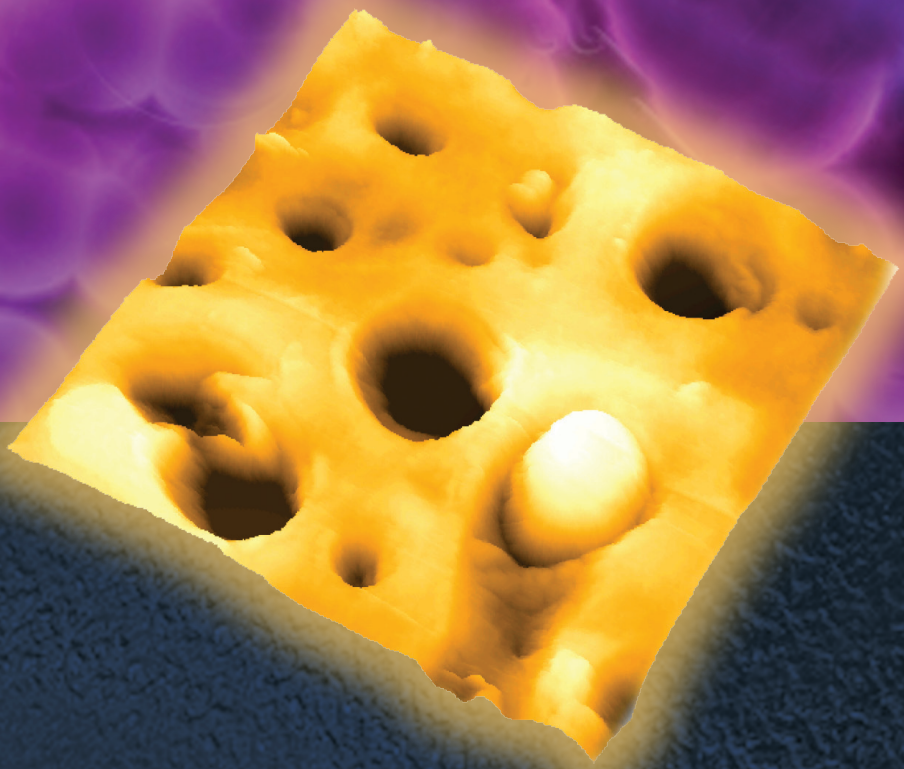
Membrane Modification

Technology and Applications



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Preface

At the turn of the twentieth century, many chemists, physicists, and biologists were studying the barrier properties of membranes. However, it was not until 20 years later when the first laboratory-scale membranes were manufactured and 50 years later when the most significant industrial breakthrough of asymmetric membranes led to greater application of membrane processes. Over the last 100 years, membrane processes have been established as an essential addition to conventional separation processes such as distillation and chemical extraction. Membrane processes have many advantages over other separation techniques that have led to their application in a wide range of industries including water treatment, biotechnology, food, pharmaceutical, and energy generation. The list continues to grow. The advantages membrane processes offer include highly selective separation, relatively low operating costs with low energy usage, and modular design with continuous and automatic operation. As more industrial applications exploit these advantages, within the second decade of the twenty-first century, there has been a resurgence of activity looking to control the barrier properties of membranes, to improve selectivity, to reduce energy consumption, and to optimize membrane applications by means of membrane surface modification. Hence, the rationale for this book, which presents an extremely timely review of membrane modification, will hopefully act as an information resource and inspiration to scientists and engineers charged with improving membrane separation processes. To that end, we have split the book into two sections: first, introducing membrane modification techniques, followed by research areas focusing on the application of modified membranes.

The underlying process of membrane separation is a selective separation achieved due to differences in the physical and chemical properties between a membrane, a solvent, and solute(s). A driving force acting on the feed solution transports the solvent or the solute, or both, to a membrane surface. The solvent can pass through the membrane, and the solute can either be retained in the feed side of the membrane or pass through the membrane depending on its size, activity, partial pressure, or charge. The simplest example of membrane separation is arguably microfiltration (MF), where suspended particles in the size range 0.05–10 μm, such as bacteria and dust particles, are separated in a liquid–liquid pressure-driven process. The separation mechanism of MF membranes is primarily controlled by steric rejection and by the sieving process of the membrane pores as the solvent passes through the membrane. Ultrafiltration (UF) membranes have pores in the size range 5–100 nm and are used to separate colloids and macromolecules with molecular weight in the range 10^4–10^6 Da. The separation mechanism of UF membranes is mainly steric; however, there is a growing acceptance that the charge differences between the solutes and the membrane surface also play a significant role. Nanofiltration (NF) and reverse osmosis (RO) are used to remove material existing as very small moieties, including synthetic dyes, agrochemicals, and aqueous salts. RO membranes ideally allow only water molecules to pass through; therefore, it is widely used on a large scale in the

desalination industry. The separation mechanism for NF is governed by the steric and charge interactions between the solute/solvent and the membrane. In all types of membrane operations, it is the chemical and physical properties of the membrane surface that control the efficiency and specificity of the separation process. Any new application of a membrane process must focus on the membrane surface, its chemical and physical characteristics, and its interaction with the components of the feed stream. This will inevitably lead to the following questions. Can the membrane surface be tailored to meet the specific needs for a given new application? Can it be modified to optimize a given separation process?

An inherent problem associated with all membrane separation processes is that of membrane fouling. During normal process operation, some feed species "foulants" are deposited on the membrane surface, changing its chemical and physical properties. This foulant material may be removed partially by standard operating procedures such as inverted flow operation and cleaning. Indeed, careful choice of the membrane material in terms of its chemical and physical interactions with the foulant(s) may reduce the buildup of foulant layers. However, if the foulant material builds up, then the fouling layers may alter the surface that interacts with the feed stream, modifying the surface roughness, hydrophobicity, charge and pore size. Membrane fouling can be reversible or irreversible, depending on the nature of the surface interaction. Both types can place economic constraints on the adoption of membrane separation processes. Thus, membrane fouling should be minimized, and again this can be achieved by modification of the membrane, with the knowledge of the foulant materials guiding the choice of base polymer membrane and the modification process.

It is worth mentioning in this preface that there are two main classes of membranes, namely, organic and inorganic. Inorganic membranes are relatively new in industrial application, and typical materials for these membranes are ceramics and zeolites, including alumina, titanium, and zirconium. Inorganic membranes have good tensile strength, have greater resistance to chemical attack, and are more applicable under extremes of temperature and pressure compared with organic membranes. However, the main drawback with these membranes is that they are extremely expensive. On the other hand, organic membranes manufactured from polymeric materials are commonly used because of their excellent bulk physical and chemical properties. They are less robust than inorganic membranes but are inexpensive and easier to construct. However, the application of polymeric membranes is currently limited due to their surface properties such as hydrophobicity and lack of functional groups. To date, a number of polymers have been used in membrane fabrication, including cellulose acetate, polysulfone, polyester, and polyamide. Unfortunately, there are a limited number of suitable polymeric materials commercially available. In addition, there has been no large-scale production of brand-new polymers within the last decade and nor is there any expected in the near future. Thus, membrane modification is one of the alternatives to increase the number and variety of membranes prepared for new and improved applications. There are two strategies for the development of novel membranes: one is to modify a bulk polymer system and subsequently prepare the membrane, and the second is to prepare the membrane from a standard polymer and then modify its surface. This last procedure can also be applied to inorganic membranes.

In this book, we have assembled the contributions from experts in the various fields that exploit membranes and have developed modification techniques to improve the efficiency of membrane operation. The book starts with an examination of the use of membrane modification to optimize the performance of membranes used in the challenging industry of nuclear power with its process streams consisting of radioactive wastes and acids that can destroy membrane functionality. Chapter 1 details the use of both polymeric and inorganic membranes in radioactive wastes processing. Membranes have been used for the separation of isotopes from gases and for liquid radioactive waste treatment. Membrane distillation (MD) is particularly useful for the concentration of low-level radioactive wastes in a small volume, appropriate for fossilization and production of clean water streams for discharge. Liquid membranes are also very attractive for nuclear technology because of their good separation ability and selectivity toward specific radionuclides. When considering membrane modification, Chapter 1 discusses the combination of different organic and inorganic materials, to obtain hybrid membranes of desirable structure and properties applicable to nuclear processing. To improve the functionality of membranes within the nuclear industry, different chemical and physical methods can be used to change the membrane surface in order to meet the challenges of the extreme environments; these include oxidation, chemical functionalization, plasma treatment, and radiation-induced grafting. The chapter concludes with case studies describing key membrane modification strategies that have benefited nuclear processing.

Chapter 2 comprehensively describes the use of impedance spectroscopy (IS) in the characterization of commercial and novel membranes. This useful technique measures impedance plots in relevant electrolyte environments to determine electrical charge parameters such as resistance and capacitance of a membrane. From these results, electrical/geometrical parameters for membranes or individual layers, such as conductivity, porosity, thickness, and dielectric constant, can be obtained. Thus, the influence of modification processes can be monitored and used to guide further strategies for improving the membrane separation processes.

We begin Chapter 3 with a discussion on the factors effecting membrane fouling. The chapter reviews recent studies in which the reduction of irreversible organic fouling and biofouling is attempted by the modification of the membrane surface. The chapter introduces the modification techniques of ultraviolet (UV)- and redox-initiated surface grafting of hydrophilic polymers, low temperature plasma treatment, physical coating/adsorption of a thin hydrophilic layer on the membrane surface, chemical reactions on the membrane surface, and surface modification of polymer membranes with nanoparticles.

Chapter 4 then expands the discussion on the use of nanoparticles in membrane modification processes. Materials in the form of nanoparticles have a large surface area to volume ratio, which infers many interesting properties on nanoparticulate systems due to the involved interfacial properties. As a consequence, nanoparticles are currently receiving a lot of interest in many industries, such as membrane technology where the control of interfacial interactions is important. Nanoparticles affect the permeability, selectivity, hydrophilicity, thermal and electrical conductivities, mechanical strength, thermal stability, and the antiviral and antibacterial properties of the polymeric membranes. Chapter 4 discusses important examples of

nanoparticles that have been incorporated into various types of polymeric membranes. The nanoparticles that are discussed include those based on silver, iron, zirconium, silica, aluminum, titanium, and magnesium, which have been applied to improve different types of membrane processes.

A common problem in water treatment using membrane processes is fouling with natural organic matter (NOM). This is the topic of Chapter 5 that discusses the modification of membranes to control fouling with NOM. The chapter describes how NF polyester thin-film composite membranes prepared by interfacial polymerization yield membranes with less fouling tendency for NOM. Another technique that can be used to improve the resistance of fouling by NOM is UV photografting. Chapter 5 discusses the results demonstrating that a membrane grafted with N-vinyl-2-pyrrolidinone (NVP) has superior properties for irreversible fouling. Discussions and analysis are based on atomic force microscopy (AFM), illustrating the importance of AFM to membrane modification characterization. AFM with its high-resolution imaging capability combined with force measurement capability is an extremely useful tool for membrane science.

