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NEW APPOACHES FOR THE DEVELOPMENT OF SOLID-CONTACT ION-SELECTIVE ELECTRODES BASED ON CARBON NANOTUBES

Enrique José Parra Arnó

Dipòsit Legal: T. 273-2012

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New approaches for the development of solid-contact ion-selective electrodes based on carbon nanotubes

Doctoral Thesis
Enrique J. Parra Arnó

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Tarragona, Spain

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Doctoral Thesis
Supervised by Dr. Pascal Blondeau
and Prof. F. Xavier Rius Ferrús

Department of
Analytical Chemistry and Organic Chemistry

UNIVERSITAT ROVIRA I VIRGILI

Tarragona, Spain

2012

Enrique J. Parra Arnó

New approaches for the development of solid-contact ion-selective electrodes based on carbon nanotubes

Tribunal members

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Prof. Pau Ballester (Institut Català d'Investigació Química)

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CERTIFY:

That the Doctoral Thesis entitled: “New approaches for the development of solid-contact ion-selective electrodes based on carbon nanotubes”, presented by ENRIQUE JOSÉ PARRA ARNÓ in order to obtain the Doctor degree, has been carried out under our supervision, at the Department of Analytical Chemistry and Organic Chemistry at the Universitat Rovira i Virgili, and all the results reported in this Thesis were obtained from experiments performed by the above mentioned Doctoral student.

Tarragona, January 19th, 2012

Dr. Pascal Blondeau   Professor F. Xavier Rius

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A mi familia adoptiva en Tarragona, Paulo Delgado y Sandra Giraldo quienes abrieron sin dudar las puertas de su casa y me convirtieron en uno más de la familia.

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“Si al franquear una montaña en la dirección de una estrella, el viajero se deja absorber demasiado por los problemas de la escalada, se arriesga a olvidar cual es la estrella que lo guía”

Antoine de Saint-Exupery (1900-1944)

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Abbreviations

$^{1}H-NMR$	Proton nuclear magnetic resonance
3DOM	Three dimensional ordered macroporous
$^{13}C-NMR$	Carbon-13 nuclear magnetic resonance
$^{31}P-NMR$	Phosphorus-31 nuclear magnetic resonance
Ω	Ohm
a_i	Activity coefficient of ion i
AIBN	Azobisisobutyronitrile initiator
B18C6	Benzo-18-crown-6 ether
CNT	Carbon nanotubes
C_b	Bulk capacitance
C_D	Diffusional pseudocapacitance
C_d	Electronic capacitance
C_{dl}	Double layer capacitance
COOH	Carboxyl function
CWE	Coated wire electrode
EMF	Electromotive force
E_i^o	Standard potential of ion i
ESEM	Scanning electron microscopy
F	Faraday constant (96485 C mol^{-1})
FT – IR	Fourier transform infrared spectroscopy
GC	Glassy carbon
Hz	Hertz
ISE	Ion-selective electrode
ISM	Ion-selective membrane
i	Primary ion i
j	Interfering ion j

$K_{i,j}^{pot}$	Potentiometric selectivity coefficient of ion i and j
KTFPB	potassium tetrakis[3,5-bis(trifluoromethyl)phenylborate
LOD	Limit of detection
MMA	Methylmethacrylate
MWCNT	Multi-walled carbon nanotube
MWCNT – B18C6	Multi-walled carbon nanotube covalently functionalized with benzo-18-crown ether
MWCNT – 1	Multi-walled carbon nanotube non-covalently functionalized with benzo-18-crown ether
MWCNT – Sq	Multi-walled carbon nanotube functionalized with squaramide salt
nA	Nanoampere
NaTFPB	sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate
NaTPB	sodium tetraphenylborate
n – BA	*n*-Butyl acrylate
o – NPOE	*o*-nitrophenyl octyl ether
PEDOT	Poly(3,4-ethylenedioxythiophene)
POT	Poly(3-octylthiophene)
PVB	Poly(vinyl butyral) resin
PVC	Poly(vinyl chloride)
R	Molar gas constant (8.314 J K^{-1} mol^{-1})
R_D	Diffusion resistance
R_S	Solution resistance
SC – ISE	Solid-contact ion-selective electrode
SD	Standard deviation
SDS	sodium dodecylsulfate
SEM	Scanning electron microscopy
Sq	Squaramide salt

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SSM	Separated solution method
SWCNT	Single-walled carbon nanotube
T	Absolute temperature (K)
TDMACl	Tridodecylmethylammonium chloride
TEM	Transmission electron microscopy
TGA	Termogravimetric analysis
V	Volt
Z	Impedance

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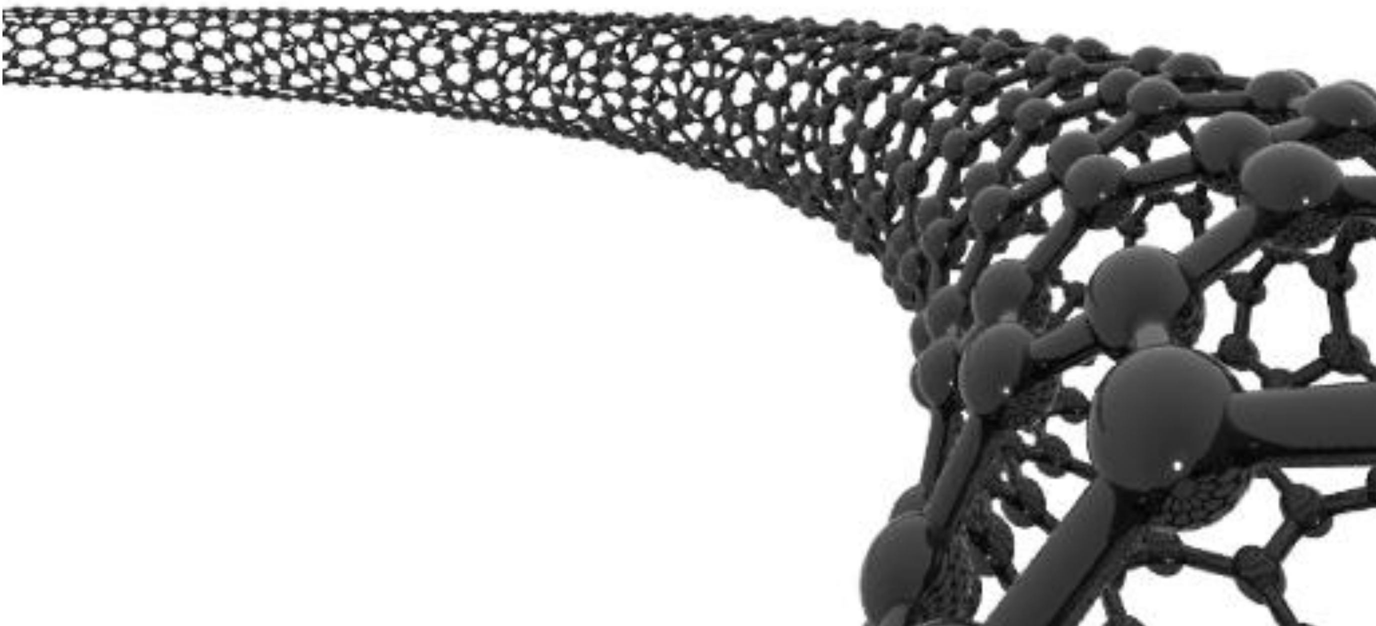
Summary



This Doctoral Thesis intends to provide an insight into the design, construction and operation of ion-selective electrodes based on multi-walled carbon nanotubes (MWCNTs).

The work done in this Doctoral Thesis can be divided into two main parts. In the first part, the incorporation of a MWCNTs layer as ion-to-electron transducer element for solid-contact ion-selective electrodes (SC-ISEs) was studied. The second part was devoted to the development of two different approaches in order to improve the potentiometric characteristics of SC-ISEs. The first approach consisted of the incorporation of new nanostructured materials based on MWCNTs into the polymeric membrane, *i.e.* the ionophore was anchored onto MWCNTs. In this way, both cations and anions were determined with increased analytical performances. The second approach was based on the introduction of an alternative polymeric matrix, a polyvinyl butyral (PVB) resin, to the conventional poly(vinyl chloride) one for the detection of anions.

The main aim of the present Doctoral Thesis is to provide different approaches for effective ions determination in SC-ISEs using MWCNTs as excellent ion-to-electron transducer and further functionalized as new nanostructured hybrid materials.

The Doctoral Thesis has been structured in different Chapters, each one containing the following information:

Chapter 1 includes a brief review of the current state of the art in potentiometric solid-contact ion-selective electrodes with a particular focus on anion detection and describes the general and specific objectives of this Doctoral Thesis.

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Chapter 2 corresponds to the experimental part where the reagents, materials, protocols, instruments and techniques are described.

Chapter 3 provides the demonstration that MWCNTs act as ion-to-electron transducer layer in SC-ISEs. The first SC-ISE is presented and characterized by potentiometry.

In **Chapter 4,** as a proof of concept and divided in two parts, new nanostructured materials based on MWCNTs and benzo-18-crown-6 ether are reported for the detection of cations.

In **Chapter 5,** a new sulfate selective electrode based on a nanostructured material, MWCNTs-squaramide salt, is reported as the first example of stable introduction of highly hydrophilic ionophore into the ion-selective membrane.

Chapter 6 describes the incorporation of a new polymeric matrix based on Poly(vinyl butyral) (PVB) resin with lower lipophilic character than conventional poly(vinyl chloride).

Finally, **Chapter 7** points out the conclusions of the Thesis. Additionally, some further works are suggested.

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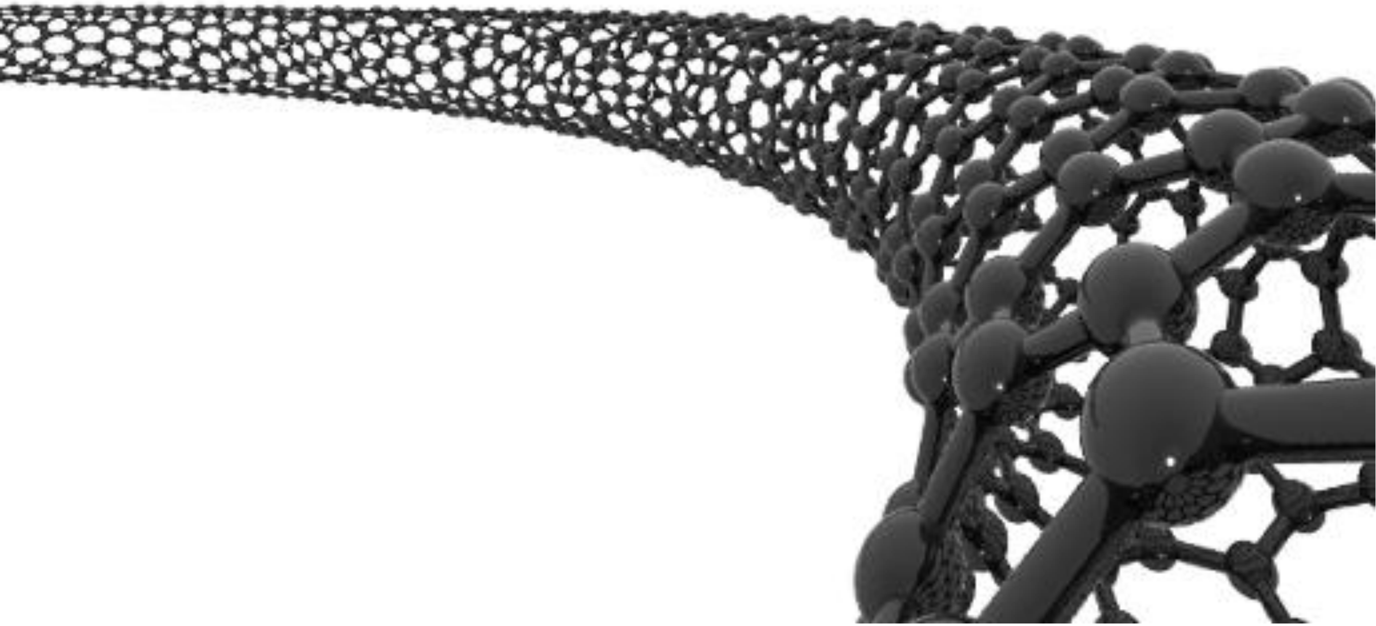
Resumen



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Esta Tesis Doctoral pretende aportar una visión del diseño, construcción y operación de electrodos selectivos de iones basados en nanotubos de carbono de pared múltiple (MWCNTs).

El trabajo realizado en esta Tesis Doctoral se puede dividir en dos partes principales. En la primera parte, se estudió la incorporación de una capa de MWCNTs como elemento transductor ion-electrón en electrodos selectivos de iones de contacto sólido (SC-ISEs). La segunda parte de este trabajo, estuvo dedicada al desarrollo de dos enfoques distintos con el fin de mejorar las características potenciométricas de los SC-ISEs. El primero de estos enfoques, fue la incorporación de nuevos materiales nanoestructurados basados en MWCNTs dentro de una membrana polimérica, donde el receptor se encuentra anclado a los MWCNTs. Así, se determinaron tanto cationes como aniones con elevados parámetros de calidad. El segundo enfoque de esta parte, estuvo dedicado a la introducción de una nueva matriz polimérica como alternativa a las membranas convencionales basadas en cloruro de polivinilo, una matriz polimérica basada en una resina de polivinil butiral.

Así, el objetivo principal de la presente Tesis Doctoral es presentar distintos enfoques para lograr una determinación efectiva de iones con SC-ISEs utilizando MWCNTs como elemento transductor ion-electrón y funcionalizado para formar los nuevos materiales híbridos nanoestructurados.

Esta Tesis Doctoral está estructurada en diferentes capítulos de la siguiente forma:

El **Capítulo 1** incluye un breve resumen de lo reportado actualmente en el campo de SC-ISEs, teniendo un enfoque particular sobre la detección

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de aniones. Así, como una descripción del objetivo general y los objetivos específicos de esta Tesis Doctoral.

El **Capítulo 2** corresponde a la parte experimental donde se describen los reactivos, materiales, protocolos, instrumentos y técnicas utilizadas en este trabajo.

El **Capítulo 3** contiene la demostración experimental del uso de MWCNTs como capa transductora ion-electrón en SC-ISEs. Aquí se presenta y caracteriza potenciométricamente el primer SC-ISE.

En el **Capítulo 4**, como demostración y dividido en dos partes se reportan materiales nanoestrucutrados basados en MWCNTs y éter benzo-18-corona-6 para la detección de cationes en muestras acuosas.

En el **Capítulo 5**, reporta por primera vez la introducción de forma estable de un receptor altamente hidrofílico dentro de una membrana selectiva a iones. Para ello se presenta un SC-ISE para sulfatos basado en un nuevo material nanoestructurado, una sal de MWCNTs-escuaramida.

El **Capítulo 6** describe la incorporación de una nueva matriz polimérica basada en una resina de polivinil butiral (PVB) la cual posee menor carácter lipofílico que el cloruro de polivinilo.

Finalmente, el **Capítulo 7** aporta las conclusiones de esta Tesis. Adicionalmente, se muestran algunas propuestas para trabajos posteriores.

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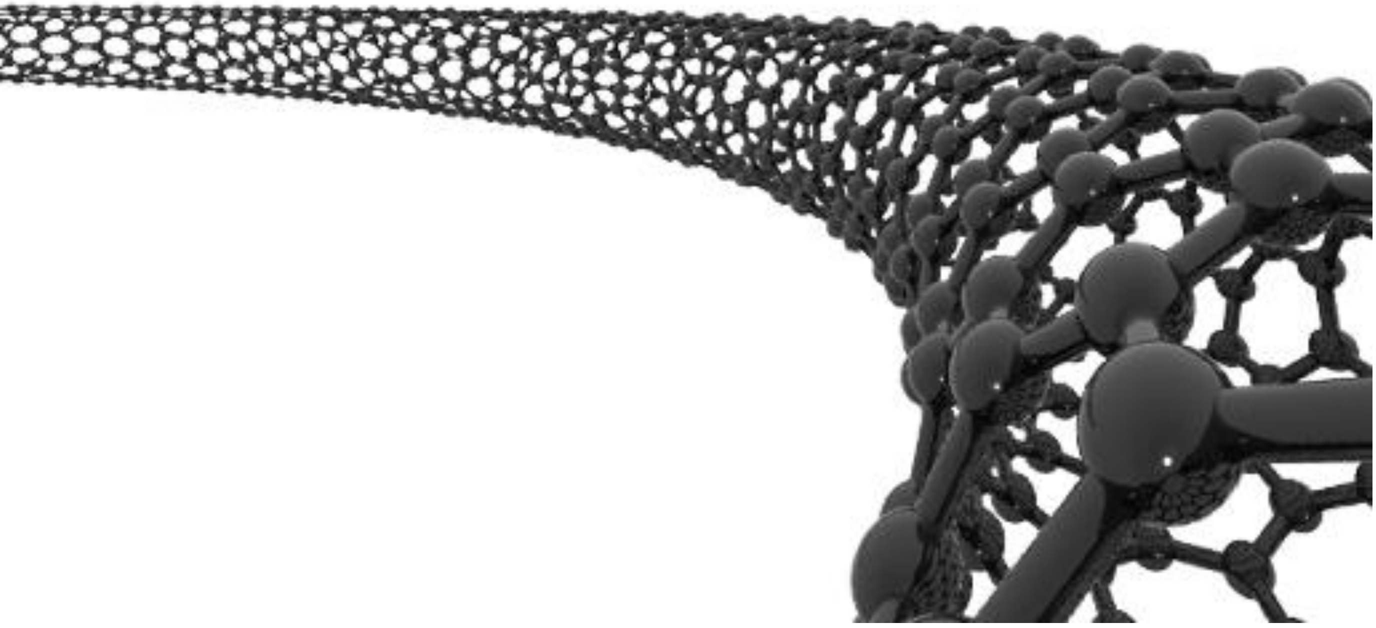
Chapter 1

Introduction



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The main aim of the present Doctoral Thesis is to study and develop alternative approaches for effective determination of ions using solid-contact ion-selective electrodes (SC-ISEs). In order to achieve such goal, multi-walled carbon nanotubes are incorporated as excellent ion-to-electron transducers. Additionally, they have been functionalized to anchor the ion-recognition element or ionophore, resulting in new nanostructured hybrid materials.

The Thesis has the following structure: first, the main concepts and principles as well as the objectives of the present work are presented in the introduction. The second Chapter contains the experimental part, where the reagents, material and procedures are described. Chapters 3, 4, 5 and 6 report the work performed to achieve the specific objectives of this Doctoral Thesis: the use of multi-walled carbon nanotubes, MWCNT, as new components of the ion-to-electron transducer layer, the introduction of new nanostructured materials into the membrane with both transduction and sensing properties for cation and anion determination and the study of poly(vinyl butyral) as new polymeric matrix for ion-selective electrodes. The conclusions and the future prospects are finally listed at the end of the Thesis.

In this introduction, the fundamentals and the state of the art in solid-contact ion-selective electrodes are reported. A particular emphasis on anion detection, so as to provide the specific knowledge on which this Thesis is based, is given.

The present introduction contains three main sections: the first section consists of a brief scientific background section dealing with potentiometry and ion-selective electrodes; the second section reviews the state of the art in anion detection using ion-selective electrodes; and the

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last section presents the main and the specific objectives of this Doctoral Thesis.

1.1. Scientific background

1.1.1. Potentiometry

Potentiometry, as analytical technique, emerged at the beginning of the last century. The measuring instruments have undergone many improvements from the old devices[1], which did not display enough resolution. As a consequence, potentiometers with much higher performance characteristics are available nowadays. Together with the measuring instruments, research on electrochemical sensing mechanisms and their components have been evolving continuously.[2]

In potentiometric analysis, the potential between two electrodes (working and reference electrodes) is measured while the electric current between these electrodes is maintained usually nearly at zero values. Potentiometric sensors offer many benefits due to their versatility and ease of use. Another advantage is the monitoring facilities, using simpler and less expensive devices than other techniques.[3] As a consequence, potentiometric measurements are frequently recorded as routine essays in control and research laboratories. Nevertheless, this kind of sensors also presents some drawbacks such as the difficulty to achieve very low limits of detection and low selectivity in some cases.

1.1.2. Ion-selective electrodes

The largest group of potentiometric sensors is represented by ion-selective electrodes (ISEs). The signal is generated by the charge separation at the interface between the membrane and the solution, due to the selective partitioning of ionic species between these two phases.[4] The potentiometric cell is composed of an ion-selective electrode, a reference electrode, with stable and known reference potential, and a high impedance potentiometer (Figure 1.1).

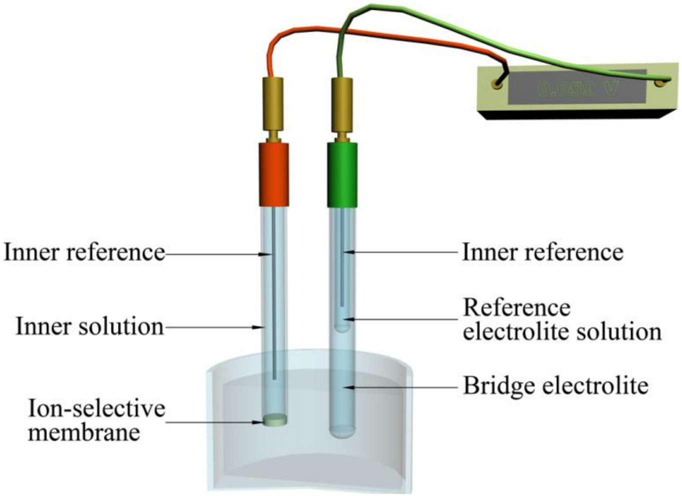

Figure 1.1. A potentiometric cell is composed by a reference electrode (green labelled) and a working ion-selective electrode (red labelled) connected to a high impedance potentiometer.

Two basic configurations of ion-selective membranes are known: 1) the crystalline based membrane, where the recognition layer is a non-water soluble pellet of specific insoluble salts; and 2) the ion-selective membrane (ISM), based on a polymer matrix containing additives, that provides selectivity against a specific ion due to one or more different interactions, *i.e.* the nature of the target (charge and size), the ability to form supramolecular assembly (host-guest) by using weak interactions and/or hydrophobic/hydrophilic forces. Therefore, ISMs are not restricted to one kind of ionophore, in contrast to crystalline based membrane. In principle, ISMs allow introducing any kind of ionophores from inorganic ion exchanger salts to organic compounds with complex molecular interactions and with either hydrophilic or lipophilic character. Because of

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these wider possibilities, ISM based ISEs have been developed more extensively than ISEs based on crystalline membranes.

Being sensors, ISEs have three main different parts: i) The ion-selective membrane (ISM) (or recognition layer) with the selective receptor, known as ionophore, entrapped in a polymeric matrix; ii) The transducer element or transducer layer to convert the ionic current into electronic current; iii) the detector, in this case a potentiometer.

The response of potentiometric sensors is based on complex phenomena[5] that depend on bulk properties of an ion-selective membrane and interfacial properties at both membrane sides governed by composition, thermodynamics and kinetics. Different theoretical models are applied to derive the potentiometric response.[5] One of the simplest sensing mechanism is the phase-boundary potential.[6] In those devices where the membrane is placed between the sample and the inner reference electrolyte, the membrane potential is divided into three separate potential contributions, two phase boundary potentials at both interfaces and the diffusion potential within the ion-selective membrane.[7] The diffusion potential is negligible in most cases[8,9], the internal phase boundary is considered constant and an electrochemical equilibrium at membrane/sample interface is assumed. As a result, the membrane potential depends only on the phase boundary potential between the membrane and the sample.

Moreover, the phase boundary potential at the interface between membrane and sample solution appears as a consequence of charge separations due to the partition ions between the organic phase (membrane) and the aqueous phase (sample). In general, the solvation energies of the anions and cations in the two phases are different.

Consequently, due to the different tendency of ions to pass into the membrane phase, an electrical double layer at the interface appears (charge separation). Furthermore, this phenomenon occurs in the membrane surface, where the electro-neutrality condition is not fulfilled.

However, in most cases a semi-empirical Nikolskii–Eisenman equation holds, linking together the sensor potential and the concentration (activity) of ions in the solution (eq. 1.1).

$$E_M = const + \frac{RT}{z_i F} \log\left(a_i + K_{i,j}^{pot} a_j^{z_i/z_j} + K_{i,l}^{pot} a_l^{z_i/z_l} + \ldots \right)$$ **Equation 1.1**

Where E_M is the EMF experimentally observed (in V); *R* is the gas constant (8.314510 J K^{-1} mol^{-1}); *T* is the absolute temperature (in K); *F* is the Faraday constant (9.6485309x10^4 C mol^{-1}); $a_i, a_j, a_l, \ldots$ are the activities of the ions present in the solution: analyte (i) and interferences $(j, l, \ldots)$; $z_i, z_j, z_l, \ldots$ are the charge number: an integer with sign and magnitude corresponding to the charge of ion: analyte (i) and interferences $(j, l, \ldots)$ respectively; and $K_{i,j}^{pot}, K_{i,l}^{pot}, \ldots$ are the potentiometric selectivity coefficient for ion $(j, l, \ldots)$ with respect to the analyte (i).

1.1.3. Solid-contact ion-selective electrodes

The classical inner solution electrodes suffer from various drawbacks such as the drying out of the inner filling solution, electrode orientation, temperature variations and the pressure range.[10] In the 1970s, the coated-wire electrodes (CWEs), with a simple and robust design[11] tried to solve these drawbacks, however they suffer from poor potential stability. The elimination of the internal filling solution from conventional ISEs gives rise to solid-contact ion-selective electrodes (SC-ISEs) (Figure 1.2). A SC-ISE is an asymmetrical sensor, where the membrane is in one side in contact with a solid-contact or a solid transducer layer instead of an inner solution, and in the another side is in contact with the sample, the aqueous solution.

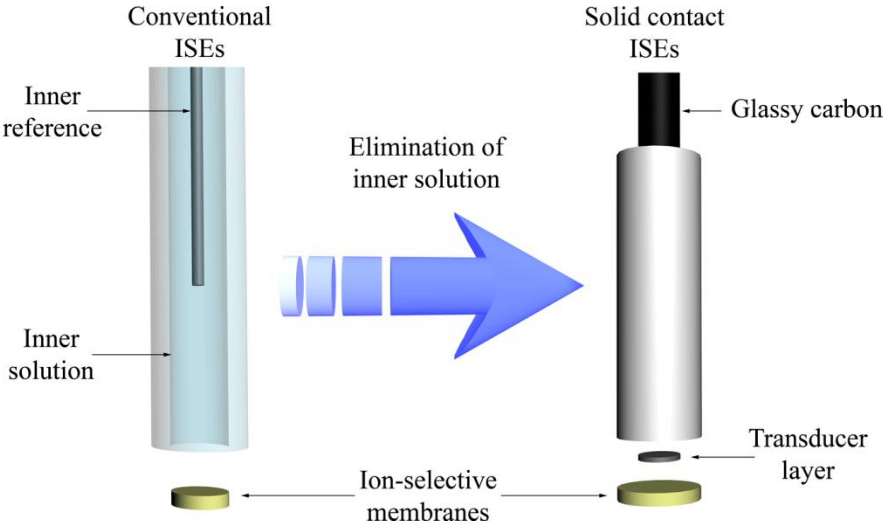

Figure 1.2. Comparison between conventional ion-selective electrodes and solid-contact ion-selective electrodes.

1.1.3.1. State of the art on solid-contact ion-selective electrodes

As mentioned above, since the year when the first CWE was reported[11], a new generation of electrodes without internal filling solution, known as SC-ISEs, started to develop. The elimination of the internal filling solution not only led to the simplicity of the design, but also improved the mechanical flexibility and robustness of the electrodes.[12] However, CWEs suffered from some drawbacks like poor reproducibility and drift potential. These limitations were related to the high charge transfer resistance at the interface between the conductor and the ISM. To overcome the drawbacks of CWEs, a layer between the conductor and the

ISM was introduced, these new configuration is known as solid-contact ion-selective electrodes (SC-ISEs).[13] This layer would act as ion-to-electron transducer which was first achieved by conducting polymers (CP).[5,14-18] This concept was extended later on by the incorporation of the transducers themselves into the ISM.[19-21]

1.1.3.2. Solid transducers

As mentioned above, and due to the poor potentiometric characteristics of the first SC-ISEs, new materials with fast and reversible ion-to-electron transduction characteristics started to attract many researchers.[5] Hence, in the early 1990s, several CPs were introduced as ion-to-electron transducer and emerged a new generation of SC-ISE[18], with CPs such as polyaniline[14], poly(3-octylthiophene)[15] and poly(3,4-ethylenedioxythiophene)[17] (Figure 1.3).

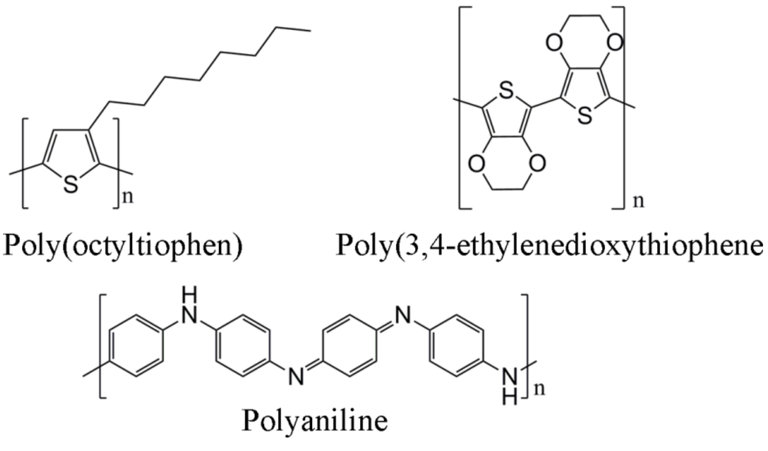

Figure 1.3. Chemical structures of some conducting polymers.

Many efforts have been done by different research teams, such as Bobacka's group[22], to explain the transduction mechanism of CPs. They observed that CPs can act as cationic or anionic exchanger depending of the charge and the mobility of ions incorporated in the doping process.

Hence, if ions approach or move away from the CPs layer a redox reaction occurs and an ion-to-electron transduction process takes place.[23]

However, CP based transducer exhibits some drawbacks[24], *e.g.* undesired secondary redox reactions, sensitivity to CO_2, O_2[5] and to light[25]. Additionally, the formation of a water layer between the ISM and the CP layer is a critical issue for trace measurements as well as for the sensor stability.[26,27]

To overcome some of these drawbacks new materials have been proposed as ion-to-electron transducers. Bühlmann's group reported the use of three-dimensionally ordered macroporous (3DOM) carbon as an ion-to-electron transducer.[28,29] The 3DOM carbon proved to be a promising candidate as a solid-contact transducer with high ionic and electrical conductivity due to well-defined interconnected pore and wall structure.

Others approaches using nanomaterials followed, *e.g.* carbon nanotubes have been extensively studied and used as ion-to-electron transducer.[30-32] The resulting electrodes display a high stability and exhibits very reproducible performance achieving Nernstian responses, low limits of detection and short responses time. In a subsequent study, electrochemical impedance spectroscopy revealed that the small resistance and a large bulk capacitance of the SWCNT based electrodes led to the formation of non-faradaic double layer charging of the porous SWCNTs responsible of the charge transfer processes.[31]

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1.1.3.3. Ion-selective membranes

Ion-selective membranes, ISMs, are an important part of ISEs. Different ion-selective membranes are described in the literature, such as solid state membranes, glass membranes[33] and polymeric membranes.[34]

Here, a polymeric matrix is used to confer mechanical stability to the membrane. In most cases its components are inert and insoluble in water. Because the polymeric matrix provides a lipophilic environment, in contrast with the hydrophilic environment in aqueous samples, the ions distribute between the two phases. Historically, polyvinyl chloride, PVC, with and without plasticizer has been commonly used as matrix and, even though the use of different polymer matrices has been demonstrated, it still remains the standard matrix for carrier-based ISEs.[35,36] Additionally, PVC membranes are easier to prepare and to deposit onto the solid transducer layers than other membranes.[37,38]

Another important component of ISMs is the lipophilic ion exchanger. This is a requirement to obtain a Nernstian response and guarantee the permselectivity (*i.e.*, the selective distribution of only some ions between the membrane and the test solution) of the membrane. They are constituted by a large, lipophilic anion and a small cation or vice-versa. Some lipophilic ion exchangers are reported in the literature, *e.g.* sodium tetraphenylborate (NaTPB) or potassium tetrakis[p-chlorophenylborate] (KTpClPB) as cation exchanger and tridodecylmethylammonium (TDMACl) chloride as anion exchanger.

