situations where the electrode surface has become irrevocably contaminated. Renewal of the surface through polishing while exposing fresh catalysts therefore bypasses the need for subsequent electrode modification.

Teixeira et al. (2005) have reported the electronic effect of substituent groups on the electrochemical behavior of the VO-salen complex in carbon paste electrode. This is related to the substituent group (electron-withdrawing and/or electron-donating) on the aromatic molecule that significantly influences the electrochemical behavior of the metal-salen complex (Hammett equation) (Fig. 5). The catalytic activity of the VO(5-X-salen) modified carbon paste electrode, where X is the substituent group, is correlated with the electron density located on the metal center and therefore with the redox potential. For example, the -NO_2 is an electron-withdrawing group, which strongly affects the distribution of charge and consequently the electron density located on the metal center shifting the redox potential to more positive values. In general, linear correlations have been found between the redox potential of the

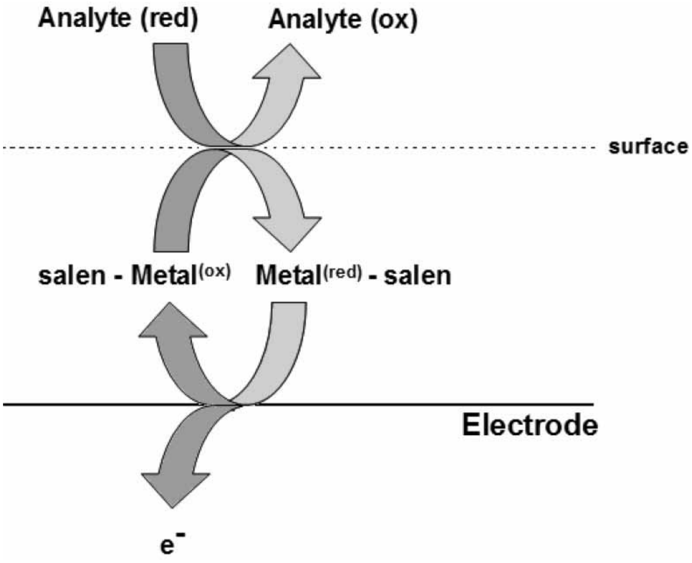


Figure 4. Schematic representation of electrocatalysis at a metal-salen modified electrode. ox = oxided species and red = reduced species.

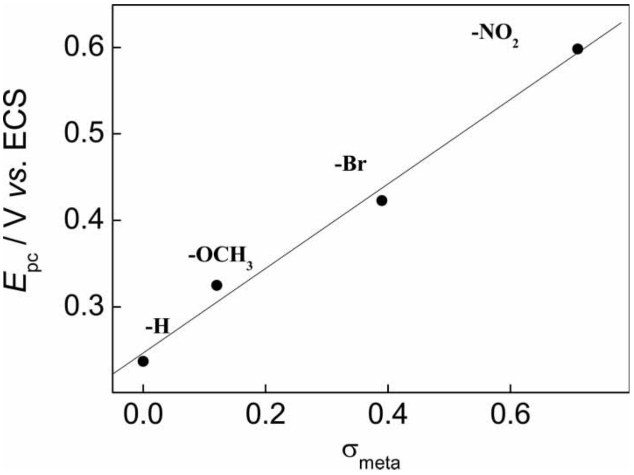


Figure 5. Cathodic peak potential of the carbon paste electrode modified with VO(X-Salen) vs. Hammett constant (Teixeira et al. 2005).

VO(X-Salen) and the catalytic activity for the reduction of hydrogen peroxide for families of substituted and unsubstituted VO-salen (Teixeira et al. 2003).

The formation of stable or saturated complexes is a factor of lack of efficiency in the catalytic process. The introduction of substituents near the coordination sites can enhance the catalytic performance of the metal-salen complex, thus preventing the early transition metal-salen complexes from forming stable and catalytically inert octahedral complexes. This design information can then be used to tune the redox properties of a given metal complex and consequently auxiliary in the development of a sensor. In this way, it can become possible to change the mechanism for electron transfer between metal-salen and analyte, and improve the sensitivity of the electrode and/or the decrease over-potential.