MD is an emerging thermally driven membrane separation process that has been applied extensively to desalination, food processing, and removal of volatile organic compounds (VOCs) from water. It has several advantages compared with other separation processes, which include higher rejections of nonvolatile solutes, lower operating temperatures than conventional distillation, and lower operating pressures than conventional pressure-driven membrane separation processes. Chapter 6 describes how a significantly higher MD permeate flux could be achieved by using novel membranes fabricated by blending fluorinated surface-modifying macromolecules (SMMs) into hydrophilic host polymers. During membrane formation by the phase inversion method, the SMMs migrate to the top polymer–air interface, changing the final characteristics of the prepared membrane. Chapter 6 also demonstrates how a comprehensive characterization strategy benefits membrane modification processes. The fabricated membranes were characterized by different techniques such as x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), contact angle measurement, gas permeate test, and liquid entry pressure (LEP) of water.

Chapter 7 examines the use of plasma treatment for the modification of polymeric membranes. Plasma treatment is carried out at the membrane surface so that the beneficial properties of the bulk material remain unchanged. Surface properties such as roughness and functionality can be altered to improve the performance of the membrane. All these processes are very quick and the time taken for modification is usually a few seconds up to a few minutes. The method uses chemicals in the gaseous form and produces very small amounts of wastes. Among all techniques of membrane surface modification, plasma treatment seems to be the most versatile and environment-friendly. The authors of Chapter 7 discuss how these benefits impact on membrane modification strategies.

There is currently a renewed interest in the use of electrospinning techniques for the fabrication of membranes. Chapter 8 reviews the use of this versatile technique for the production of nanofiber webs or membranes. The chemical and physical properties of nanofiber membrane surfaces play an important role in their application to filtration, biomedical materials, tissue engineering scaffolds, drug delivery

carriers, for reinforcement in composite materials and electronics, antibacterial materials, and within the food processing industry as membrane bioreactors. Chapter 8 gives an overview of various surface modification techniques applied to enhance the bulk and surface properties of nanofiber membranes, rendering them suitable for specific applications.

Over the last 50 years, pervaporation (PV) has been developed as a technology with particular use in dehydration of solvents, alcohol/water separation, VOC removal from water, and separation of organic mixtures. Chapter 9 reviews the improvement of PV performance using membrane modification with a discussion on different strategies for surface modification of synthetic polymeric membranes and composite polymer/inorganic membranes.

The focus of this book then changes to be more application-based and demonstrates how the modified membranes have benefited different fields. An examination and a review of membrane modification to improve membrane crystallization processes are reported in Chapter 10. In this innovative process, the crystallization of biomolecules is enhanced to produce crystals with controlled structure and polymorphism. The chapter describes the theoretical and experimental correlations between the physicochemical properties of membranes, kinetics of nucleation, and characteristics of the final product. Membrane modification techniques using copolymers or additives are discussed in the context of controlling nanoscale physical and chemical characters of membranes for improved crystallization.

One of the most recent developments in the field of membrane technology has been the successful commercialization of polymer membrane processes for gas separation/purification. Chapter 11 argues that membrane modification can meet the remaining challenges for this technique, which include achieving higher selectivity for the relevant application while maintaining equivalent productivity and preserving the acceptable membrane performance, thermal stability, and chemical resistance in the presence of aggressive feeds. The most widely used modification strategies for the improvement of gas separation membranes are thermal treatment, polymer blending, and cross-linking. Cross-linking is achieved by a number of methods, including thermal, ion beam, and UV-irradiation treatment, or by chemical cross-linking.

Another emerging area where membrane modification is proving to be invaluable is that of polymer electrolyte membranes (PEMs) used for the construction of fuel cells, batteries, electrolyzers, sensors, and actuators. Chapter 12 discusses how membrane modification can meet the strong demand for the design of PEMs with particular properties. PEMs can be fabricated using electron beams obtained from accelerators, which have the advantage to be applied using simultaneous and preirradiation techniques. Various types of high-energy radiation, such as γ-rays and electron beams, can be used in radiation-induced grafting, irrespective of the morphology of the starting polymer. Chapter 12 reviews the latest progress in using electron beam for the preparation of PEMs for proton exchange membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) applications using novel radiation-induced grafting techniques. Chapter 13 continues the discussion on membrane modification for DMFC improvements, with a special focus on polymeric membranes based on sulfonated poly (ether ether ketone) (SPEEK). The modification strategies discussed for SPEEK include clay nanocomposite fabrication with

compatibilizer, composite SPEEK and boron orthophosphate membrane, tungstosilicic acid supported on silica–aluminum oxide, and SPEEK membrane blended with charged SMMs.

Chapter 14 covers the important area of the textile industry and how membrane modification can improve the separation processes in this industrial sector, which is recognized as one of the worst global polluters of water sources. The ability of NF to separate small and neutrally charged molecules from textile wastewater streams has gained a lot of attention in recent years. Chapter 14 provides an overview with case studies on the latest development of NF fabrication technology and puts this in the context of problems associated with the use of other treatment processes in the textile industry, thus demonstrating the advantages of NF in removing dye components and dissolved salts. Membrane fouling within the textile industry is also reviewed with emphasis on unraveling the mechanisms involved in guiding techniques such as membrane modification aimed at the reduction of fouling. Among the available practical solutions, the development of fouling-resistant NF membranes is the most sustainable one and is currently attracting considerable attention. Membrane modification strategies include changing the chemical functionality or the physical structure of the membrane. Hydrophilic groups and/or charged functional groups can be immobilized onto membrane surfaces using coating, blending, or grafting techniques to reduce fouling during the processing of the highly variable process streams of the textile industry.

In the final chapter, we have pooled the thoughts of the contributors to suggest some of the ways in which membrane modification may contribute to the development and application of membranes in the future.

We thank all the authors who have contributed to the writing of this book. We very much appreciate their willingness to devote their valuable time and efforts to this task and for the delivery of the high-quality chapters in time. We believe that membrane scientists and technologists from different disciplines and research fields will find this book stimulating and essential for their research and academic projects.

Nidal Hilal, Mohamed Khayet, and Chris J. Wright
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Editors

Nidal Hilal holds a chair in nanomembranology and water technologies at Swansea University. He is also the founding director of the Centre for Water Advanced Technologies and Environmental Research (CWATER) at Swansea University in the United Kingdom. Currently, he is establishing a Center of Excellence in Membranes and Desalination at Masdar Institute of Science and Technology in Abu Dhabi. This institution is being founded in collaboration with MIT. He obtained a PhD in chemical engineering from the University of Wales in 1988. His research interests lie broadly in the identification of innovative and cost-effective solutions to real-world process engineering problems within the fields of chemical engineering, nano-water, membrane technology, water treatment including desalination, colloid engineering, and nano-engineering applications of atomic force microscopy (AFM). He is now internationally recognized as a world leader in developing and applying the force measurement capability of AFM to the study of membrane separation and engineering processes at the nanoscale level. He has pioneered the application of AFM to chemical and process engineering problems and recently published a book in this area. His research has led to the use of AFM in the development of new membranes with optimized properties for difficult separations. He has published 5 books, 21 invited book chapters, and around 300 articles in the refereed scientific literature. He has chaired international conferences and delivered numerous invited lectures around the world. In recognition of an outstanding research contribution, he was awarded senior doctorate (Doctor of Science) by the University of Wales in 2005. He was also awarded the Kuwait Prize for Water Resources Development in the Arab World for the year 2005. This prize is regarded as the "Arab Nobel Prize" and is one of the highest scientific honors for intellectual achievement to be awarded in the Middle East.

Professor Hilal is the editor-in-chief for the international journal *Desalination*, is on the editorial boards of a number of international journals, and is a member of the advisory boards of several multinational organizations. He is a registered European Engineer, a Chartered Engineer in the United Kingdom, and a fellow of the Institution of Chemical Engineers. Hilal has carried out extensive consultancy for industry, government departments, research councils, and universities on an international basis.

Mohamed Khayet was born in Marrakech, Morocco, in 1966, and graduated from the Faculty of Sciences, University Cadi Ayyad of Marrakech (Morocco), in 1990. Funded by the Spanish Agency of International Cooperation (AECI), he pursued his doctoral studies at the Faculty of Physical Sciences, Department of Atomic Molecular and Nuclear Physics, University Complutense of Madrid (UCM, Spain), and received his PhD degree from UCM in 1997. He joined the Department of Applied Physics I (UCM) in 1997, serving as an assistant and then as an associate professor. Funded by UCM, he undertook a postdoctoral visit at the Industrial Membrane Research Institute (IMRI) in Ottawa (Canada) during the period 2000–2001. Currently, he is the professor of thermodynamics, statistical physics, and renewable energy applications in the Department of Applied Physics I (UCM) and is director of the UCM research group *Membranes and Renewable Energy.*

He has published over 100 scientific papers in international refereed journals and has written several invited book chapters and 3 books. He has given over 70 presentations at scientific conferences, workshops, and congresses. He is author of two patents in the field of membrane science and technology and has supervised national and international projects as well as research and academic studies. He is referee of a number of international journals and a member of the editorial boards of the following international journals: *Desalination*, *Applied Membrane Science and Technology*, *Membrane Water Treatment*, *Polymers and Membranes*. His current research interests include future desalination technologies, renewable energy, membrane fabrication characterization, membrane processes, modeling, and transport phenomena.

Chris J. Wright is a reader in bionanotechnology and membrane separation within the Multidisciplinary Nanotechnology Centre (MNC) at Swansea University. At Swansea, he is an executive member of the Centre for NanoHealth and is an associate director of the Centre for Complex Fluids Processing. He graduated from the University of Wales in 1996 with a PhD in biochemical engineering. In 2001, he was awarded a prestigious Advanced Research Fellowship by the Engineering and Physical Research Council (EPSRC), United Kingdom, in recognition of his innovative research applying AFM to the characterization of membrane and biological surfaces. This 5-year award allowed him to establish an internationally recognized research group exploiting the capabilities of AFM. His innovative research developing AFM force measurement capabilities to study biological interfaces has

been adopted by many other researchers and industry. In 2006, he was appointed Portfolio Director for Process Engineering within the College of Engineering at Swansea University and is now director of PhD studies within the MNC.

His research interests include the control of polymer surfaces for improved membrane separation and tissue engineering and the control of biofilms and the combination of AFM with advanced light microscopy methods. An underlying theme of this research is the application of nanotechnology to health care. His research has been sustained through major grants from government, charity, and industry. He is on the editorial board of the *Journal of Nanoengineering and Nanosystems* and is a member of the EPSRC College for the assessment of research grants. He has over 80 peer-reviewed international publications with 15 invited book chapters and review articles.