Finally, and probably they are the most important components of the membrane, the ion receptors known as ionophores. These ionophores are the responsible for the selectivity of the membrane. The ionophore must have stronger affinity to the target analyte (also known as primary ion) than to the other interfering or secondary ions. Therefore, the ionophores are synthesized according to the nature of each analyte (charge, shape and size) as well as considering the ability to form supramolecular assembly (host-guest) by weak van der Waals forces, hydrogen bonds, metal coordination and hydrophilic/lipophilic forces.[39]

1.1.4. Carbon nanotubes

These allotropes of carbon re-discovered by Iijima in 1991[40] have been the centre of interest in many fields. Their name is derived from their long, hollow structure with the walls formed by one-atom-thick sheets of graphene. They can be classified into two groups: carbon nanotubes (CNTs) of a single wall, known as single-walled carbon nanotubes (SWCNTs); and multi-walled carbon nanotubes (MWCNTs), made of several coaxial SWCNTs in a single tube (Figure 1.4). SWCNTs can have either metallic or semiconducting behaviour, depending on the rolling vectors of the graphene sheet; while MWCNTs show metallic behaviour. Both types of CNTs have unusual properties, which are valuable for nanotechnology, electronics, optics and other fields of materials science and technology. Their outstanding properties are the consequence of their chemical structure and high surface-to-volume ratio. These properties make the CNTs an excellent nanomaterial for the transduction between heterogeneous phases[41] and have been incorporated in different devices as field effect transistor (FETs)[42,43], capacitors[44], nanoelectrodes[45] and recently in our research group SWCNTs have been successfully used in carbon nanotubes FETs[46-54], potentiometric ion-selective sensors[30,32,55], direct hydrocarbon detection potentiometry[56] and real time potentiometric bio-sensors.[57,58]

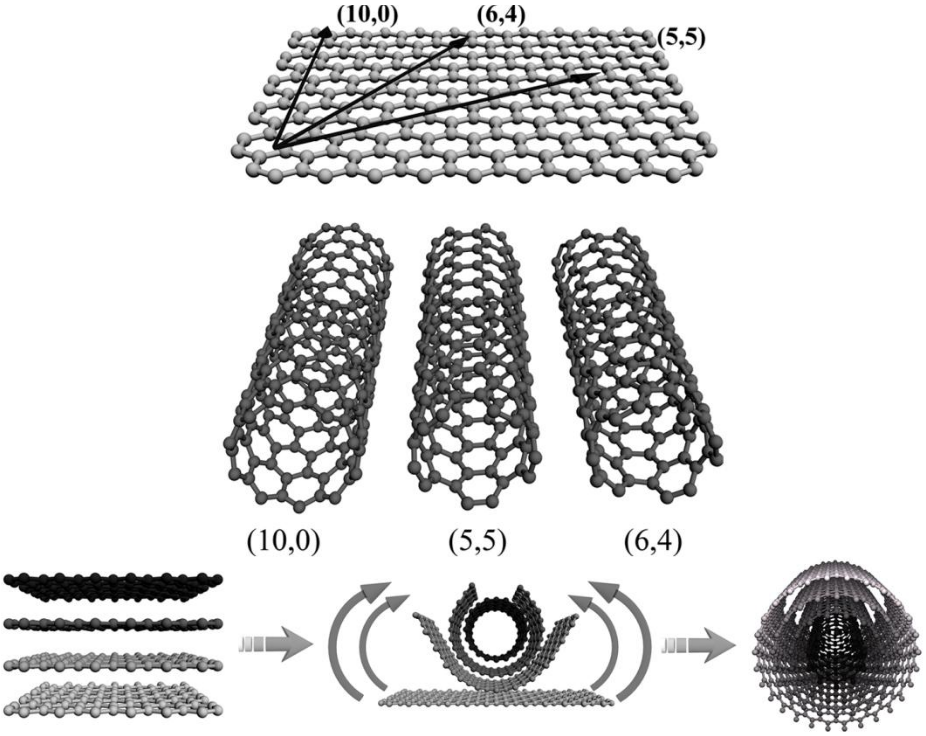

Figure 1.4. The chemical structure of SWCNTs and MWCNTs can be visualized as folding either one or several graphene sheets in defined directions. The wrapping vectors define either semiconducting (*e.g.* 6,4) or metallic (*e.g.* 5,5) behaviour of SWCNTs.

1.2. Ion detection

1.2.1. Cations as analytes

Since the first ISE was introduced, many cation-selective electrodes have been reported.[59] These electrodes are suitable for the detection of cations in real samples with high accuracy, *e.g.* it was estimated that in the United States about 200 million clinical assays of K^+ are made every year with valinomycin-based ISEs.[39] Cation recognition is indeed a well-developed and mature area of supramolecular chemistry so that selective synthetic receptors have been reported for the most common cations.[60] Furthermore, the design of cation receptor is not as challenging as the

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design of anion receptor. Cations are smaller than isoelectronic anions[61] and therefore have a higher charge to radius ratio. This means that electrostatic binding interactions are highly effective. Additionally, cations are less sensitive to pH and they do not suffer from a high degree of solvation in aqueous samples.

Therefore, cation determination through ion-selective electrode is routinely employed in various fields such as clinical, physiology, process control, and environmental analysis.[39]

1.2.2. Anions as analytes

The rapid detection of anions is important in many areas such as to monitor the environment or in clinical analysis. Much research is focussed nowadays towards the development of reliable and simple ways to selectively detect anions.[62]

Anion recognition using the principles of supramolecular chemistry and the design of anion ionophores are less developed than the field of ionophores for cations.[63-65] The first publication on cation and anion receptors appeared almost at the same time: the cation complexation by crown ethers was reported in 1967 by Pedersen[66], and the first anion-selective sensor was reported in 1966 by Frant and Ross[67] followed, in 1968, by Park and Simmons with the first synthetic inorganic anion receptors.[68] However, the field of cation receptors developed faster than the anion receptors. Compared to cation-selective electrode, the slower development of anion ISEs may be related to various differences between anions and cations:[3]

- Ionic size: anions are relatively larger than cations and therefore require larger binding sites, *e.g.* Cl^- (1.67 Å) ions have larger ionic

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radius than K^+ and this latter, a moderately sized cation, has the same ionic radius as the smallest anion, F^- (1.33 Å).

- Geometry: anions have many different shapes, *e.g.* spherical Cl^-, linear SCN^-, tetrahedral SO_4^{2-} and trigonal planar NO_3^-.
- pH window: several anions are present only in a narrow range of pH and the ionisation state can be variable, *e.g.* $H_2PO_4^-$ (pK_{a2} 7.21) and HCO_3^{2-} (pK_{a2} 10.329) anions in an acidic/neutral and basic environment, respectively.
- Solvation: anions undergo strong hydration in comparison to cations of similar size, whereas the solvation by organic solvents is generally less favourable.

Most of polymeric membrane based ISEs consist of a polymeric matrix, ionophore, ionic exchanger and membrane solvent. The nature and the amount of these components determine the characteristics of the sensor.[69] Selectivity of potentiometric sensors is determined by the ion-selective membrane (ISM)[3] and is governed by the partition coefficients of anions. The relative partition is determined by the relative dehydration energies given by the Hofmeister series. Although this series was first established to study the effect of different salts on the solubility of proteins, it can be applied to our case, because it arranges anions according to their decreasing hydrophobicity (and therefore degree of aqueous solvation).[60,70]

$ClO_4^- > SCN^- \approx I^- > \text{salicylate}^- > NO_3^- > Br^- > NO_2^- \approx Cl^- > HCO_3^- > H_2PO_4^- \approx F^- \approx SO_4^{2-}$

In this series of anions, perchlorate is much more hydrophobic than sulfate. Therefore, this sequence indicates that anion sensors based on ion-exchange membranes (containing only the lipophilic ion exchanger, in

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absence of ionophore) are limited to the determination of the relatively most lipophilic anions in solution, because of the high affinity of the lipophilic anion towards the lipophilic polymeric matrix. In practice this means that to be detected accurately, hydrophilic anions must be present in the test sample in much higher concentrations than the more lipophilic ones (see table 1.1). In order to improve the selectivity towards hydrophilic anions, the presence of artificial receptors that bind selectively the anion are mandatory. The presence of the selective receptor favours the introduction of the analyte into the membrane, and improved selectivities can be achieved over the more lipophilic anions present in the same solution.[3]

Table 1.1. **The radius, *r*, width of hydration shell, Δr, number of water molecules in this shell, n, and the electrostatic contribution of the molar Gibbs energies of hydration of ions, $\Delta_{hyd}G^*$.**[71]

Ion	r/nm	Δr/nm	n	$\Delta_{hyd}G^*$/kJ mol^{-1}
CO_3^{2-}	0.178	0.076	4.0	-1300
SO_3^{2-}	0.200	0.059	3.6	-1230
SO_4^{2-}	0.230	0.043	3.1	-1145
F^-	0.133	0.079	2.7	-345
NO_3^-	0.179	0.044	2.0	-275
IO_3^-	0.181	0.043	2.0	-270
Cl^-	0.181	0.043	2.0	-270
CN^-	0.191	0.038	1.9	-260
NO_2^-	0.192	0.037	1.9	-255
Br^-	0.196	0.035	1.8	-250
$H_2PO_4^-$	0.200	0.033	1.8	-245
SCN^-	0.213	0.029	1.7	-230
I^-	0.220	0.026	1.6	-220
ClO_4^-	0.250	0.019	1.4	-180
$B(C_6H_5)_4^-$	0.421	0.004	0.9	15

1.2.3. State of the art in anion detection

As explained above, the detection of anionic species, in many cases, is challenging because of the different shapes, charges, sizes and solvation capability of anions. Therefore, the development of better and different anion-selective electrodes with suitable selectivity is required. In this context, several SC-ISEs for anion detection have been reported. It is important to remark that no significant advances in terms of selectivity have been reported in the last ten years. The Hofmeister series continues to be the usual determining factor in anion detection field. However, large efforts have been focussed on developing new sensors able to detect anions under specific conditions. In addition, new technologies have been reported in order to have robust, easy to build and miniaturized solid-contact ion-selective electrodes, incorporating materials than could be

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used in mass production techniques. In this context, conducting polymers emerged as novel ion-to-electron transducers for many researchers[5]. Nevertheless, recently, the efforts have been focussed on the incorporation of nanostructured materials as ion-to-electron transducers[30] or free membranes system. In these latter systems, the membrane is suppressed so that the recognition event is achieved through specific interactions with the receptor anchored to the transduction element[57] or by specific interactions between the transducer itself and the analyte[56]. Additionally, several authors have applied the knowledge acquired in the cation detention field to develop a proof of concept for the construction of anion sensors. Here a brief review of the last decade is reported showing the recent efforts in solid-contact anion-selective electrodes development, from the last CWE to the newest nanostructured materials.

Gorski *et al.* developed in 2009 a nitrite selective electrode based on a metalloporphyrin as anion-selective ionophore demonstrating that carbon paste with mineral oil, metalloporphyrin and ionic additives in the same amount, act as ionophore in ISM as well as electron- and ion- conducting species to ensure the ion-to-electron transduction. In the same way, they showed that the presence of mineral oil avoids the water layer formation between the conductor wire and the ISM because of the lipophilicity of transduction layer[72]. The motivation to develop new sensors is not only the achievement of better potentiometric performance parameters but also to solve problems in actual applications. In this way, Kumar *et al.*, reported in 2010 a CWE for monohydrogen phosphate as an indicator for the end point determination in the potentiometric titration of phosphate solution. They used a poly(vinyl chloride) (PVC) membrane containing a macrocycle polyamide as ionophore without any ion exchanger and with anti-Hofmeister behaviour (*i.e.* $HPO_4^{2-} > SO_4^{2-} > OAc^- > NO_3^- > ClO_4^- >$

$Cl^- > I^-$), revealing the recognition mechanism of monohydrogen phosphate via hydrogen bond of the ionophore[73]. However, the electrodes showed sub-Nernstian sensitivity, shorter linear range and slower response time than PVC based membranes.

Obtaining very stable and reproducible signal with potentiometry sensors is still challenging, especially in anionic sensing, due to the absence of a fast transduction ion-to-electron between the membrane and the conductor and the presence of a water layer between el conductor wire and the ISM. However, again, from the experience with cations, some scientists proposed to improve the signal stability using conducting polymers. Additionally, SC-ISEs have been widely used in flow injection analysis (FIA). Because FIA needs robustness, small and fast response sensors easy to incorporate to the system so that SC-ISEs are the suitable candidates. As a proof of concept, in 2001, Kovacs *et al.* proposed miniaturized electrodes using polypyrrol (PPy) as transducer to be incorporated into FIA systems obtaining good stability and low limits of detection (0.5 µM) for anionic surfactants and with the ability of processing 30 samples/h[74]. Also, PPy has been proposed for the construction of miniaturized planar screen printed electrodes in 2002 by Zielinska *et al.*, obtaining sensors with longer lifetime for chloride detection when PPy was doped with hexacyano ferrate (II) instead of chloride[75]. In 2003, using an anodic current in the range of microamperes per square centimetre, Michalska *et al.* lowered the limit of detection for chloride selective electrode based on tridodecylmethylammonium chloride ISM by 3 orders of magnitude. They attributed this effect to the compensation of the leakage of doping chloride cause by self-discharging property of PPy and the modification of ion fluxes in the membrane due to the anodic current applied[76]. Additionally, other authors proposed SC-ISEs

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using different CP (*i.e.* Poly(3-octylthiopene) (POT)[77-79] and polyaniline (PANI)[80]) with low limits of detection, wide linear ranges and good stabilities for chloride selective electrodes. Nevertheless, a thorough selectivity study of proposed electrodes is still missing.

Additionally, it is known that the principal drawback of conducting polymers acting as ion-to-electron transducer is the presence of secondary reactions with redox interferences. To solve this weakness, in 2006 Khripoun *et al.* developed a nitrate selective electrode using PANI that was buffered with electron-ion-exchanging resin. Thus, buffering the transducer layer against the changes of redox and acidity conditions improved the stability and the piece-to-piece reproducibility of SC-ISEs.[81]

In an effort to improve the selectivity and sensitivity of SC-ISEs based on CP, Kim *et al.* introduced a new monohydrogen phosphate selective electrode based on a Schiff's base-transition metal complex, the polyterthiophene-appended uranyl-salophen complex (TUS). Here, the phosphate ions were easily accessed due to the uranyl-salophen complex recognition sites in the CP/poly-TUS films. Workable in a small pH window (*i.e.* 7.5-8.5) they reported good electrochemical properties (rapid response time, near-Nernstian slope and significant anti-Hofmeister series behaviour) but short electrode lifetime.[82]

Zhu *et al.* described a new approach where the transducer material (*i.e.* carbon nanotubes) was dispersed into the membrane resulting in a cocktail with both transduction properties and recognition for sodium. In addition, they incorporated ionic liquids instead of plasticizer to obtain a plasticizer-free membrane improving the potential stability and exchanger character against different anions[20].

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Wilson *et al.*, in another approach to improve the electrochemical properties, linked covalently the ionophore to a polymeric support compatible with the ISM. They proposed to resolve mixtures of sulphide and perchlorate anions using electrodes based on metal-phtalocyanine complexes. The resulting sensors showed longer-life time with improved stability due to the absence of ionophore leakage[83].

To summarize, the main efforts have been focussed on developing miniaturized devices with stable signal and longer lifetime. In addition, the new materials and configurations made low-cost electrodes possible. The incorporation of screen printing process allowed making cheaper devices due to mass production. Whereas the elimination of inner internal solution in ISEs is a breakthrough, some drawbacks still remain to be overcome related to some electrochemical properties.

A summary of the characteristics corresponding to the papers reviewed above is presented in table 1.2.

Table 1.2. Summary of the different approaches to detect anions.

Ref	Transducer	Analyte	Main characteristics
72	Carbon Paste	NO_2^-	Similar potentiometric parameters than ISEs. No water layer
73	CWE	HPO_4^{2-}	Worst potentiometric parameters than ISEs Anti-Hofmeister series behaviour
74	PPy (CP)	Anionic surfactants	Incorporation into FIA More than 30 samples/h
75	PPy (CP)	Cl^-	Miniaturized planar ISE Longer lifetime because of Fe^{2+} presence
76	PPy (CP)	Cl^-	Lower LOD by smaller current
77	POT (CP)	Cl^-	Screen printed ISE
78	POT (CP)	Cl^-	Improved Selectivity More stable signal
79	POT (CP)	Cl^-	Lower impedance, same potentiometric parameters
81	PANI (CP)	NO_3^-	No redox reactions with the CP
82	Poly-TUS	HPO_4^{2-}	Transducer-receptor all-in-one / No PVC Workable in small pH range / Anti-Hofmeister behaviour
20	CNT cocktail	Anion exchanger	Transducer dispersed into the polymeric matrix
83	Polyacrylamine	S^-/ClO_4^- mixtures	Receptor covalently linked to a polymeric support

1.2.4. Alternative approaches for solid-contact ion-selective electrodes

The incorporation of ionophores in hydrophobic polymeric membranes has led to ISEs with excellent potentiometric properties and widely used in many fields such as clinical analysis.[39] However, their lifetime can be determined by the lipophilicity of the ionophore due to the leaching of the active components from the ISM to the sample.[84]

The ISM is usually a polymeric matrix that consists of a high molecular weight PVC with a plasticizer, an organic liquid with high boiling point required to increase the polarity of the membrane to favour the partition of ions.[3] However, the PVC matrix often suffers from leaching of their components to the sample solution, which limits the lifetime of the electrodes[85] and restricts their applicability. In fact, it is known that these components can contaminate the samples and rapidly

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deteriorate the potentiometric properties of ISEs.[86] Many efforts have been focussed to overcome these limitations, some examples are the use of self-plasticizing polyacrylate-based membranes[87], the covalent confinement of the active ingredients to the polymer matrix[84,88] or to embedded nanoparticles[89]. In this context, the covalent immobilization of all active components of ISM in nanopores[90] represented an alternative to the traditional construction of ISEs.

Moreover, not only leaching of ISM components into the sample is harmful, but also the adsorption of proteins and cells onto the electrode surface[91,92], known as biofouling. In addition to the biofouling, the extraction of hydrophobic components from the sample to the polymeric matrix can also result in drifts and gradual loss of selectivity.[93,94] In order to overcome those drawbacks, superhydrophobic fluorous polymer based ISMs have been reported[95,96]. Because the extremely poor solvation capacity of these membranes, they hinder the extraction of highly lipophilic components. However, this poor solvation makes the ISMs often incompatible with commercially available ionophores limiting therefore their applicability.

To conclude, many efforts have been done in order to obtain very stable ISEs with excellent potentiometric properties. However, some drawbacks inherent to the components used in ISEs have still to be solved (*e.g.* leaching out of components of polymeric matrix; undesired reactions, light sensitivity or presence of a water layer near the transducing materials).

In order to solve these drawbacks new approaches have to be suggested. Thereby, in this Thesis, new proposals to overcome or reduce the anion detection drawbacks will be discussed. The incorporation of new

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nanostructured transducer material, the chemical modification of hydrophilic receptors in order to keep them into the polymeric membrane and the use of an alternative polymeric matrix will be proposed and discussed in this work.

1.3. Objectives

The main objective of this Doctoral Thesis is the design, development, characterization and application of solid-contact ion-selective electrodes based on multi-walled carbon nanotubes for the determination of inorganic cations and anions in aqueous media.

This general objective is achieved through a series of specific objectives:

- Demonstration that a layer of purified multi-walled carbon nanotubes can act as an effective ion-to-electron transducer in solid-contact ion-selective electrodes.
- Development of a new nanostructured hybrid material, based on multi-walled carbon nanotubes linked to benzo-18-crown-6 ether, which displays both ion-to-electron transduction and selective recognition properties.
- Development of a new nanostructured hybrid material, based on multi-walled carbon nanotubes linked to squaramide-based macrocycle, for the selective determination of sulfate using a solid-contact ion-selective electrode.
- Study of poly(vinyl butyral) resin as a new polymer matrix for the construction of solid-contact ion-selective electrodes.

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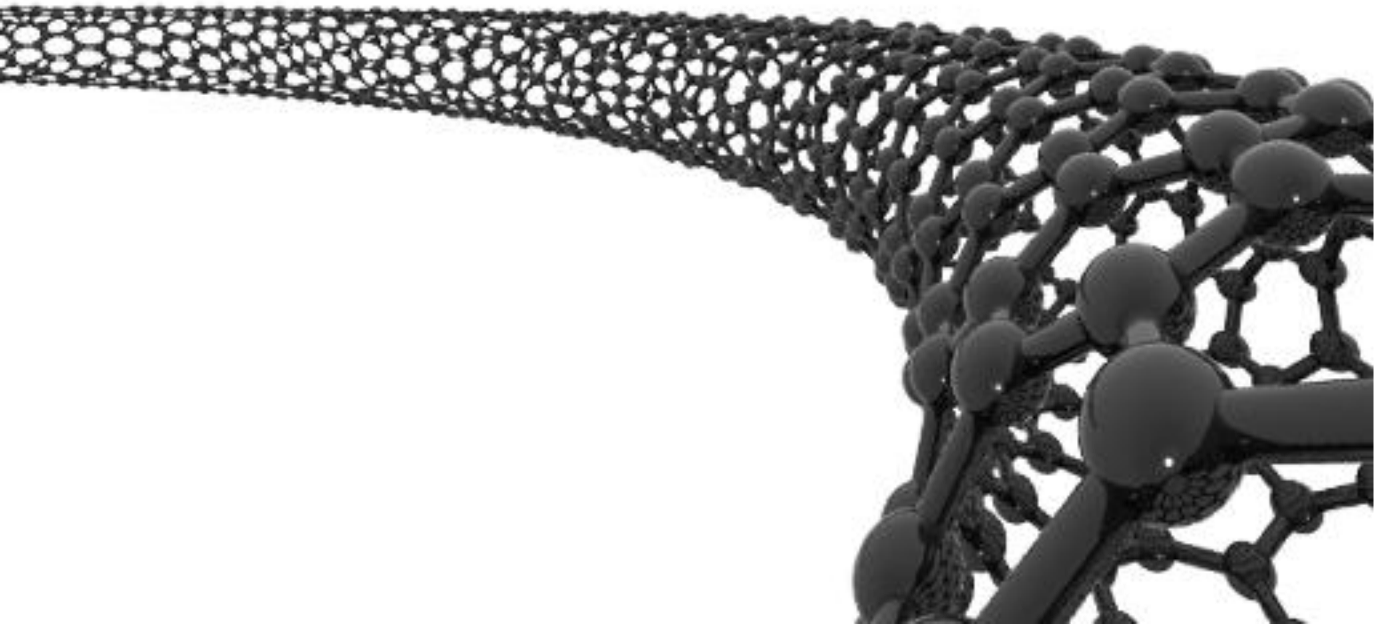
Chapter 2

Experimental part



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2.1. Introduction

The techniques, devices and protocols described in this Chapter have been collected from the experimental part of the different Chapters throughout the Thesis. Here, the reagents and material are listed together with the description of development and construction of the electrodes. Finally, a detailed description of the characterization techniques employed along this work is included.

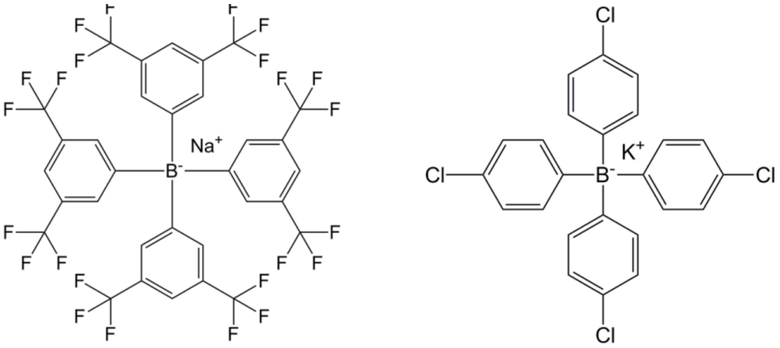
2.2. Reagents

2.2.1. Carbon nanotubes

Multi-walled carbon nanotubes (MWCNT) with > 99% purity, 150 μm average length and 10-20 nm diameter were obtained from HEJI, Inc. (Zengcheng City, China).

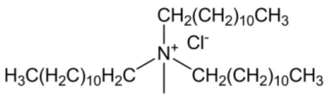
2.2.2. Lipophilic salts

In order to assure the membrane neutrality and the ionic exchange different selectophore® grade lipophilic salts were obtained from Fluka: sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate (NaTFPB), potassium tetrakis(4-clorophenyl)borate (KTClPhB) and tridodecylmethylammonium chloride (TDMACl). The structure of these compounds is displayed in Figure 2.1.



Sodium tetrakis[3,5-bis (trifluoro-methyl)phenyl]borate

Potassium tetrakis (4-chlorophenyl)borate



Tridodecylmethylammonium chloride

Figure 2.1. Lipophilic salts used in this work.

2.2.3. Polymeric matrix

Three different polymeric membranes were used in this work: an acrylic based matrix, a poly(vinyl chloride) matrix (PVC) and a poly(vinyl butyral) resin (PVB).

To synthesize the acrylic based membrane the following reagents were employed from Sigma-Aldrich: methyl methacrylate (MMA), n-butyl acrylate (nBA), radical precursor azobisisobutyronitrile (AIBN) previously re-crystallized in methanol, benzene, petroleum ether (b.p. 80-100 ºC), hexane and dichloromethane. Likewise, Poly(vinyl chloride) high molecular weight (PVC), 2-Nitrophenyl octyl ether (NPOE), Tetrahydrofuran (THF) were purchased from Fluka. Polyvinyl butyral resin BUTVAR® B-98 (PVB) was obtained from Quimidroga, S.A.

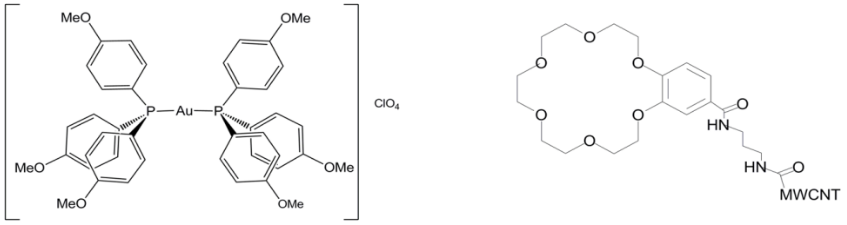
2.2.4. Analytical grade salts

In order to prepare the different cation and anion standard solutions analytical grade salts were purchased form Fluka: sodium perchlorate ($NaClO_4$), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium acetate ($NaCH_3COO$), sodium monohydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium bromide (NaBr), sodium nitrate ($NaNO_3$), sodium bromide (NaBr), sodium nitrate ($NaNO_3$), lead nitrate ($Pb(NO_3)_2$), zinc nitrate ($Zn(NO_3)_2$), calcium nitrate ($Ca(NO_3)_2$), copper nitrate ($Cu(NO_3)_2$), cadmium nitrate ($Cd(NO_3)_2$), magnesium nitrate ($Mg(NO_3)_2$).

2.2.5. Receptors

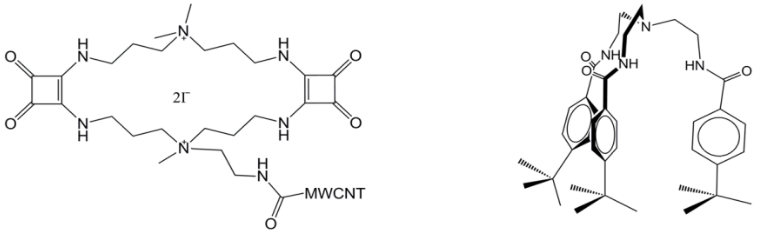
For the synthesis of the receptors used in this work described in each Chapter the following reactive were used, additionally the structures are shown in Figure 2.2:

- For the synthesis of the gold complex used as ionophore for perchlorate in Chapter 3 analytical grade gold (III) chloride tetrahydrate, potassium nitrate, lithium acetate, potassium chloride and tris(4-methoxyphenyl)phosphine were acquired from Sigma-Aldrich.
- In Chapter 4, thionyle chloride ($SOCl_2$), 1,3-diaminopropane, N,N′-Dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), 4′-carboxybenzo-18-crown-6, benzo-18-crown-6 (B18C6) were purchased for the synthesis of the hybrid nanostructure material MWCNT-B18C6.
- The squaramide-based receptor were synthesized and provided by A. Costa’s group (Departament de Química, Universitat de les Illes Balears, Palma de Mallorca, Illes Balears).
- In Chapter 6, the nitrate selective receptor was synthesised following a previous procedure starting from trien and 2-aminoethylcarboxylic acid.[1]



Gold complex
Perchlorate ionophore[2]

Hybrid material
B18C6 lead and potassium ionophore[3]



Squaramide salt
Sulfate ionophore[4]

Tris-[2-(4-tert-butylbenzoyl) aminoethyl]amine. Nitrate ionophore[1]

Figure 2.2. Ionophores used in this work.

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2.2.6. Dispersants

Two different surfactants, used as dispersing agents, were used throughout this work. In Chapter 3, sodium dodecyl sulfate (SDS) was employed as the first surfactant to afford suitable aqueous MWCNTs dispersion that was sprayed onto the glassy carbon conductive layer. In Chapter 4, poly(ethylene-co-acrylic acid) (PEAA) was used to obtain dispersions of the MWCNTs or of the nanostructured materials that were incorporated in the ion-selective membrane.

2.3. Materials and instruments

- Sigradur G glassy carbon rods were obtained from HTW (Thierhaupten, Germany).

- Teflon blocks were obtained from RS Amidata (Pozuelo de Alarcón, Spain).

- Abrasive paper (Carbimet 600/P1200) and alumina with different grain size (30, 5, 1 and 0.03 µm Micropolish II) were obtained from Buehler (Lake Bluff, Illinois, USA).

- Hydrophobic Polytetrafluoroethylene (PTFE) membrane filters (Ø: 47 mm Ø pore: 0.20 µm) were obtained from Albet, LabScience, Germany.

- Double junction reference electrode (Ag/AgCl/KCl 3 M) containing LiAcO 1 M as electrolyte bridge, type 6.0729.100, Metrohm AG, Switzerland.

- High input impedance precision electrochemistry EMF interface EMF-16 (impedance 10^{13} Ω), Lawson Lab, USA.

- High input impedance Keithley programmable electrometer, model 6514 (impedance >2x10^{14} Ω). Keithley, UK.
- Milli-Q PLUS reagent-grade water system (Millipore), France.
- pHmeter GLP21, Grison Instruments SA., Spain.
- Silica furnace chamber, HST 12/600, Carbolite, UK.
- Tip sonicator, Ultrachallprocessor UP200S, Dr. Hielscher, Germany.
- Sonicator Bath (100 W), Selecta, Spain.
- Thermostatic circulator, model 9112, polyscience, USA.
- Environmental scanning electron microscope (ESEM, Quanta 600), scanning electron microscope (SEM, JEOL/JSM-6400) and transmission electron microscope (TEM, JEOL/1011) in the Technical and Scientific Services of our university (SRCiT).

2.4. Procedures

Unless otherwise indicated, the procedures described below were used along the experimental work in this Thesis.

2.4.1. Purification of carbon nanotubes

The MWCNTs were previously purified at 500 ºC in a quartz tubular oven with dry air flow-rate 100 cm^3 min^{-1} during 45 minutes in order to remove any amorphous carbon content. When carboxylated MWCNTs were needed, the oxidized MWCNTs described above were refluxed in 3 M nitric acid for 4 hours.[5] The resulting carboxylated MWCNT were filtered and thoroughly washed with Milli-Q water. The final carboxylated

MWCNTs were dried overnight at 80 ºC, and stored under dry conditions until used.

As an alternative to the acid purification described above and when highly carboxylated MWCNTs were needed, MWCNT were refluxed in H_2SO_4/HNO_3 (3:1) for 30 min. Then filtered on a Millipore membrane (Polycarbonate PC, 0.10 µm) and the solid on the filter was washed with Milli-Q water, dried to afford MWCNT-COOH and stored under dry conditions until used.

2.4.2. Deposition of carbon nanotubes

2.4.2.1. Spraying

0.2% wt. MWCNT powdered in a miller and dispersed in 10 ml 1 % SDS solution was used.[6] The dispersion was homogenized using a tip-sonicator for 30 min. Then a spray-gun containing the dispersion was placed at 30 cm from the top of the electrode. To achieve a homogenous deposition, the MWCNT dispersion was sprayed for 2 s, dried by hot air-blower, thoroughly washed with water and dried with the hot air-blower again. This procedure was repeated 35 times to obtain a layer thickness around 35 µm.

2.4.3. Ion-selective membranes

2.4.3.1. Deposition

All the membranes were deposited by drop casting of 50 µl of ion-selective membrane or sensing cocktail containing the polymeric matrix in THF on the top of the electrodes.

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2.4.3.2. Conditioning

In order to reach lower limits of detection, two basic steps were performed.[7] First; the electrodes were placed in a relatively concentrated solution (10^{-3} M) of the primary ion for 24 h. Then, the electrodes were washed with Milli-Q water and placed in a diluted solution of the primary analyte (10^{-8} or 10^{-9} M) for 48 h. However, calibration curves for a common and rapid test could be obtained either without the second stage or reducing the time.