CONCLUSIONS AND OUTLOOK

Electrochemical modified electrodes based on metal-salen complexes have been employed for biological, environmental, food, industrial and pharmaceutical analysis over the past decade. The potentiometric electrodes modified with salen-complexes are easy to prepare and show very good sensitivity and wide dynamic range. High selectivity, low detection limit, rapid response and high stability make these ISE suitable for measuring the concentration of many analytes in wide variety of samples without need of pre-concentration and/or pre-treatment steps. The amperometric/voltammetric metal-salen modified electrodes show electrocatalytic effect toward various analytes, resulting in either a decrease in over-potentials, or an increase in peak currents, or both. Finally, it is shown that a modified electrode with a molecular film of Fe(salen)Cl mimics the catalytic functions of peroxidase for determining hydrogen peroxide.

The synthesis of new metal-salen complexes and their use as ionophore in potentiometric ion-selective electrodes or as a modifier in amperometric/voltammetric electrodes will pave the way for applications of such electrochemical electrodes for the determination of various analytes of interest in many samples.

REFERENCES

Achard, T., Belokon, Y.N., Fuentes, J.A., North, M., and Parsons, T. 2004. Influence of aromatic substituents on metal(II)salen catalysed, asymmetric synthesis of α-methyl α-amino acids. *Tetrahedron*, 60: 5919–5930.

Ambroziak, K. and Szypa, M. 2007. A synthesis of unsymmetrical chiral salen ligands derived from 2-hydroxynaphthaldehyde and substituted salicylaldehydes. *Tetrahedron Lett.*, and refs. therein, 48: 3331–3335.

Amini, M.K., Khorasani, J.H., Khaloo, S.S., and Tangestaninejad, S. 2003. Cobalt(II) salophen-modified carbon-paste electrode for potentiometric and voltammetric determination of cysteine. *Anal. Biochem.*, 320: 32–38.

Aranha, P.E., dos Santos, M.P., Romera, S., and Dockal, E.R. 2007. Synthesis, characterization, and spectroscopic studies of tetradentate Schiff base chromium(III) complexes. *Polyhedron*, and ref. therein, 26: 1373–1382.

Atkins, R., Brewer, G., Kokot, E., Mockler, G.M., and Sinn, E. 1985. Copper(II) and nickel(II) complexes of unsymmetrical tetradentate Schiff base ligands. *Inorg. Chem.*, 24: 127–134.

Audebert, P., Capdevielle, P., and Maumy, M. 1991. Synthesis and characteristics of new redox polymers based on copper containing units; evidence for the participation of copper in the electron transfer mechanism. *New J. Chem.*, 15: 235–237.

Azzem, M.A., Mohamed, Z.F., and Fahmy, H.M. 1995. Electrocatalytic reduction of some imino compounds on a glassy carbon electrode electrochemically modified with a new copper-salen complex. *J. Electroanal. Chem.*, 399: 121–125.

Badr, I.H.A. 2006. Potentiometric anion selective of polymer-membrane electrodes based of cobalt, chromium, and aluminium salens. *Anal. Chim. Acta*, 570: 176–185.

Bedioui, F., Labbe, E., and Gutierrez-Granados, S. 1991a. Electrooxidative polymerization of cobalt, nickel and manganese salen complexes in acetonitrile solution. *J. Electroanal. Chem.*, 301: 267.

Bedioui, F., Labbe, E., Gutierrez-Granados, S., and Devynck, J. 1991b. Electrooxidative polymerization of cobalt, nickel and manganese salen [salen = ethylenebis(salicyldiiminato)] complexes in acetonitrile solution. *J. Electroanal. Chem.*, 301: 267–274.

Bergamini, M.F., Teixeira, M.F.S., Dockal, E.R., Bocchi, N., and Cavalheiro, E.T.G. 2006. Evaluation of different voltammetric techniques in the determination of Amoxicillin using a carbon paste electrode modified with [N,N′-ethylenebis(salicylideneaminato)] oxovanadium(IV). *J. Electrochem. Soc.*, 153: E94–E98.

Brett, C.M.A. and Oliveira-Brett, A.M. 1998. *Electroanalysis*; Compton, R.G. (ed.); Oxford University Press: New York, pp. 37–41.

Bu, X.R., Jackson, C.R., Van Derveer, D., You, X.Z., Meng, Q.J., and Wang, R.X. 1997. New copper(II) complexes incorporating unsymmetrical tetradentate ligands with *cis-*N_2O_2, chromophores: synthesis, molecular structure, substituent effect and thermal stability. *Polyhedron*, 16: 2991–3001.