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1 Membranes in Nuclear Science and Technology: Membrane Modification as a Tool for Performance Improvement

Grazyna Zakrzewska-Trznadel
and Mohamed Khayet

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1.1 MEMBRANES AND MEMBRANE PROCESSES APPLIED IN NUCLEAR SCIENCE AND TECHNOLOGY

1.1.1 Membranes for the Separation of Isotopes

The idea of applying membranes in nuclear technology came from the work of Graham, who, in the middle of the nineteenth century, reported the possibility of separating gaseous mixtures by molecular diffusion. Later, the process was studied for the separation of isotopes of light elements such as neon, hydrogen, nitrogen, or carbon. During the 1940s and 1950s, the method was employed in the United States for the enrichment of ^{235}U, the fissionable natural uranium isotope. Since the concentration of ^{235}U in natural uranium is very low (0.711 wt%), the separation of this isotope is only possible by the application of a multistage process and a separation cascade with a large number of separating units. The crucial element of the system for isotopic enrichment is a membrane or porous barrier, the characteristics of which influence the stage separation factor and the size of the stage required to handle the desired stage flows. The preparation of such a material with fine pores of size range 6–40 nm, and a high bulk and surface porosity, presents a difficult technological problem.

Membranes for gaseous diffusion can be homogenic or composite, consisting of a porous, permeable support and a thin membrane layer with a small pore size. The information on the uranium technology applied during the Manhattan Project and the materials used for preparing the membranes is still being classified; however, it is known that the French technology uses sintered and anodic alumina, gold and silver alloys, nickel, Teflon, porcelain, or zirconium (Burggraaf and Cot 1996; Hsieh 1996). Composite membranes can be manufactured, for example, by sintering metallic powder with a ceramic material or by coating a metallic, porous support with a Teflon emulsion.

The development of membranes for uranium enrichment has led to the still growing market of ceramic membranes in France (Hsieh 1996). The characterization techniques of barriers suitable for the separation of isotopes by gaseous diffusion include adsorption methods, x-ray analysis, electron microscopy, mercury intrusion methods, permeability measurements with liquids or gases, and separation efficiency measurements. Various methods are used for preparing the membranes for gaseous diffusion, including etching with strong acids such as nitric acid for gold and silver alloys, sintering, pressing, or extrusion of the fine powders of metals or metal oxides such as nickel or alumina, as well as anodic oxidation (alumina). The use of metal oxides is beneficial because of their resistance to corrosive hydrofluoric acid, which is generated from uranium hexafluoride used in gaseous diffusion technology. Typically, the membranes in gaseous diffusion are operated at elevated temperatures of 60°C–200°C and under a pressure of up to 3.3 bars.

It was proved that isotopes other than uranium, such as those of Ar, Ne, O, and H, could also be separated by gaseous diffusion (Fain and Brown 1974). The membranes developed for this purpose are made from alumina, gold, or glass (Konishi et al. 1983; Evans et al. 1983). Attempts were made to use polymeric membranes for separating the isotopes. The membranes from polyethylene terephthalate (PET),

polyethylene (PE), polytetrafluoroethylene (PTFE), cellulose acetate (CA), and polyvinylidene chloride (PVC) were tested for the separation of hydrogen isotopes in a gaseous phase (Marcea 1983). For the separation of water isotopomers, which include heavy water (HDO), heavy oxygen water ($H_2{}^{18}O$) and tritiated water, the membranes prepared from regenerated cellulose, CA, and porous barriers from PTFE were studied. The Institute of Nuclear Chemistry and Technology (Warsaw, Poland) applied PTFE membranes for the enrichment of HDO and $H_2{}^{18}O$ in the process of membrane distillation (MD). The isotope separation effect of HDO/H_2O was also studied with cellulose membranes (Chmielewski et al. 1991; Zakrzewska-Trznadel et al. 1996). Polyphosphazene membranes for the separation of the water isotopomers were tested in the Pacific Northwest Laboratory (Nelson et al. 1996; Duncan and Nelson 1999). In the Korean Atomic Research Institute (Daejeon), an MD cascade was constructed for testing the enrichment of heavy oxygen water ($H_2{}^{18}O$) for medical applications in positron emission tomography (Kim et al. 2004). Using various membranes and membrane processes, the isotopes of chlorine (Campbell 1985), carbon (Fritz et al. 1987), and lithium (Whitworth et al. 1994) were separated. Nanofiltration (NF) membranes with complexing agents were applied for the separation of the gadolinium and neodymium isotopes (Chitry et al. 2001).

1.1.2 Membranes for Liquid Radioactive Waste Treatment

1.1.2.1 Properties of Membranes Selected for Radioactive Waste Treatment

Radioactive wastes are generated in the power generation cycle and during the dismantling of nuclear installations. The wastes from nuclear power reactors include miscellaneous waste, secondary waste, and chemical and detergent wastes. The radioactive wastes are generated at other stages of the nuclear cycle, such as in fuel fabrication plants, in spent fuel reprocessing installations, and during uranium enrichment and environmental remediation. Institutional activities such as radiopharmaceutical production and the application of radioisotopes in medicine, industry, and research also produce liquid radioactive wastes. The treatment of liquid radioactive wastes involves the concentration of radioactive species in a small volume and the conversion of this concentrate into an inert matrix, such as concrete, ceramics, or glass. Several processes are adopted for the treatment of the liquid waste, such as precipitation, evaporation, ion exchange and, in recent years, membrane methods. The efficiency of the treatment is measured by evaluating two characteristics: the decontamination factor (DF) (Equation 1.1) and the volume reduction factor (VRF) (Equation 1.2):

$$\mathrm{DF} = \frac{A_\mathrm{o}}{A_\mathrm{f}}, \tag{1.1}$$

$$\mathrm{VRF} = \frac{V_\mathrm{o}}{V_\mathrm{f}}, \tag{1.2}$$

where A_o is the specific activity of the waste before treatment, A_f is the specific activity of the waste after treatment, V_o is the initial volume of the waste, and V_f is the final volume of the waste.

Membranes employed for radioactive waste treatment have to fulfill very strict requirements, appropriate to the target applications. In addition to their separation ability, good permeability, and long lifetime, the membrane modules should have sufficient resistance to the ionizing radiation and a geometry enabling easy cleaning. Both types of materials, organic and inorganic, are applied for the preparation of membranes for liquid radioactive waste treatment (Zakrzewska-Trznadel 2008; Vienna Technical Reports Series 2004). The benefits of using polymeric membranes are their relatively low price and their wide commercial availability. Polymer membranes can be easily manufactured and arranged in various configurations and can be modified for specific applications. The advantages of the inorganic materials come from their high resistance to the aggressive chemical environment, high temperature, and ionizing radiation.

Polymeric membranes can be formed as flat sheets, tubes, or hollow fibers. The foils are also arranged as spiral-wound or pleated filters. The modular design of the membrane apparatus permits easy development of the filtration area and the scale-up of the process. The configuration of the membrane is very important from an operational point of view because it determines the flow hydrodynamics in the membrane system. Hydrodynamic conditions promoting turbulence and good mixing reduce the boundary layers and enhance the mass transport through the membrane (Zakrzewska-Trznadel et al. 2009; Cojocaru et al. 2009a,b). The appropriate design of the filtration segment facilitates cleaning of the membranes, which is a common procedure within the filtration cycles. Flat sheet membranes in plate and frame modules with narrow channels and hollow fiber membranes are susceptible to fouling. However, the former are easier to clean. In spiral-wound modules, the spacer promotes turbulence, thereby reducing the concentration and temperature polarization as well as the fouling of the membrane. The flow in the tubular membrane modules is easily made turbulent, which is also beneficial to their application.

In nuclear applications, membrane fouling is a particular problem. Frequent cleaning of the membranes creates secondary wastes that are radioactive and require additional treatment. Thus, the elimination of the phenomena that lead to membrane fouling is a key issue in the design of membrane installations.

One of the critical characteristics of membranes is their radiation stability. Membrane materials exposed to ionizing radiation may undergo structural changes, leading to an alteration of their permeation and separation characteristics, faster aging, or polymer degradation. A number of publications have reported studies on the effects of irradiation on the polymers applied for the preparation of the membranes (Ramachandhran and Misra 1985, 1986; Chmielewski and Harasimowicz 1992, 1997). They showed that for most polymers, the threshold values of the radiation doses that cause the structural changes of the membrane are sufficiently high; therefore polymeric membranes can be applied for low- and medium-level radioactive waste treatment for reasonable periods of time.

1.1.2.2 Pressure-Driven Membrane Processes

Membrane processes offer one-stage separation for all the dissolved components of radioactive waste, from suspended matter to ionic species. During the last decade, membrane technology has been gradually introduced into the nuclear industry. The pressure-driven membrane processes like reverse osmosis (RO), ultrafiltration (UF), or microfiltration (MF) have found application in radioactive waste treatment. RO involves a semipermeable, dense membrane that is able to reject all dissolved low-molecular-weight organics and multivalent and monovalent ions. The applications reported in the nuclear industry are for laundry nuclear wastes, mixed laboratory wastes, and institutional wastes (Sen Gupta et al. 1996; Zakrzewska-Trznadel and Harasimowicz 2002, 2004; Zakrzewska-Trznadel 2003; Arnal et al. 2000, 2003a,b; IAEA-TECDOC-911 1996). NF was employed for boric acid recovery and recycling, for lanthanides/actinides separation, and for the treatment of uranium mill effluents (Macnaughton et al. 2002; Hwang et al. 2002). Laundry wastes and uranium containing effluents from mill and mine operations can be treated by UF (Karlin et al. 2001; Kryvoruchko et al. 2004). UF in combination with complexation or inorganic sorbents is an effective method for processing different waste streams from nuclear applications (Hooper 1997; Smyth et al. 1998, 1999; Ramachandhran and Misra 1998). Polymer-enhanced ultrafiltration (PEU) and micellar-enhanced ultrafiltration (MEUF) were tested for the removal of metallic impurities from model solutions (Xiarchos et al. 2008). They were also proven as methods for the removal of radionuclides from liquid radioactive wastes (Zakrzewska-Trznadel and Harasimowicz 2002, 2004). MF is employed in remediation activities and for the dewatering of precipitate from treatment procedures (Mann and Todd 2000; Brown et al. 1991). It should be noted that RO and NF involve polymer membranes. Inorganic membranes, in addition to polymeric barriers, are in common use in UF and MF. The modification of the membranes used in the pressure-driven processes aims not only to improve the separation characteristics, but also to increase the wear resistivity and the chemical and radiation stability.

1.1.2.3 Electric Membrane Processes

Electric membrane processes, including electroosmosis, electrodialysis, and membrane electrolysis, are studied for different applications along the power generation cycle (Andalaft et al. 1997; Hobbs 1999; Hegazy et al. 1999). The novel anion exchange membrane was applied to separate ^{125}I and ^{36}Cl ions by electrodialysis (Inoue et al. 2004). The membrane exhibited high selectivity for iodine ions over chlorine ions, and the ratio of electroconductive membrane permeabilities of ^{125}I and ^{36}Cl was 6.2, while the diffusion membrane permeabilities of the two components were almost the same.