2.4.4. Development of the ion-selective electrodes

Glassy carbon rods (length 50 mm, Ø 3 mm) were inserted into a hard body Teflon (length 40 mm, external diameter 6 mm and internal diameter 3 mm) by mechanical pressure. The top of the electrode was polished using abrasive paper (Carbimet 600/P1200) and subsequently treated with alumina of different grain-size (30, 5, 1 and 0.03 μm Micropolish II).

In this work two different configuration of electrodes are described (Figure 2.3). The first configuration is named as conventional configuration; these electrodes have three parts well differentiated: conductor (glassy carbon rod), transducer (MWCNT layer) and sensor layer (or ion-selective membrane). In the other configuration, only two parts can be differentiated: conductor (glassy carbon rod) and the membrane cocktail containing receptor and transducer in all-in-one hybrid material dispersed in a polymeric matrix.

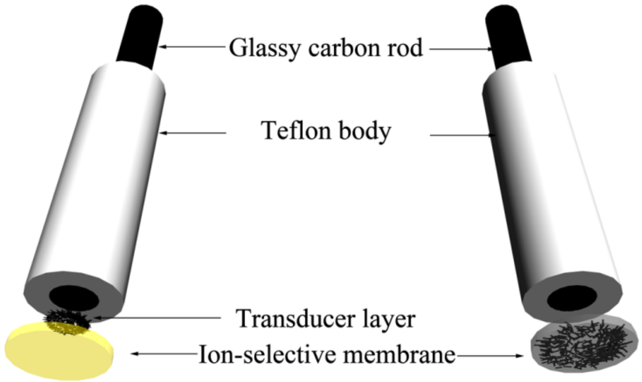

Figure 2.3. Solid-contact ion-selective electrodes developed. Left: SC-ISE developed with two differenced layers: transduction and recognition (ISM). Right: new SC-ISE with transduction and recognition elements in only one layer.

2.5. Electrochemical characterization

2.5.1. Potentiometry

Real time EMF measurements were performed using high impedance Keithley electrometer and/or multichannel EMF-16 Lawson. The EMF was recorded in a two electrodes system, working and reference electrodes, at 22.0±0.5 ºC. Potential values were corrected for liquid junction potentials according to the Henderson equation and the activity coefficients were calculated by the Debye-Hückel approximation.

2.5.1.1. Direct potentiometric measurements

The calibration curves for the different analytes were obtained by successive additions of different concentrated analyte solutions (addition method). Moreover, when the limit of detection was calculated, the method of continuous dilution with adding Milli-Q water (dilution method) was used.[8]

2.5.1.2. Selectivity measurements

Potentiometric selectivity coefficients ($K_{i,j}^{pot}$) were calculated by the separate solution method (SSM).[9] The calibration curves for the interfering ions are measured. If they are Nernstian, $K_{i,j}^{pot}$ is calculated with equation 2.1. However, if the slope is significantly lower than Nernstian, maximal limiting values can be calculated from measurements at high activity of the interfering ion.

$$\log K_{i,j}^{pot} = \frac{E_j^{\circ} - E_i^{\circ}}{RT} z_i F + \log\left(\frac{a_i}{a_j^{z_i/z_j}}\right)$$ **Equation 2.1**

E_i° and E_j° stand for the potential contribution of analyte and interference, respectively. a_i and z_i are the activity and the charge of the analyte, respectively, while a_j and z_j are the same terms for the interfering ion. R, T and F have their usual meaning.

2.5.1.3. Water layer test

In order to show the presence/absence of a water layer between the ion-selective membrane and the carbon nanotubes transducer or the glassy carbon, the water layer test was performed. This water layer has harmful effects since it can favour the presence of the atmospheric gases like O_2 or CO_2, diffused through the ion-selective membrane. The presence of O_2 can favour redox side-reactions while CO_2 can change the pH of the interface, what may result in response drifts. This procedure follows three steps[10]: in the first and the third step the potential was recorded in a 10^{-3} M of the primary analyte solution, in the second step the electrode was submerged into a 10^{-3} M interference ion solution.

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2.5.1.4. Intermediate and long term stability

The intermediate and long term potential stabilities were assessed by measuring the EMF during 5 and 24 hours, respectively, in a thermostatic bath fixed at 22.0±0.5 ºC, using a starting 10^{-5} M analyte solution and adding after 45 min an analyte solution to reach a final concentration of 10^{-3} M analyte.

2.5.2. Electrochemical impedance spectroscopy

Electrochemical measurements were performed by using a three electrode electrochemical cell: working electrode, counter electrode (glassy carbon rod) and the reference electrode. The impedance spectra were recorded in the frequency range 100 kHz-10 mHz and in a concentrated electrolyte solution of the primary ion (10^{-3} M). Impedance measurements were recorded using two different devices: i) an Autolab general purpose electrochemical system, Autolab frequency response analyser system (AUT20.FRA2-AUTOLAB, Eco Chemie, B.V) and ii) electrochemical Analyser/Workstation (Model 600 Series, CH Instruments). The impedance spectra were then fitted to an equivalent electrical circuit by using the CH or the Autolab impedance analysis software.

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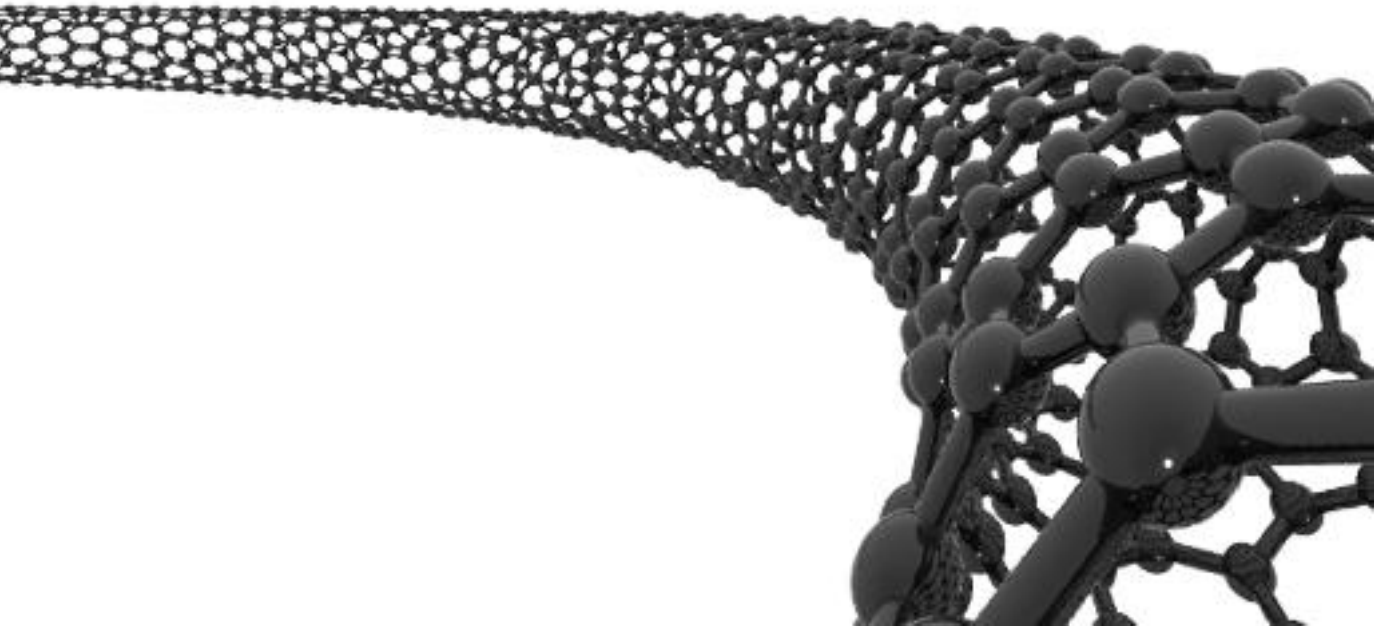
Chapter 3

Multi-walled carbon nanotubes ion-to-electron transducer layer



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3.1. Introduction

The objective of this Chapter is to assess the performance of multi-walled carbon nanotubes as ion-to-electron transducers. In previous studies, our group showed that single-walled carbon nanotubes can act as ion-to-electron transducers in ion-selective electrodes (ISEs). Additionally, it is well known that semiconductor carbon nanotubes are needed in field effect transistors based on carbon nanotubes (CNTFETs). However, because the transduction mechanisms in ISEs and CNTFETs are different, there is an interest to determine whether the multi-walled metallic carbon nanotubes could also act as transducers in ISEs in a similar way as the semiconductor single-walled CNTs.

Hence, an ion-selective electrode based on multi-walled carbon nanotubes as transducer and a gold complex as ionophore for perchlorate determination is presented. This novel approach of solid-contact ion-selective electrode (SC-ISE) was developed to overcome most of the drawbacks of conventional ion-selective electrodes based either on internal solution (*e.g.* inner filling solution drying out, electrode orientation, temperature variations, the pressure range, …) or based on conducting polymers (*e.g.* water layer, undesired redox reactions, …). The new SC-ISE showed very low limit of detection, rapid response time and stable potential in time. The content of this Chapter was published in The Analyst, 134 (2009) 1905-1910.

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3.2. Ion-selective electrodes using multi-walled carbon nanotubes as ion-to-electron transducers for the detection of perchlorate

Enrique J. Parra[†], Gastón A. Crespo[†], Jordi Riu[†], Aurora Ruiz[‡] and F. Xavier Rius[†]

3.2.1. Abstract

A solid-contact ion-selective electrode using for the first time multi-walled carbon nanotubes (MWCNT) for the transducer material was developed for detecting perchlorate in water. To demonstrate the excellent ion-to electron transducer ability of the MWCNTs, a 15 μm thick layer of carboxylated MWCNT was deposited between an acrylic membrane selective to perchlorate ions and a glassy carbon rod used as the substrate and electrical conductor. The electrodes showed a Nernstian response of 57 mV/decade (standard deviation of 3 mV/decade along time and different electrodes) across a wide linear range of 10^{-6} to 10^{-2} M. The limit of detection was $10^{-7.4}$ M of perchlorate. The response time was less than 10 s for activities higher than 10^{-6} M and the intermediate-term potential stability shows a small drift of 0.22 mV h-1 recorded over 5 hours. The electrode displays selectivity comparable to liquid-contacted ISEs containing the same membrane.

3.2.2. Introduction

Perchlorate ions occur both naturally and as a result of chemical synthesis. They are noted for their high solubility, high solvation capacity and high reduction potential in water; properties which make perchlorate ions both chemically stable and a serious risk to human health.[1]

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During recent decades, different methods for determining perchlorate ions in water samples have been developed, including atomic absorption spectrometry,[2] spectrophotometry,[3,4] ion chromatography[5,6] and mass spectrometry.[7] However, electrochemical detection offers several advantages over these methods such as ease of use, low cost, direct detection, miniaturisation and fast response times.[8]

The simplest electrochemical technique is potentiometry. Nowadays, conventional potentiometric ion-selective electrodes (ISE) with an internal solution[9] are highly selective, highly sensitive and have low limits of detection. Solid-contact electrodes can be miniaturized in a more cost-effective manner than conventional ISEs which use an inner solution. The latter, depending on how they are designed, suffer from various drawbacks such as the inner filling solution drying out, electrode orientation, temperature variations and the pressure range.[10]

Recently, new nanostructured materials such as three-dimensionally ordered macropores (3DOM)[11], fullerenes[12], platinized porous silica[13] and single walled carbon nanotubes (SWCNT)[14] have been used to provide transducer layers that can work effectively as ion-to-electron transducers in solid-contact ISEs. This is because the large contact area between the ion-selective membrane and the electronically conducting nanostructured material generates a large double-layer capacitance that stabilizes the potential.[11,15] In addition, carbon nanotubes have a notable charge-transfer capability between heterogeneous phases and can be easily deposited over many surfaces, making them ideal for solid-contact electrodes.[16]

The electrical properties of SWCNT depend on their helicity and diameter.[17] In multi-walled carbon nanotubes (MWCNT) the conduction essentially occurs through the outer shell, but interactions with the inner shells may also change the electronic properties.[18] MWCNT are basically metallic and should be excellent ion-to-electron transducers in ISE; however, they have yet to be tested.

In this article we report the first solid-contact ISE (SC-ISE) that uses for the first time networks of MWCNT as the transducer layer. As a proof-of-concept, we report the performance characteristics of an ISE used to selectively detect perchlorate. Selectivity is achieved by using a ion-exchange polymeric membrane selective to perchlorate which contains the synthesized perchlorate salt (bis[tri-(p-metoxyphenyl)phosphine] gold (I) perchlorate)[19] (Figure 3.1). The new SC-ISE showed improved performance parameters like limit of detection, response time, potential stability and reproducibility over previous electrodes with the same gold complex but without MWCNT. Electrochemical impedance spectroscopy (EIS) was used to determine the electrical performance of the new internal solid-contact material. In addition, a potentiometric water test was carried out to establish the potential stability of the new ISE and the influence of the interfacial water layer.

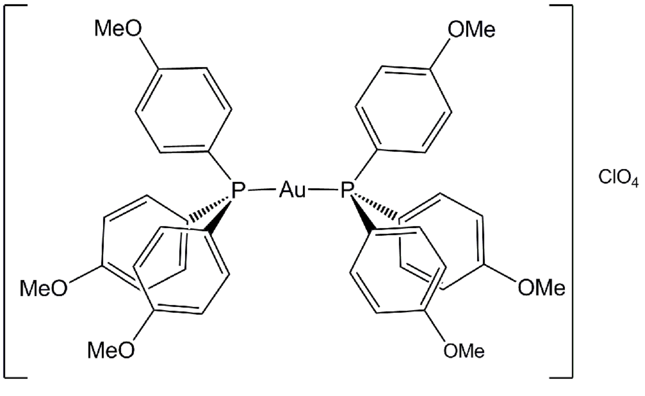

Figure 3.1. The ion-exchange salt used in the membrane (bis[tri-(p-metoxyphenyl)phosphine] gold (I) perchlorate).

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3.2.3. Experimental section

3.2.3.1. Reagents

Fluka (Buchs, Switzerland) provided the sodium perchlorate monohydrated ($NaClO_4{\cdot}H_2O$) selectophore product and the azobisisobutyronitrile (AIBN). Aldrich (Tres Cantos, Spain) provided sodium dodecyl sulfate (SDS), methyl methacrylate (MMA), n-butyl acrylate (nBA), reagent grade benzene, dichloromethane, ethanol, acetone, tetrahydrothiophene, high boiling point petroleum ether (80–100ºC), analytical grade gold(III) chloride tetrahydrate, potassium nitrate, lithium acetate, potassium chloride and tris(4-methoxyphenyl)phosphine. Multi-walled carbon nanotubes (MWCNT) with >95% purity and 10-20 nm in diameter were obtained from HEJI, Inc. (Zengcheng City, China). Deionized and charcoal-treated water (18.2 MΩ·cm specific resistance) were obtained using a Milli-Q PLUS reagent-grade water system (Millipore, Billerica, Massachusetts, USA). Sandpapers and alumina were obtained from Buehler (Lake Bluff, Illinois, USA). Sigradur G glassy carbon rods were obtained from HTW (Thierhaupten, Germany). Teflon blocks were obtained from RS Amidata (Pozuelo de Alarcón, Spain). Environmental scanning electron microscope (ESEM) images were taken using a Quanta 600 (FEI Company, Inc.) provided by the Technical and Scientific Service of our university.

3.2.3.2. Synthesis of gold complex

The bis[tri-(p-metoxyphenyl)phosphine] gold (I) perchlorate was obtained following the procedure proposed by Usón and Laguna[20] and its purity was confirmed using ^{1}H and ^{31}P NMR spectra, recorded on a Varian Gemini 400 MHz spectrometer. Chemical shifts are relative to $SiMe_4$ (^{1}H)

as internal standard or H_3PO_4 (^{31}P) as external standard. Infrared spectrum confirmed the presence of uncoordinated perchlorate anion. This spectrum was obtained using a Jasco FT/IR-600 Plus ATR.

3.2.3.3. Preparation of the polymeric matrix

A modified version of Heng and Hall's procedure was used to synthesize the acrylic polymeric matrix.[21] The membrane was prepared using a 1:10 ratio of MMA and nBA respectively. 0.40 g of MMA and 5.54 g of nBA were mixed in 3 ml of dry benzene. The solution was degassed for 15 min by bubbling with a nitrogen stream, after which 2.8 mg of AIBN initiator was added. After 12 h, the polymer solution was cooled at room temperature, and then a volume of petroleum ether (80–100ºC fractions) equivalent to 10 times the overall volume of the polymeric solution was added under vigorous stirring. White flaky precipitates were formed. The final precipitate was dried under vacuum (0.1 Torr) for 24–48 h before the ion-selective membrane was prepared for the perchlorate.

3.2.3.4. Preparation of the ion-selective membrane for perchlorate

The composition of the membrane was as follows: 98% wt. was made up of the acrylic matrix prepared following the previous section and 2.0% wt. (19.98 mmol Kg^{-1}) was made up of bis[tri-(p-metoxyphenyl)phosphine] gold (I) perchlorate. The membrane was prepared by dissolving the components in 2 ml of dichloromethane and applying external stirring for 30 min.

3.2.3.5. Preparation of the electrodes

Before being deposited over the glassy carbon tip (3 mm Ø), MWCNT were previously purified in two steps: 1) they were baked at 500ºC in a tubular oven with dry air atmosphere for 45 minutes in order to remove amorphous carbon and 2) they were refluxed in 3 M nitric acid for 4 hours.[22] After cooling, the resulting carboxylated MWCNT were filtered, thoroughly washed with water and dispersed in an aqueous solution containing 1% wt. of SDS and 0.2% wt. of MWCNT in order to prevent bundles of MWCNT from forming. 15 ml of the MWCNT solution was sprayed on the top side of a polished glassy carbon rod shielded with Teflon wrapping. The polishing procedure was started with sandpaper 600/P1200 and then followed by alumina 25 and 10 µm.

The last step was the deposition of the ion-selective membrane. About 100 µl of the membrane was drop cast onto the MWCNT network that had been previously deposited on top of the glassy carbon. The membrane was left to dry for approximately 24 hour at room temperature (22 ± 2 ºC).

3.2.3.6. Potentiometric measurements

Electromotive forces (EMF) were measured at room temperature (22 ± 2 °C) in stirred solutions with an EMF16 interface (Lawson Labs, Malvern, PA, USA). A double-junction Ag/AgCl/3 M KCl reference electrode (type 6.0729.100, Metrohm AG, Switzerland) containing a 1 M lithium acetate electrolyte bridge was employed. All measurements were corrected using the Henderson equation[23] and the Debye–Hückel approximation.[24] The calibration curves of the perchlorate were plotted by recording the instrumental signal after consecutive additions of different analyte concentrations (concentration method). The electrode was

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conditioned for 48h in a 10^{-11} M ClO_4^- solution before measurements were taken so as to prevent the membrane equilibrium from causing ion fluxes at low concentrations. The limit of detection (LOD) was determined using Milli-Q water and by following the continuous dilutions procedure (dilution method). In this case the electrode was conditioned for 48h in 10^{-6} M of perchlorate ion and then for 24h in 10^{-4} M of perchlorate ion.

3.2.3.7. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was carried out using a one-compartment, three-electrode electrochemical cell. The working electrode was a glassy carbon rod sprayed with a layer of MWCNT (area 0.07 cm^2) and the counter electrode was a glassy carbon rod. All measurements were taken at room temperature (22 ± 2 °C). All electrochemical impedance measurements were taken using an Autolab general purpose electrochemical system and an Autolab frequency response analyser system (AUT20.FRA2-AUTOLAB, Eco Chemie, Utrecht, The Netherlands). The impedance spectra were recorded in the 100 kHz – 0.01 Hz frequency range and then fitted to an equivalent electrical circuit (previously reported by our research group[14]) for electrodes with SWCNT as the transducer layer.

3.2.4. Results and discussion

3.2.4.1. Characterization of MWCNT

A spaghetti-like layer (15 µm thick) of MWCNT was sprayed over the surface of the glassy carbon. The porosity of the layer allows a very high contact surface between the ion-selective membrane and the MWCNT network. The density of the MWCNT also ensures that there is electrical contact with the conducting wire and that there is no direct contact between the polymeric membrane and the conducting wire.

3.2.4.2. Electrochemical impedance spectroscopy

Figure 3.2 shows the complex impedance plots for the GC/MWCNT electrode in which the spectrum is dominated by a 90° capacitive line that extends down to low frequencies (0.3 Hz). At high frequencies, only a slight deviation from the capacitive line can be observed, indicating a fast transduction across the MWCNT film/electrolyte solution. The value obtained for the capacitance (C_d=200 μF) after the fitting is in the same order of magnitude as that reported for a layer of SWCNT with a thickness of 10 μm.[16]

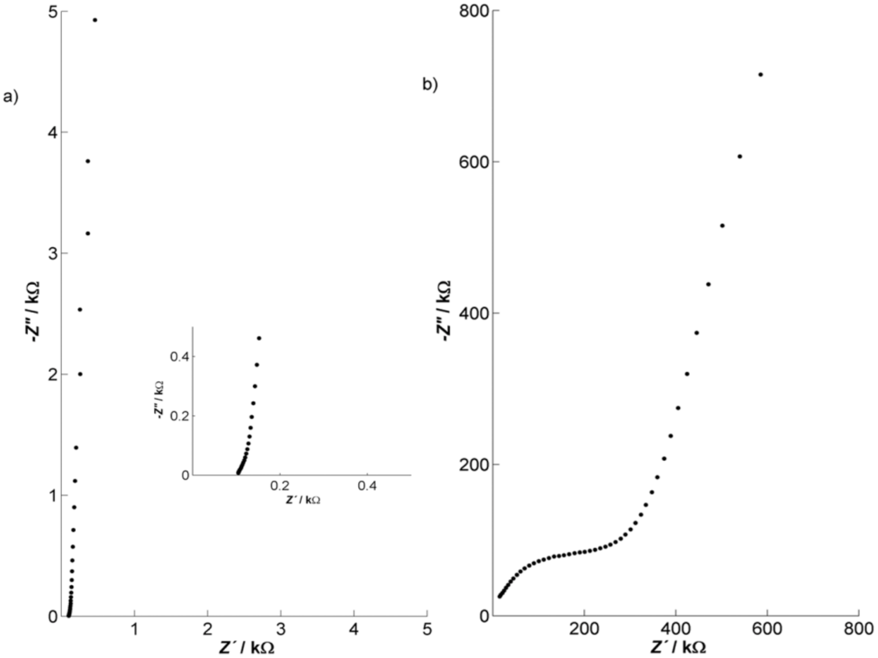

Figure 3.2. Experimental data obtained from Electrochemical Impedance spectrum analysis (EIS). a) Impedance plot of GC/MWCNT recorded at E_{dc}=0.2 V, range 0.3 Hz – 10 kHz. ΔEac=10 mV in 0.01 M $NaClO_4$. Thickness of 15 µm. Inset: range 3 Hz-10 kHz. Fitting values, Rs=102 Ω; Cd= 200 µF. b) Electrochemical Impedance plot of GC/MWCNT/ISM recorded at E_{dc}=0.2 V, range 0.01 Hz – 100 kHz. ΔEac=10 mV in 0.01 M $NaClO_4$. Thickness of 85 µm.

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The impedance measurement of the GC/MWCNT/ISM is shown in Figure 3.2b. This type of spectrum shows the behaviour of the membrane in the electrode. At high frequencies the signal is mainly dominated by the resistance and geometric capacitance in parallel with the membrane, thus revealing a small semicircle between 0.1-200 kHz. On the other hand, at low frequencies a diffusional component (45º line) appears which is related to diffusion of the analyte from the solution into the ISM.

3.2.4.3. Ion-selective electrodes performance parameters

Figure 3.3 shows the change of potential over time for different solutions with increasing activities of perchlorate. Short response times and a high short-term potential stability are observed. As expected, the lowest concentration of perchlorate gives the longest response times because of the longer equilibration time. Thus, concentrations between 10^{-8} and 10^{-7} M have response times of about 1 min, whereas concentrations higher than 10^{-6} M have response times of less than 10 s. The absence of an internal solution improves the response time of the solid-contacted ISE.[25]

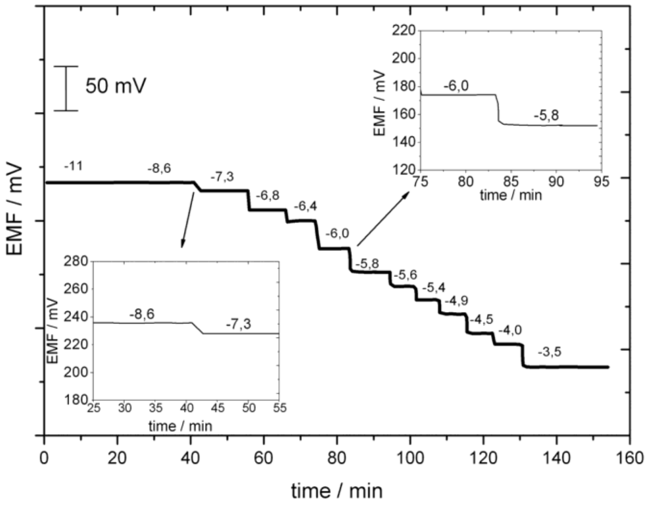

Figure 3.3. EMF values for different solutions displaying increasing ClO_4^- activities recorded over time. Expansions of selected ranges are represented in the insets.

The sensitivity and the linear range of the electrode were evaluated by carrying out several calibration curves between 10^{-11} and 10^{-2} M. The electrode saturates and the EMF values are constant for perchlorate concentrations above 10^{-2} M. The values were based on 12 measurements taken with 6 electrodes (two measurements for each electrode) over three months. In Figure 3.4, the error bars represent the range between the minimum and maximum value for the 12 measurements at each activity value and show that a near-Nernstian slope of 57 mV / decade (SD=3 mV), and a linear range from 10^{-6} to 10^{-2} M were obtained.

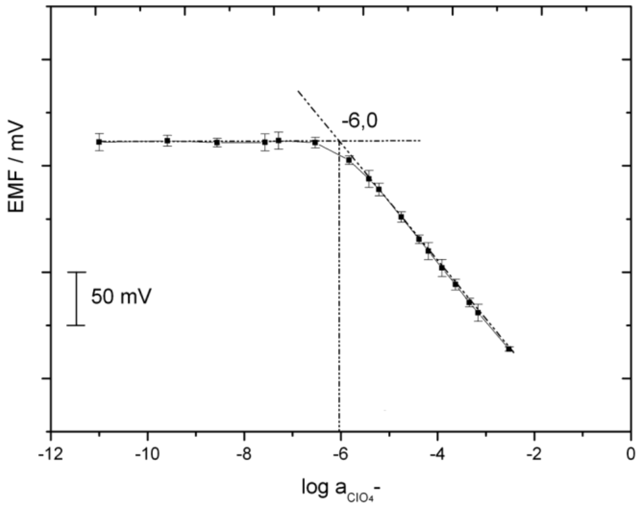

Figure 3.4. EMF dependence on log a_{ClO-} for perchlorate ion-selective electrode, conditioned in 10^{-11} M for 2 days.

In addition, the EMF was measured for five hours using a perchlorate concentration of $10^{-4.4}$ M to determine the intermediate-term potential stability. We obtained a small drift of 0.2 mV h^{-1}. A similar potential stability has also been shown by other solid transducers such as conducting polymers and SWCNT.[15]

The limit of detection (LOD) was obtained using Lai *et al.*'s[11] dilution method. This involves different initial concentration solutions; the starting concentration playing a particularly important role in determining the LOD. Figure 3.5 shows that the lower the concentration of the conditioning and the starting solutions, the lower the LOD obtained. With a starting concentration of 10^{-4} M of perchlorate, a LOD of $10^{-6.0}$ is obtained, whereas if the initial concentration is decreased to $10^{-6.0}$ M of perchlorate, the LOD is reduced to $10^{-7.4}$ M.

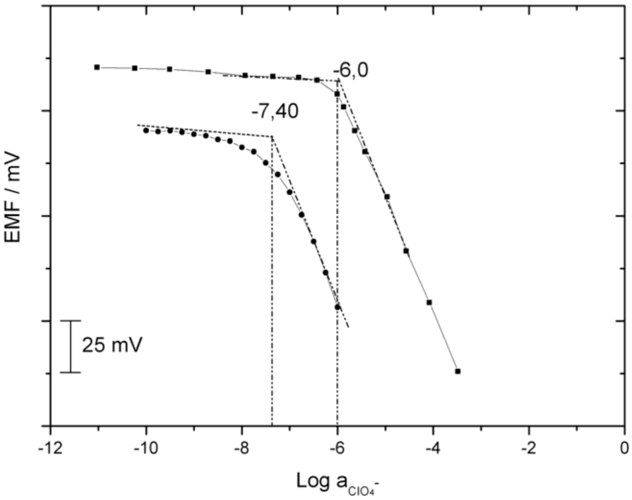

Figure 3.5. Limit of detection for the ISE determined using the dilution method. (-•- starting at 10^{-6} M of perchlorate. -▪- starting at 10^{-4} M of perchlorate).

The behaviour shown in Figure 5 can be explained by the fact that the membrane is exposed to the concentrate solutions of perchlorate in the conditioning solution. This perchlorate is then released from the membrane phase back into the test sample when the membrane is exposed to more diluted solutions.

A preliminary selectivity study was carried out in which the potentiometric selectivity coefficients for different ions were determined in accordance with the IUPAC separated solutions method. This method uses the Nicolsky-Eisenman equation[26] to determine the selectivity coefficient ($K_{A,B}^{pot}$). The results are shown in Table 3.1. The $K_{A,B}^{pot}$ values were compared with the values obtained by Sánchez-Pedreño *et al.*[19] for the same gold complex.

Table 3.1. Potentiometric selectivity coefficient.

Ion	$K_{A,B}^{pot}$	
	Present	Ref[19]
NO_3^-	-3.2	-3.2
SO_4^{2-}	-3.7	-5.0
Cl^-	-3.9	-5.0

3.2.4.4. Water layer test

A water layer test was conducted to show the effect of the water layer between the ion-selective membrane and the MWCNT network. This water layer has harmful effects since it can allow atmospheric gases such as O_2 or CO_2 to be diffused through the ion-selective membrane. The presence of O_2 can favour redox side-reactions whereas CO_2 can change the pH of the interface, which may result in response drifts. This procedure follows three steps.[14] In the first and third steps the potential was recorded in a solution of sodium perchlorate. A very slight negative drift was observed (Figure 3.6), indicating that the primary ion is not accumulated in the water layer. In the second step the electrode was submerged into a $1 \cdot 10^{-4}$ M sodium nitrate solution. The final equilibrium is reached immediately after changing the sample from the primary ion to the interfering nitrate ion, suggesting that the perchlorate is rapidly replaced by nitrate in the membrane. Figure 3.6 shows a very small positive potential drift, which indicates that ClO_4^- is hardly replaced by NO_3^- in the water film formed between the ion-selective membrane and the MWCNT layer. The equilibrium is quickly reached again when the interfering solution is replaced with the initial $1 \cdot 10^{-4}$ M ClO_4^- solution, this causing a slight negative drift. These results indicate that only a reduced or inexistent water layer is formed in our electrode.[27] The highly hydrophobic character of the MWCNT network could be the reason for the absence of the water layer.

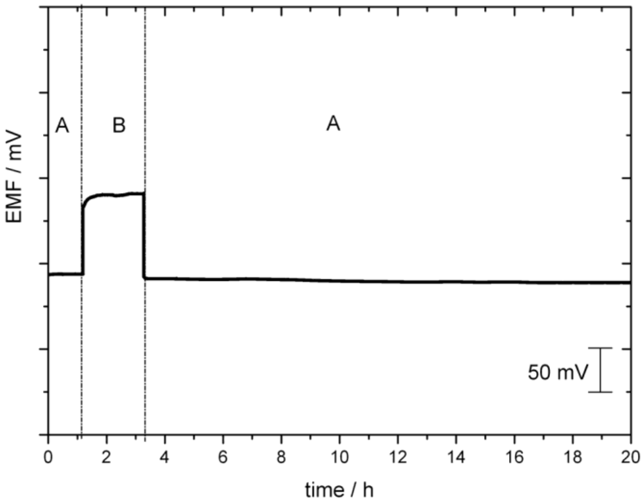

Figure 3.6. Water layer test. The EMF was recorded successively in (A) $KClO_4$ 10^{-4} M and (B) KNO_3 10^{-4} M.

3.2.4.5. Performance parameters

Table 3.2 shows that the all solid-contact ISEs containing MWCNT as the ion-to-electron transducer have important potentiometric characteristics when used for detecting perchlorate. Most of these potentiometric characteristics, like for instance response times and LOD, are better than those reported by Sánchez-Pedreño *et al*.,[19] who used an ISE made with a PVC membrane with an internal solution.