Campbell, E.J. and Nguyen, S.B.T. 2001. Unsymmetrical salen-type ligands: high yield synthesis of salen-type Schiff bases containing two different benzaldehyde moieties. *Tetrahedron Lett.*, 42: 1221–1225.

Canali, L. and Sherrington, D.C. 1999. Utilization of homogeneous and supported chiral metal(salen) complexes in asymmetric catalysis. *Chem. Soc. Rev.*, 28: 85–93.

Cattrall, R. 1997. *Chemical Sensors*; Compton, R.G. (ed.); Oxford University Press: New York, pp. 13–22.

Cozzi, P.G. 2004. Metal-Salen Schiff base complexes in catalysis: practical aspects. *Chem. Soc. Rev.*, and refs. therein, 33: 410–421.

Dahm, C.E. and Peters, D.G. 1994. Catalytic reduction of Iodoethane and 2-Iodopropane at carbon electrodes coated with anodically polymerized films of nickel(II) salen. *Anal. Chem.*, 66: 3117–3123.

Dahm, C.E., Peters, D.G., and Simonet, J. 1996. Electrochemical and spectroscopic characterization of anodically formed nickel salen polymer films on glassy carbon, platinum, and optically transparent tin oxide electrodes in acetonitrile containing tetramethylammonium tetrafluoroborate. *J. Electroanal. Chem.*, 410: 163–171.

Dalton, C.T., Ryan, K.M., Wall, V.M., Bousquet, C., and Gilheany, D.G. 1998. Recent progress towards the understanding of metal-salen catalysed asymmetric alkene epoxidation. *Top. Catal.*, 5: 75–91.

de Azevedo-Marques, A.P., Dockal, E.R., Skrobot, F.C., and Rosa, I.L.V. 2007. Synthesis, characterization and catalytic study of [N,N′-bis(3-ethoxysalicylidene)-m-xylylenediamine]-oxovanadium(IV) complex. *Inorg. Chem. Commun.*, 10: 255–261.

Fakhari, A.R., Raji, T.A., and Naeimi, H. 2005. Copper-selective PVC membrane electrodes based on salens as carriers. *Sens. and Actuat., B*, 104: 317–323.

Fatibello-Filho, O., Marcolino, Jr, L.H., and Teixeira, M.F.S. 2007. Unpublished results.

Ganjali, M.R., Poursaberi, T., Basiripour, F., Salavati-Niassari, M., Yousefi, M., and Shamsipur, M. 2001. Highly selective thiocyanate poly(vinyl chloride) membrane electrode based on cadimium-Schiffs base complex. *Fresenius J. Anal. Chem.*, 370: 1091–1095.

Ganjali, M.R., Poursaberi, T., Hosseini, M., Salavati-Niasary, M., Yousefi, M., and Shamsipur, M. 2002. Highly selective iodide membrane electrode based on a cerium salen. *Anal. Scienc.*, 18: 289–292.

Ganjali, M.R., Mizani, F., Emami, M., Salavati-Niasari, M., Shamsipur, M., Yousefi, M., and Javanbakht, M. 2003a. Novel liquid membrane electrode for selective determination of monohydrogenphosphate. *Electroanal.*, 15: 139–144.

Ganjali, M.R., Rezapour, M., Pourjavid, M.R., and Salavati-Niasary, M. 2003b. Highly selective PVC-membrane electrodes based on Co(II)-salen for determination of nitrite ion. *Anal. Scienc.*, 19: 1127–1131.

Ganjali, M.R., Norouzi, G., Golmohammadi, M., Rezapou, M., and Salavati-Niasan, M. 2004. Novel bromide PVC-based membrane sensor based on iron(III)-salen. *Electroanalysis*, 16: 910–914.

Ganjali, M.R., Emani, M., Javanbakht, M., Salavati-Niasari, M., Samsipu, M., and Yousefi, M. 2005. Novel Triiodide ion-selective polymeric membrane sensor based on mercury-salen. *Sens. and Actuat. B.*, 105: 127–131.

Ganjali, M.R., Norouzi, P., Hatambeygi, N., and Salavati-Niasari, M. 2006. Anion recognition: fabrication of a highly selective and sensitive HPO_4^{2-} PVC sensor based on a oxo-molybdenum-salen. *J. Braz. Chem. Soc.*, 17: 859–865.