In electric membrane processes, anion- and cation-exchange membranes are used. Sodium super ion conducting ceramic membranes—NaSICON—were studied for the separation of sodium from radioactive wastes produced by the US Department of Energy (Fountain et al. 2008). Nafion and NaSICON membranes were tested for the electrochemical separation and recycling of sodium hydroxide from high salt content radioactive wastes (Hobbs 1999; Kurath et al. 1997).

1.1.2.4 Thermal Processes: MD

MD is one of the emerging *nonisothermal* membrane separation processes, known for about 50 years but still requiring development for its industrial implementation. MD refers to the thermally driven transport of vapor through porous hydrophobic membranes, the driving force being the vapor pressure difference between the two sides of the membrane pores. Simultaneous heat and mass transfer occurs in this process, and different MD configurations include direct contact MD, sweeping gas MD, vacuum MD, and air gap MD.

MD is an effective process for desalination, the concentration of salts and acidic solutions, and distilled water production; it can also be applied to water and wastewater treatment (Hogan et al. 1991; Gryta 2002; Couffin et al. 1998; Khayet 2011). The use of this process for low-level radioactive waste treatment leads to a concentration of radioactive species in a small volume, appropriate for fossilization and the production of clean water streams and for discharge (Zakrzewska-Trznadel 1998; Zakrzewska-Trznadel et al. 1999). MD units can be employed in the front end of liquid radioactive waste processing to improve the economy of the treatment by an initial concentration before evaporation or in the back end to obtain better separation of the radionuclides and produce clean effluents.

The membranes used for MD processes are hydrophobic, porous barriers made from PTFE polypropylene (PP) or polyvinylidene fluoride (PVDF). All modifications lead to an increase in the membrane hydrophobicity in order to avoid membrane wettability, thereby making the membrane useful for longtime operation.

1.1.2.5 Liquid Membranes

Liquid membranes are very attractive in nuclear technology because of their good separation ability and their selectivity toward specific radionuclides. Many applications of such membranes in the radioactive waste processing field are reported. They are applied to different waste streams for the recovery of selected components of the waste and the separation of fission products from spent fuel reprocessing waste (Kocherginsky et al. 2002; Happel Streng et al. 2003; El-Reefy et al. 1996; El-Said et al. 2002). All types of liquid membranes, including bulk, emulsion, supported, and inclusion liquid membranes, have been tested for nuclear applications: Facilitated transport using an appropriate carrier enhances the separation ability and the selectivity of the membrane. It can also improve the kinetics of the transport through the membrane. Chemical modification of the carrier makes the liquid membrane more selective to specific substances.

The organic liquids used for liquid membranes are as follows: dichloromethane, chloroform, kerosene, chlorobenzene, *n*-octane, *n*-decane, *n*-dodecane, and *n*-tetradecane. The most popular carriers are crown ethers, calixarenes, phosphoroorganic compounds (e.g., D2EHPA and CYANEX 302), hydroxyoximes (e.g., LIX 65N and SME 529), and amines (e.g., ALAMINA 336 and tri-*n*-octylamine). In general, liquid membranes are used mostly to decrease the radiotoxicity of the liquid waste, but not to reduce its volume. In radioactive waste management, liquid membranes are first applied to remove ^{90}Sr and ^{137}Cs from acidic or alkaline solutions (Kocherginsky et al. 2002; Happel Streng et al. 2003).

The removal of actinides from reprocessing acidic waste solutions is advantageous in terms of minimizing the radioactive discharge to the natural environment. The separation of plutonium using supported liquid membranes was extensively studied, as well as U(VI) and Pu(IV) selective transport over fission products and minor actinide contaminants (Lakshmi et al. 2004; Sriram et al. 2000; Kedari et al. 1999).

1.1.3 Other Applications of Membranes in Nuclear Technology

Membrane separation techniques are being considered as feasible methods for cleaning the exhaust gases discharged from nuclear facilities such as nuclear power plants and spent fuel processing plants. The exhaust gases contain radioactive aerosols, fission products, and radioactive corrosion products, which have to be separated from the gas streams before discharge. For the removal of noble gases, especially ^{85}Kr and $^{133+135}Xe$, from reactor atmospheres, silicone rubber, siloxane rubber membranes, and different polyarylane–siloxane block copolymers were tested (Stern and Leone 1980; Ohno et al. 1977; Stern and Wang 1980). In recent years, the research has focused on the application of hollow fiber membranes from polyimide, oriented PP, or flat sheet membranes from PET (Sasaki et al. 2003; Nörenberg et al. 2001). The use of membrane techniques for removing the tritium generated in nuclear reactors or spent fuel processing plants from the gas effluents has been reported (Le Digabel et al. 2002; Ishida et al. 2000; Hirata et al. 1995; Hayashi et al. 1995; Bridesell and Willms 1998). Some aspects of this research focused on the assurance of tritium for future fusion reactors (Violante et al. 1995; Tosti et al. 2000; Konishi et al. 1998; Heinze et al. 2003).

1.1.4 Preparation of Membranes

Membrane manufacturing techniques depend on the material applied and on the required membrane characteristics. Based on the preparation materials used, the basic types of membranes include polymeric, inorganic, and hybrid polymeric–inorganic membranes. Both the polymeric and the inorganic membranes can be applied to radioactive wastes processing. Inorganic membranes are of greatest interest because of their good stability and their resistance toward different types of radiation: α, β, and γ. In most cases, commercial membranes that were proved in other industrial applications are employed after testing their stability under ionizing radiation.

Taking into consideration the separation principles and the structure, three types of membranes can be distinguished: porous, dense, and liquid membranes. The most common techniques available for preparing the membranes are sintering, stretching, extrusion, track etching, phase inversion, and coating. For composite membranes, methods such as plasma polymerization, interfacial polymerization, and dip coating can be employed (Mulder 1991).

1.1.5 Modification of Membranes

Membranes manufactured in primary processes can be modified for different applications by changing the material's chemical properties or by changing the pore size.

The combination of different materials, organic and inorganic, to obtain hybrid membranes of a desirable structure and properties applicable for nuclear purposes is also possible.

Different chemical and physical methods are used for membrane modification (Van der Bruggen 2009). The properties of membranes can be modified by introducing ionic groups, which can alter the character of the membrane surface from hydrophobic to hydrophilic (Bolong et al. 2009; Rana et al. 2005; Wei et al. 2010; Zhou et al. 2009). This modification is important since it can reduce fouling of the membranes. Hydrophilization can be attained by using methods such as chemical oxidation, plasma treatment, chemical functionalization, or radiation-induced surface grafting. Surfactant modification and self-assembly of the hydrophilic nanoparticles are other methods for membrane surface modification. Another approach is to modify the polymer before membrane formation, by incorporating the hydrophilic additives into the membrane matrix. This can be achieved by sulfonation, carboxylation, or nitration.

Chemical oxidation is achieved by introducing oxygen-containing groups into the membrane surface, using oxidants such as potassium permanganate, nitric acid, and chromic acid, or redox initiators such as ferric chloride. They can oxidize the membrane surface to create active sites where surface graft polymerization is conducted.

Chemical functionalization is achieved by attaching specific functional groups that give new character to the membrane surface. Such groups are bonded with membrane surface groups by ionic or polar bonds and can cause the hydrophilization of the membrane.

Plasma treatment in the presence of oxygen forms peroxides on the membrane surface that undergo further decomposition and form oxygen-containing radical groups, such as hydroxyls, carbonyls, or carboxyls. The technique can also be used for preparing membranes for surface graft polymerization. In this process, synthetic monomers are attached to the peroxide groups formed by the plasma treatment. The monomers then polymerize on the membrane surface, forming a thin layer with properties different from those of the initial material.

Radiation-induced grafting is another modification method that utilizes ultraviolet or ionizing radiation to produce active sites on the membrane surface for attaching different kinds of groups (IAEA-TECDOC-1465 2005). The polymerization of the monomer grafted to these active sites results in membranes with different properties. The most common monomers used for radiation-induced grafting are vinyl acetate, *N*-vinyl pyrrolidone, acrylic acid, metacrylic acid, or *N*-vinyl pyridine.

Radiation-based technologies are employed for the development of a new class of materials, namely, stimuli-responsive polymers and membranes that can be applied in nuclear science and technology. It is foreseen that temperature-sensitive or pH-sensitive membranes can be used in a variety of novel applications, including separation processes in the nuclear field, for the recovery of uranium from seawater.

Inorganic membranes can also be modified according to their future applications. Ceramic membranes present many advantages, such as mechanical and chemical resistances, thermal stability, nonswelling properties, and easy cleaning, and are very

attractive for nuclear technologies. However, separation based on size exclusion does not give sufficient selectivity for a wide range of applications. The recent research on the modification of ceramic membranes by alcohol adsorption demonstrated a simple method for modifying the membrane properties (Dafinov et al. 2002). The chemisorbed alcohol causes hydrophobization of the surface imparted by the alkyl chains and, in consequence, decreases water transport. The ceramic membrane with the adsorbed layers presents a high stability against acids, down to pH = 1. This shows the potential for the use of such modified membranes with highly acidic solutions, for example, in wastes originating from fuel reprocessing. The emerging field of the study presents the application of nanostructured materials and nanoparticles embedded in the membrane matrix to produce functionalized membranes with controlled fouling resistance (Kim and Bruggen 2010).

1.2 REMOVAL OF RADIONUCLIDES WITH SURFACE-MODIFIED MEMBRANES; LABORATORY EXPERIMENTS: UF AND MD

1.2.1 Case Study: Application of Surface-Modified Membranes Based on Polysulfone and Polyethersulfone in UF/Complexation Process for the Removal of ^{60}Co from Water Aqueous Solutions

UF coupled with complexation by water-soluble polymers was tested to assess the membrane surface modification for the removal of radioactive cobalt (^{60}Co) from water solutions. The experiments were conducted with porous membranes prepared using PES and modified PES membranes made using surface-modifying macromolecules (SMMs). Both the modified and the unmodified membranes were prepared by a simple phase inversion technique in a single casting step from a blend dope containing PES and an SMM. During the membrane formation, the SMM migrates toward the top air–polymer interface, rendering the membrane surface hydrophobic. SMMs are oligomeric fluoropolymers synthesized by polyurethane chemistry and tailored with fluorinated end groups (Khayet et al. 2003, 2006). The prepared membranes are named hereafter, SMM3/PES and SMM41/PS. A commercial PES membrane supplied by Millipore, having a 10 kDa molecular weight cutoff (MWCO), was used for comparison. A typical UF setup equipped with a stainless steel membrane cell of an effective filtration area of 14.52×10^{-4} m^2 was employed in the experiments (Figure 1.1).