Table 3.2. Response parameters of the ClO_4^- ISE.

Characteristic	Present	Ref[19]
Slope (mV/decade)	57	56.7
Linear range (M)	10^{-6}-10^{-2}	$5x10^{-6}$-$1x10^{-2}$
LOD (M)	$4x10^{-8}$	$1.1x10^{-6}$
Response time (s)	<10	<14
Long-time stability(h)	>5	--

3.2.4.6. Applications

In order to test the ISE in real samples, it was used to determine the concentration of perchlorate in drinking water and tap water to assess it could be practically applied to the selective determination of perchlorate. The analysis was carried out by direct potentiometry using the standard addition method at different known concentrations of perchlorate (10, 100 and 1000 ppm) in order to compare these results with the ones given by Sánchez-Pedreño *et al.*[19] (See Table 3.3).

Table 3.3. Determination of perchlorate ion in drinking water and tap water.

Samples	Perchlorate (ppm)		
	Added	Found[a]	Recovery (%)
Drinking water	10	10.5 (0.5)	105
	100	107 (16)	107
	1000	1059 (58)	106
Tap water	10	9.8 (0.3)	98
	100	99 (1)	99
	1000	989 (42)	99

[a] Mean (standard deviation of three determinations)

Very good recovery values were obtained for the different concentration levels and the two matrices assayed.

3.2.5. Conclusions

We have developed a new solid-contact potentiometric ISE using carboxylated MWCNT as the transducer layer to detect perchlorate. Crespo *et al.*[14,16] have demonstrated that the transduction behaviour of single walled carbon nanotubes can be attributed to a high double layer capacitance in the carbon nanotube's ion-selective membrane. The same behaviour is observed with MWCNT, proving that these are also efficient transducer elements in solid-contact ion-selective electrodes. In contrast with conducting polymers, where the transduction mechanism is based on ion-exchange mechanisms and redox reactions, the new transducer is more robust against any redox side-reactions that might occur in the electrode. The absence of a water layer in the interface between the ion-selective

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membrane and the transducer layer may be a consequence of the hydrophobicity of the MWCNT, as with other nanostructured carbon materials. ISE used to detect perchlorate show a near-Nernstian response, low limit of detection, stability over time and on electrodes, and good selectivity. In general, the present solid-contact ISE showed better performance than the similar electrode that has been previously reported. Moreover, the new solid-contact ISE can be built easily and for a very reasonable cost and, because it is an all-solid state electrode, it is easier to miniaturize. A straightforward way to miniaturize this ISE would be using screen-printing, which is reported to be a reproducible and low-cost technique for the construction of miniaturised planar solid-state thick-film sensors. These miniaturized ISEs are aimed to be reliable and maintenance-free, having fewer limitations in temperature and pressure range than standard ISEs. Furthermore, the low-cost screen-printing fabrication technique allows these miniaturised planar sensors to be disposable, which is very convenient when the user wants to analyse a small volume of sample avoiding cross-contamination between measurements.

3.2.6. Acknowledgments

We would like to thank the Spanish Ministry of Science and Innovation, MICINN, for supporting the work through the project grant CTQ2007-67570/BQU. EP thanks the Universitat Rovira i Virgili for the economic support.

3.2.7. References

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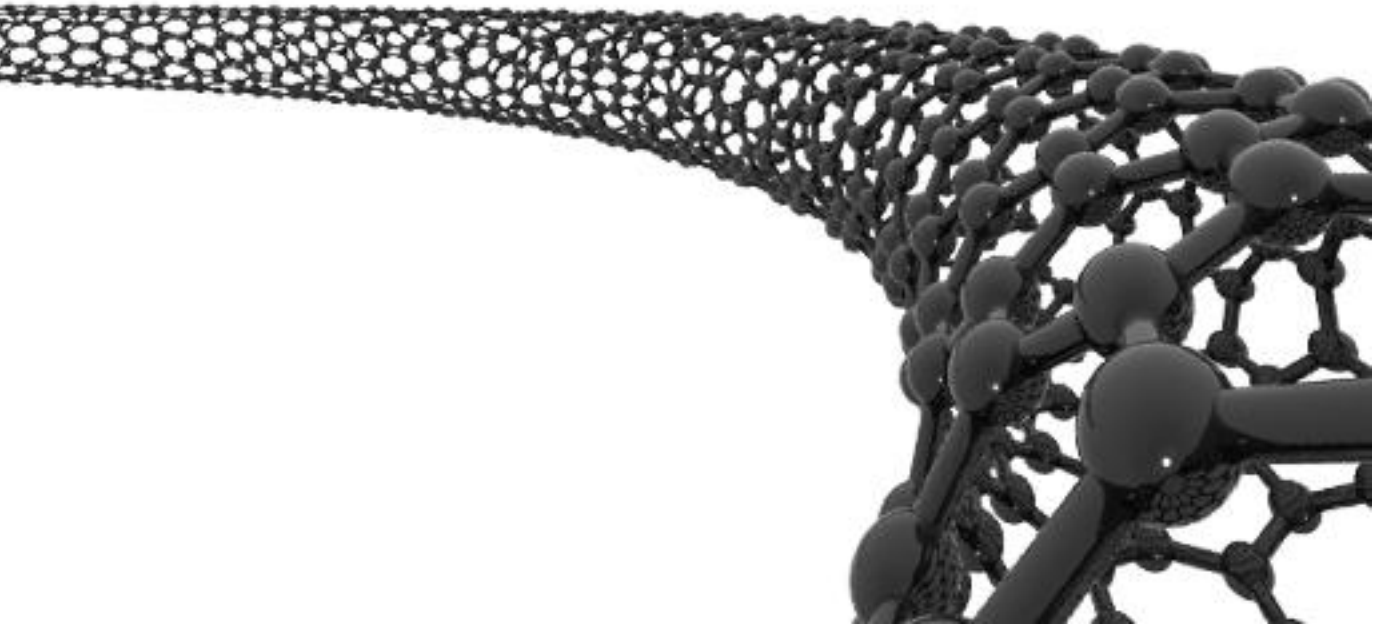
Chapter 4

Ion-selective electrode based on new hybrid materials with both transduction and recognition properties



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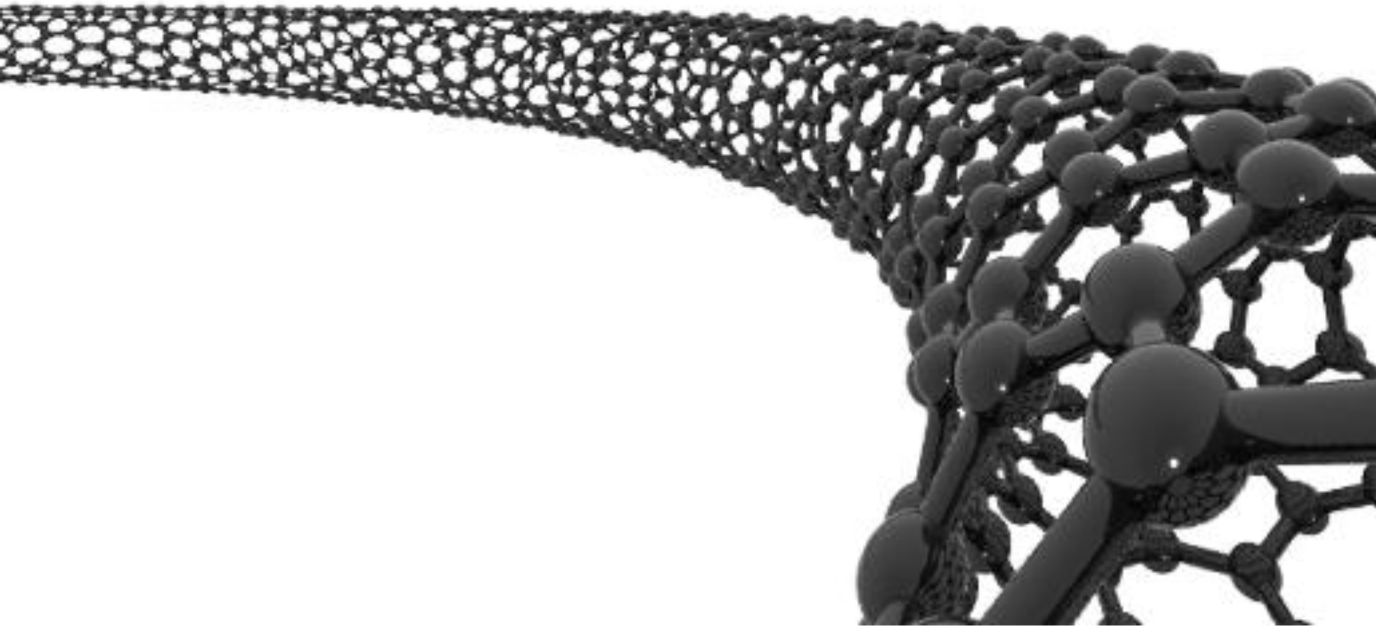
4. Introduction

In the previous Chapter, the incorporation of multi-walled carbon nanotubes (MWCNTs) as ion-to-electron transducer in a perchlorate selective electrode demonstrated to be an effective way to construct very stable, robust and ease-to-build ion-selective electrode (ISE). The drawbacks from conventional ion-selective electrode containing inner solution such as the leakage of the internal solution to the ion-selective membrane, electrode orientation, temperature variations and the pressure workable range were suppressed. In addition, multi-walled carbon nanotubes showed their superiority compared to traditional conducting polymer with the insensitiveness to light and redox species.

Nevertheless, some problems related to the ion-selective membrane still remains: for instance, the loss of some membrane components to the test solution. This migration is due to the trend to all species to reach the extraction equilibrium established between the hydrophobic membrane matrix and the hydrophilic aqueous sample solution. This leakage is the reason for the limited stability of the electrodes in long terms or the gradual increase of the limits of detection of the electrodes. This type of leakage should be avoided not only because the sensors lose their performance characteristics but, because in particular cases, these components can contaminate the sample solution. In this context, we propose two novel approaches to link the ionophore to the MWCNTs giving rise to a nanostructured hybrid material, with both recognition and transduction properties.

Part 4.1

Covalent functionalization of multi-walled carbon nanotubes



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4.1.1. Introduction

As first approach, we propose to covalently link the ionophore to the MWCNTs giving rise to a nanostructured hybrid material, with both recognition and transduction properties. Moreover, as the recognition element is linked to the non-extractable carbon nanotubes, the leakage problem can be avoided.

As a proof of concept, we selected a well-known neutral ionophore, the benzo-18-crown-6 ether to selectively detect lead. The ionophore has been covalently linked to multi-walled carbon nanotubes. In contrast to the previous Chapter where the transducer and the recognition elements are introduced separately, here the new hybrid material was dispersed into the polymeric material of the ion-selective membrane. In this way, the new solid-state ion-selective electrode was developed and characterized.

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4.1.2. An effective nanostructured assembly for ion-selective electrodes. Ionophore covalently linked to carbon nanotubes for Pb^{2+} determination*

Enrique J. Parra, Pascal Blondeau, Gastón A. Crespo and F. Xavier Rius.

We report on the synthesis of a new hybrid material, *i.e.* benzo-18-crown-6 covalently linked to multi-walled carbon nanotubes and its use in solid-state ion-selective electrodes both as receptor and ion-to-electron transducer. This new concept leads to potentiometric sensors with extremely high selectivity.

The development of solid material transducers that can reversibly and efficiently convert a chemical event into an electronic signal has generated a new wave of potentiometric electrodes. Solid-contact ion-selective electrodes (SC-ISEs) have indeed emerged as the most promising potentiometric sensors because of their excellent analytical performance, robustness and easy handling.[1] Conducting polymers were the most common transducers able to convert ions into electrons by taking advantage of the redox properties of these materials. Conducting polymers were introduced into the polymeric membrane in a non-covalent manner resulting in a significant signal stability improvement compared to coated wire elements.[2] Nanostructured materials such as single-walled carbon nanotubes (SWCNTs), on the other hand, have proved to be excellent ion-to-electron transducers in ISEs because they improve the stability of the signal without having any of the intrinsic drawbacks.[3,4] In addition, several

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[*] Supplementary information (SI): Experimental procedures for MWCNT-B18C6 hybrids, as well as additional analytical measurement of the SC-ISE at the end of this Chapter.

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types of CNTs with different degrees of functionalization have been reported to be successful transducers for both analytical and biological applications.[5-7] Nevertheless, these devices are still awkward to construct since the transducer and the recognition elements are introduced separately. Some progress has been made by incorporating multi-walled carbon nanotubes (MWCNTs) dispersion into the ion-selective membrane (ISM), which makes it much easier to develop new electrodes without affecting the potentiometric performance.[8-10]

The production of devices with long operating life times still remains a challenge for potentiometric sensors. One of the sources of the deterioration of the membrane can be found in the frequent loss of their components into samples. Therefore, if the performance parameters are to remain stable there is a strong need for the recognition element to be immobilized in the ISM. Two alternative approaches have been reported so far: the covalent immobilization of the ionophore on the functional groups of the polymeric membrane[11] and the covalent linkage of the ionophore to gold nanoparticles entrapped in the ISM[12]. In the first approach, the need for a high degree of functional moieties in the polymers that form the basis of the membrane dramatically affects the selectivity of the sensor. In the second approach, the ISM based on the receptor-gold-nanoparticle structure has excellent sensing properties. Nevertheless, this approach requires the ion exchanger/ionophore ratio to be carefully adjusted if the selectivities are to be comparable to the ISEs using the same ionophore. Moreover, both approaches use inner solution ISEs due to the lack of a chemically integrated solid transducer.

In this paper we report for the first time an integrated ionophore-transducer material with both recognition and transduction properties that

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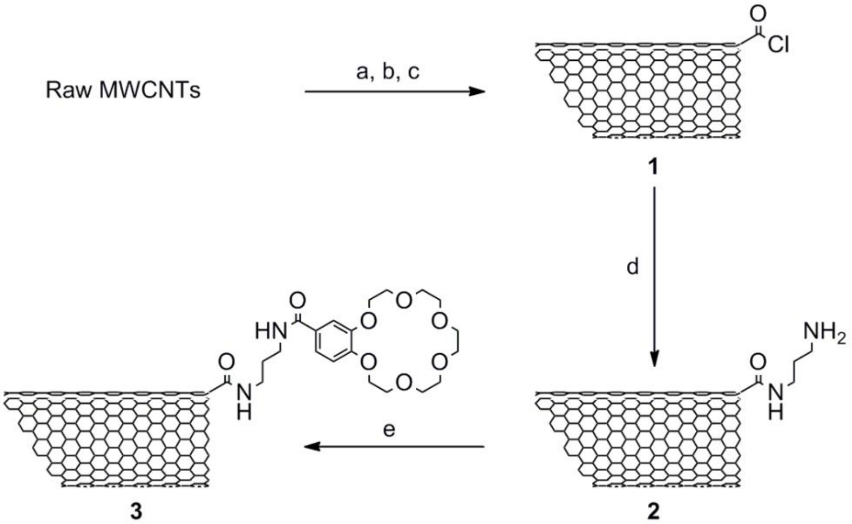
can be used to develop solid-contact ion-selective electrodes with improved performance characteristics. This new approach tends to overcome the problem of ionophore leaching without compromising the sensitivity and selectivities of the potentiometric sensors. In recent years, considerable efforts have been made to reliably incorporate artificial and biological receptors into the CNT structure.[13-15] In this context, we have selected Benzo-18-crown-6 (B18C6) as the lead ionophore[16] to be covalently grafted to the MWCNTs. The hybrid material is subsequently incorporated into the membrane preparation. Applying this methodology, we develop a very practical SC-ISE with ionophores that have very low mobilities and which therefore ensure the constant composition of the ISM.

B18C6 was covalently attached to the MWCNTs with a short 3-carbon chain spacer in three steps (Scheme 4.1.1). First, raw MWCNTs were purified and oxidized to introduce carboxylic groups into the MWCNTs.[17] These acid moieties were activated as acid chlorides and then reacted with 1,3-diaminopropane to afford **2**.[18] Subsequently, 4'-carboxybenzo-18-crown-6 was activated by standard coupling reagents to react with MWCNTs **2** to give MWCNT-B18C6 hybrids **3**. The degree of functionalization was evaluated by thermogravimetric analysis under N_2 atmosphere and showed a weight loss of 15.0% at 600 ºC (Figure S4.1.1, SI). Compounds **1**, **2** and **3** were characterized by Fourier transform infra-red [FT-IR] and Raman spectroscopy techniques as well as elemental analysis. The FT-IR spectra of MWCNTs **1** display the characteristic bands at 1714 cm^{-1} for the C=O stretching vibrations of acid groups as well as at 1576 cm^{-1} for the C=C stretching of the carbon nanotube (Figure S4.1.2, SI).[19] The FT-IR spectrum of **2** and **3** shows a similar trend with a new band at 1637 cm^{-1} due to the C=O stretching of the CONH amide bond. It is worth noting that a new, sharp band is detected at 1120 cm^{-1} due to the C-O stretching of the crown ether macrocycle in the spectrum of **3**. Elemental analysis confirmed the functionalization of MWCNTs with a significantly increased percentage of nitrogen content (Table T4.1.1, SI).



a) T= 365 ºC, 90 min. b) H_2SO_4/HNO_3 (3:1), reflux, 30 min. c) $SOCl_2$ reflux, 24 h. d) 1,3-diaminopropane, reflux, 120 h. e) 4'-carboxybenzo-18-crown-6, CH2Cl2, DCC, HOBt, 48 h.

Scheme 4.1.1 Synthesis of MWCNT-B18C6 hybrids.

Given that the MWCNTs are introduced into the polymeric membrane, the absence of MWCNTs bundles are essential if the electrode is to be effective.[8,9] Here, the Poly(ethylene-*co*-acrylic acid) (PEAA) was used to ensure good dispersion of MWCNTs and MWCNT hybrids, and the dispersion was then characterized by TEM (Figure S4.1.6, SI†). Three ISMs were prepared to compare the mobility of the ionophore in the ISMs: dispersed MWCNT-B18C6 and NaTFPB[20]; dispersed MWCNTs, B18C6 and NaTFPB (free receptor membrane); dispersed MWCNTs and NaTFPB without ionophore (blank membrane).

Figure 4.1.1 shows the characteristic potentiometric response of the ISEs developed as a function of time at different increasing activities of Pb^{2+} for the three membrane compositions studied here with their corresponding error bar. The response was almost Nernstian displaying a slope 28.7±0.5 mV decade^{-1} and a linear range between 1.58×10^{-6} and 10^{-3} M Pb^{2+} (the slope for the blank membrane was 27.1±0.6 mV with a linear range from 3.16×10^{-6} to 10^{-3} M Pb^{2+} and 25.7±0.7 mV with a linear range from 2.00×10^{-5} to 10^{-2} M Pb^{2+} for the free receptor membrane). No changes were observed in response time for the different lead activities within the linear range (c.a. $t_{95\%} \leq 15$ s). The limit of detection (LOD) was calculated using the conventional addition method,[21] (*i.e.*, successive additions starting from 10^{-8} M Pb^{2+}), for the MWCNT-B18C6 system (c.a. $10^{-5.8}$ M Pb^{2+}; for free receptor and blank membranes the LODs were $10^{-4.7}$ and $10^{-5.5}$ M Pb^{2+}, respectively). In addition, when the dilution method was used starting at 10^{-2} M Pb^{2+}, the LOD for the MWCNT-B18C6 electrode was lower (c.a. $10^{-6.4}$ M Pb^{2+}, Figure S4.1.4, SI).[22]

The intermediate-term potential stability was evaluated by measuring the EMF for 24 hours using a 10^{-3} M Pb^{2+} solution. A drift of 360±92 mV h^{-1} was obtained for the MWCNT-B18C6 membrane (Figure S4.1.5, SI), which is comparable with the drift obtained for the blank membrane (300±52 mV h^{-1}). In contrast, the drift of the MWCNT+B18C6 membrane is almost twice as much (590±29 mV h^{-1}) confirming the increased stability of the membrane containing MWCNT-B18C6. A comparable potential stability was also found when SWCNT or MWCNT were deposited as solid layer transducers and not entrapped in the membrane matrix (400 and 200 mV h^{-1}, respectively).[4,6] The increased stability observed for MWCNT-B18C6 membrane respect to the MWCNT+B18C6 membrane is related to the loss of the membrane components. Leaching out of the ionophore from the MWCNT+B18C6 membrane was evidenced by Mass spectroscopy in the conditioning solution after one month whereas such feature was not observed for the hybrid MWCNT-B18C6 membrane (FigureS4.1.7 and S4.1.8, SI). Additionally, probably because of the highly hydrophobic character of the MWCNTs entrapped in the polymer network, no water layer is detected at the interface between the membrane and the conducting substrate of the electrode (Figure S4.1.9, SI).[23]

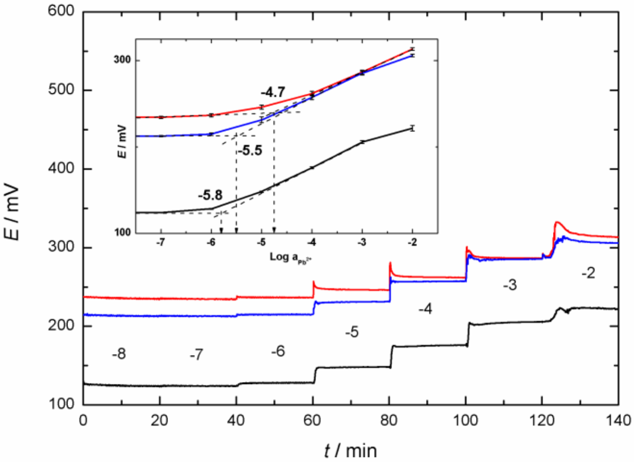


Figure 4.1.1 Time response for the MWCNT/Pb^{2+}-ISEs. *Black:* MWCNT-B18C6 membrane. *Red:* free receptor ion-selective membrane. *Blue:* blank membrane. The inset shows the corresponding calibration curves. The error bars associated to each ion-selective membrane type represent the range of the three EMF values recorded for three different electrodes.

ISE based on B18C6 ionophore have been reported to be selective for K$^+$, Sr$^+$ and Pb^{2+} with respect to their respective interferences.[16] In this context, the ISE was used for detection of Pb^{2+} considering only dications as interferences. Potentiometric selectivity coefficients ($K^{pot}_{Pb^{2+},J}$) were calculated for five divalent interferences (Cu^{2+}, Zn^{2+}, Ca^{2+}, Cd^{2+} and Mg^{2+}, Figure 4.1.2) using the separate solution method (SSM).[24,25] The selectivity coefficients dramatically increased by three to four logarithmic orders of magnitude when the MWCNT-B18C6 was used instead of the free receptor membrane. The grafting of B18C6 on the MWCNTs is mainly localised at the open ends and the side walled defects of the CNTs so the ionophore molecules are close to each other. This favours the formation of sandwich complexes between two ionophore molecules and the lead ion which provides an increased affinity.[26,27] This specific configuration, in which the ionophore is anchored to the carbon nanotubes, may be responsible for the impressive selectivity coefficients reported for this specific ion. The cooperative effect is definitely not present in those membranes that contain the free ionophore. These selectivity coefficients increased by two to three orders of magnitude with respect to those obtained with a previous lead IS-ISE that had B18C6 as the ionophore.[16] Furthermore, the selectivities shown here are higher than for previous IS-ISEs reported with other lead ionophores.[28]

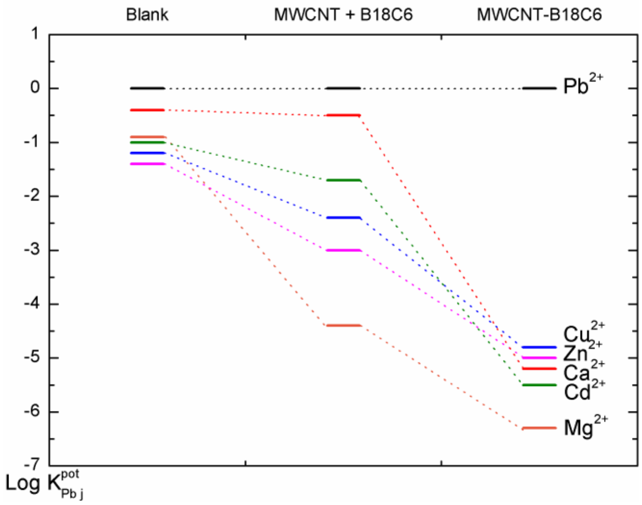


Figure 4.1.2 Potentiometric selectivity coefficients of Pb^{2+}-selective membranes determined by SSM at the 10 mM level. The first column shows the blank membrane (MWCNTs and NATFPB), the second column the free B18C6 membrane (MWCNTs, B18C6 and NaTFPB) and the third column the MWCNT-B18C6 membrane (MWCNT-B18C6 hybrids and NaTFPB).

The electrochemical characterization of the various ISMs mentioned above was performed by electrochemical impedance spectroscopy (EIS). The characteristic complex plane impedance plot for asymmetric sensors is observed for the MWCNT-B18C6 hybrid SC-ISE (Figure S4.1.10, SI). The high-frequency semicircle is related to the bulk impedance of the membrane composed of bulk resistance ($R_b \approx 520$ kΩ) and the geometric capacitance ($C_g \approx 20$ pF) in parallel. At the low frequency a Warburg diffusion component is detected. The fact that the bulk resistance is greater than that of the free membrane is in agreement with the immobilization of the receptor on the MWCNTs. As a result of the reduced mobility of the ionophore in the membrane, the bulk resistance increases from 150-184 kΩ to 520 kΩ. However, the current exchange between membrane and solution, in the very small phase boundary, should not be affected. Nernstian responses are indeed obtained in all the experiments, which indicates that the current exchange is optimal (Figure S4.1.11, SI). Furthermore, the shape of the impedance spectrum for the MWCNT-B18C6 hybrid membrane indicates that it behaves differently from the rest of the membranes studied (Figure S4.1.11-4.1.13, SI). For the MWCNT-B18C6 hybrid membrane there is one semicircle at high frequency whereas for both the free receptor and blank membranes there are two. These differences could be caused by the free carboxyl group of the MWCNTs that is in the free receptor and the blank membrane but not in the hybrid membrane, where this group has been functionalized. The carboxyl group in the membrane, then, may generate an additional charge transfer resistance.

By using the hybrid system of ionophores linked to multi-walled carbon nanotubes, both molecular recognition and ion-to-electron transduction have been successfully carried out on a single material in

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potentiometric solid-contact ion-selective electrodes. These electrodes are easier to produce than solid-contact electrodes, which show the recognition and transduction events in two separate layers. They have an excellent Nernstian response, much higher selectivity and intermediate-term potential stability. The fact that the ionophore does not leach out from the membrane means that the sensor is very stable and reproducible. This report not only proves a concept, it describes a hybrid material that can overcome some of the drawbacks of ionophores, thus opening up new routes for immobilizing hydrophilic receptors in hydrophobic phases and extending the sensing capabilities of ISEs.

4.1.2.1. Notes and references

Financial support from the Spanish Ministerio de Ciencia e Innovación (Project CTQ2010-18717) is gratefully acknowledged.

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4.1.3. Supplementary information (SI)

4.1.3.1. Chemicals and reagents

The multi-walled carbon nanotubes (MWCNT) were purchased from HeJi in bulk form with >99% purity, 150 μm average length and 10-20 nm diameter. The reagents thionyle chloride ($SOCl_2$), 1,3-diaminopropane, N,N′-Dicyclohexylcarbodiimide (DCC), 1-Hydroxybenzotriazole (HOBt), 4′-Carboxybenzo-18-crown-6, benzo-18-crown-6 (B18C6), Poly(ethylene-co-acrylic acid) (PEAA) and analytical grade lead, zinc, calcium, copper, cadmium and magnesium nitrate salts were purchased from Sigma–Aldrich. Poly(vinyl chloride) high molecular weight (PVC), 2-Nitrophenyl octyl ether (NPOE), Tetrahydrofuran (THF) and sodium tetrakis[3,5-bis(trifluoro-methyl)phenyl]borate (NaTFPB) were of selectophore® grade from Fluka. Deionized and charcoal-treated water (18.2 MΩ•cm specific resistance) were obtained with Milli-Q PLUS reagent-grade water system (Millipore). Sandpapers and alumina were obtained from Buehler. Sigradur G glassy carbon rods were obtained from HTW. Teflon blocks were obtained from RS Amidata. Environmental scanning electron microscope (ESEM) images were taken on a Quanta 600 (FEI Company, Inc.) in the Technical and Scientific Services of our university.

4.1.3.2. Synthesis of MWCNT-B18C6 hybrids

As-purchased MWCNTs (100 mg) were oxidized in a silica furnace chamber in order to selectively remove any amorphous carbon impurity (T = 365 ^{o}C, air flow-rate = 100 cm^3 min^{-1}, t = 90 min). Subsequently, the MWCNTs were refluxed in H_2SO_4/HNO_3 (3:1) for 30 min. The MWCNTs were then filtered on a Millipore membrane (Polycarbonate PC, 0.10 μm) and the solid on the filter was washed with Milli-Q water and dried to afford MWCNT-COOH as a black solid (60 mg).

To MWCNT-COOH (20 mg) in DMF (1 mL) was added $SOCl_2$ (20 mL) and the mixture was stirred with refluxing overnight. The resulting material was decanted and the supernatant was removed. Dry THF (5 mL) was then added, the mixture was centrifuged and the supernatant was removed. This operation was repeated 5 times. The solid was then filtered on a Millipore membrane (PTFE, 0.22 µm) and washed several times with CH_2Cl_2 and diethyl ether affording **1** as a black solid (20 mg).

Compound **1** (20 mg) was subsequently refluxed in 1,3-diaminopropane (1 mL) for 5 days. The reaction mixture was then filtered on a Millipore membrane (PTFE, 0.22 µm) and the solid on the filter was washed several times with CH_2Cl_2 and diethyl ether obtaining **2** as a black solid (22 mg).

To a mixture of 4′-Carboxybenzo-18-crown-6 (0.2 mmol, 71.2 mg), DCC (0.2 mmol, 40.6 mg), HOBt (0.2 mmol, 27 mg) in dry CH_2Cl_2 (2 mL) was added compound **2** (10 mg) in DMF/CH_2Cl_2 (1:1, 2 mL). The reaction mixture was stirred during 48 h at room temperature and then filtered on a Millipore membrane (PTFE, 0.22 µm) and the solid on the filter was washed several times with DMF, CH_2Cl_2 and diethyl ether affording **3** as a black solid (20 mg).

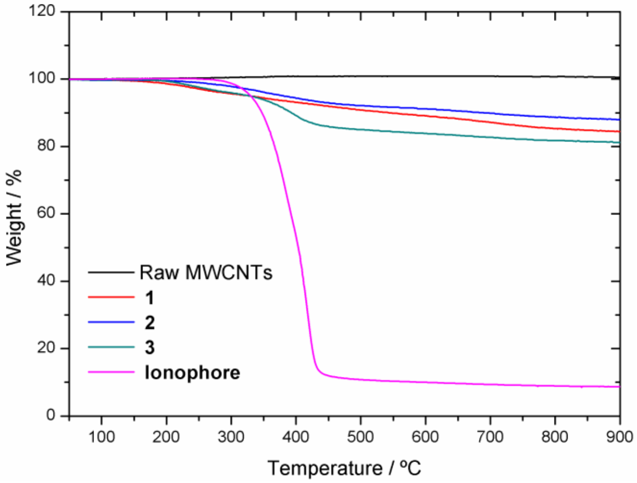

Figure S4.1.1 TGA of raw MWCNTs, 1, 2, 3 and the ionophore 4′-Carboxybenzo-18-crown-6 (10 ºC min^{-1} in N$_2$).

For a typical TGA experiment, 1-2 mg of MWCNTs were placed in the sample holder in the furnace of a Mettler Toledo TGA/SDTA851 instrument and the material was heated up at a rate of 10 ºC min^{-1} in N$_2$, while the weight was recorded continuously. The degree of functionalization at 600ºC is 10%, 8% and 15% for **1**, **2** and **3** respectively.

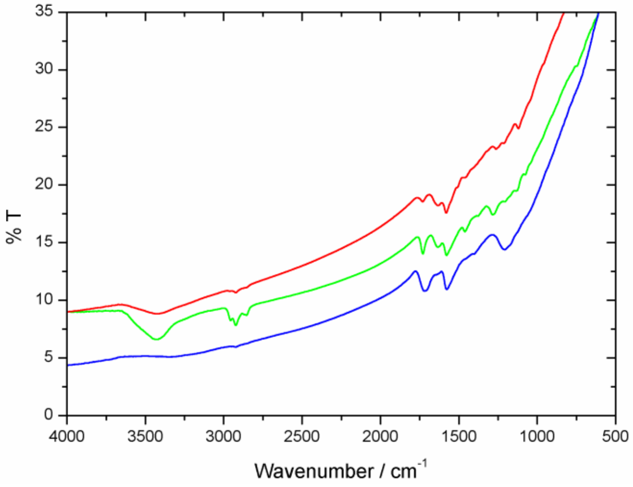

Figure S4.1.2 FTIR spectra for 1 (blue), 2 (green) and 3 (red).