Goldsby, K.A., Blaho, J.K., and Hoferkamp, L.A. 1989. Oxidation of nickel(II) bis(salicylaldimine) complexes: solvent control of the ultimate redox site. *Polyhedron*, 8: 113–115.

Hobday, M.D. and Smith, T.D. 1973. *N, N′*-ethylenebis(salicylideneiminato) transition metal ion chelates. *Coord. Chem. Rev.*, and refs. therein, 9: 311–337.

Hoferkamp, L.A. and Goldsby, K.A. 1989. Surface-modified electrodes based on nickel(II) and copper(II) bis(salicylaldimine) complexes. *Chem. Mater.*, 1: 348–352.

Holm, R.H., Everett-Jr, G.W., and Chakravorty, A. 1966. Metal complexes of Schiff bases and *β*-ketoamines. Prog. *Inorg. Chem.*, and ref. therein, 7: 83–214.

Irie, R., Noda, K., Ito, Y., Matsumoto, N., and Katsuki, T. 1990. Catalytic asymmetric epoxidation of unfunctionalized olefins. *Tetrahedron Lett.*, 31: 7345–7352.

Jacobsen, E.N. 1993. In *Catalytic Asymmetric Synthesis*; Ojima, I. (ed.); VCH: New York, pp. 159–202.

Jacobsen, E.N. and Wu, M.H. 1999. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E.N., Pfalz, A., and Yamamoto, H. (eds.); Springer: New York, and refs. therein, 1309–1326.

Jacobsen, E.N., Zhang, W., and Guler, M.L. 1991. Electronic tuning of asymmetric catalysts. *J. Am. Chem. Soc.*, 113: 6703–6704.

Jain, A.K., Gupta, V.K., Ganeshpure, P.A., and Raisoni, J.R. 2005. Ni(II)-selective ion sensor of salen type Shiff base chelates. *Anal. Chim. Acta*, 553: 177–184.

Jamasbi, E.S., Rouhollahi, A., Shahrokhian, S., Haghgoo, S., and Aghajani, S. 2007. The electrocatalytic examination of cephalosporins at carbon paste electrode modified with CoSalophen. *Talanta*, 71: 1669–1674.

Janata, J. 1989. *Principles of chemical sensors*; Plenum Press: New York, 112–116.

Kaik, M. and Gawroński, J. 2003. Facile monoprotection of *trans*-1,2-diaminocyclohexane. *Tetrahedron: Asymmetry*, 14: 1559–1563.

Kuska, H.A., Farona, M.F., Pappas, P., and Poterton, S. 1972. Unsymmetrical tetradentate complexes of copper(II). *J. Coord. Chem.*, 1: 259–268.

Kwiatkowski, E. and Kwiatkowski, M. 1984. Metal complexes with unsymmetrical tetradentate Schiff bases. *Inorg. Chim. Acta*, 82: 101–109.

Lee, N.H., Lee, C.S., and Jung, D.S. 1998. Selective oxidation of benzylic hydrocarbons to carbonyl compounds catalyzed by Mn(III) salen complexes. *Tetrahedron Lett.*, 39: 1385–1388.

Liou, Y.W. and Wang, C.M. 2000. Peroxidase mimicking: Fe(Salen)Cl modified electrodes, fundamental properties and applications for biosensing. *J. Electroanal. Chem.*, 481: 102–109.

Liu, G.D., Li, Z.Q., Huan, S.S., Shen, G.L., and Yu, R.Q. 2000. Electro-catalytic oxidation of ascorbic acid at a cobalt-salen polymer modified electrode and analytical applications. *Anal. Lett.*, 33: 175–192.

Maeda, T., Takeuchi, T., Furusho, Y., and Takata, T. 2004. Design and synthesis of chiral poly(binaphthyl salen zinc complex) and application of the asymmetric field based on its helical conformation to a catalytic asymmetric reaction. *Polym. Sci., Part A: Polym. Chem.*, 42: 4693–4703.

Mao, L.Q., Yamamoto, K., Zhou, W.L., and Jin, L.T. 2000. Electrochemical nitric oxide sensors based on electropolymerized film of M(salen) with central ions of Fe, Co, Cn, and Mn. *Electroanal.*, 12: 72–77.