To assess the permeability of each membrane, the permeate flux of the distilled water (J_w) was measured for the SMM-modified membranes, the unmodified PES membrane, and the commercial PES membrane. It was observed that the SMM-modified membranes exhibited lower permeation rates than the commercial PES and the unmodified membrane. The flux of the distilled water was highest for the PES commercial membrane (168.6 kg/m^2 h) and for the prepared unmodified PES membrane (127.6 kg/m^2 h). For the modified membranes, SMM3/PES and SMM41/PES, the permeate fluxes were lower at 41.3 and 39.5 kg/m^2 h, respectively (Table 1.1).

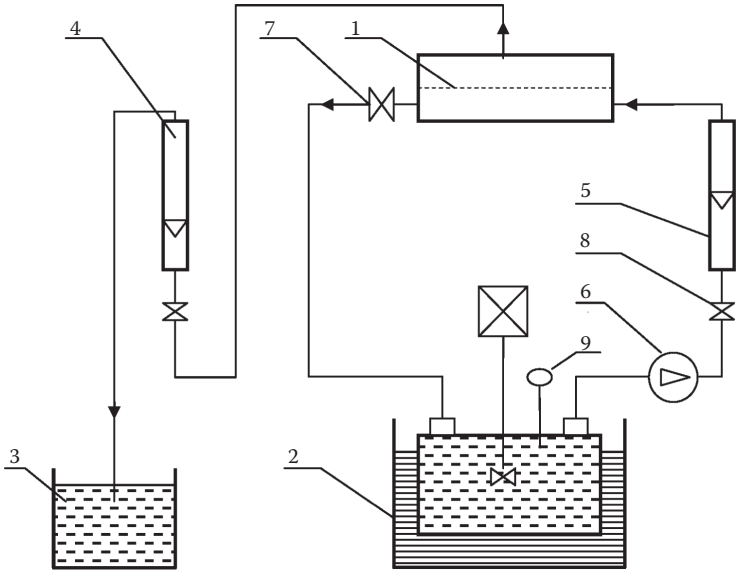

FIGURE 1.1 Setup for ultrafiltration experiments. 1: Membrane module; 2: feed tank; 3: permeate tank; 4: permeate flow meter; 5: feed flow meter; 6: pump; 7: feedback valve; 8: control valve; and 9: thermometer.

Before the UF experiments, to reduce the adsorption of the radioactive cobalt in the unit, the UF system was pretreated by circulating nonradioactive 0.1 g/dm^3 $Co(NO_3)_2 \cdot 6H_2O$ aqueous solution for 1 h. The electrical conductivity of this solution was about 100 μS/cm. With this solution for each tested membrane, the permeation flux (J_s) and the retention factor (R_s) of the cobalt ions were determined. For all tested UF membranes, the retention of the cobalt ions was not high. The highest retention factor was 51.7%, which was achieved for the SMM3/PES membrane. To enhance the efficiency of the cobalt ions removal, a macromolecular complexing agent, allowing the formation of larger molecules with the cobalt ions, was added in further experiments. Polyethyleneimine (PEI) (1 g/dm^3) was introduced for the complexation of the Co^{2+} ions. The pH of the solution was adjusted with 10% HNO_3 at the optimal value (pH = 6). In these conditions, the permeation flux ($J_{Co/PEI}$) and the retention factor ($R_{Co/PEI}$) for the hybrid UF/complexation process were determined (Table 1.1).

TABLE 1.1
Permeation Characteristics of Membranes

Membrane	J_w (kg/m^2 h)	J_s (kg/m^2 h)	$J_{Co/PEI}$ (kg/m^2 h)	R_s (%)	$R_{Co/PEI}$ (%)
Commercial PES	168.6	83.1	55.2	29.2	93.6
Unmodified PES	127.6	85.1	58.7	44.2	70.8
Modified SMM3/PES	41.3	26.5	20.2	51.7	98.7
Modified SMM4/PES	39.5	24.0	17.7	48.2	96.7

TABLE 1.2
Decontamination Results for 0.1 g/dm³ $Co(NO_3)_2 \cdot 6H_2O$ Aqueous Solution Containing ^{60}Co

Membrane	A_F (kBq/dm³)	A_R (kBq/dm³)	A_P (kBq/dm³)	DF	A_m (counts/100 sec)
Commercial PES	6.94	1.70	0.103	44	2941
Unmodified PES	6.77	2.84	0.067	75	1532
Modified SMM3/PES	6.75	2.82	0.022	223	401
Modified SMM41/PES	6.89	3.65	0.034	163	600

Note: Cobalt ions complexed by 0.1 g/dm³ polyethyleneimine (PEI).

The SMM-modified membranes exhibited the highest retention of the Co^{2+} ions. It was over 98% for the SMM3/PES membrane and 97% for the SMM41/PES membrane. Under the same conditions, the retention of the prepared unmodified PES was only 71%.

A radioactive solution containing ^{60}Co of the total radioactivity of ca. 4000 counts/100 sec was employed as a radioactive feed. The respective radioactivity counting rate (pulse/sec), treated as the intensity of the γ-radiation of a 5 cm³ liquid sample containing ^{60}Co, was measured by a γ-analyzer, LG-1B (INCT). The obtained values were compared with the radiation intensity of the ^{60}Co standard sample. Therefore, the specific activity of the feed (A_F), the retentate (A_R), and the permeate (A_P) were calculated. The parameters (R), (DF), and (J) were determined when the radioactive solutions were treated. In all the experiments, the transmembrane hydrostatic pressure was maintained at 0.22 MPa and the feed flow rate at 40 l/h. Substantially high DFs for radioactive ^{60}Co were obtained for the SMM-modified membranes used in the UF/complexation process: 223 for SMM3/PES and 163 for SMM41/PES (Table 1.2). For the unmodified membranes, the DFs were lower: 44 for the commercial PES membrane and 75 for the prepared unmodified PES membrane. Additionally, the SMM-modified membranes showed smaller adsorption of the radioactive cobalt than the modified membranes, which was beneficial, taking into account the considered applications. After a 2 h operation, the adsorption of ^{60}Co by the SMM-modified membranes was four to five times smaller than that of the unmodified PES membrane.

The washing tests showed that the adsorption of the radioactive substances occurred in all tested membranes. Subsequent cleaning cycles with water and chemicals (alternant acidic and base washing) did not result in the complete removal of radioactivity, owing to the deep adsorption inside the membrane pores and the strong binding of the radioactive species within the membrane matrix. The variation of the radioactivity of the membrane during the operation, interrupted by water washing cycles, is shown in Figure 1.2. It is apparent that the effect of the subsequent cleaning procedures decreases over time and that the radioactivity of the membrane stabilizes at the level corresponding to persistent sorption in the membrane material.

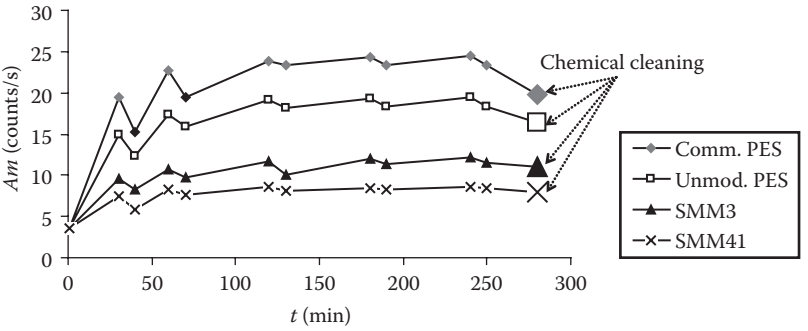

FIGURE 1.2 Changes of membrane radioactivity in polymer-enhanced UF removal of ^{60}Co from a water solution after water washing cycles and chemical cleaning.

More radical chemical cleaning resulted in a decline in the membrane-bound activity; however, it remained significant. The lowest adsorption observed at the SMM3 and SMM41 membranes predestines these materials to nuclear applications, namely, radioactive waste treatment.

1.2.2 Case Study: Surface-Modified Membranes Applied for the Treatment of Radioactive Wastes by MD

Direct contact membrane distillation (DCMD) is an effective process applied for the concentration of dissolved matter in water solutions. The process can be considered a feasible method for liquid radioactive waste treatment and, in some cases, it can effectively serve in reducing the hazard connected with its toxicity.

Four porous composite hydrophobic/hydrophilic membranes were tested for the removal of selected radionuclides from water solutions. The membranes were also prepared by the phase inversion method using SMMs. Two hydrophilic polymers, PES and PS, were used. Each polymer was dissolved in the solvent/nonsolvent mixture and the macromolecules SMM3 or SMM41 were then added to the polymer casting solutions, to construct the membranes denoted as SMM3/PES, SMM41/PES, SMM3/PS, and SMM41/PS. For comparison, the commercial PTFE membranes, supported by a PP net (TF200, Gelman: thickness 178 μm, average pore size of 0.20 μm and porosity of 80%), were used. DCMD experiments were conducted using the setup shown in Figure 1.3. The feed liquid was brought in direct contact with the hydrophobic side of the membrane, while the distilled water collecting the permeate was brought in direct contact with the hydrophilic side of the membrane. The effective membrane area was 7.55×10^{-4} m^2, and the bulk feed and the permeate were kept at 49°C and 24°C, respectively. To circulate both the feed and the permeate, peristaltic pumps were used, and for measuring the temperatures inside the test cell, two Pt100 thermometers were applied.

To determine the water vapor permeability (permeate flux J_w) in the DCMD process, distilled water was used as the feed. To avoid the adsorption of the radioactive species in the system before using the solutions containing ^{60}Co, ^{137}Cs, and ^{85}Sr radioisotopes,

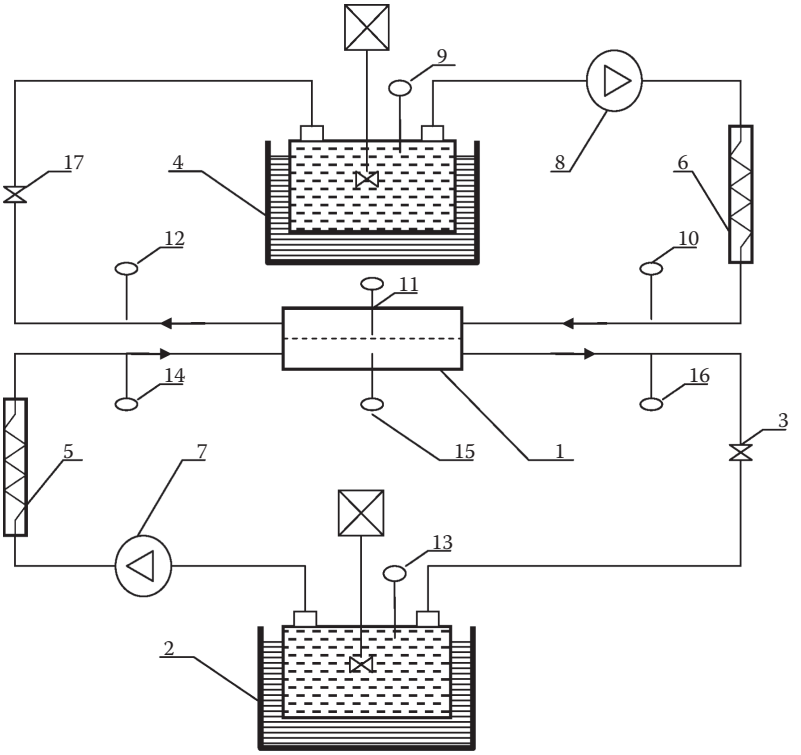

FIGURE 1.3 Setup for membrane distillation experiments. 1: Membrane module (test-cell); 2: feed tank; 3, 17: control valves; 4: distillate tank; 5, 6: heat exchanger; 7, 8: peristaltic pumps; and 9, 10, 11, 12, 13, 14, 15, 16: thermometers.

the solutions of the same nonradioactive ions as salts, $Co(NO_3)_2 \cdot 6H_2O$, CsCl, and $SrCl_2 \cdot 6H_2O$ in concentrations equivalent to the conductivity of 1000 μS/cm, were first circulated through the DCMD apparatus to saturate the unit. Finally, small volumes of radioactive solutions containing ^{60}Co, ^{137}Cs, or ^{85}Sr in 0.1 M HCl were added, to establish the feed activity between 4000 and 4500 counts/100 sec for the 50 cm^3 sample. For all the tested membranes, the initial conductivity of the permeate was 9–16 μS/cm and the activity was between 400 and 440 counts/100 sec. The results are shown in Table 1.3.