FTIR spectra were recorded with a Jasco FT/IR-600 PLUS spectrometer on KBr pellet. In addition to the characteristic bands, the C=O stretching vibrations of acid groups are shifted from 1714 cm^{-1} for **1** up to 1727 and 1730 cm^{-1} for **2** and **3** respectively. Noteworthy, the formation of a second amide in final compound **3** results as the loss of a peak at 1282 cm^{-1} present in spectrum of **2**, which could be attributed to the C-N stretching of the free amine in **2**.

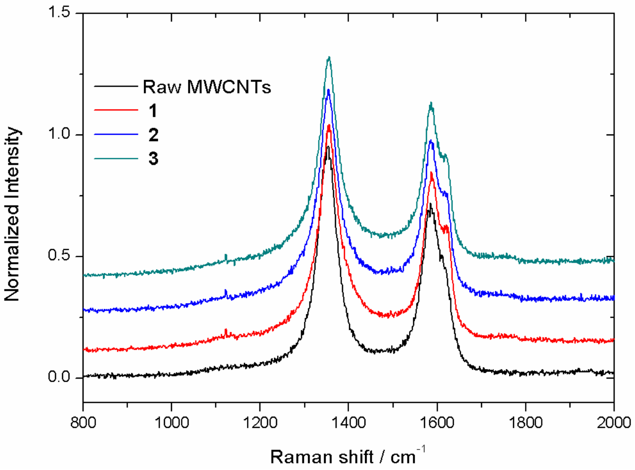

Figure S4.1.3 Raman spectra of raw MWCNTs, 1, 2, 3 excited at 514 nm.

Raman spectra were recorded with an Invia Renishaw Raman microspectrometer (50 × objective) using a 514 nm laser line from an Ar laser. The Raman spectrum corresponding to the functionalized nanotubes is very similar to that of raw MWCNTs. There are no changes in the frequency of the tangential stretching mode (G band at 1585 cm^{-1}) and disorder one (D band at 1355 cm^{-1}). Slight difference is displayed by the ratio D/G from raw MWCNTs to **3** (1.30; 1.24; 1.26; 1.23 for raw MWCNTs, **1**, **2** and **3** respectively). Raman spectroscopy shows indeed that the ratio of the tangential stretching mode and the disorder mode peak was not affected by covalent synthesis.

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Table T4.1.1. Elemental analysis for raw MWCNTs, 1, 2 and 3.

Sample	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Raw MWCNT	98.81	0.20	-
1	82.44	1.11	-
2	83.96	1.45	4.70
3	72.12	1.78	4.61

The elemental analysis of the samples was performed with a Thermofinnigan Instrument (1110 CHNS-O).

4.1.3.3. Preparation of ISE membranes and electrodes

Since the ionophore content was 15 wt. % of the MWCNT hybrids, a considerable amount of MWCNT-B18C6 was required to reach 1% ionophore in the ISM cocktail (6.67% of the total membrane weight). Due to the high dry matter content in the membrane, a higher ratio (3:1) of plasticizer/polymer was required.[7] sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was used as a lipophilic cation exchanger to ensure the cation permselectivity of ISMs (30% mol ratio NaTFPB/B18C6).

The membrane cocktails were prepared in two steps: first, CNTs (MWCNT-B18C6 or MWCNT-COOH) with 5 mg of PEAA in 1 ml of THF were dispersed using a sonicator bath and, second, NaTFPB (30% per mole of ionophore) and PVC:NPOE in a 1:3 ratio were mixed to obtain a total of 100 mg of membrane. The sonicator bath was used until complete dissolution of components. Three different membranes were prepared: MWCNT-B18C6 membranes: the amount of MWCNT-B18C6 hybrid required to have an equivalent of 1% w/w of ionophore in 1 ml of THF (amount of CNT-B18C6 according to the TGA analysis). Free receptor membranes were prepared with the same composition as the MWCNT-B18C6 membranes, with the only difference of ionophore as free form (c.a. 1% w/w). Blank membranes were prepared following the same composition as the previously described membranes but without adding ionophore. All the membranes were prepared by drop casting 50 µl of membrane cocktail onto the polished end of a glassy carbon rod (3 mm ∅) followed by solvent evaporation at room temperature.

4.1.3.4. EMF measurements

Potentiometric responses were recorded with a high-input impedance (10^{13} Ω) 16-channel EMF-16 interface (Lawson Labs) at room temperature (22 ± 2 ºC). A double-junction Ag/AgCl/3 M KCl reference electrode (type 6.0729.100, Metrohm AG) containing a 1 M lithium acetate electrolyte bridge was employed. All measurements were corrected with the Henderson equation[1] and the Debye–Hückel approximation[2] and were done with three electrodes to evaluate the reproducibility of the sensors.

Potentiometric selectivity coefficients ($K_{Pb,J}^{pot}$) were calculated employing the separate solution method (SSM) using 10 mM nitrate solutions of the primary ion Pb^{2+} and interferences: Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} as previously described.[3]

The calibration curves for lead were obtained by successive additions of different lead solutions (addition method, black in Figure S4.1.4). The electrode was conditioned 24 h in a 10^{-3} M Pb^{2+} solution and then 48 h in a 10^{-9} M Pb^{2+} solution before measurements to avoid ion fluxes at low concentration due to the lack of membrane equilibrium. The limit of detection (LOD) calculated for this calibration curve using the addition method was $10^{-5.8}$ M. The limit of detection was also calculated using the continuous dilution procedure with Milli-Q water (dilution method, red in

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Figure S4.1.4).[4] In this case the electrode was conditioned for 48 h in 10^{-2} M of Pb^{2+} obtaining a value of $10^{-6.4}$ M.

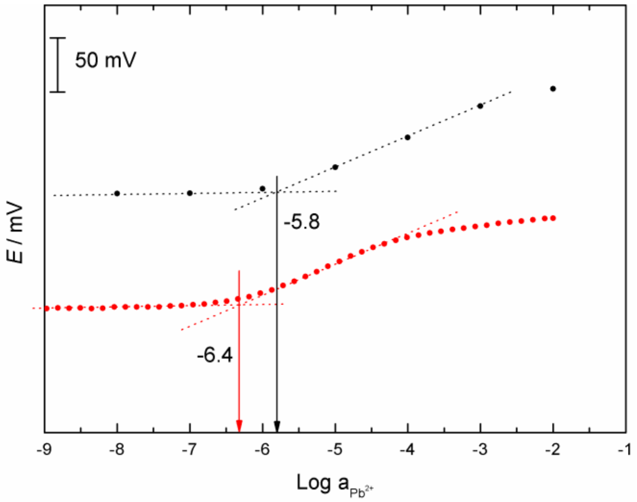

Figure S4.1.4 Limit of detection. (black) LOD obtained by addition method. (red) LOD obtained by dilution method.

The intermediate-term potential stability (Figure S5) was also assessed by measuring the EMF during 24 hours using a starting 10^{-5} M Pb^{2+} solution and adding after 45 min a Pb^{2+} solution to reach a final 10^{-3} M Pb^{2+} solution.

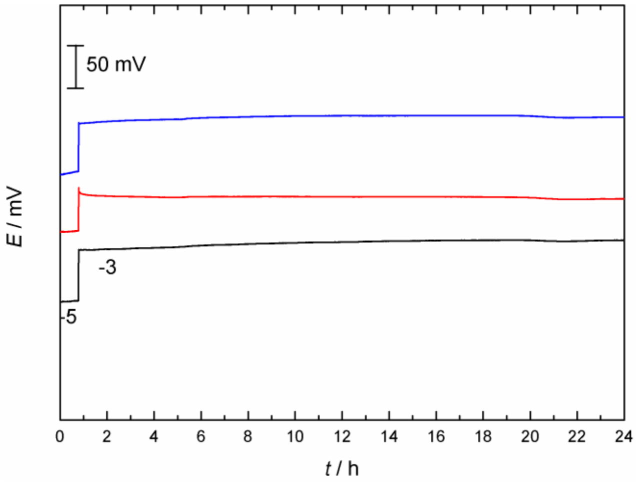

Figure S4.1.5 Intermediate-term potential stability of the electrode over 24 hours for an activity change from 10^{-5} M Pb^{2+} to 10^{-3} M Pb^{2+}. *Black:* MWCNT-B18C6 membrane, *red:* Free receptor ion-selective membrane and *blue:* blank membrane.

4.1.3.5. Optical characterization

The membranes were characterized using environmental scanning electron microscopy (ESEM, Quanta 600) and Transmission electron microscopy (TEM, JEOL model 1011). Figure S6 shows a TEM image for MWCNT-B18C6 membrane where the low density network of dispersed carbon nanotubes is observed. A 60 µm membrane thickness was estimated by ESEM.

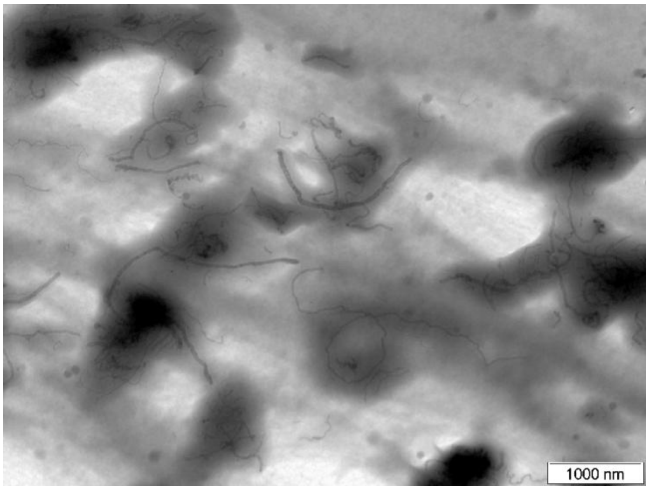

Figure S4.1.6 Transmission electron microscopy image of ion-selective membrane with MWCNT-B18C6 hybrid.

4.1.3.6. Mass spectroscopy analysis

Mass spectroscopy analysis of the conditioning solution of MWCNT+B18C6 and MWCNT-B18C6 membrane ISEs were achieved to detect the presence of leaching components of the polymeric membrane. Experimentally, the aqueous solution (1 month conditioning) was concentrated under reduced pressure and the resulted material subjected to mass analysis (Figure S4.1.7 and S4.1.8). Figures S4.1.7 and S4.1.8 present the Mass spectrum of MWCNT + B18C6 and MWCNT-B18C6 membranes respectively. In the conventional membrane, the mass of the ionophore was detected (Figure S4.1.7, M=330.19 gmol^{-1}) whereas in the hybrid membrane, such mass was not present. This experiment accounts for the leaching out of the ionophore when it is not covalently linked to the MWCNTs.

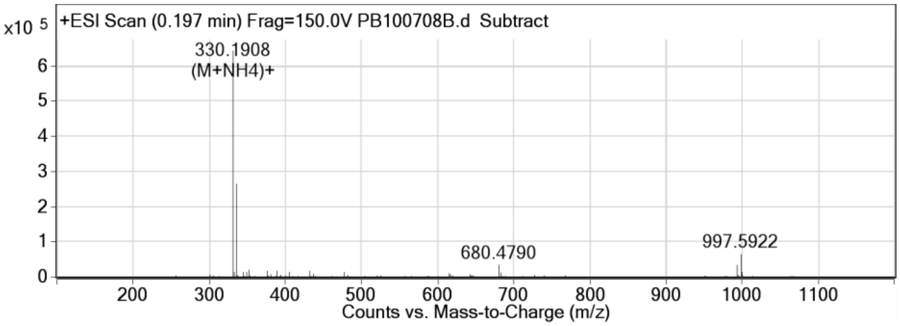

Figure S4.1.7. Mass spectrum of conditioning solution of MWCNT+B18C6 membrane.

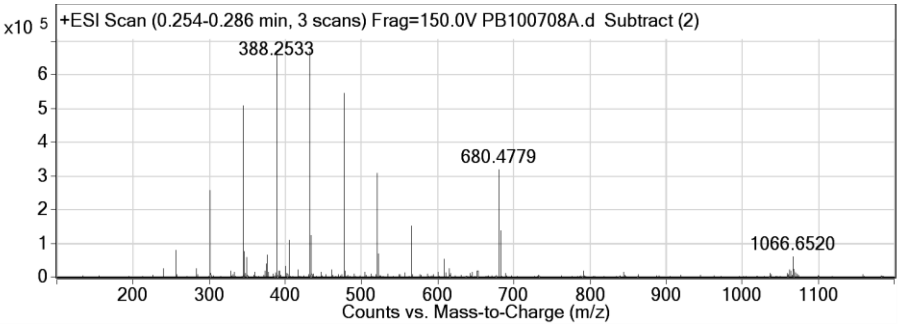

Figure S4.1.8. Mass spectrum of conditioning solution of MWCNT-B18C6 membrane.

4.1.3.7. Water layer test

In order to show the effect of the water layer between the ion-selective membrane and glassy carbon, the water layer test was performed. This water layer has harmful effects since it can favour the presence of the atmospheric gases like O_2 or CO_2, diffused through the ion-selective membrane. The presence of O_2 can favour redox side-reactions while CO_2 can change the pH of the interface, what may result in response drifts. This procedure follows three steps[5]: in the first and the third step (area A,

Figure S4.1.9) the potential was recorded in a 10^{-3} M Pb^{2+} solution, in the second step (area B, Figure S4.1.9) the electrode was submerged into a 10^{-3} M Mg^{2+} solution. The water layer test was recorded for the three different membranes (Figure S4.1.9): MWCNT-B18C6 membrane, MWCNT + B18C6 membrane and blank membrane. The same responses were observed for the three membranes, no water layers were detected due to the high hydrophobic character of the MWCNTs inside membrane.

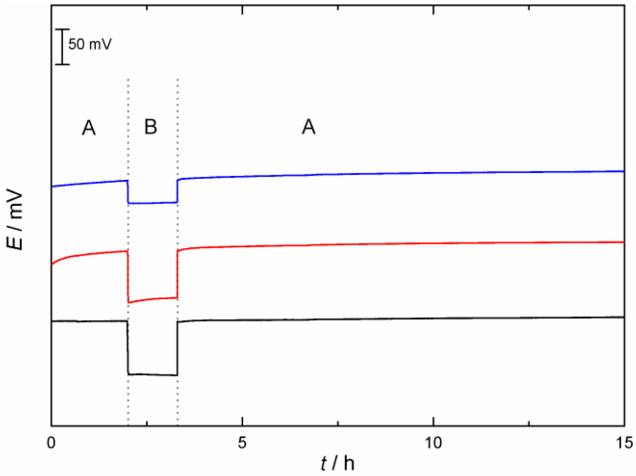

Figure S4.1.9 Water layer test of Pb^{2+} selective electrodes. *Area A*: solution of 10^{-2} M Pb^{2+}. *Area B*: solution of 10^{-2} M Mg^{2+}. *Black:* MWCNT-B18C6 membrane, *red:* free receptor ion-selective membrane and *blue:* blank membrane.

4.1.3.8. Electrochemical impedance spectroscopy (EIS)

All electrochemical impedance measurements were made using a potentiostat/galvanostat Autolab PGSTAT128N with frequency response analyser electrochemical impedance module (FRA2) (AUTOLAB, Eco Chemie). EIS was performed in a three-electrodes electrochemical cell. The working electrode was a glassy carbon rod with a drop casted on it (area 0.07 cm^2)[6], the counter electrode was a glassy carbon rod and the reference electrode was a single junction Metrohm Ag,AgCl/3M KCl (type 6.0733.100, Metrohm AG). All measurements were performed at room temperature (22 ± 2 °C). The impedance spectra were recorded in a frequency range (100 kHz – 10 mHz). The impedances were recorded for four different composition of membranes: membrane with dispersed MWCNT-B18C6 (Figure S4.1.10), membrane containing only PVC (Figure S4.1.11), membrane containing dispersed MWCNT-COOH (Figure S4.1.12), membrane with dispersed MWCNT-COOH and B18C6 (Figure S4.1.13)

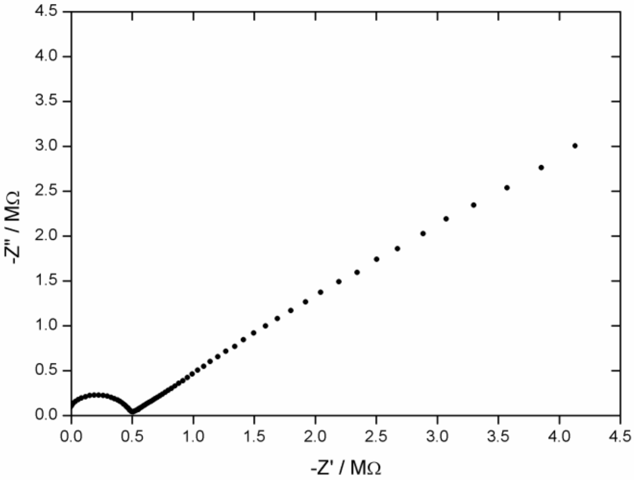

Figure S4.1.10 Complex plane impedance plot of MWCNT-B18C6 electrode in 10^{-3} M $Pb(NO_3)_2$ solution. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz-10 mHz, Amplitude = 0.1V.

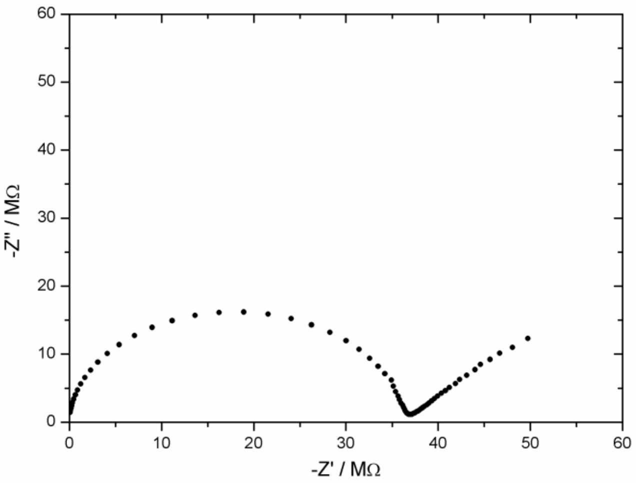

Figure S4.1.11. Complex plane impedance plot of the membranes with PVC: NPOE electrode in 10^{-3} M $Pb(NO_3)_2$. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz -10 mHz, Amplitude = 100 mV. Parameters from the RC circuit R_b=35.5 MΩ ; C_g=14 pF (Time constant: 1.7 ms).

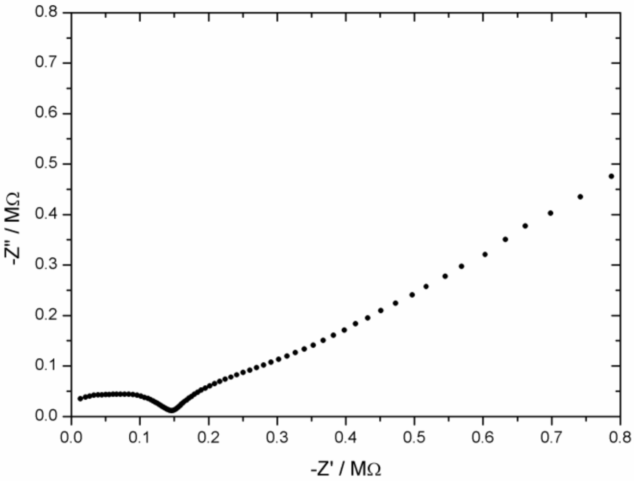

Figure S4.1.12. Complex plane impedance plot of MWCNT-COOH electrode in 10^{-3} M $Pb(NO_3)_2$ solution. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz-10 mHz, Amplitude = 100 mV. Parameters from the RC circuit R_b=184 kΩ ; C_g=54 pF; (Time constant: 0.06 ms). Second RC R_{ct}=287 kΩ ; C_{dl}= 1.2 μF; (Time constant: 0.9 s).

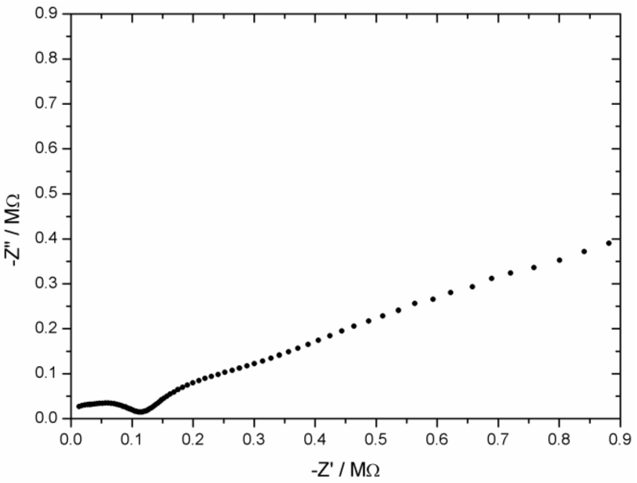

Figure S4.1.13. Complex plane impedance plot of MWCNT-COOH with B18C6 free electrode in 10^{-3} M $Pb(NO_3)_2$ solution. Experimental conditions: E_{dc}=0.2 V, Frequency range =100 kHz-10 mHz, Amplitude = 100 mV. Parameters from the RC circuit R_b=150 kΩ ; C_g=30 pF (Time constant: 0.007 ms). Second RC R_{ct}=407 kΩ ; C_{dl}= 0.8 μF (Time constant: 0.5 s).

4.1.3.9. References

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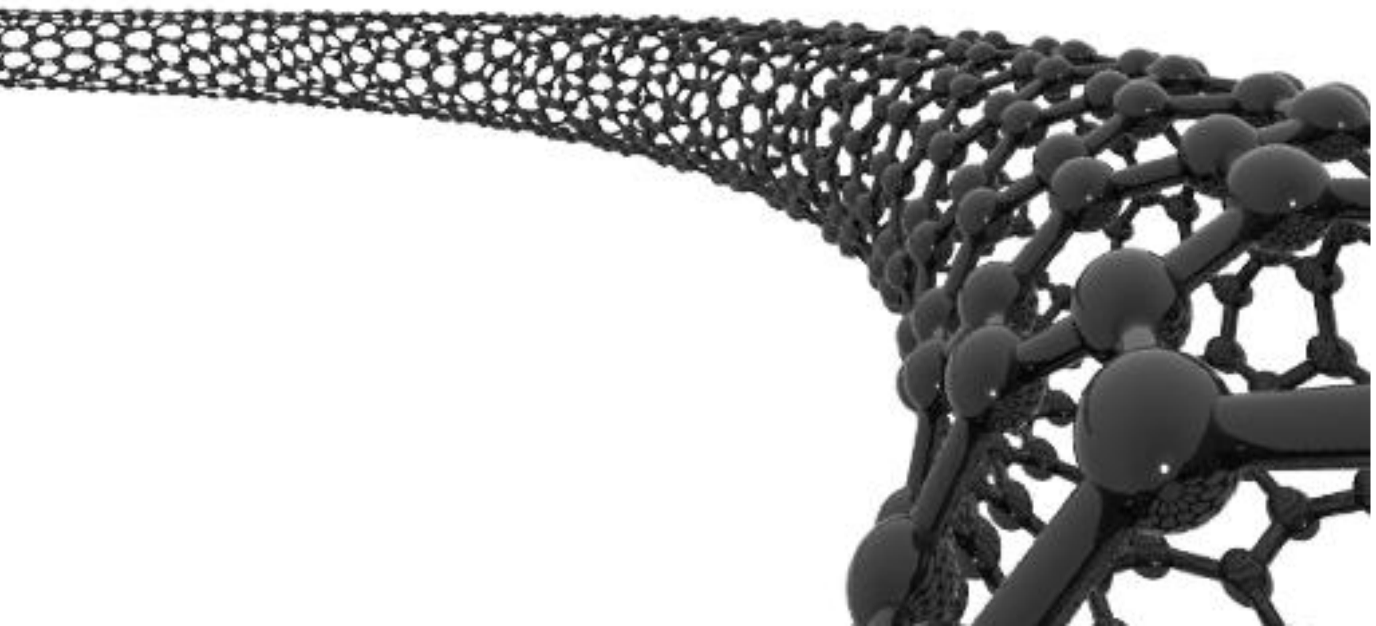
Part 4.2

Non-covalent functionalization of multi-walled carbon nanotubes



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4.2.1. Introduction

In the first section of this Chapter, we reported on the covalent immobilization of the ionophore to the multi-walled carbon nanotubes (MWCNTs) so as to avoid the leakage of the ionophore to the aqueous solution. The resulting nanostructure hybrid assemblies, unlike the previous Chapter, were dispersed in the polymeric membrane. The aim of the previous study was not limited to the development of a new sensor but more importantly to demonstrate that this new methodology, *i.e.* to link the ionophore to the transducer, was promising in the context of SC-ISEs, since the analytical performances were maintained.

However, the main limitations of these new ion-sensors came from the carbon nanotube functionalization process: the presence of unreacted moieties on the MWCNT structure, the low loading capacity and the use of polymer dispersant (pH sensitive in the latter case). To extent the new methodology to real test samples, the performance parameters must be studied thoroughly. For instance, the study of the sensor developed to determine lead using MWCNT-B18C6 hybrids was limited to the detection of divalent cations, although clearly the ionophore also interacts with some monovalent cations as potassium.

In this section we propose to further explore this field by applying an alternative approach for the MWCNT functionalization: the non-covalent functionalization of the ionophore onto the MWCNTs. This linkage is based on a pyrene group covalently bonded to the ionophore and interacting with the nanotube by π-π stacking interactions. The approach presented in this section, in a similar way as the one presented in the previous section, aims to overcome the drawbacks of conventional

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electrodes without reducing the analytical performances of the resulting ion-selective sensors.

We attached a pyrene group to the ionophore, benzo-18-crown-6 ether, in order to non-covalently anchor the ionophore to the MWCNTs for the selective detection of monovalent cation such as potassium. Similarly to the previous part, the new material was dispersed into the polymeric material of the ion-selective membrane but did not require polymeric dispersant. In this way, the new solid-state ion-selective electrode were developed and characterized. Using this new approach, more selective charged ionophores, which are, in many cases, insoluble in the organic solvents used to generate the polymeric matrices, can be incorporated in the membrane and thus be able to recognize anions.

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4.2.2. Potassium selective sensor based on non-covalent functionalization of the ionophore onto multi-walled carbon nanotubes

4.2.2.1. Introduction

Nanostructured materials such as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotube (MWCNTs) have emerged as excellent ion-to-electron transducers in solid-contact ion-selective electrodes (ISEs).[1-3] They indeed improve the stability of the potentiometric signal without suffering from external interferences such as light or redox species to name a few.[4,5] Moreover, these devices could be easily constructed by incorporating multi-walled carbon nanotubes dispersion directly into the ion-selective membrane (ISM).[6,7] The electrodes are therefore more robust and easier to develop compared to the conventional ones, where the transducer and the recognition layer are introduced separately, while their potentiometric performance are maintained. In this context, we have taken advantage of covalently linking the ionophore to the MWCNTs and introducing the resulting hybrid into the polymeric matrix to build a lead sensor.[8,9] This nanostructure assembly faced one of the remaining issues of ISEs, *i.e.* the leakage of the ionophore from the polymeric membrane. This result would indeed address the production of devices with long operating life time. Furthermore, we have recently investigated the role of MWCNTs functionalization process on the analytical performances of the ISEs.[9] In order to increase the loading capacity of such nanostructures, a dendrimer approach was therefore reported and the resulting ISEs characterized. However, several aspects still need to be considered to maintain at high level the sensor analytical performance parameters. Selectivity is such an issue. In this regard, MWCNTs functionalization strategies as well as the surfactant requirement are critical aspects. By covalent linking the ionophore to the MWCNT structure, enough available anchoring sites are mandatory to reach a high loading capacity. Nevertheless, carbon nanotube chemistry is still complex to control[10-12] and incomplete reactions result as unreacted moieties that could participate in the recognition event and therefore alter the sensor selectivity. In addition, the surfactant requirement often implies pH interference and ion exchanger properties because of the charged groups along its backbone.[13] To address these issues, we present herein a non-covalent functionalization of MWCNTs with pyrene-benzo-18-crown-6 ionophore **1** (Figure 4.2.1). The pyrene group is anchored onto the MWCNTs walls by π-π stacking interactions[14,15] and the B18C6 moiety selectively recognizes potassium K^+ [16,17]. The analytical performances of the resulting solid-contact ion-selective electrode (SC-ISE) were therefore fully characterized and the ionophore reduced mobility inside the ion-selective membrane (ISM) demonstrated by electrochemical impedance spectroscopy (EIS).

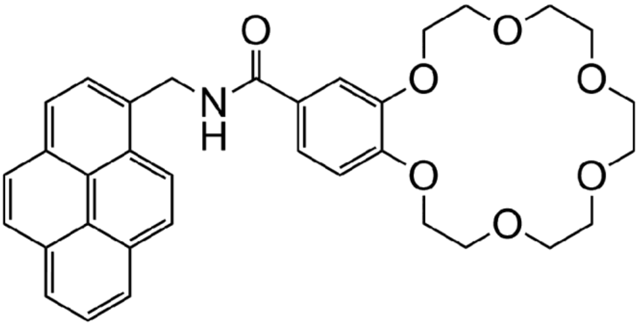

Figure 4.2.1 Pyrene-B18C6 ionophore **1**.

4.2.2.2. Experimental part

The multi-walled carbon nanotubes (MWCNT) were purchased from HeJi in bulk form with > 99 % purity, 150 μm average length and 10-20

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nm diameter. Synthesis of **1**: A mixture of pyrenemethylamine hydrochloride (270 mg, 1.01 mmol), *N*-methylmorpholine (NMM) (102.1 mg, 1.01 mmol), N,N′-dicyclohexylcarbodiimide (DCC) (174 mg, 0.84 mmol), 1-hydroxybenzotriazole (HOBt) (113 mg, 0.84 mmol) and 4′-carboxybenzo-18-crown-6 (300 mg, 0.84 mmol), in 50 mL DMF/CH_2Cl_2 (1:1) was stirred overnight at room temperature. After evaporation of the solvent, the crude was purified by silica gel column chromatography (CH_2Cl_2/MeOH, 9:1). The resulting solid was precipitated in cold methanol and recrystallized in THF as white crystals (405 mg, 85 %). ^1H NMR (500 MHz, CD_3CN) δ 8.48 (d, J = 16.0 Hz, 1H, CH_{Ar}), 8.27 (m, 4H, CH_{Ar}), 8.07 (m, 4H, CH_{Ar}), 7.58 (s, 1H, NH), 7.41 (m, 2H, CH_{Ar}), 6.91 (d, J = 16.2 Hz, 2H, CH_{Ar}), 5.28 (d, J = 6.3 Hz 2H, CH_2), 4.15 (m, 4H, CH_2), 3.72 (m, 4H, CH_2), 3.56 (m, 12H, CH_2). ^{13}C NMR (CD_3CN, 100 MHz) δ 133.8, 128.7, 128.5, 128.2, 128.1, 127.7, 127.3, 126.3, 126.2, 125.8, 124.3, 121.2, 112.2, 111.8 (CH_{Ar}, C_{Ar}), 71.2, 71.2, 71.1, 70.9, 69.7, 69.6, 68.8, 68.7 (CH_2). ESI-MS *m/z* 592.2 $(M+Na^+)^+$.

Functionalization of MWCNTs: 10 mg of MWCNTs were added to **1** (10 mg) in 10 ml of THF. The mixture was treated using an ultrasonic bath (100 W) for 3 h at room temperature. The solid was then filtered on a Millipore membrane (PTFE, 0.22 µm) and washed several times with THF, CH_2Cl_2 and diethyl ether affording MWCNT-**1** as a black solid. The degree of functionalization was evaluated by thermogravimetric analysis (TGA) under N_2 atmosphere and showed a weight loss of 36.0 wt.% at 600 ºC.

The solid-contact ISEs were fabricated by following a previous reported procedure.[8] Because the ionophore content was 36 wt.% of the MWCNT hybrids, 2.8 % of the total membrane weight was required to reach 1 wt. % of the ISM. In all membrane preparations, a poly(vinyl chloride)/2-nitrophenyl octyl ether (PVC/NPOE) ratio of (3:1) was employed and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB) was used as cation exchanger (30 % mol ratio NaTFPB/B18C6). First, MWCNTs were dispersed in 1 ml of tetrahydrofuran (THF) using a ultrasonic bath (100 W) and, second, NaTFPB (30 % per mole of ionophore) and PVC:NPOE were mixed to obtain a total of 100 mg of membrane. All the membranes were prepared by drop casting 50 µl of membrane cocktail onto the polished end of a glassy carbon rod (3 mm ∅) followed by solvent evaporation at room temperature. The resulting electrodes were immersed into 0.01 M KCl solution for 24 h before measurements, and stored in the same solution. Potentiometric and electrochemical impedance measurements were performed as previously reported.[8] All data are the average of three electrodes.