Mao, L.Q., Tian, Y., Shi, G.Y., Liu, H.Y., Jin, L.T., Yamamoto, K., Tao, S., and Jin, J.Y. 1998. A new ultramicrosensor for nitric oxide based on electropolymerized film of nickel salen. *Anal. Lett.*, 31: 1991–2007.

Meyerhoff, M.E., Badr, I.H.A., and Mitchell-Koch, J.T. 2005. Highly selective optical and potentiometric fluoride ion sensors based on thin polymeric films doped with aluminum(III)- porphyrins and salens as ionophores. *Abstracts of papers of the American Chemical Society*, 230: U301–U301 260.

Miomandre, F., Audebert, P., Maumy, M., and Uhl, L. 2001. Electrochemical behavior of iron(II) salen and poly(iron-salen). Application to the electrocatalytic reduction of hydrogen peroxide and oxygen. *J. Electroanal. Chem.*, 516: 66–72.

Ordaz, A.A., Rocha, J.M., Aguilar, F.J.A., Granados, S.G., and Bedioui, F. 2000. Electrocatalysis of the reduction of organic halide derivatives at modified electrodes coated by cobalt and iron macrocyclic complex-based films: Application to the electrochemical determination of pollutants. *Analysis*, 28: 238–244.

Palucki, M., Finney, N.S., Pospisil, P.J., Guler, M.L., Ishida, T., and Jacobsen, E.N. 1998. The mechanistic basis for electronic effects on enantioselectivity in the (salen) Mn(III)-catalyzed epoxidation reaction. *J. Am. Chem. Soc.*, 120: 948–954.

Pietikäinen, P. and Haikarainen, A. 2002. Synthesis and catalytic activity of new chiral unsymmetrical Mn(III)-Schiff-base complexes containing salicylaldehyde and 1-(2-hydroxyphenyl)ketone units. *J. Mol. Catal. A: Chem.*, 180: 59–65.

Rodyagina, T.Y., Gaman'kov, P.V., Dmitrieva, E.A., Chepurnaya, I.A., Vasil'eva, S.V., and Timonov, A.M. 2005. Structuring redox polymers poly[M(Schiff)] (M = Ni, Pd; Schiff = Schiff bases) on a molecular level: methods and results of an investigation. *Russian J. Electrochem.*, 41: 1101–1110.

Salimi, A., Mamkhezri, H., and Mohebbi, S. 2006. Electroless deposition of vanadium-Schiff base complex onto carbon nanotubes modified glassy carbon electrode: Application to the low potential detection of iodate, periodate, bromate and nitrite. *Electrochem. Comm.*, 8: 688–696.

Sasaki, I., Pujol, D., and Gaudemer, A. 1987. Non-symmetric Schiff base Co(II) complexes. Synthesis and catalytic activity in the oxidation of 2,6-Di-tert-butylphenol by molecular oxygen. *Inorg. Chim. Acta*, 134: 53–57.

Shagisultanova, G.A. and Kuznetsova, N.N. 2003. Conducting and photoactive polymers on the basis of transition metal complexes: electrochemical synthesis. *Russian J. Coord. Chem.*, 29: 703–709.

Shahrokhian, S., Souri, A., and Khajehsharifi, H. 2004. Electrocatalytic oxidation of penicillamine at a carbon-paste electrode modified with cobalt salophen. *J. Electroanal. Chem.*, 565: 95–101.

Shahrokhian, S., Karimi, M., and Khajehsharifi, H. 2005. Carbon-paste electrode modified with cobalt-5-nitrolsalophen as a sensitive voltammetric sensor for detection of captopril. *Sensors and Actuators, B: Chemical*, 109: 278–284.

Shamsipur, M., Sadeghi, S., Naeimi, H., and Sharghi, H. 2000. Iodide ion-selective PVC membrane electrode based on a recently synthesized salen-Mn(II) complex. *Polish J. of Chem.*, 74: 231–238.

Shin, C.K., Kim, S.J., and Kim, G.J. 2004. New chiral cobalt salen complexes containing Lewis acid BF_3; a highly reactive and enantioselective catalyst for the hydrolytic kinetic resolution of epoxides. *Tetrahedron Lett.*, 45: 7429–7433.

Sukwattanasinitt, M., Nantalaksakul, A., Potisatityuenyong, A., Tuntulani, T., Chailapakul, O., and Praphairakait, N. 2003. An electrochemical sensor from a soluble polymeric Ni-salen complex. *Chem. Mat.*, 15: 4337–4339.