It can be observed that the commercial TF200 membrane exhibited higher permeate flux (2.1 $kg/m^2 h$) than the SMM-modified membranes. This was because the SMM-modified membranes were prepared with a high concentration of PES and PS polymers, leading to pore sizes of an order of magnitude lower than those of the membrane TF200.

The DCMD results showed that the rejection of Co^{2+}, Cs^-, and Sr^{2+} ions, as well as the radioactive isotopes ^{60}Co, ^{137}Cs, and ^{85}Sr, was almost complete. No changes in the electrical conductivity and the specific radioactivity in the permeate samples collected at the beginning and the end of the experiments (after 4 h) were observed.

TABLE 1.3
Removal of Radionuclides of ^{60}Co, ^{85}Sr, and ^{137}Cs by MD Process

Membrane	J_w (kg/m² h)	ρ_F (μs/cm)	ρ_D (μs/cm)	R (%)	A_F (kBq/dm³)	A_D (Bq/dm³)	DF
TF200	2.10	982[a]	2	99.18	7.15	3.9	1833
		996[b]	3	99.70	2.85	7.2	396
		1017[c]	14	98.62	3.66	1.2	3050
SMM3/PES	0.86	977[a]	4	99.59	7.03	3.7	1900
		983[b]	14	98.57	2.90	7.2	403
		1005[c]	15	98.51	2.69	6.2	434
SMM41/PES	0.72	1000[a]	46	95.40	7.02	4.5	1560
		982[b]	21	97.86	2.91	14.5	201
		980[c]	20	97.96	3.70	9.1	407
SMM3/PS	0.44	978[a]	7	99.28	7.07	2.5	2828
		992[b]	3	99.70	2.87	8.5	338
		984[c]	20	97.97	3.68	2.0	1840
SMM41/PS	0.35	975[a]	16	98.31	7.01	1.4	5007
		994[b]	3	99.70	2.88	4.5	640
		994[c]	10	98.99	3.69	1.0	3690

[a] ^{60}Co.
[b] ^{85}Sr.
[c] ^{137}Cs.

It was concluded that the SMM-modified membranes could be used effectively for rejecting the radioactive compounds in water solutions. Moreover, the radioactivity of the SMMs membranes after 4 h DCMD experiments was substantially lower than that of the commercial membrane TF200 (Table 1.4), suggesting a smaller adsorption of the radionuclides on the SMM-modified membrane, which can be regarded as an advantageous property and important for further application in nuclear technologies.

TABLE 1.4
Radioactivity of the Membrane after 4 h MD Experiments with ^{60}Co, ^{85}Sr, and ^{137}Cs Solutions

	A_m (counts/100 sec)				
	Commercial Membrane	Modified Membranes			
Solution	TF200	SMM3/PES	SMM41/PES	SMM3/PS	SMM41/PS
^{60}Co	1799	487	679	574	691
^{85}Sr	584	282	152	101	54
^{137}Cs	917	358	447	251	334

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2 Use of Impedance Spectroscopy for Characterization of Modified Membranes

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2.1 INTRODUCTION

It is well known that membrane charge can play an important role in the transport of electrolyte and charged particles across membranes and their electrical characterization has been of great importance since the beginning of membrane processes applications (Helfferich 1962; Laksminarayanaiah 1969; Compañ et al. 1997; Vallejo et al. 1999). Usually, the determination of an effective fixed charge concentration in the membranes (bulk) and the number of ions transported across them is made from the membrane potential (MP) measurements (Demish and Pusch 1980; Kimura et al. 1984; Benavente and Fernández-Pineda 1985; López et al. 2001), while the streaming potential (SP) gives information on the membrane–solution electrical interface, such as

the surface charge density and the isoelectric point; however, the characteristic adsorption parameters, such as Gibbs energy and the number of accessible sites, can also be determined by using the appropriate models (Benavente et al. 1993; Molina et al. 1999; de Lara and Benavente 2007). In particular, SP measurements are commonly used for determining membrane changes at both the pore wall and the membrane surface, associated with fouling, membrane material modification, and deterioration or age (Childress and Elimelech 1996; Benavente and Jonsson 1998; Pointié 1999; Fievet et al. 2003). The membrane electrical resistance (or conductivity) is also an electrical parameter of major significance in the case of charged membranes, such as those used in electrodialysis, electrochemical devices, and fuel cells. The conductivity and the dielectric constant, both intrinsic and material parameters, are determined from the electrical resistance and the capacitance values obtained from impedance spectroscopy (IS) measurements. IS can be carried out with the membranes in dry and wet (solution embedded) states (Benavente et al. 2010a,b) or in "working conditions," that is, in contact with the electrolyte solutions, which is termed electrochemical impedance spectroscopy (EIS) (Mälmgren-Hansen et al. 1989; Asaka 1990; Benavente et al. 1997; Oleinikova et al. 2000; Li and Zhao 2004; Freger and Bason 2007).

IS is a nondestructive ac technique for the electrical characterization of solid and liquid systems. It is also used for determining the interfacial effects or for monitoring the system changes associated with the time evolution of the impedance (Mijovic and Bellucci 1996; Hamdy et al. 2006). IS has emerged with the development of instruments that are capable of measuring impedance in a wide range of frequencies (between 10^{-6} and 10^{9} Hz), and it allows the determination of the electrical properties of heterogeneous systems formed by a series array of layers with different electrical and/or structural properties, such as membrane/electrolyte systems. This permits a separate evaluation of the electrical contribution of each layer by using the impedance plots and the equivalent circuits as models, where the different circuit elements are related to the structural/transport properties of the systems (Buck and Ciani 1975; Macdonald 1987). In particular, in the case of EIS measurements carried out with membranes in working conditions, separate contributions of the membranes and the solution are usually obtained, except for membranes with a high charge or solution content. In addition, if composite/asymmetric membranes are studied, the analysis of the impedance plots might allow the separate evaluation of the electrical contribution associated with dense and porous layers and even the estimation of the geometrical parameters (Coster et al. 1992; Cañas et al. 2001; Torras et al. 2007).

The research described above, which has used IS, demonstrates that it can provide qualitative and quantitative information, obtained from impedance measurements, and that the technique can be applied to determine the modification of different commercial and experimental membranes with diverse structures (porous, dense, and composites) and materials. These modifications are associated with membrane fouling and aging, as well as changes purposely made to optimize the membrane performance. Most of the impedance measurements were carried out with the membranes in contact with the electrolyte solutions at different concentrations (electrode/electrolyte (c)/membrane/electrolyte (c)/electrode system), and the impedance curves for the electrolytes alone, without any membrane in the cell system, were also considered

to verify the measurement. In addition, the results obtained without electrolyte solution (electrode/membrane/electrode system) are presented in some cases to provide complementary information. The fitting of theoretical models to the experimental data allows the determination of the electrical parameters, although geometrical parameters for the membrane, or the layers forming a composite membrane, such as porosity and/or thickness, might also be estimated from these results. The differences found in the impedance plots, the equivalent circuits, and the parameters associated with the original and the modified membranes give information on the effect of the modification on the electrical and transport behavior of the membrane.

2.2 THEORY

When a linear system is perturbed by a small v(t) voltage, its response, the electric current i(t), is determined by a differential equation of nth order in i(t) or by a set of n differential equations of the first order. If v(t) is a sine wave input (Equation 2.1):

$$v(\mathrm{t}) = V_\mathrm{o} \sin \omega t, \tag{2.1}$$

the current intensity i(t) is also a sine wave (Equation 2.2):

$$i(\mathrm{t}) = I_\mathrm{o} \sin(\omega t + \phi), \tag{2.2}$$

where V_o and I_o represent the maximum voltage and intensity, respectively, while $\omega = 2\pi f$ is the angular frequency.

A transfer function, the admittance function, can be defined as $Y^*(\omega) = |Y(\omega)|e^{j\phi}$, where $|Y(\omega)|$ represents the amplitude and ϕ is the phase angle. The impedance function, $Z(\omega)$, is the inverse of the admittance function, $Z(\omega)=[Y^*(\omega)]^{-1}$, and since both the amplitude and the phase angle of the output may change with respect to the input values, the impedance is expressed as a complex number, $Z = Z_{\mathrm{real}} + jZ_{\mathrm{img}}$, where Z_{real} is the real part and Z_{img} is the imaginary part.