4.2.2.3. Results and discussion

Pyrene-B18C6 ionophore **1** was synthesized according to standard coupling reaction between pyrenemethylamine hydrochloride and 4′-carboxybenzo-18-crown-6 with 85 % yield. Non-covalent functionalization was then achieved by treatment of MWCNTs with **1** in tetrahydrofuran giving a yield of 36.0 wt.% (TGA). Three membranes were then prepared and labelled as follows: MWCNT-1 (with the ionophore anchored to the MWCNT), MWCNT+B18C6 (with the ionophore in free form) and blank (with no ionophore). Noteworthy, the dispersion of MWCNT-1 in THF was stable over weeks so that MWCNT-1 did not require the additional use of surfactant. Besides, the loading capacity was improved dramatically compared to the covalent approach

(36.0 wt. % *vs.* 15 wt. %). Non-covalent functionalization of CNTs has indeed been widely reported for device construction due to both high loading capacity and ease of process.[18] Figure 4.2.2 shows the characteristic potentiometric response of the ISEs developed as a function of time. The response displayed a Nernstian character with a slope of 56.9±0.9 mV decade^{-1} and a linear range between 3.09x10^{-6} and 10^{-2} M K$^+$ for the MWCNT-1 electrode. In contrast, the sensitivity decreased when using both MWCNT+B18C6 and blank membranes with 51.7±0.7 mV decade^{-1} and 49.4±2.0 mV decade^{-1} respectively. The limit of detection (LOD) displayed again a slight improvement for the MWCNT-1 with respect to the two other systems described here: 10$^{-5.9}$, 10$^{-5.8}$ and 10$^{-5.6}$ M K$^+$ for MWCNT-1**,** MWCNT+B18C6 and blank respectively. Lowering the detection limit is indeed in good agreement with the immobilization of ionophore.[19] Moreover, non-covalent functionalization was not altering the linear range of the electrode. We previously reported that the covalent functionalization reduced the linearity of one order of magnitude at high level (from 10^{-2} M down to 10^{-3} M)[9], which accounted for coextraction of sample anions from the aqueous solution into the ISE membrane.[20] Such behaviour was not detected here and confirmed the effectiveness of the functionalization strategy. Comparable response times were measured within the linear range in the three cases (c.a. $t_{95\%} \leq 15$ s). Moreover, the long-term potential stability was evaluated by measuring the EMF for ninety hours using a 10^{-3} M K$^+$ solution. A small drift of 334.0±0.2 µV h^{-1} was obtained for the MWCNT-1 membrane which was also comparable to the one recorded for MWCNT+B18C6 and blank (332.1±0.1 and 338.4±0.1 µV h^{-1}, respectively). Noteworthy, leaching out of the ionophore from the MWCNT+B18C6 membrane was evidenced by mass spectroscopy in the conditioning solution whereas such behaviour was not observed when the ionophore was physically immobilized in the hybrid MWCNT-1 membrane. In addition, probably because of the highly hydrophobic character of the MWCNTs entrapped in the polymer network, no water layer was detected at the interface between the membrane and the conducting substrate of the electrode.[21]

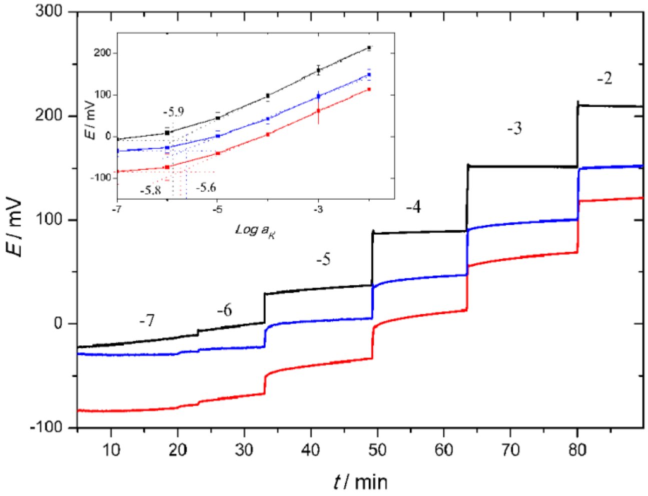

Figure 4.2.2 Time response for the MWCNT/K$^+$-ISEs when adding different amounts of the primary analyte. *Black:* MWCNT-1 membrane. *Red:* MWCNT+B18C6 membrane. *Blue:* blank membrane. The inset shows the corresponding calibration curves.

Potentiometric selectivity coefficients ($K^{pot}_{K^+,J}$) were calculated for five secondary ions, both monovalent and divalent cations (NH_4^+, Na^+, Li^+, Ca^{2+} and Mg^{2+}, Table 4.2.1) using the separate solution method (SSM).[20,22] For the interfering anions in which no response was observed using the new hybrid sensor MWCNT-1, the selectivity coefficient was not calculated to avoid biased values that could give misleading results.[20,23,24] However, as an example, the entire calibration curve is shown for Ca^{2+} in Figure 4.2.3, with the three different assayed membranes (MWCNT-**1,** MWCNT+B18C6 and blank membrane). Whereas Ca^{2+} gave a selectivity coefficient (in logarithmic terms) of -4.0 and -5.2 for the blank and the MWCNT+B18C6 systems respectively, almost no potentiometric response

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was detected in the case of the hybrid system (slope 13.3 mV/dec). Li^+ presents a comparable behaviour. Due to the large difference in cation sizes[25], B18C6 is very selective against Mg^{2+}, so that no response was observed for this latter cation using both the MWCNT+B18C6 and MWCNT-1 electrodes. Ammonium, on the contrary, is the highest interfering cation because of its comparable size and hydration energy. Interestingly, the hybrid system showed a slight increase in selectivity respect to NH_4^+ (from -0.9 to -1.5 for the MWCNT+B18C6 and MWCNT-1 respectively) while the selectivity towards Na^+ was maintained (from -2.5 to -2.3 for the MWCNT+B18C6 and MWCNT-1 respectively). In the covalent functionalization scheme performed in the previous work,[8] the selectivity coefficients were dramatically increased by 3 to 4 orders of magnitude from the free system to the covalent one.[8] We attributed this exceptional feature to the specific configuration of the ionophore covalently linked to the MWCNTs forming a 2:1 sandwich complex with Pb^{2+}; the latter feature could be hardly reached with the non-covalent functionalization described here. Nevertheless the selectivity coefficient were maintained and even slightly improved for some interferences when comparing the MWCNT+B18C6 and MWCNT-1. This aspect might point to probable interactions between the cation and the MWCNTs walls due to the closer arrangement of the ionophore onto the MWCNTs walls.[26] Since in almost all covalently immobilized ionophores, the selectivity is reduced compared to the free ionophore[27,28], the non-covalent system MWCNT-1 presented here is therefore part of the few sensors that report a maintained selectivity pattern with immobilized ionophores.[24,29]

Table 4.2.1. Potentiometric selectivity coefficients of K^+-selective membranes determined by SSM at the 10 mM level.

	Blank		MWCNT+B18C6		MWCNT-1	
	Slope (mV/dec)	Log $K_{K^+,j}$	Slope (mV/dec)	Log $K_{K^+,j}$	Slope (mV/dec)	Log $K_{K^+,j}$
NH_4^+	57.0±0.3	-0.6±0.1	48.7±0.8	-0.9±0.1	49.3±1.6	-1.5±0.4
Na^+	42.1±4.5	-2.5±0.1	33.9±0.5	-2.5±0.1	42.1±3.4	-2.3±0.6
Li^+	25.9±5.4	-4.3±0.1	26.3±1.8	-4.6±0.2	13.5±1.7	*
Ca^{2+}	33.6±0.7	-4.0±0.2	22.7±2.1	-5.2±0.1	13.3±0.9	*
Mg^{2+}	31.9±4.0	-5.6±0.3	-1.1±0.1	*	6.9±0.4	*

*not calculated considering the reduced response

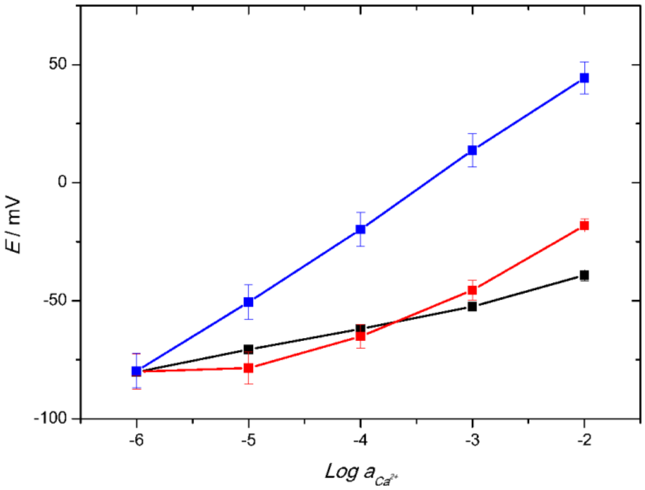

Figure 4.2.3 Calibration curves for the MWCNT/K^+-ISEs for Ca^{2+} interference. *Black:* MWCNT-1 membrane. *Red:* MWCNT+B18C6 ion-selective membrane. *Blue:* blank membrane.

The electrochemical characterization of the ISMs mentioned above was performed by electrochemical impedance spectroscopy (EIS). The characteristic complex plane impedance plot for asymmetric sensors was observed in all cases (Figure 4.2.4). The high-frequency semicircle is related to the bulk impedance of the membrane composed of bulk resistance and the geometric capacitance in parallel.[30] At the low frequency a Warburg diffusion component was detected. The bulk resistance increased from the blank to the MWCNT-1 electrode (38, 50 and 108 kΩ for blank, MWCNT+B18C6 and MWCNT-1 electrodes respectively). A similar trend was indeed displayed by the geometric capacitance ($C_g \approx$ 2.9, 2.5 and 1.3 pF for blank, MWCNT+B18C6 and MWCNT-1 electrodes respectively). The bulk resistance of the hybrid MWCNT-1 was much higher than that of the MWCNT+B18C6 membrane because of the immobilization of the receptor on the MWCNTs. Therefore, as a result of the reduced mobility of the ionophore in the membrane, the bulk resistance increased.

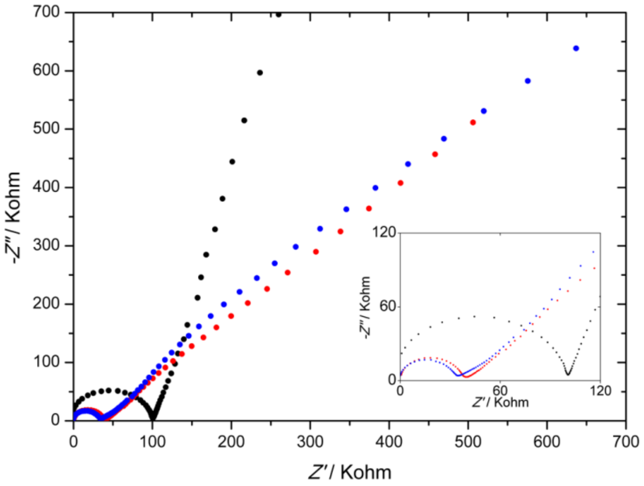

Figure 4.2.4 Complex plane impedance plot of MWCNT based electrode in 10^{-3} M KCl solution. Black: MWCNT-1 electrode, Red: MWCNT+B18C6 and blue: blank

4.2.2.4. Conclusions

By using the hybrid system of ionophores non-covalently anchored to multi-walled carbon nanotubes, solid-contact ion-selective electrode have been successfully constructed and applied to the determination of potassium. Both molecular recognition and ion-to-electron transduction were therefore carried out on a single material. Moreover, the limitations of covalent functionalization for the construction of the SC-ISE, such as loading capacity and surfactant requirement, have been overcome. We

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have demonstrated that non-covalent functionalization of MWCNTs ensured the constant composition of the ion-selective membrane while the resulting suitable sensitivity, selectivity and reproducibility represented a considerable advantage over conventional SC-ISEs. This approach represents a major advance towards easy-to-build and reproducible SC-ISEs. However, the immobilization of highly selective ionophores, electrically charged, still remains to be achieved to confirm this result and it is currently carried out in our laboratory.

4.2.2.5. Acknowledgments

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4.2.2.6. Notes and references

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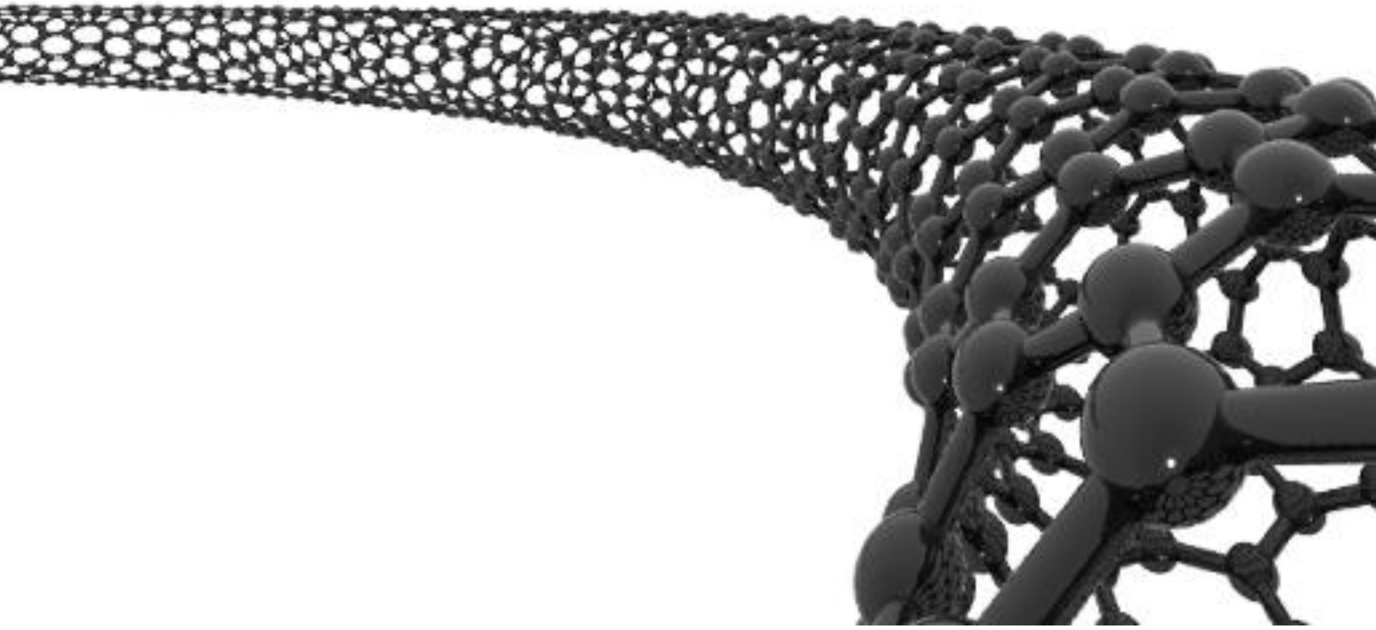
Chapter 5

Nanostructured hybrid materials for anion sensing



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5.1. Introduction

In the previous Chapter a hybrid MWCNT-ionophore material using a neutral receptor, entrapped into the polymeric membrane of the ion-selective electrode, was presented as a proof of concept to detect ions, specifically Pb(II). Here the aim of this Chapter is to go a step further towards anion detection. Similarly, a hybrid material based on MWCNTs, in which the charged ionophore is covalently linked to the nanotube, is employed for the detection of sulfate. The main novelty here is arising from the ionophore, a squaramide-based macrocycle which has high capacity to bind highly solvated divalent anions in aqueous media. The positively charged ionophore fits very well with divalent anions, such as sulfate and monohydrogen phosphate, based on the shape, size, electrostatic interactions and hydrogen bonding of the receptor. Traditionally, polymeric ion-selective membranes are based on lipophilic poly(vinyl chloride) so that the highly hydrophilic anions, such as sulfate and phosphate, because of their very large negative molar free energy of hydration, are very difficult to enter in the hydrophobic matrix and, therefore, are difficult to determine with this type of ISE. In addition, most of the charged ionophores have a hydrophilic character and tend to leach to the aqueous phase if simply entrapped in the hydrophobic matrix. To overcome these problems, we proposed to link covalently the ionophore to MWCNTs. The leakage of the charged ionophore to the solution will be avoided while the high affinity of the resulting receptor, embedded in the ion-selective membrane, should give increased analytical performances compared to conventional electrodes.

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This work was done in collaboration with Dr. Gastón A. Crespo from the same research group at the URV, Dr. Pau Ballester from Institute of Chemical Research of Catalonia (ICIQ), Tarragona, and Dr. Antoni Costa from Department of Chemistry, Universitat de les Illes Baleares, Palma de Mallorca.

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5.2. All-solid state ion-selective electrodes based on nanostructured assembly using a charged ionophore for sulfate detection

5.2.1. Introduction

The development of new sensors for anionic species continues to be a rich area of research.[1] Sulfate is a highly widespread anion, and its determination in environmental, industrial and pharmaceutical fields, is an important task. The existing methods for sulfate determination have several drawbacks such as time consuming and high limits of detection (*i.e.* gravimetric methods)[2], poor selectivity and reproducibility (*i.e.* optical methods)[2]; complexity and high equipment cost (chromatographic and chromate-electrophoretic methods).[3,4] Therefore, the attention has been focused on the determination of sulfate by methods that could overcome these drawbacks.[5] Potentiometry is one of the simplest electrochemical techniques[6], being also very fast and cheap. However, due to the highly hydrophilic characteristics of sulfate (the molar free energy of hydration, Δ_{hyd} G, has been evaluated as -1080 kJ mol^{-1}, compared, for instance, to -300 kJ mol^{-1} for nitrate)[7], the construction of ISEs for such anion is very demanding.[8-10] The development of solid-contact ion-selective electrodes (SC-ISEs) is a promising area within the field of potentiometric sensors because of their analytical performance, robustness and easy handling.[11] Nanostructured materials such as carbon nanotubes (CNTs) have proved to be excellent ion-to-electron transducers in ISEs because of the improvement of signal stability.[12-16] Some progress has been made by incorporating MWCNTs dispersion into the ion-selective membrane (ISM), which makes electrodes much easier to develop without compromising the potentiometric performance characteristics.[17-19] Recently, a novel nanostructured material has been reported[19], these novel

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material incorporate the receptor and the transducer element in a single hybrid material able of displaying both recognition and transducer properties. Moreover, the novel nanostructure material open the way to the incorporation of hydrophilic ionophores into the hydrophobic nature of the ion-selective membrane.

Squaramides are ideal components for molecular sensing devices due to their quenching and binding abilities.[20,21] Using the hydrogen bond donor capabilities of squaramides together with two tetraalkylammonium groups to complement the charges of sulfate anion, a macrocyclic receptor was synthesized by Costa *et al.* (Figure 5.1).[21] In this way, a simple molecular sensor that uses the exclusive binding abilities of two squaramide units included within an anionic recognition site has been reported for monitoring sulfate in water.[22] Remarkably, the binding of monovalent anions such as halides, nitrate, acetate, and others is negligible owing to the electroselectivity imposed by the tetraalkylammonium groups. On the other hand, the preference for tetrahedral sulfate is accounted for the structural constraints of the hydrogen bond donor array of the squaramide units, favouring the binding of sulfate over other divalent anions.

Here we report the development of a new solid-contact sulfate selective electrode based on squaramide-based macrocyle as a proof of concept of the incorporation of hydrophilic ionophores into hydrophobic ion-selective membranes.

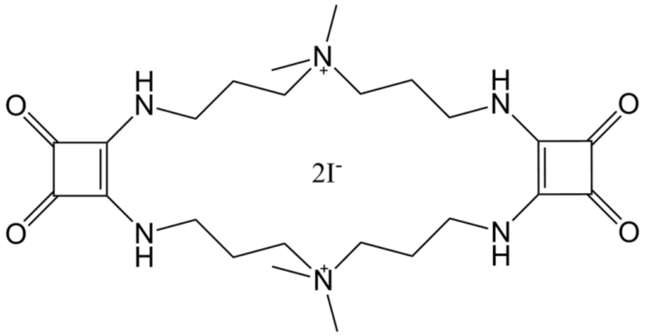

Figure 5.1. Structure of squaramide-based receptor for sulfate recognition.

5.2.2. Experimental part

5.2.2.1. Chemicals and reagents

The MWCNTs were purchased from HeJi in bulk form with > 99 % purity, 150 μm average length and 10-20 nm diameter. The squaramide-based receptor were synthesized and provided by A. Costa's group (Departament de Química, Universitat de les Illes Balears, Palma de Mallorca, Illes Balears). The reagents N,N′-dicyclohexylcarbodiimide (DCC), 1-hydroxybenzotriazole (HOBt), poly(ethylene-co-acrylic acid) (PEAA), acetone and analytical grade sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium acetate ($NaCH_3COO$), disodium hydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium bromide (NaBr), sodium nitrate ($NaNO_3$) salts and 1-butyl-3-methylimidazolinium hexafluorophosphate were purchased from Sigma–Aldrich. Poly(vinyl chloride) high molecular weight (PVC), 2-nitrophenyl octyl ether (NPOE), tetrahydrofuran (THF) and tridodecylmethylammonium chloride (TDMACl) were of selectophore® grade from Fluka. Deionized and charcoal-treated water (18.2 MΩ•cm specific resistance) were obtained with Milli-Q PLUS reagent-grade water system (Millipore). Sandpapers and alumina were obtained from Buehler. Sigradur G glassy carbon rods were obtained from HTW. Teflon blocks

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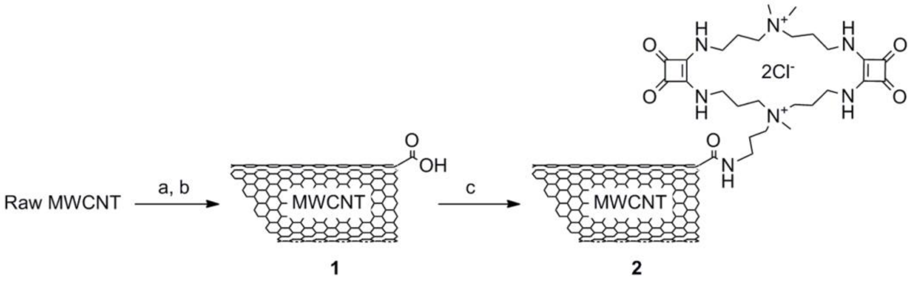
were obtained from RS Amidata. Hydrophobic PTFE membrane filters (Ø: 47 mm $Ø_{pore}$: 0.20 μm) were obtained from Albet, LabScience.

5.2.2.2. Synthesis of multi-walled carbon nanotubes squaramide hybrid nanostructure material

As-purchased MWCNTs (100 mg) were oxidized in a silica furnace chamber in order to selectively remove any amorphous carbon impurity (T= 365 ºC, air flow-rate = 100 cm^3 min^{-1}, t = 90 min) without affecting the structure of the nanotubes. Subsequently, the MWCNTs were refluxed in concentrated H_2SO_4/HNO_3 (3:1) for 30 min. The MWCNTs were then filtered on a Millipore membrane (Polycarbonate PC, 0.10 µm) and the solid on the filter was washed with Milli-Q water and dried to obtain carboxylated carbon nanotubes (MWCNT-COOH) as a black solid (60 mg).

To a mixture of squaramide-based receptor (0.2 mmol, 117.91 mg), DCC (0.2 mmol, 40.6 mg), HOBt (0.2 mmol, 27 mg) in DMSO (2 mL) was added compound **1** (10 mg) in DMSO (2 mL). The reaction mixture was stirred during 48 h at room temperature and then filtered on a Millipore membrane (PTFE, 0.22 µm) and the solid on the filter was washed several times with DMSO, DMF, CH_2Cl_2 and diethyl ether obtaining 2 (MWCNT-Sq) as a black solid (20 mg) (see Schema 5.1).



a) T= 365 ºC, 90 min. b) H_2SO_4/HNO_3 (3:1), reflux, 30 min. c) 3, DCC, HOBt, DMSO 48 h.

Scheme 5.1. Synthesis of MWCNT–Sq hybrids 2.

5.2.2.3. Electrodes preparation

The glassy carbon rods (GC) (50 mm length and 3 mm ø), inserted into a Teflon body (4 mm length, 3 mm internal diameter and 5 mm external ø), act as the ion-selective electrode support as well as the electrical contact between the ion-selective membrane and the potentiometer. The electrode was polished with abrasive paper (Buehler Carbimet 600/P1200) followed by alumina of different sizes (30, 5 and 1 μm Buehler Micropolish II) and cleaned with ultrasonic tip sonicator after each size of alumina. The final surface was cleaned several times with acetone.

5.2.2.4. Membranes preparation

Since the ionophore content was 20 wt. % of the MWCNT hybrids (according to TGA analysis), a considerable amount of squaramide-carbon nanotubes hybrid nanostructure material (MWCNT-Sq) was required to reach 1% ionophore in the ISM cocktail (5 mg MWCNT-Sq in 100 mg of membrane). Due to the high dry matter content in the membrane, a higher ratio (3:1) of plasticizer/polymer was required. TDMACl was used as a lipophilic anion exchanger to ensure the anion permselectivity of ISMs.

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The membrane cocktails were prepared in two steps: first, CNTs (MWCNT-Sq or MWCNT-COOH) with 5 mg of PEAA (if necessary) in 1 ml of THF were dispersed using a sonicator bath and, second, TDMACl (different amounts per mole of ionophore) and PVC:NPOE in a 1:3 ratio were mixed to obtain a total of 100 mg of membrane. The sonicator bath was used until complete dissolution of components.

Different membranes were prepared: MWCNT-Sq membranes: the amount of MWCNT-Sq hybrid required to have an equivalent of 1% w/w of ionophore in 1 ml of THF. Free receptor membranes were prepared with the same composition as the MWCNT-Sq membranes, with the only difference of the ionophore introduced as free form (c.a. 1% w/w). Blank membranes were prepared following the same composition as the previously described membranes but without the presence of ionophore. All the membranes were prepared by drop casting 50 μl of membrane cocktail onto the polished end of a glassy carbon rod (3 mm ø) followed by solvent evaporation at room temperature.

5.2.2.5. Electrochemical measurements

Potentiometric responses were recorded with a high-input impedance (10^{13} Ω) 16-channel EMF-16 interface (Lawson Labs) at room temperature (22 ± 2 ºC). A double-junction Ag/AgCl/3 M KCl reference electrode (type 6.0729.100, Metrohm AG) containing a 1 M lithium acetate electrolyte bridge was employed. All measurements were corrected with the Henderson equation and the Debye–Hückel approximation. All the experiments were carried out with three different electrodes to evaluate the reproducibility. Potentiometric selectivity coefficients ($K^{pot}_{SO_4^{2-},j}$) were calculated employing the separate solution method (SSM)[23,24] using a

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range from 10^{-6} to 10^{-2} M sodium salts solutions of the primary ion SO_4^{2-} and interferences: Cl^-, HPO_4^{2-}, $H_2PO_4^-$, CH_3COO^-, Br^- and NO_3^-. The calibration curves for sulfate were obtained by successive additions of different sulfate solutions.[23] The electrode was conditioned 24 h in a 10^{-3} M SO_4^{2-} solution and then 48 h in a 10^{-9} M SO_4^{2-} solution before performing measurements to avoid ion fluxes at low concentration due to the lack of membrane equilibrium.[25]

5.2.3. Results and discussion

5.2.3.1. Synthesis of squaramide-carbon nanotubes hybrid nanostructure material

Squaramide-based receptor was covalently attached to the MWCNTs with a short 3-carbon chain spacer in three steps (Scheme 1). First, raw MWCNTs were purified and oxidized to introduce carboxylic groups into the MWCNTs. These acid moieties were activated by standard coupling reagents to react with receptor to give MWCNT–Sq hybrids 2. The degree of functionalization was evaluated by thermogravimetric analysis under N_2 atmosphere and showed a weight loss of 20.0 % at 600 ºC (Figure 5.2). Elemental analysis confirmed the functionalization of MWCNTs with a significantly increased percentage of nitrogen content (Table 5.1).

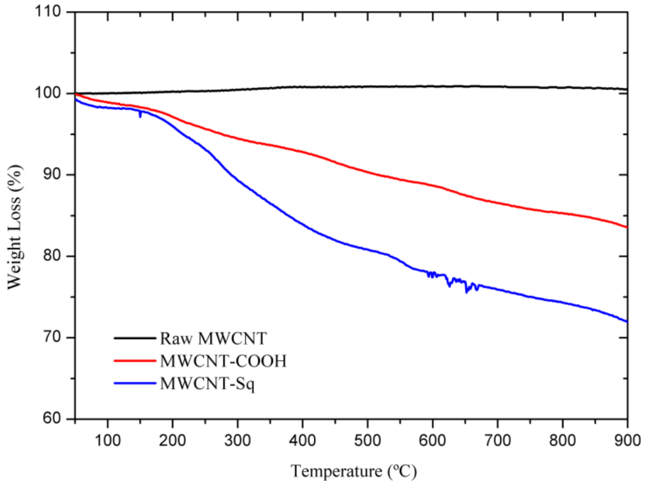

Figure 5.2. TGA of raw MWCNTs, 1 and 2 (10 ºC min^{-1} in N$_2$).

Table 5.1. Elemental analysis for raw MWCNTs, 1 and 2

Sample	**Carbon (%)**	**Hydrogen (%)**	**Nitrogen (%)**
Raw MWCNT	98.81	0.20	-
1	82.44	1.11	-
2	71.15	1.40	3.12

5.2.3.2. Dispersing agent

The application of large amounts of carbon nanotubes is limited mainly because of their low dispersability in aqueous and organic media. In previous works, this drawback was solved using poly(ethylene-co-acrylic acid) (PEAA) as dispersing agent for MWCNT hybrid material.[19] However, due to the presence of carboxyl group PEAA–MWCNTs based membrane suffered from pH interference. In contrast, **2** gives stable dispersions without PEAA addition due to the introduction of quaternary ammonium groups. Therefore, both membranes with and without PEAA were studied. **2** (5 mg), ion exchanger (200% per mol of ionophore) and polymeric matrix (PVC/NPOE) were kept the same to obtain 100 mg of membrane in both cases. The responses of the electrodes to changes of sulfate ion concentration and the calibration curve are shown in Figure 5.3.

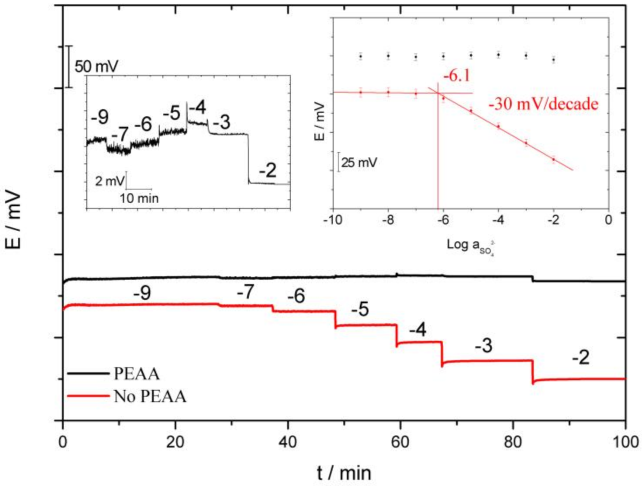

Figure 5.3. Time response for the SO$_4^{2-}$ ISEs. Black: hybrid material dispersed with PEAA. Red: hybrid material dispersed without PEAA. The right inset shows the corresponding calibration curves. The error bars associated to each ion-selective membrane type represent the range of the three EMF values recorded for three different electrodes. The left inset shows a zoom on the hybrid material dispersed with PEAA.