Tarabek, J., Rapta, P., Kalbac, M., and Dunsch, L. 2004. In situ spectroelectrochemistry of poly(N,N′-ethylenebis(salicylideneiminato)Cu(II)). *Anal. Chem.*, 76: 5918–5923.

Teixeira, M.F.S., Dockal, E.R., Lázaro, S.R., and Longo, E. 2003. Redox chemistry of substituted oxovanadium(IV) salen and correlations with Hammett parameters and molecular orbital, In *54th Annual Meeting of the International Society of Electrochemistry*, São Pedro, Brazil, pp. 810.

Teixeira, M.F.S., Marcolino-Junior, L.H., Fatibello-Filho, O., Dockal, E.R., and Cavalheiro, E.T.G. 2004a. Voltammetric determination of dipyrone using a N,N'ethylenebis (salicylideneaminato)oxovanadium(IV) modified carbon-paste electrode. *J. Braz. Chem. Soc.*, 15: 803–808.

Teixeira, M.F.S., Marino, G., Dockal, E.R., and Cavalheiro, E.T.G. 2004b. Voltammetric determination of pyridoxine (Vitamin B-6) at a carbon paste electrode modified with vanadyl(IV)-Salen complex. *Anal. Chim. Acta*, 508: 79–85.

Teixeira, M.F.S., Dockal, E.R., and Cavalheiro, E.T.G. 2005. Sensor for cysteine based on oxovanadium(IV) complex of Salen modified carbon paste electrode. *Sens. and Actuat. B*, 106: 619–625.

Teixeira, M.F.S., Marcolino-Junior, L.H., Fatibello-Filho, O., Dockal, E.R., and Bergamini, M.F. 2007. An electrochemical sensor for L-dopa based on oxovanadium-salen thin film electrode applied flow injection system. *Sens. and Actuat. B*, 122: 549–555.

Tsumaki, T. 2003. Nebenvalenerzingverbindungen. IV. Über einige innerkomplexe Kobaltsalze de Oxyaldimine. *Bull. Chem. Soc. Jpn.*, 13: 252–260.

Umezawa, Y., Bühlmann, P., Umezawa, K., Tohda, K., and Amemiya, S. 2000. Potentiometric selectivity coefficients of ion-selective electrodes, Part I. Inorganic cations. *Pure Appl. Chem.*, 10: 1851–2082.

Verschuren, P.G., van der Baan, J.L., Blaauw, R., de Beer, D., and van den Heuvel, J.C. 1999. A nitrate-selective microelectrode based on a lipophilic derivative of iodocobalt(III)salen. *Fresen. J. Anal. Chem.*, 364: 595–598.

Vilas-Boas, M., Freire, C., Castro, B., Christensen, P.A., and Hillman, A.R. 1997. New insights into the structure and properties of electroactive polymer films derived from [Ni(salen)]. *Inorg. Chem.*, 36: 4919–4929.

Vilas-Boas, M., Freire, C., Castro, B., and Hillman, A.R. 1998. Electrochemical Characterization of a Novel Salen-Type Modified Electrode. *J. Phys. Chem. B*, 102: 8533–8540.

Walsh, C. 1979. *Enzymatic Reaction Mechanisms*; W. H. Freeman: New York.

Xu, L., Yuan, R., Chai, Y.-Q., and Wang, X.-L. 2005. A novel salicylate-selective electrode based on a Sn(IV) complex of salicylal-imino acid Shiff base. *Anal. Bioanal.Chem.*, 381: 781–787.

Yuan, R., Chai, Y.Q., Liu, D., Gao, D., Li, J.Z., and Yu, R.Q. 1993. Schiff-Base complexes of cobalt(II) as neutral carriers for highly selective iodide electrodes. *Anal. Chem.*, 65: 2572–2575.

Zhang, W., Loebach, J.L., Wilson, S.R., and Jacobsen, E.N. 1990. Enantioselective epoxidation of unfunctionalized olefins catalyzed by salen manganese complexes. *J. Am. Chem. Soc.*, 112: 2801–2803.

Zhang, Z., Xing, L., Cai, W., Ren, C., and Jiang, L. 2004. Use of microelectrodes for electrochemical measurement of nitric oxide in natural seawater. *Chin. J. Ocean. Limn.*, 22: 373–380.