The overall admittance (Equation 2.3) for a parallel resistor–capacitor (RC) circuit is given by the sum of the conductance ($1/R$) and capacitance contributions, where the resistance (R) represents the dissipative component of the dielectric response, while the capacitance (C) describes the storage component. The impedance function for that circuit is

$$(1/Z^*) = (1/R) + (j\omega C). \tag{2.3}$$

These expressions correlate the impedance components with the electrical parameters of the system. Moreover, the impedance can be separated into the real and imaginary parts by algebraic manipulation and the impedance components are related to the electrical parameters of the system by the following expressions:

$$Z_{\mathrm{real}} = \left(R \Big/ \left[1 + (\omega RC)^2\right]\right); \quad Z_{\mathrm{img}} = -\left(\omega R^2 C \Big/ \left[1 + (\omega RC)^2\right]\right). \tag{2.4}$$

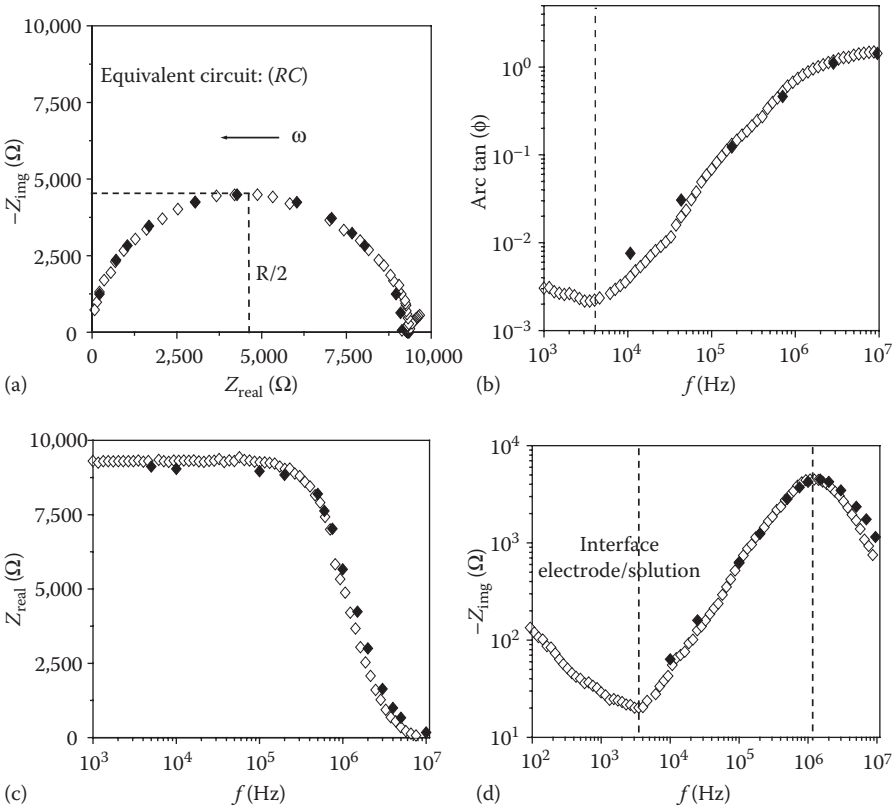

FIGURE 2.1 Different impedance plots for the electrode/electrolyte solution (c)/electrode system. (a) Nyquist plot, (b) phase angle ϕ vs. frequency, Bode plots: (c) Z_{real} vs. frequency, and (d) $-Z_{img}$ vs. frequency. (◇) Experimental values and (◆) calculated values for a certain number of frequencies.

The analysis of the impedance data can be carried out by a complex plane method using the Nyquist plot ($-Z_{img}$ vs. Z_{real}). The equation for a parallel RC circuit gives rise to a semicircle in the $Z^*(\omega)$ plane, as that shown in Figure 2.1a, which has intercepts on the Z_{real} axis at $R_\infty(\omega \to \infty)$ and $R_0(\omega \to 0)$, where $(R_0 - R_\infty)$ is the resistance of the system. The maximum of the semicircle equals 0.5 $(R_0 - R_\infty)$ and occurs at such a frequency that $\omega RC = 1$; $\tau = RC$ is the relaxation time (Macdonald 1987).

The impedance plot shown in Figure 2.1a ($-Z_{img}$ vs. Z_{real}, or the Nyquist plot) corresponds to an electrochemical cell (electrode/NaCl solution/electrode) and the equivalent circuit consists of a resistance (R) in parallel with a capacitor (C), which is represented as (RC), while Figure 2.1b shows the variation of the phase angle $\phi = \text{arc tan}(Z_{img}/Z_{real})$ with frequency (ϕ vs. f), but other typical impedance representations correspond to the variation of Z_{real} and $-Z_{img}$ with frequency (Bode plots), as indicated in Figure 2.1c and 2.1d. This latter representation allows the determination of the interval of frequency associated with a given relaxation process, between 10^4 and 10^7 Hz, with a maximum frequency around 2×10^6 Hz, for the NaCl solution

represented in Figure 2.1, while an almost constant value for a frequency lower than 10^6 Hz can be observed in Figure 2.1c. However, a slight variation seems to exist at the lowest frequencies, usually associated with the interfacial effects, which is more evident in Figure 2.1b. As can be seen, the different types of plots shown in Figure 2.1 provide complementary information on the sample studied, but all of them show a unique relaxation process; a semicircle in Figure 2.1a and a symmetric and well-defined peak in Figure 2.1d.

The fitting of the experimental points shown in the Nyquist plot using a nonlinear program has permitted the determination of the following electrical resistance and capacitance values: $R = (22{,}500 \pm 12{,}300)\ \Omega$ and $C = (5.2 \pm 0.3) \times 10^{-12}$ F. These results were used for the calculation of the Z_{real} and Z_{img} values for certain frequencies using Equation 2.4, and are also represented in Figure 2.1 as dense symbols. The good agreement between the experimental and the calculated data can be considered a test of the correctness of the circuit selected and the values obtained.

When a membrane is placed in the middle of the electrochemical cell, the total system, electrode/electrolyte (c)/*membrane*/electrolyte (c)/electrode, can be considered as a heterogeneous system formed of two different subsystems (electrolyte solution and membrane), and the membrane contribution may be obtained separately if its dielectric properties are sufficiently different from those corresponding to the electrolyte solution. In these cases, two different contributions, associated with each of the relaxation processes in one of the subsystems, may be obtained. As an example, Figure 2.2a and 2.2b show the impedance plots for a dense and symmetric polyamide membrane in contact with an NaCl solution, and two subcircuits and two semicircles in the Nyquist plot, or two symmetric and narrow peaks in the Bode plot, one of them associated with the membrane (f_{max} at 5000 Hz) and the other associated with the electrolyte solution (f_{max} between 1 and 2 MHz), were obtained. In the case of the composite RO or NF membranes, three different contributions for the electrolyte, the porous sublayer, and the dense layer can be obtained. However, the impedance curves depend not only on the membrane structure, but also on the membrane material, and its hydrophilic/hydrophobic character might mask some processes. This point is clearly shown in Figure 2.2c and 2.2d, where the impedance plots for a regenerated cellulose membrane with a high water uptake (W) are presented, with W between 70% and 85% (Vázquez et al. 2008). Due to the electrolyte content in this membrane, a unique relaxation process for the membrane system was obtained, with the equivalent circuit represented as $R_{sm}C_{sm}$, which does not allow the separate determination of the membrane electrical parameters and those associated with the electrolyte solution between the electrodes and the membrane surfaces; in this case, R_m can only be determined if the electrolyte is independently measured (R_e), taking into account the series association rule for electrical resistance ($R_{me} = R_e + R_m$). On the other hand, for this system, the presence of the membrane is more evident, considering the Bode plot (Figure 2.2d), since the wider width of the curve and the shift of its maximum to a lower frequency are indications of a more dense contribution.

In many cases, complex systems present a distribution of relaxation times and the resulting plot is a depressed semicircle, which is associated with a nonideal capacitor or a constant phase element (CPE), and its impedance is expressed by $Q(\omega) = Y_0(j\omega)^{-n}$, where Y_0 represents the admittance and n is an experimental parameter ($0 \leq n \leq 1$)

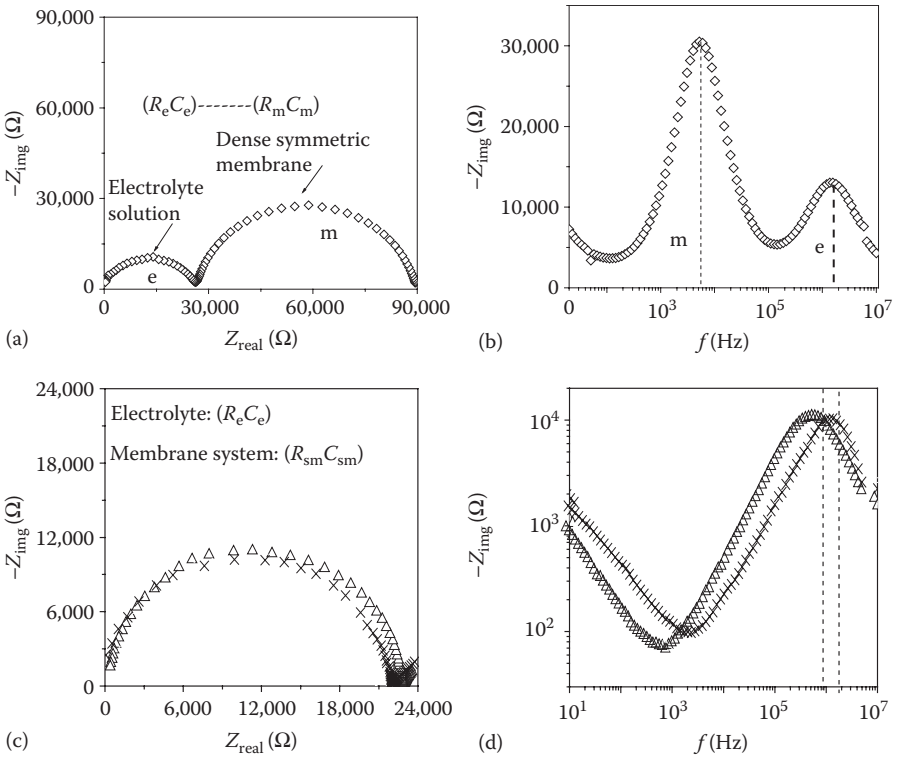

FIGURE 2.2 Nyquist and Bode plots for two different electrode/electrolyte/membrane/electrode systems. (a, b) Dense and symmetric polyamide membrane. (c, d) Dense and symmetric highly hydrophilic regenerated cellulose membrane.

(Macdonald 1987). In these cases, an equivalent capacitance (C^{eq}) can be determined (Jonscher 1983):

$$C^{eq} = \left(RY_0\right)^{(1/n)}/R. \tag{2.5}$$

A particular case is obtained when $n = 0.5$, then the circuit element corresponds to a "Warburg impedance" (W), which is associated with a diffusion process according to Fick's first law.

Once the membrane's electrical resistance and capacitance are obtained by the fit of the impedance plots to the circuit models, the membrane conductivity (σ) and the dielectric constant (ε_r) of the symmetric samples, or the dense active layer of the composite membranes, can be determined if the geometrical parameters are known, taking into account the expressions for the homogeneous conductors and the plane-plate capacitors, respectively:

$$\sigma = \Delta x_m / R_m S_c, \tag{2.6}$$

$$C = \varepsilon_o \varepsilon_r S_a / \Delta x_m, \tag{2.7}$$

where Δx_m is the membrane thickness, ε_o and ε_r are the permittivity of the vacuum and membrane dielectric constant, respectively, while S_a corresponds to the surface where the charge is adsorbed ($S_a \approx S_m$, for the dense membrane/layer), and S_c represents the cross section for the charge transport.

These examples clearly show how the EIS measurements allow the estimation of the membrane electrical parameters (R_m and C_m); however, they also indicate the possibility of obtaining "qualitative" information on the membrane structure, which can also be of great interest. In any case, it should be pointed out that impedance is an extensive magnitude (it depends on the sample area), and for that reason, comparisons of the type of curves and the concentration dependence instead of particular values are usually made. In addition, IS measurements with the dry and wet membranes, but without an electrolyte solution between the electrode and the membrane surface, can also be performed and complementary information, mainly related to the membrane material itself or the interfacial (electrode/membrane) effects, can be obtained.