Noteworthy, there is no response from the electrodes built using a dispersion of MWCNTs with PEAA. However, when the MWCNTs are dispersed into de polymeric matrix without PEAA, the electrodes show a Nernstian response as seen in the inset of Figure 5.3. This is a clear evidence of the interference of PEAA (pKa=4.25) which is a weak acid[26,27]. At pH ≈ 5.5 the carboxylic groups of PEAA are present as carboxylate salt so that electrostatic interactions between the carboxylate and the counter cation of sulfate might be well occurring. Indeed a slight cationic response is detected at first which is then followed by a slight anionic response. The ionic interaction has no effect in the case of divalent cation-selective electrodes.[19]

5.2.3.3. Counterion influence

The presence of the primary anion inside the membrane is mandatory to ensure the electrochemical equilibrium, at the membrane-test solution interface, as explained by the phase boundary potential theory.[28] In order to achieve such chemical equilibrium inside the membrane, we need to ensure that any native anion has been exchanged by the primary anion, *i.e.* sulfate. The conventional procedure is the membrane conditioning in a solution that contains a relatively high concentration of the primary ion. Since it is possible to previously obtain the ionophore with different counterions, the influence of the counterion was studied by employing free-ionophore with counterions with increasing lipophilicity (SO_4^{2-}, Cl^- and $B(PhCl)_4^-$). The electromotive force recorded for different sulfate additions is shown in Figure 5.4. All electrodes were conditioned 24 h in a 10^{-3} M SO_4^{2-} solution followed by 48 h in a 10^{-9} M SO_4^{2-} solution before performing the measurements.[25]

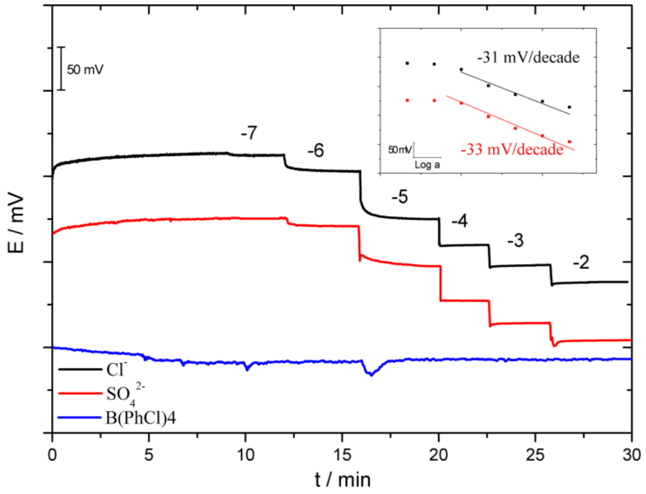

Figure 5.4. Time response for the MWCNT/SO_4^{2-}ISEs when changing the sulfate ion concentration in the test sample. Black: hybrid material with chloride as counterion. Red: hybrid material with sulfate as counterion. Blue: hybrid material with tetrakis(*p*-chlorophenyl) borate as counterion. The inset shows corresponding calibration curves for the SO_4^{2-}ISEs with Cl^- and SO_4^{2-} counterions.

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The calibration curves are shown in the inset of Figure 4. Nernstian responses were observed for counterions with some hydrophilic character (SO_4^{2-} and Cl^-). However, no response was observed for the more lipophilic counterion tetrakis(*p*-chlorophenyl)borate. This behaviour could be due to the absence of ionic interchange equilibrium between the sample and the membrane. Nevertheless, since polymeric membranes containing only an anion exchanger are able to act as ion exchanger membrane, a potentiometric response should be detected. Because neither cationic nor anionic detection was shown, a more complex equilibrium should occur. It might be based on the leaching of the hydrophilic content of the ISM remaining a high lipophilic salt Tridodecylmethylammonium tetrakis(*p*-chlorophenyl)borate in the polymeric membrane. This is supported by the ionophore/anion exchanger ratio employed here which is 1:2. In this latter case, neither anionic nor cationic exchange should be observed.

The selectivities against different anions of the ion-selective membranes developed with squaramide salts containing two different hydrophilic counterions (Cl^- and SO_4^{2-}) were studied (Figure 5.5). No significant differences between chloride and sulfate salts were observed. This result is in agreement with a complete conditioning process that involves the exchange between the counterion and the sulfate.

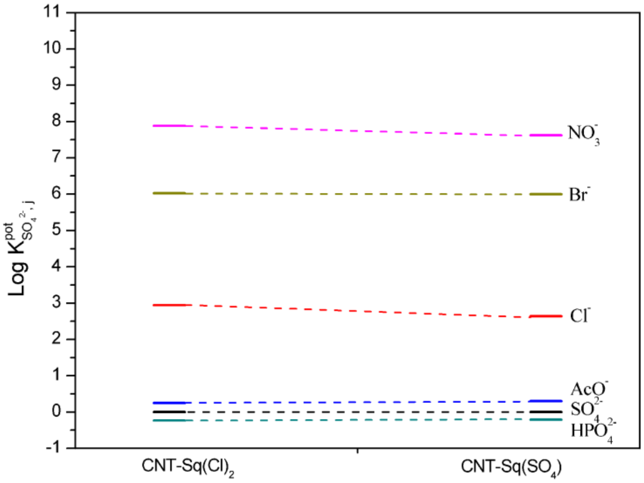


Figure 5.5. Potentiometric selectivity coefficients, determined by SSM at the 10 mM level, of the squaramide-MWCNTs SO_4^{2-}-selective membranes containing Cl^- and SO_4^{2-} counterions.

5.2.3.4. Different ion exchanger content

A significant parameter to study was the ion exchanger content of the membranes (Figures 5.6). It has been demonstrated that ionophore/ion exchanger ratio directly influence the sensitivity and selectivity of ISE.[29] To carry out this analysis four different membranes were prepared by varying the amount of ion exchanger from 0% to 200% per mol of ionophore content of the membrane (*i.e.* 0, 50, 100 and 200%) while keeping the rest of components at a constant value (5 mg **2** and polymeric matrix (PVC/NPOE ratio 1:3) to obtain 100 mg of membrane).

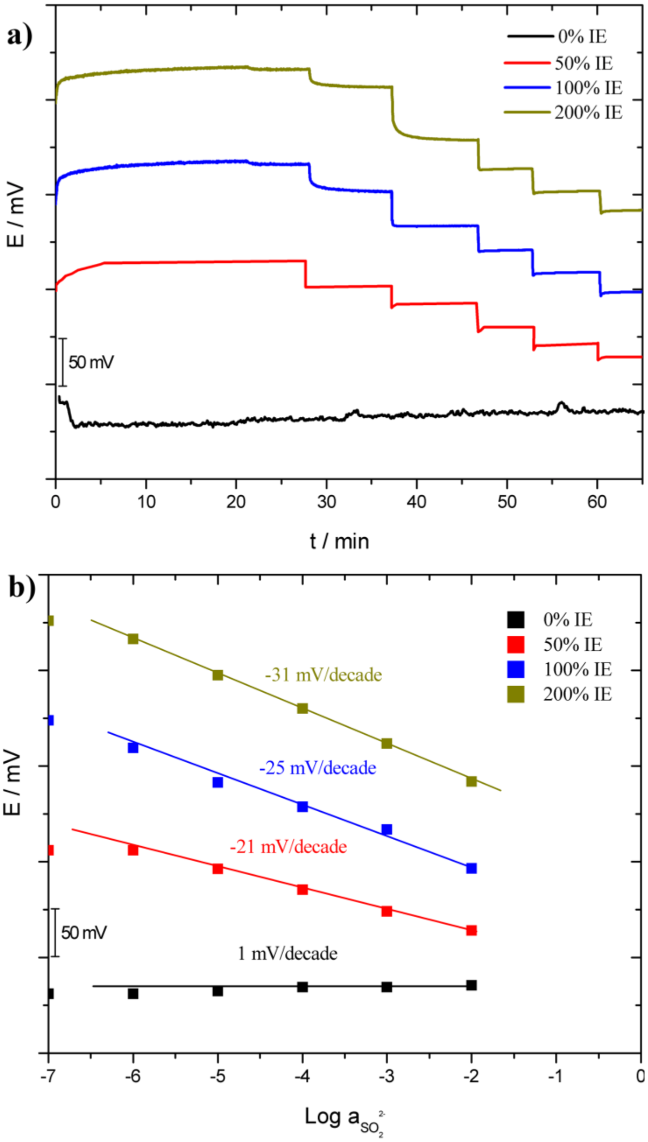


Figure 5.6. a) Time response for the MWCNT/SO_4^{2-}ISEs with different amounts of anion exchanger when changing the sulfate ion concentration in the test sample. b) Corresponding calibration curves for the MWCNT/SO_4^{2-}ISEs.

Different responses related with the amount of ion exchanger were obtained. From no response (0% ion exchanger content) to a Nernstian response (200% of ion exchanger per mol of ionophore) were observed while intermediate slopes were obtained when the contents of ion exchanger were in between these two extreme values. This observation is in good agreement with previous reports.[30,31] Noteworthy, without anion exchanger, no potentiometric response was observed indicating that the charged ionophore is not actuating and requires the use of the anion exchanger.[32]

As shown in Figure 5.7, the higher the amount of ion exchanger, the slightly higher the estimated selectivity coefficients. Nevertheless, the response of the selective membrane is still very pronounced towards more lipophilic salts such as nitrate or bromide, which represent a high degree of interference from these anions if they are present in the test solution. A selectivity pattern following the Hofmeister series is indeed observed.

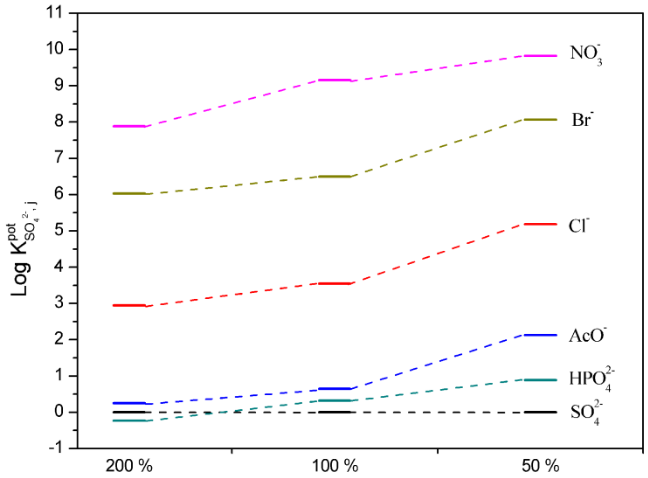


Figure 5.7. Potentiometric selectivity coefficients of SO_4^{2-}-selective membranes with different amounts of ion exchanger per mol of ionophore determined by SSM at the 10 mM level.

5.2.3.5. Ionic liquid incorporation into ion-selective membrane

It is known that the relative tendency of a certain anion to enter into a membrane is the balance between two energies, one resulting from the anion–water interaction and the other reflecting the anion–membrane interactions.[33] The response of the PVC based membranes basically displays the well-known Hofmeister series which determines that the anion selectivity is related to the partition coefficients between water and the membrane.[34] In spite that some reports demonstrated the use of very selective receptor to enhance the selectivity towards hydrophilic anions[35,36], the selectivity pattern in ISEs is strongly influenced by the partition coefficient of each ion between the polymeric matrix and the aqueous solution. Some modification of the polymer matrix have been reported to increase the polarity of the organic media, nevertheless such modification of the chemical composition of the membrane is challenging because the chemistry to be used involves groups that binds anions, which therefore modify the selectivity.[9] An alternative to enhance selectivity towards hydrophilic anions has been recently reported by the introduction of ionic liquids.[33,37]

Here, a potentiometric sulfate electrode was developed by incorporating the 1-butyl-3-methylimidazolinium hexaflourophosphate as ionic liquid (IL) into the polymeric matrix (Figure 5.8) to try to obtain ISMs with modified Hofmeister series behaviour, favouring the extraction of hydrophilic sulfate anions from the sample by reducing the difference in dielectric constants between water and the membrane phases.

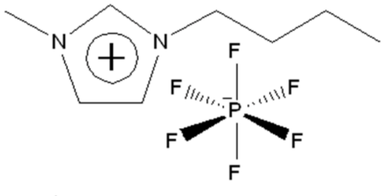


Figure 5.8. Structure of the ionic liquid 1-butyl-3-methylimidazolinium hexaflourophosphate (IL) used to enhance the hydrophilicity of ion-selective membranes.

As first experiment, the sulfate ionophore was incorporated into the membrane as Coll *et al.* proposed, in order to study our system under the same conditions (41.84% w/w PVC, 25.11% w/w NPOE, 25.94% w/w IL and 7.11% w/w ionophore). The resulting curves are shown in Figure 5.9.

With the incorporation of squaramide as ionophore for sulfate the system proposed by Coll *et al.*[33] did not give any response to sulfate addition. The ISM does not contain any anion exchanger in this latter case since it was reported that the ionic liquid plays its role in this new configuration. Nevertheless, in our electrodes the ion equilibrium is not detected and the presence of anion exchanger should be therefore considered.

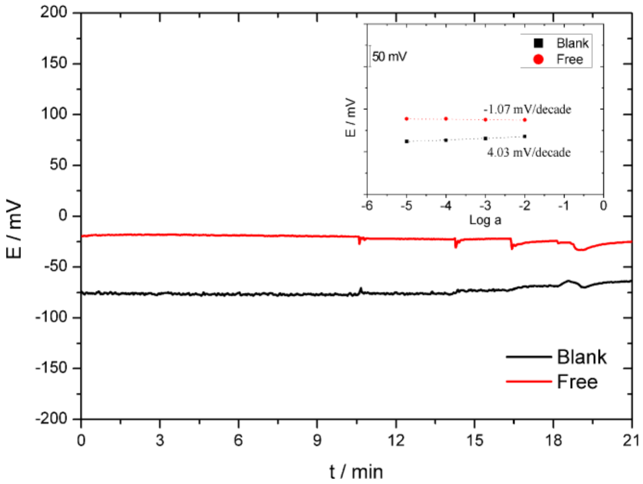


Figure 5.9. Time response for the SO_4^{2-} ISEs when changing the sulfate ion concentration in the test sample based on squaramide ionophore with the proposed composition by Coll *et al.* Inset: calibration curves.

To study the effect of ionic liquid content, four different membranes were prepared varying the content of IL (15% w/w, 25% w/w, 35% w/w and 50% w/w of IL) while keeping constant the amount of all other components. No significant changes were observed, but with 50% w/w of IL a slope of -12 mV/decade was obtained (Figure 5.10). Higher amounts of IL liquid seem to favour the entrance of sulfate into the membrane but only a sub-Nernstian response was obtained. Further increase of IL content was not considered since IL leaching out from the ISM was detected by mass spectroscopy. Additionally a cationic response can be observed with lower IL content, *i.e.* 15% w/w. This is usually attributed to the PVC impurities that act as cation exchanger.[29]

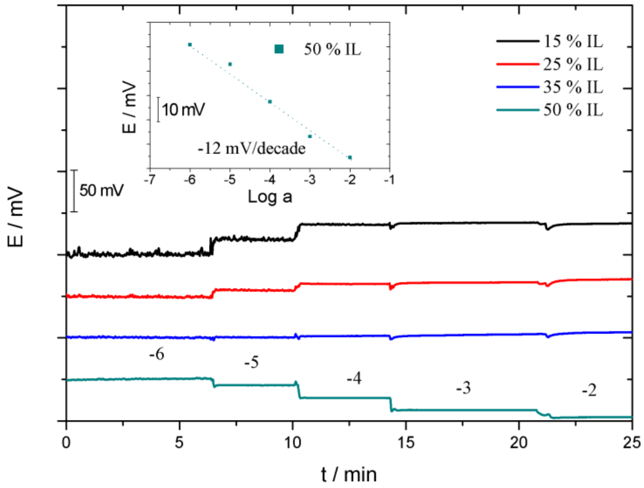


Figure 5.10. Time response for the SO_4^{2-} ISEs when changing the sulfate ion concentration in the test sample based on squaramide ionophore with different amounts of ionic liquid in the membrane. Inset: calibration curve for the SO_4^{2-} ISEs based on squaramide ionophore with 50% IL.

In order to study the effect of IE on IL system, a 25 % IL content membrane was studied adding different amounts of IE into the membrane (17% w/w, 50% w/w and 100% w/w); the recorded response is shown in Figure 5.11. At the highest content of IE a small slope of -6 mV/decade was obtained, this agrees with the effect of IE into the response of the electrode already demonstrated in previous experiments.

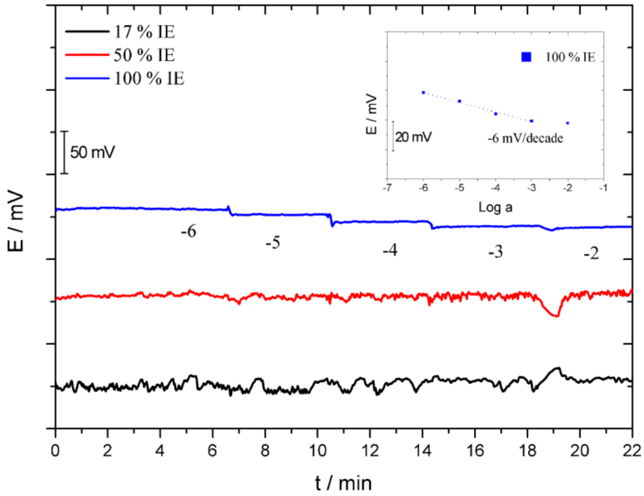


Figure 5.11. Time response for the SO_4^{2-}ISEs when changing the sulfate ion concentration in the test sample based on squaramide ionophore with different amounts of ion exchanger in the ion-selective membrane. Inset: calibration curve for the SO_4^{2-}ISEs based on squaramide ionophore with 100% IE.

Finally, using the composition already optimized (1% w/w ionophore, 200% of IE per mol of ionophore, with 2:1 NPOE/PVC) small amounts of IL were incorporated into the membrane (1% and 5%). No response was observed with the presence of IL (Figure 5.12).

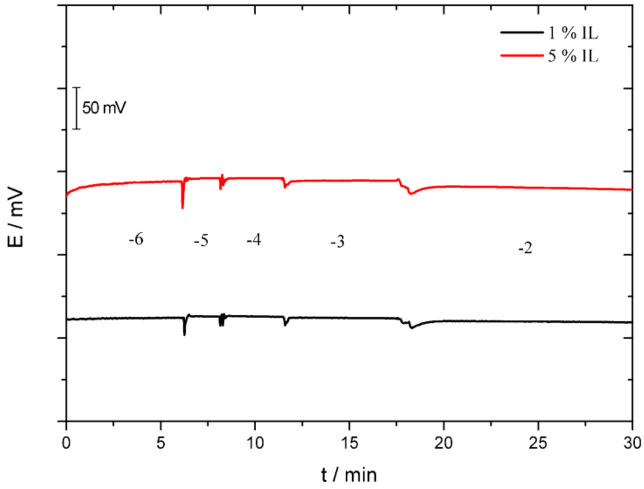


Figure 5.12. Time response for the SO_4^{2-}ISEs when changing the sulfate ion concentration in the test sample, based on squaramide ionophore with different amounts of ionic liquid in the ion-selective membrane.

Although IL have been reported to improve the selectivity of hydrophilic anion~~s~~ sensors[33,37], in our system the ionic liquid seems to make difficult the sulfate detection since a Nernstian response has never been obtained

5.2.3.6. Potentiometric analysis

Finally, using the optimized parameters a calibration curve was estimated. The parameters used were: 1% of ionophore (5 mg of hybrid material), 200% ion exchanger per mol of ionophore and polymeric matrix PVC/NPOE in a ratio 1:3 in order to obtain 100 mg of membrane, all the components were dispersed on 1 ml of THF. The obtained results are shown in Figure 5.13, where the errors bars are the average of three different electrodes measured consecutively; A Nernstian response was obtained (-30 mV/decade) with fast responses times (< 10 s) with a linear range between 10^{-6} to 10^{-2} M SO_4^{2-} and limit of detection of $7.9x10^{-7}$ M SO_4^{2-}.

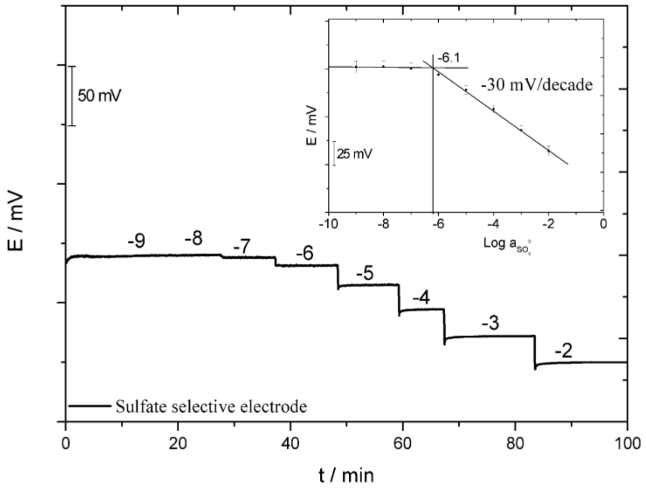


Figure 5.13. Time response for the MWCNT/SO_4^{2-}ISEs when changing the sulfate ion concentration in the test sample. The inset shows the corresponding calibration curve. The error bars in the inset represent the average of the three EMF values recorded for three different electrodes.

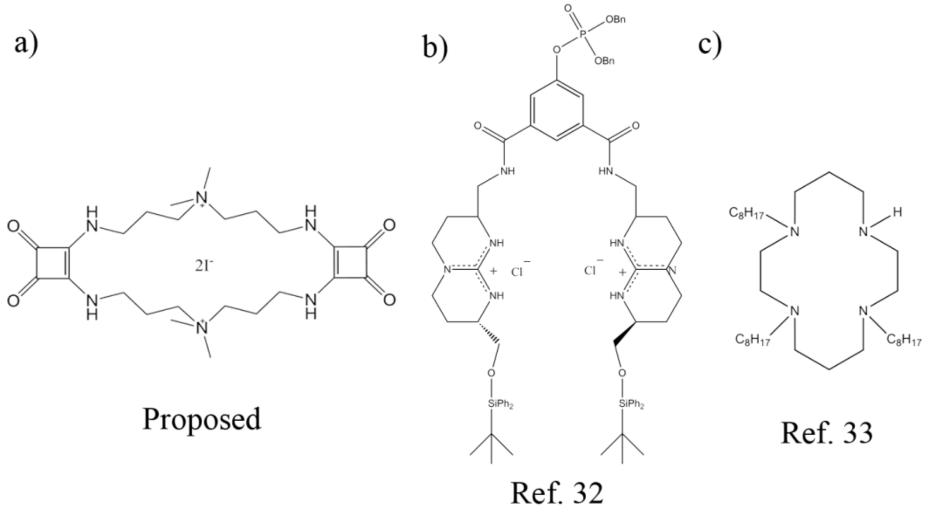
To summarize the electrochemical parameters of the proposed membrane are listed in table 5.2. In this table a comparison with two different sulfate electrodes previously published is also provided.[32,33]

Table 5.2. Potentiometric quality parameters for the proposed electrode and comparison to other two electrodes previously reported.

Parameter		Proposed*	Ref. 32*	Ref. 33**
Slope (mV/decade)		-30	-27	-30
Limit of detection (M)		$8x10^{-7}$	$1x10^{-6}$	$1x10^{-4}$
Linear range (M)		$1x10^{-1}$–$1x10^{-6}$	N/R	$1x10^{-1}$–$4x10^{-5}$
Selectivity coefficients	Br^-	6.0	2.4	-0.96
	Cl^-	2.9	-0.2	-1.16
	CH_2COO^-	0.2	-1.7	-1.70
	NO_3^-	7.8	4.3	N/R
	HPO_4^{2-}	-0.2	-0.9	N/R

*Separated solution method. **Fixed interference method. N/R: Not Reported

The system proposed by Fibbioli *et al.* is based on an internal solution electrode containing a membrane with an entrapped bis(guanidinium) ionophore (Figure 5.14b).[32] In this latter case, the selectivity deviates slightly from the Hofmeister series even though lipophilic anions such as bromide and nitrate are strong interferences. Coll *et al.*, using polyazacycloalkane derivate as ionophore (Figure 5.14c)[33], introduced the ionic liquid into the membrane showing dramatic increase of selectivity against more lipophilic anions such as bromide. However, the large amount of receptor needed (7.11% w/w) represents a significant drawback for this electrode based on internal solution. In contrast, the optimum amount of ionophore in our proposed system was 1% w/w and no changes were observed when increasing this amount. Although, the results of selectivity for the tested anions in our proposed electrode were poorer than in the mentioned works, Nernstian response, better linear range and lower limit of detection were obtained.



Proposed

Ref. 32

Ref. 33

Figure 5.14. Structural formulas of ionophores (Ph = phenyl, Bn = benzyl)

The high selectivity coefficients obtained means that the electrode developed here will suffer from strong interferences when trying to determine sulfate anions in samples containing at the same time anions less hydrophilic than sulfate. The squaramide based receptor demonstrated very high selectivity for sulfate against monovalent anions in aqueous medium. Nevertheless, entrapped into the polymeric matrix of ISM the receptor is not able to confirm this high selectivity. It might happen that the receptor is not able to adopt the right conformation in the organic medium of the polymeric membrane in order to selectively complex sulfate anion or simply that the more hydrophobic anions than sulfate tend to be extracted by the polymeric membrane independently of the ionophore entrapped. In addition, the high hydrophilic character of sulfate anions makes harder the extraction into a lipophilic medium like the PVC based ISM.

5.2.4. Conclusions

A sulfate-selective electrode based on a new hybrid material was developed and its performance parameters were studied and optimized.

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Nernstian response (-30 mV/decade), low limit of detection (8x10^{-7} M) and good linear range (1x10^{-1}–1x10^{-6} M) were obtained. Nevertheless, high potentiometric selectivity coefficients for more lipophilic anions were obtained. However, we here demonstrated the possibility of incorporating hydrophilic ionophores in a hydrophobic membrane overcoming therefore the limitation of conventional ISM. Further work has to be done in order to achieve better determination results using ion-selective electrodes and hydrophilic anions.

5.2.5. References

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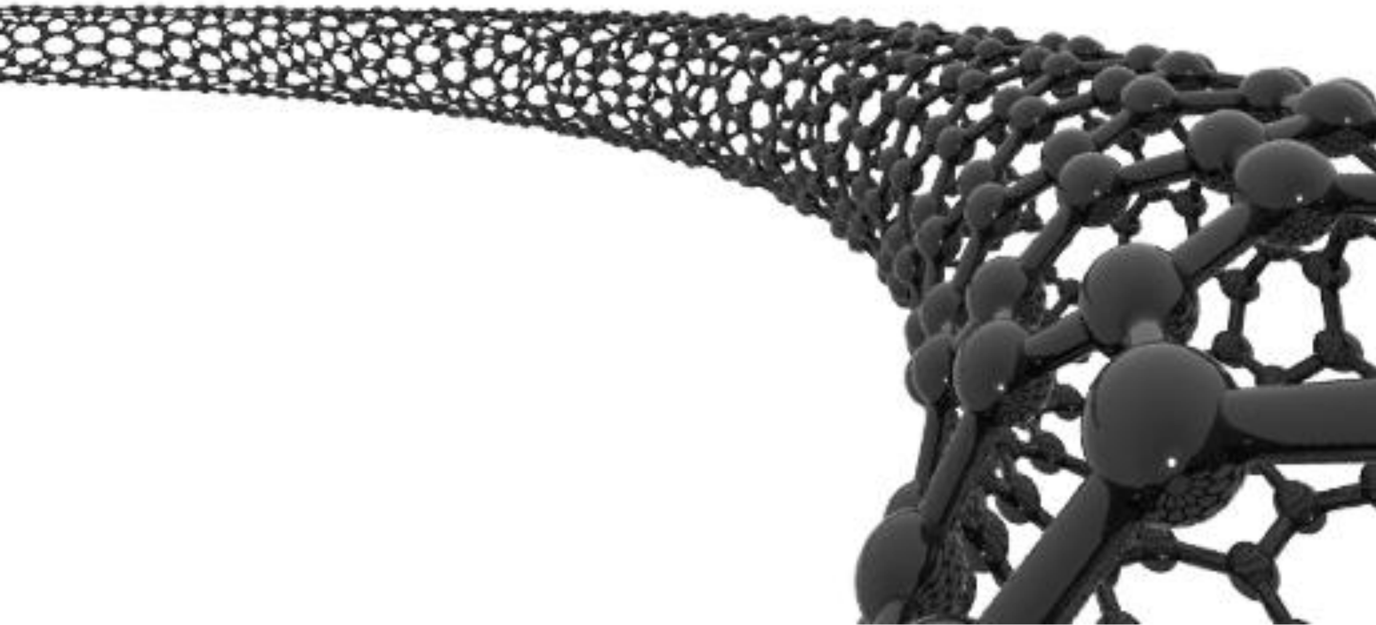
Chapter 6

New polymeric matrix for ion-selective electrodes



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6.1. Introduction

Throughout this work different approaches for the detection of ions in aqueous media using solid-contact ion-selective electrodes have been presented. Nevertheless, the selectivity pattern of the ISEs is highly influenced by the polymeric membrane itself (usually PVC based membrane). Two main aspects intervene in the detection, specifically, in the extraction equilibrium between the immiscible layers: the lipophilicity of the polymeric membranes and the free energy of hydration of the ions, particularly anions. In this Chapter, we aim at studying the influence of the polymeric membrane structure on the selectivity pattern by reducing the lipophilic character of the matrix. We propose here a new ion-selective membrane based on polyvinyl butyral for the detection of nitrate as a model analyte. This work was carried out in collaboration with Dr. Gastón A. Crespo and Dr. Francisco J. Andrade from our University.

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6.2. New polymeric matrix for ion-selective membranes

6.2.1. Introduction

Anion receptor design and synthesis are less developed than the cation counterparts. Anion recognition is indeed very challenging and the small number of selective anion receptors can be related to the various differences between anions and cations. For instance anions are relatively large and therefore require receptors with a much larger binding site. In addition, anions have many different shapes, *e.g.*, spherical halides, linear SCN^-, trigonal planar NO_3^-, and tetrahedral $H_2PO_4^-$. Moreover, anions are more strongly hydrated than cations, whereas the solvation by organic solvents is reduced. In addition, several anions may be present in a narrow pH window, *e.g.* the pairs $HPO_4^{2-}/H_2PO_4^-$ and HCO_3^-/CO_3^{2-} anions in acid and basic environments, respectively.[1,2]

For ion-selective membrane based on polymers, the anion selectivity is governed by the partition coefficient of anions. The partition is determined by the lipophilic character of the membrane and the relative dehydration energies of the anionic species. As a consequence, the selectivity of a conventional ISE follows the Hofmeister series[3]: $ClO_4^- > SCN^- \approx I^- >$ salicylate$^- > NO_3^- > Br^- > NO_2^- \approx Cl^- > HCO_3^- > H_2PO_4^- \approx F^- \approx SO_4^{2-} \approx HPO_4^{2-}$. Hydrophilic anions, such as sulfate or dihydrogen phosphate, suffer therefore strong interference from more lipophilic anions, such as nitrate or perchlorate. This selectivity pattern is particularly critical in many practical applications including clinical analysis of blood/serum anions such as chloride where hydrophobic anions could be also present.[4]

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The polymeric membrane consists usually of a high molecular weight poly(vinyl chloride) (PVC) with a plasticizer, a high boiling organic liquid such as *o*-nitrophenyl octyl ether (NPOE) or dioctyl sebacate (DOS). The plasticizer is required to decrease the glass transition temperature of the matrix as well as to increase the polarity of the membrane for the partition of ions. The variation of polymer matrix type can be used to achieve more polar environment in order to optimize the analytical performances such as sensor sensitivity and selectivity.[2] First, polar membranes with increased polarity vary the solvation of anions in the membrane phase.[5] And second, the high binding ability receptor could give, to some extent, a deviation from the Hofmeister series.[6]

In principle, the use of a less lipophilic polymeric membrane could help to overcome the problem that brings the Hofmeister behaviour, thus promoting a better competition between anions and reducing the strong interference from the more lipophilic anions. The polyvinyl butyral (PVB) is a hydrophilic polyacetal produced by the condensation of polyvinyl alcohol with n-butyraldehyde in the presence of an acid catalyst.[7] The final structure can be considered to be a random ter-polymer of vinyl butyral, vinyl alcohol and vinyl acetate (Figure 6.1).[8] The proportions of x, y and z are controlled to obtain PVB resins with different properties. Different polyvinyl butyral resins are available on the market depending on the hydroxyl group content. Here in this study, the commercial PVB resin used, a Butvar B-98, which contain the higher amount of hydroxyl groups (x=80%, y=18% and z=2%). PVB polymer possesses increased polarity compared to PVC so that this enhanced hydrophilic character could result as a selectivity pattern variation.

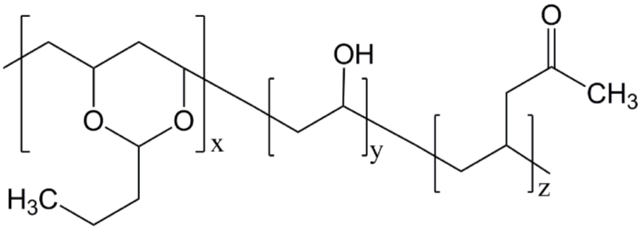

Figure 6.1. Polyvinyl butyral resin.

Nitrate is an important anion in environmental and biological analysis.[9,10] Because it has direct impacts on health, excessive amount of nitrate in waters indicates a level of pollution, mainly due to the abuse of fertilizers. Various methods including fluorescence,[11,12] flow injection analysis spectrophotometry,[13-16] electrochemical methods based on modified electrodes,[9,17] and nitrate-selective electrode[18,19] have been developed for the determination of this anion in various media. Among these methods, potentiometric detection based on ion-selective electrodes (ISEs) provides a rapid, simple, and inexpensive way of determining this ion in different samples. Nevertheless, selectivity is an analytical parameter that could be improved, *i.e.* almost all nitrate selective electrodes are based on ion-selective membranes that provide Hofmeister-type selectivities[20,21], therefore, they suffer from interferences caused by the presence of more hydrophobic anions.

Few nitrate receptors have been introduced in ISM for the production of nitrate selective electrode.[22-26] For instance, tripodal tris(2-aminoethyl)amine (tren) derivatives which are capable of binding nitrate via properly positioned hydrogen bonding groups have been proposed as pH-insensitive receptors for nitrate.[27] Here, we report the development of a new solid-contact nitrate selective electrode based on Tris-[2-(4-tert-butylbenzoyl)aminoethyl]amine[22] (Figure 6.2) with a new polymeric ion-selective membrane based on polyvinyl butyral. Analytical performances were fully characterized as well as some preliminary experiments in real samples performed.

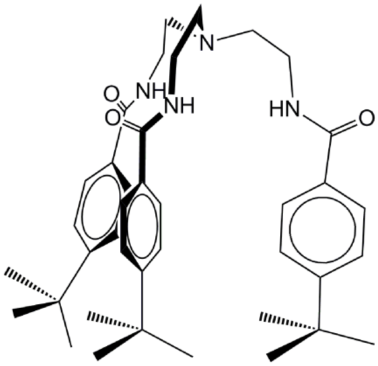

Figure 6.2. Tris-[2-(4-tert-butylbenzoyl)aminoethyl]amine (1).

6.2.2. Experimental section

6.2.2.1. Chemicals reagents and material

The multi-walled carbon nanotubes (MWCNT) were purchased from HeJi in bulk form with > 99% purity, 150 µm average length and 10-20 nm diameter. Acetone and analytical grade sodium sulfate (Na_2SO_4), sodium chloride (NaCl), sodium bromide (NaBr), sodium nitrate ($NaNO_3$), sodium monohydrogen phosphate (Na_2HPO_4), sodium dihydrogen phosphate (NaH_2PO_4), sodium acetate ($NaCH_3COO$), sodium perchlorate ($NaClO_4$) salts and poly(vinyl chloride) high molecular weight (PVC) were purchased from Sigma–Aldrich. Polyvinyl butyral resin BUTVAR® B-98 (PVB) was obtained from Quimidroga, S.A., 2-nitrophenyl octyl ether (NPOE), valinomycin, tetrahydrofuran (THF), potassium tetrakis(4-clorophenyl)borate (KTClPhB) and tridodecylmethylammonium chloride (TDMACl) were of selectophore® grade from Fluka. Deionized and charcoal-treated water (18.2 MΩ•cm specific resistance) were obtained with Milli-Q PLUS reagent-grade water system (Millipore). Sandpapers and alumina were obtained from Buehler. Sigradur G glassy carbon rods

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were obtained from HTW. Teflon blocks were obtained from RS Amidata. Hydrophobic PTFE membrane filters (Ø: 47mm and $Ø_{pore}$: 0.20 μm) were obtained from Albet, LabScience.

The synthesis of receptor 1 was performed following a previously described procedure.[22]

6.2.2.2. Multi-walled carbon nanotubes purification

Before being used MWCNTs were purified as follows: MWCNTs were baked at 500 ºC in a tubular oven with dry air atmosphere for 45 minutes in order to remove amorphous carbon.[28]

6.2.2.3. Electrodes preparation

The glassy carbon rods (GC) (50 mm length and 3 mm diameter) were inserted into a Teflon body (4 mm length, 3 mm internal diameter and 5 mm external diameter). The electrode was polished with abrasive paper (Buehler Carbimet 600/P1200) followed by alumina of different sizes (30, 5 and 1 μm Buehler Micropolish II) and cleaned with ultrasonic tip sonicator after each size of alumina. The final surface was cleaned several times with acetone.

6.2.2.4. Membranes preparation

PVC membranes: 0.5% w/w MWCNT were dispersed in 1 ml of THF using a sonicator bath and then the required amount of tridodecylmethylammonium chloride (TDMACl) and PVC:NPOE in a 1:2 ratio were added to obtain a total of 100 mg of membrane. The sonicator bath (100W) was used until complete dissolution of components.

PVB membranes: 0.5% w/w MWCNT were dispersed in 1 ml of THF using a sonicator bath and then the required amount tridodecylmethylammonium chloride (TDMACl) and PVB resin was added to obtain a total of 100 mg of membrane. The sonicator bath was used until complete dissolution of components.

6.2.2.5. Electrochemical measurements

Potentiometric responses were recorded with a high-input impedance (10^{13} Ω) 16-channel EMF-16 interface (Lawson Labs) at room temperature (22 ± 2 ºC). A double-junction Ag/AgCl/3 M KCl reference electrode (type 6.0729.100, Metrohm AG) containing a 1 M lithium acetate electrolyte bridge was employed. All measurements were corrected with the Henderson equation and the Debye–Hückel approximation and were done with three electrodes to evaluate the reproducibility of the sensors. Potentiometric selectivity coefficients ($K^{pot}_{NO_3^-,j}$) were calculated employing the separate solution method (SSM)[29,30] using a range from 10^{-5} to 10^{-3} M sodium salts solutions of the primary ion NO_3^- and interferences: Cl^-, Br^-, ClO_4^- and SO_4^{2-}. The calibration curves for nitrate were obtained by successive additions of different nitrate solutions.[29] The electrode was conditioned 24 h in a 10^{-3} M NO_3^- solution and then 48 h in a 10^{-9} M NO_3^- solution before measurements to avoid ion fluxes at low concentration due to the lack of membrane equilibrium.[31]

6.2.3. Results and discussion

6.2.3.1. PVC *vs.* PVB

Three blank membranes were prepared (*i.e.* PVB with and without plasticizer and PVC with plasticizer) not incorporating ionophore but the anion exchanger TDMACl (*i.e.* 1% w/w) and 0.5% w/w of MWCNT. The selectivity coefficients were calculated for three monovalent and one divalent secondary anions (Cl^-, Br^-, ClO_4^- and SO_4^{2-}) (Figure 6.3). The selectivity was recorded by measuring the calibration for each anion in the range of 10^{-5} M to 10^{-3} M (Figure 6.4). Nitrate anion is an interesting target since it possesses a medium hydrophilic character compared to the highly hydrophilic sulfate and the highly lipophilic perchlorate.

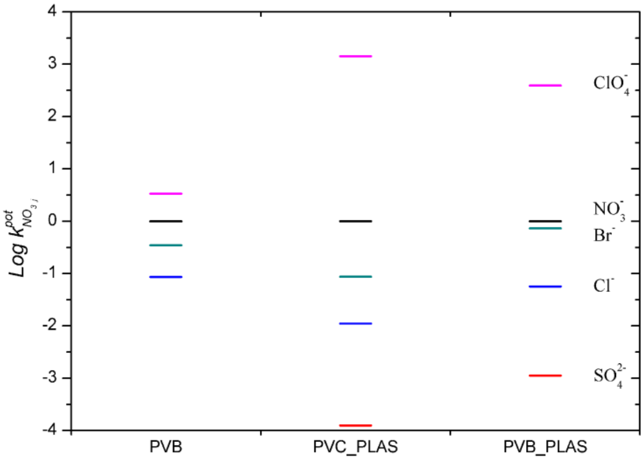

Figure 6.3. Selectivity coefficients for blank membranes, *i.e.* not containing ionophore: (PVB) without plasticizer and (PVB_PLAS) and (PVC_PLAS) with plasticizer.

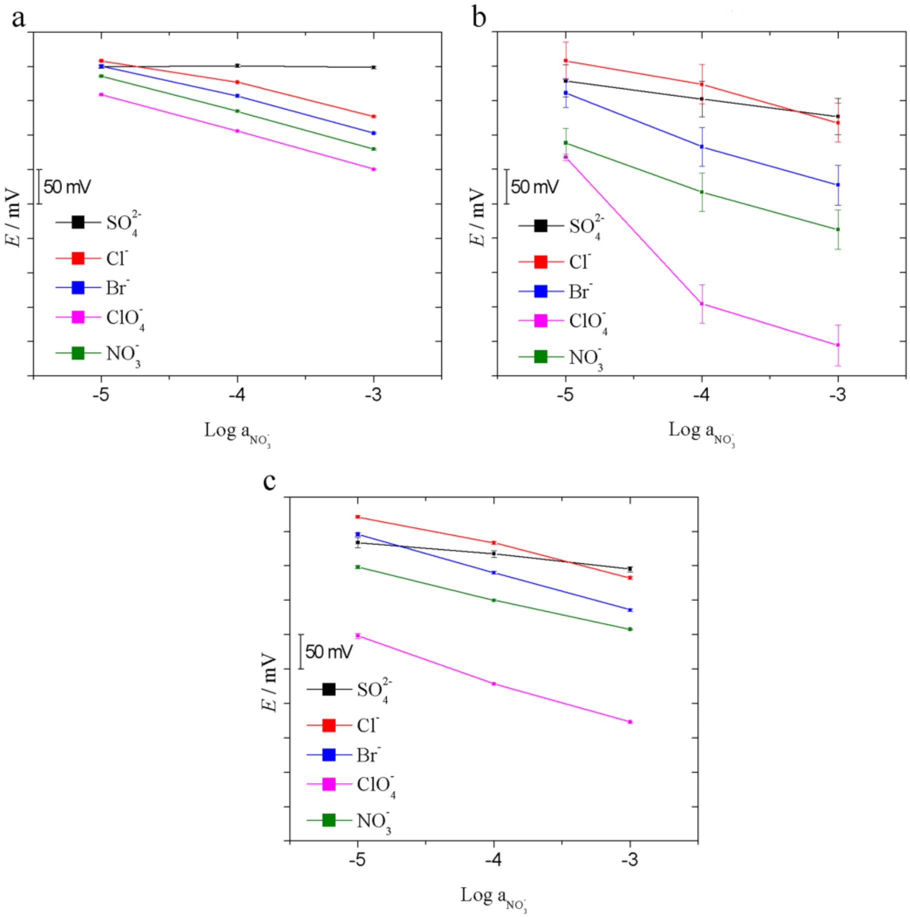

Figure 6.4. Calibration curves for blank membranes: a) PVB without plasticizer and plasticized b) PVB and c) PVC against 5 anions.

A slight variation in the selectivity coefficients was observed from PVC to PVB membranes with plasticizer. The reduced lipophilicity of the PVB membrane, due to the high content of polar groups, results as a smaller gap between the selectivity coefficients of each anion (Figure 6.3). Nevertheless, no changes in the Hofmeister series order were depicted. In contrast, the ISM based on PVB without plasticizer displayed a dramatic variation of the selectivity coefficients, *i.e.* the ClO_4^- suffered two orders of magnitude decrease whereas both Br^- and Cl^- suffered one order of magnitude increase. Noteworthy, no potentiometric response to sulfate ions was observed. Further experiments with other divalent hydrophilic

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anions, such as phosphate and carbonate, should be performed to understand this phenomenon. It should also be compared to monovalent hydrophilic anions (*e.g.* dihydrogen phosphate) to assess whether this behaviour is due to either the hydrophilic character of the membrane or the anion charge. The differences in selectivity are therefore levelled in a narrow range (1.5 and 5 orders of magnitude for PVB and PVC respectively). Even though the loss of anionic response was detected for the more hydrophilic anions such as sulfate, PVB could present interesting features for anion detection by potentiometry.

The assayed membranes containing ion exchanger showed anionic response in presence of nitrate (Figure 6.5). A shorter linear range was observed for the PVB based electrode (*i.e.* 10^{-4} to 10^{-2} M NO_3^- and 10^{-5} to 10^{-2} M NO_3^- for PVB and PVC respectively). However, an increased sensitivity was obtained (*i.e.* -55 mV/decade and -46 mV/decade for PVB and PVC respectively). The limit of detection was comparable for the two polymeric systems studied here ($10^{-4.8}$ M and $10^{-5.0}$ M NO_3^-). Since the selectivity of the electrode was modified while the analytical parameters maintained, we decided to introduce a selective ionophore into the PVB based ISM.

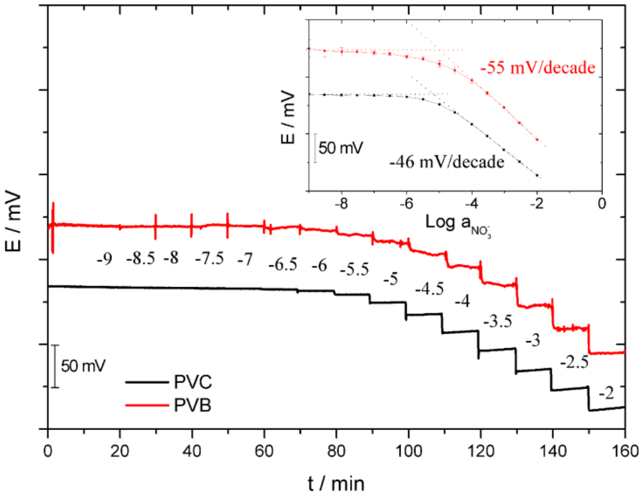

Figure 6.5. EMF *vs.* time plots for two different polymeric ion exchanger membranes against nitrate. Inset: calibration curves for the respective membranes.

6.2.3.2. Ion exchanger influence

A nitrate selective membrane based on PVB resin with tris-[2-(4-tert-butylbenzoyl)aminoethyl]amine, compound **1**[22] (see Figure 6.2) as ionophore was therefore studied. As the PVB resin was employed for the first time to build ISEs some parameters have to be optimized. The first one is the anion exchanger concentration. While keeping the level of ionophore constant (1 % w/w)[22] the amount of ion exchanger tridodecylmethylammonium chloride (TDMACl) was varied (*i.e.* 10%, 50% and 100% w/w of ion exchanger).

Figure 6a shows the potentiometric response of the three membranes. Membranes containing 50% and 100% TDMACl showed similar linear range (*i.e.* 10^{-6} to 10^{-2} M NO_3^-) and limit of detection (7.9×10^{-7} M and 5.0×10^{-7} M, respectively). These results are comparable to the PVC membrane (*i.e.* linear range: 10^{-5} to 10^{-1} M NO_3^- and limit of detection: 2.5×10^{-6} M)[22]. In both cases (50% and 100% TDMACl), the sensitivity was the same -55 mV/decade. In contrast, lower content of TDMACl shortened the linear range and reduced the limit of detection (*i.e.* 10^{-4} to 10^{-2} M NO_3^- and $5.0x10^{-5}$ M, respectively).

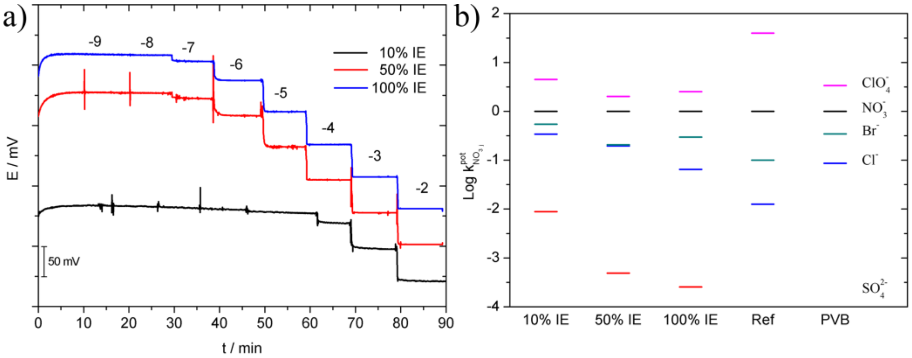

Figure 6.6. a) EMF *vs.* time plots for different ion exchanger (IE) contents membranes based on PVB resin. b) Selectivity coefficients for membranes based on PVB resin. Ref. stands for results obtained by Ortuño *et al.*[22] and PVB stands for blank membrane with 1% IE without ionophore.

The selectivity coefficients observed on the PVB membranes under study (10%, 50% and 100% IE Figure 6.6b) were lower for perchlorate anion by one order of magnitude compared to the previous report by Ortuño *et al*. However, these selectivity coefficients were higher for hydrophilic anions (Br^- and Cl^-) also by one order of magnitude compared to the reference (Ortuño *et al*.[22]). Taking into account these results, we can state that the interference from lipophilic anions can be reduced because of the lower lipophilicity of PVB polymeric matrix. In contrast, the interference from the medium hydrophilic anions considerably increased. Here, the interference from high lipophilic ions is reduced, but the interference due to the presence of more hydrophilic ions is enhanced. It maybe due to the high solvation energy of these ions.

The optimal response was obtained when 50% TDMACl was used, because of the reduced selective coefficients for lipophilic ions and wider linear range. In contrast, when 100% IE was used, the ion-selective membrane showed the same response as the ion exchanger membrane (PVB at Figure 6.6b).

6.2.3.3. Other quality parameters: water layer test, long term stability and pH influence

Figure 6.7 shows the results of the water layer test for PVB membranes containing 50% IE.[32] First, the signal was recorded at 10^{-3} M of nitrate, without any drift in the electrical response during this period. Then, a fast shift is observed, suggesting that the nitrate is rapidly replaced by chloride. Finally, the signal returns to its initial value in the solution of nitrate. A possible water layer can be discarded because the signal to the primary ion has the same value before and after being exposed to interfering ion. It is very important to note that the hydrophobic character of the MWCNT entrapped into the polar PVB matrix could still hinder the formation of a water layer.

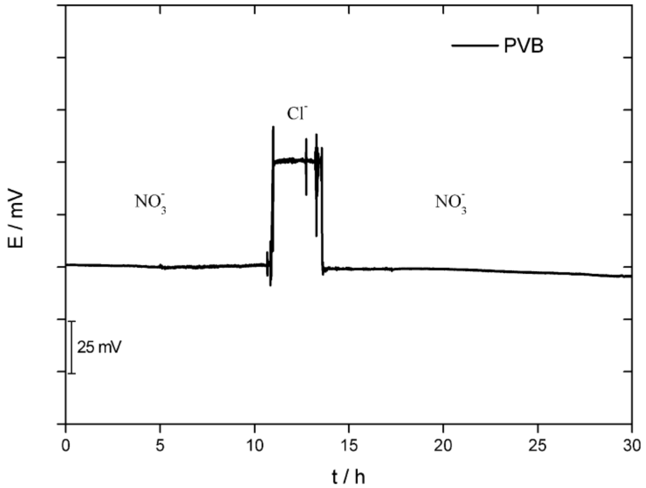

Figure 6.7. Water layer test for the membrane based on PVB resin containing 50% IE at 10^{-3} M NO_3^- and Cl^-.

The long-term stability was evaluated by measuring the EMF for 120 h using a 10^{-3} M NO_3^- solution. A drift of 27.9±0.1 µV h^{-1} was obtained for the PVB membrane. The stability of PVB based electrodes is better than previous reports incorporating other solid transducers, such as conducting polymers[33] and SWCNTs.[34-39]

The influence of pH was studied because of the molecular structure of the PVB. An universal buffer (containing 1 mM sodium borate, sodium acetate and sodium dihydrogen phosphate) fine-tuned with NaOH or HCl 0.1 M, was used to scan a wide range of pH values. No significant effect from the pH variation was detected in a range of 4 to 12 pH units (Figure 6.8). Therefore, electrodes based on PVB membranes can be used directly in samples displaying a wide range of pH values.

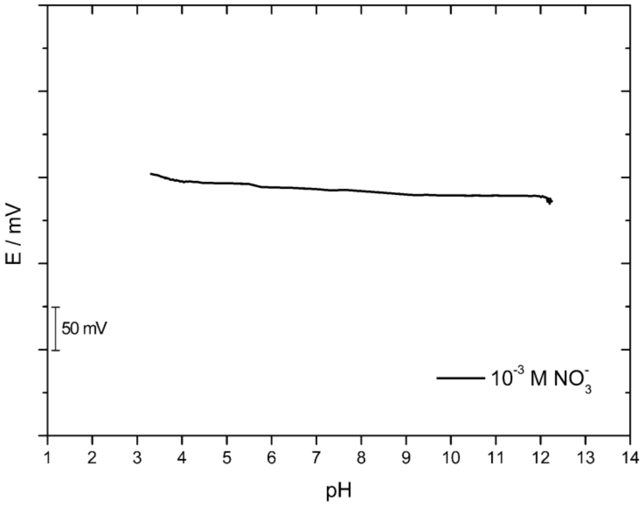

Figure 6.8. EMF *vs.* pH plot for nitrate ion-selective electrode based on PVB resin.

6.2.4. Conclusions

Ion-selective electrodes based on a new polymeric membrane were described. Poly vinyl butyral membrane gave comparable potentiometric behaviour with respect to PVC membranes. Higher stability and easier construction make PVB based membranes excellent candidates for ion-selective electrodes construction. Furthermore, this new generation of ion-

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selective electrodes based on PVB membranes suffered lower interferences from lipophilic anions and the interval of selectivity coefficients was reduced in almost two orders of magnitude respect to conventional PVC membranes containing the same ionophore, because of the higher polarity of the ion-selective membrane. However, the potentiometric response towards divalent hydrophilic anions such as sulfate was lost. These preliminary results indicate that these new membranes are promising for the analysis in real samples without suffering from biofouling because the presence of lipophilic species, *i.e.* biological species can adhere in the lipophilic membrane resulting in a complete failure of the electrode[40]. Further studies have to be performed to optimize the membrane preparation and be able to afford better selectivity coefficients.

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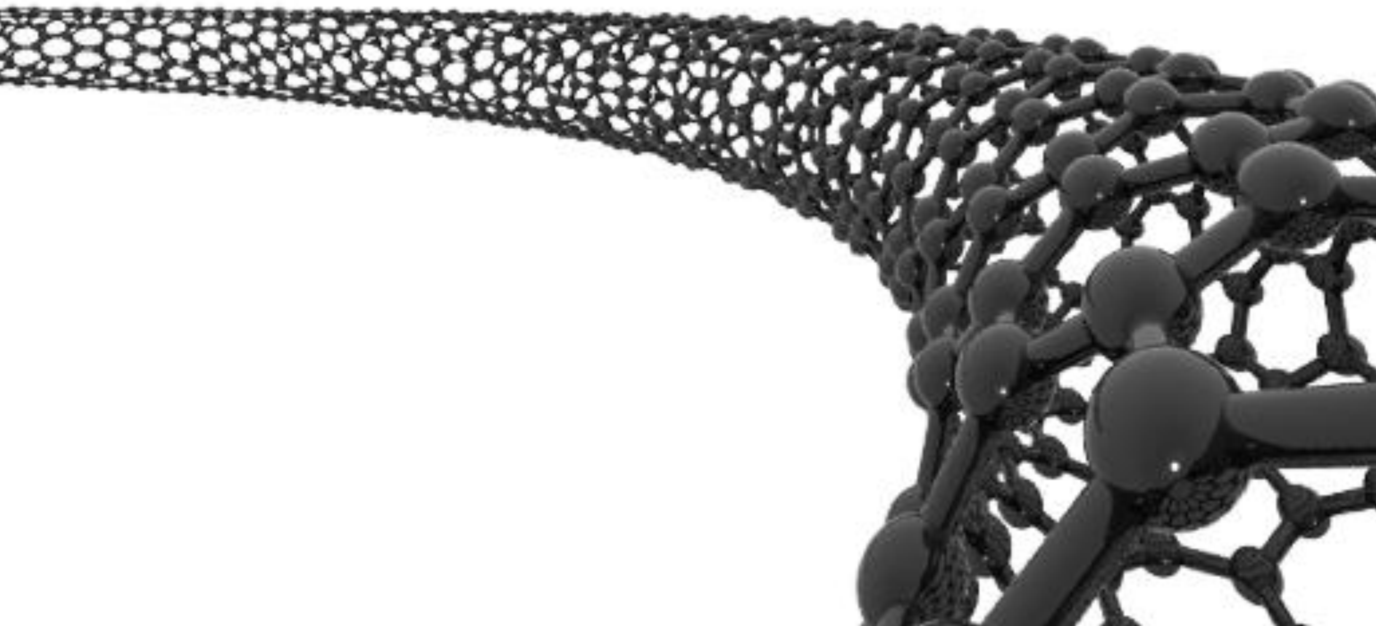
Chapter 7

Conclusions



7.1. Conclusions

The present Thesis reports the development, characterization and application of the first solid-contact ion-selective electrodes based on multi-walled carbon nanotubes. To demonstrate the concept of MWCNTs-based ISEs, different approaches were proposed: i) the implementation of MWCNTs as ion-to-electron transducer, ii) the covalent and non-covalent functionalization of MWCNTs with neutral and charged ionophores, and iii) the analysis of alternative polymeric matrix.

The ion-to-electron transducer property of MWCNTs was demonstrated by developing a new solid-contact potentiometric ISE for perchlorate detection. As previously reported, the transduction behaviour of MWCNTs was attributed to a high double layer capacitance resulting from the large interface between MWCNTs and the ion-selective membrane. The resulting perchlorate selective electrode did not suffer the drawbacks from conventional ISEs (*e.g.* CPs), such as redox side-reactions. In addition, the ISE was used to determine perchlorate anions in water and it showed excellent potentiometric properties. Moreover, the perchlorate SC-ISE was robust, easy-to-build and easy-to-miniaturize.

The concept of new hybrid materials capable to show both molecular recognition and ion-to-electron transduction properties were demonstrated in Chapter 4. The incorporation of a hybrid nanostructured material based on benzo-18-crown-6 ether covalently and non-covalently linked to MWCNTs confirmed not only the excellent potentiometric properties mentioned above, but also the fact that the ionophore did not leach out from the membrane. This work not only proved a concept, it described a hybrid material that can overcome some of the drawback of ionophores, thus opening up new routes for immobilizing hydrophilic receptors in hydrophobic phases and extending the sensing capabilities of ISEs.

A step further was the incorporation of a selective anion receptor covalently linked to MWCNT. In this work, a sulfate selective receptor, a hydrophilic squaramide–based macrocyle, was selected a suitable candidate. The receptor was anchored on the MWCNTs and the resulting material incorporated into the ISM giving rise to sulfate-selective electrode with good potentiometric properties, *i.e.* sensitivity, limit of detection and stability. However, high potentiometric selectivity coefficients were determined for more lipophilic anions. By this study, the incorporation of synthetic hydrophilic ionophores in a hydrophobic membrane was achieved but could not significantly reduce the high interference from highly lipophilic anions.

As last, a new polymeric matrix was suggested for the construction of anion-selective electrode in order to reduce the strong Hofmeister bias usually detected in PVC based electrodes. Thus, poly(vinyl butyral), *i.e.* a more polar resin than PVC, was used for ISEs construction. PVB based membranes showed good potentiometric properties when compared with PVC based membranes. The PVB based membranes were easier to build and possessed higher stability than PVC based membranes. Additionally, SC-ISEs based on PVB polymeric membranes suffered lower interferences from lipophilic species due to the higher polarity of the resulting ISM. Nevertheless, the potentiometric response towards divalent hydrophilic species such as sulfate was lost.

In some cases ion sensing by conventional ISE can be a challenging field. In this context, we have reported three different approaches to reach suitable potentiometric detection for ions. First, it was demonstrated that

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MWCNTs can work as an efficient ion-to-electron transducer layer. Second, the incorporation of hybrid nanostructured materials leads to high reproducible ISEs with excellent potentiometric properties offering the opportunity to incorporate hydrophilic receptor into the ISM. Last but not least, polymer matrix with higher polar character based PVB resin represents a promising alternative to PVC membranes and further work has to be done to understand the exchange mechanism of PVB based ISE.

7.2. Future prospects

Recently, cocktails containing carbon nanotubes were easily incorporated into non-conventional substrates for real life applications[1,2]. This innovation together with the hybrid nanostructure material approach will probably enable the incorporation of a new generation of ion-sensors for real life applications.

Furthermore, because SC-ISEs based on MWCNTs are very reproducible, easy-to-build and low cost devices with real possibility of miniaturization by screen-printing for instance, miniaturized disposable MWCNTs based sensors can be obtained.

However, a lot has still to be done to understand mechanism in the nanostructured assemblies. Some questions have to be raised: Can we incorporate any kind of receptor into the membrane? Does the membrane character really affect the ionophore sensing properties? Additionally, further have to be done in order to achieve better results with divalent hydrophilic anions.

Moreover, the study of new polymeric matrix showed that further and deeper analyses have to be done in order to optimize and to understand the mechanism of the new polymeric matrix.

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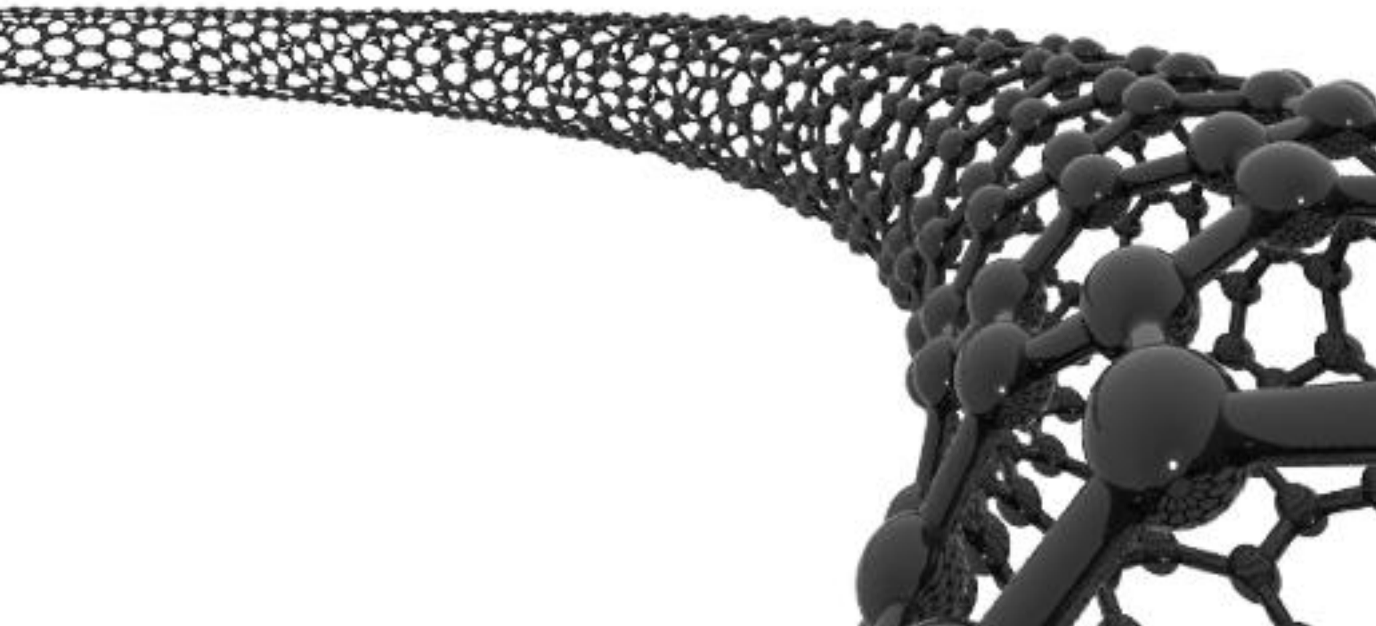
Scientific contributions



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Papers directly resulting from the Doctoral Thesis

- Enrique J. Parra, Gastón A. Crespo, Jordi Riu, Aurora Ruiz and F. Xavier Rius. "Ion-selective electrodes using multi-walled carbon nanotubes as ion-to-electron transducers for the detection of perchlorate". Analyst. **2009**, 134, 1905-1910.

- Enrique J. Parra, Pascal Blondeau, Gastón A. Crespo, F. Xavier Rius. "An effective nanostructured assembly for ion-selective electrodes. An ionophore covalently linked to carbon nanotubes for Pb^{2+} determination". Chemical communications. **2011**, 47, 2438-2440.

- Enrique J. Parra, Pascal Blondeau, F. Xavier Rius. "Non-covalent functionalization of multi-walled carbon nanotubes by selective ionophore for potassium potentiometric sensor". In preparation.

Papers indirectly resulting from the Doctoral Thesis

- Gaelle Kerric, Pascal Blondeau, Enrique J. Parra, Gastón A. Crespo, F. Xavier Rius. "Nanostructured assemblies for ion-sensors: functionalization of multi-walled carbon nanotubes by benzo-18-crown-6 for determination of Pb^{2+}". In preparation.

Oral communications

- Enrique J. Parra, Pascal Blondeau, Gastón A. Crespo and F. Xavier Rius. "Nanostructured assembly in potentiometric sensors: Improving selectivities with lead-ionophore covalently linked to carbon nanotubes". IV Workshop de Nanociencia y Nanotecnología Analítica. **2010**. Zaragoza, Spain. Flash presentation.

Posters

- Enrique J. Parra, Gastón A. Crespo, Jordi Riu and F. Xavier Rius. "Perchlorate ion-selective electrodes using multi-walled carbon nanotubes as ion-to-electron transducers". II Workshop de Nanociencia y Nanotecnología Analítica. **2008**. Tarragona, Spain

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