In addition to the impedance, other derived quantities, such as the dielectric modulus (M), the complex dielectric constant (ε), or susceptibility (χ), can be calculated from the IS measurements; their interrelations have been tabulated elsewhere (Macdonald 1987). Complementary information on the dielectric response of a given system can be obtained from the different impedance plots and the related magnitudes. It is important to point out the different nature of these magnitudes: extensive or sample geometry dependent in the case of impedance or admittance, and intensive or characteristic of homogeneous materials in the case of conductivity and the dielectric constant.

2.3 APPLICATION OF IMPEDANCE SPECTROSCOPY TO MEMBRANES

2.3.1 Membranes

To show the potential of the impedance measurements for determining a membrane, modifications associated with both manufacture effects, in terms of changes in the material and/or structure, and working process effects, such as fouling or age, were considered. This chapter will describe the research on commercial and experimental membranes from different materials and with diverse structures (porous, dense, and composites) used in filtration processes, charged membranes, or those presenting working modifications. The membranes used to demonstrate the potentiality of IS are:

1. A commercial composite polyamide/polysulfone membrane for reverse osmosis (HR95) from DSS (Denmark). The characteristic membrane parameters, such as total thickness, hydraulic permeability, and rejection, are: $\Delta x_m = (165 \pm 5)$ μm, $L_p = 8.5 \times 10^{-12}$ m/(sec Pa), and $\sigma = 99.5\%$, respectively (Jonsson and Benavente 1992).

2. Two experimental composite membranes consisting of a sulfonated-polysulfone support and a polyamide–polyethylene glycol top layer (PS/PA–PEG). Samples with two different PEG concentrations, 5 and 25 wt%, are characterized. These membranes (PS/PA–PEG5 and PS/PA–PEG25, respectively) were obtained and kindly submitted by Dr. X. Zhang and Professor R. García-Valls (Department Ingeniería Química, Universidad Rovira y Virgili, Tarragona, Spain), and the membrane preparation is extensively explained by Benavente et al. (2005).
3. A regenerated cellulose/polypropylene supported ultrafiltration RC70PP membrane with 10 kDa cutoff (DSS) (Pelaez et al. 2010); a Tefzel ethylene tetrafluoroethylene (ETFE) laser-perforated film (LZ200 from DuPont Fluoropolymers, Detroit, MI) with 8×8 holes of 150 μm pore radius and a center-to-center distance of 400 μm (González-Pérez et al. 2009); and a composite structure formed with the RC70PP membrane plus the ETFE perforated film. The interest of this system is double, because as a layered system it allows the possibility of individual layers and complete structure measurement to check the series association or to see possible interfacial/material effects that affect the total structure; moreover, the ETFE/RC70PP composite structure studied was considered as a possible encapsulation system for biomimetic membranes (Vogel et al. 2009).
4. Two experimental poly(ether ether ketone) (PEEK) membranes for methanol fuel cell application, one with a zirconium modification to reduce the methanol crossover (samples PEEK-sn-0 and PEEK-sn-Zr, respectively), which were prepared and kindly submitted by Dr. S. Nunes (GKSS, Germany) (Nunes et al. 2002; Silva et al. 2006). To observe the electrical changes only due to membrane material modification, impedance measurements with these membranes were performed both in contact with the NaCl solutions and in a dry state.
5. A flat, flexible, and symmetric commercial ceramic membrane by Degussa (Germany), with a composite structure formed by a fibrous stainless steel network covered by a sublayer of Al_2O_3 particles plus an external layer of ZrO_2, with a pore size of 0.1 μm and 80–100 μm thickness, according to the supplier (Augustin et al. 2002). Changes due to membrane fouling as a result of protein (BSA) filtration were determined and correlated with a flow reduction and the SP results (de Lara and Benavente 2009). These samples will be named Z100S (clean membrane) and Z100S+BSA (fouled membrane).

2.3.2 Typical Impedance Spectroscopy Experimental System

We now discuss how IS measurements are made in the laboratory. IS measurements are performed with an impedance analyzer (Solartron 1260, United Kingdom), which is controlled by a computer and uses Ag/AgCl or Pt electrodes. The experimental data are corrected by software as well as the influence of connecting cables

and other parasite capacitances. The measurements are carried out using 100 different frequencies in the range 10–10^7 Hz, at a maximum voltage of 0.01 V and a room temperature of (25 ± 2)°C.

An electrochemical test cell similar to that described in Pelaez et al. (2010) is used for the IS measurements in "working conditions," meaning that the membranes are placed between the two half-cells in contact with NaCl aqueous solutions at the same concentration (electrode/solution (c)/*membrane*/solution (c)/electrode system); different NaCl concentrations between 0.001 and 0.05 *M* are typically measured. Before use, the membranes are maintained in contact with a solution of the studied concentration over a certain time ($10 \leq t(h) \leq 24$), depending on the membrane structure. In the case of dry membranes, the test cell consists of a Teflon structure on which two Pt electrodes are placed and screwed down (system: electrode/*membrane*/electrode) (Ramos et al. 2010). We will now discuss, in turn, the IS of these different membranes.

2.4 RESULTS AND DISCUSSION

2.4.1 Reverse Osmosis Membrane

The impedance plots for the composite HR95 membrane are shown in Figure 2.3, where two different contributions associated with the membrane (*m*) and the electrolyte solution between the electrodes and the membrane surfaces (*e*) can clearly be observed. To check this assumption, the impedance data obtained with the electrolyte alone, without any membrane in the measuring cell, are also plotted in Figure 2.3. As can be observed, a parallel RC circuit with only a relaxation process and a maximum frequency of around 10^6 Hz (similar to that in Figure 2.1) was obtained for the electrolyte solution measured alone (R_eC_e). The circuit associated with the composite polyamide/polysulfone HR95 membrane shows two subcircuits,

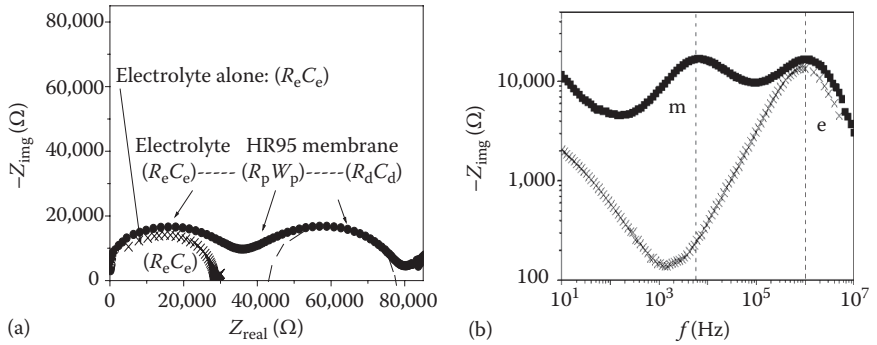

FIGURE 2.3 (a) Nyquist and (b) Bode plots for the electrode/0.002 *M* NaCl solution/HR95 membrane/0.002 *M* NaCl solution/electrode (•) and the electrode/0.002 *M* NaCl solution/electrode (×) systems.

one for each layer, plus the electrolyte contribution, that is: (i) A parallel association of a resistance and a capacitor for the dense active layer (R_dC_d); (ii) A resistor in parallel with a Warburg impedance for the porous sublayer (R_pW_p); and (iii) the parallel RC circuit associated with the electrolyte solution placed between the membrane and the electrodes, which hardly differs from that obtained with the electrolyte alone. This point is also observed in Figure 2.3b, where the relaxation process associated with the membrane appears at a lower frequency ($f_{max} \approx 5000$ Hz), in agreement with the value indicated for the dense polyamide membrane (Figure 2.2b), but a certain asymmetry can be observed in Figure 2.3, which is attributed to the porous sublayer.

The data shown in Figure 2.3a were fitted using a nonlinear program to determine the values of the different circuit elements, and the variation of R_p and R_d with the NaCl concentration is shown in Figure 2.4a. The decrease in electrical resistance with the increase in salt concentration is due to the concentration dependence of the electrolyte embedded in the dense layer matrix (R_d) or filling the voids of the support (R_p). However, the capacitance for the dense membrane layer has little dependence on the salt concentration, as can be observed in Figure 2.4b, and an average value of $C_d = (1.5 \pm 0.3) \times 10^{-9}$ F for the whole range of concentrations was obtained, while the porous sublayer Warburg impedance (a diffusion-related parameter) slightly increases with the increase in the NaCl concentration.

It should be noted for simplicity reasons that a two-layer model has been assumed for the HR95 reverse osmosis membrane, but a more complex structure, including an "intermediate layer" with gradual changes in the pore radii/porosity from one layer to another (three-layer model), could be more realistic (Zholkovskij 1995). In this context, the compaction or partial inclusion of the intermediate layer due to membrane aging determined by IS measurements for nanofiltration membranes shows the utility of this technique for membrane modification characterization (Benavente and Vázquez 2004).

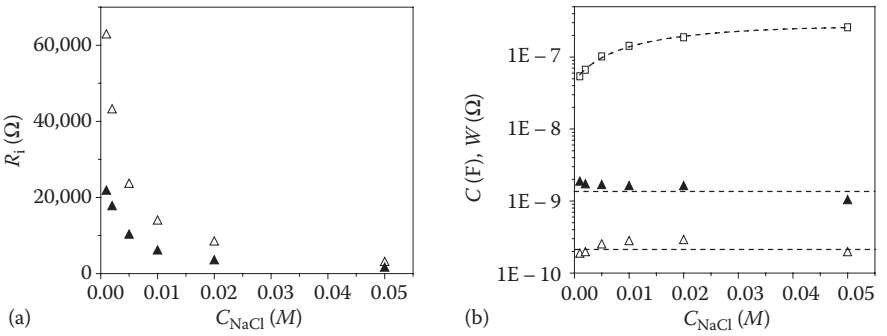

FIGURE 2.4 Concentration dependence for the (a) electrical resistance of the porous (Δ) and dense (▲) layers of the HR95 membrane; (b) dense layer capacitance (▲), porous layer Warburg impedance (□), and porous layer equivalent capacitance (Δ) calculated using Equation 2.5.

2.4.2 Polysulfone–Polyamide/Polyethylene Glycol Membrane: Effect of PEG Content

The EIS characterization of the polysulfone–polyamide/PEG membranes was carried out not only to determine separately the contribution of the porous support and the PEG-modified top layer, but also to correlate the electrical changes with the PEG content. Figure 2.5a shows an SEM micrograph of the cross section of the PS/PA–PEG membrane; the porous polysulfone structure and the dense polyamide top layer where the PEG is mainly located can be clearly observed in this figure (Benavente et al. 2005).

Impedance plots (Nyquist and Bode plots) for the PS/PA–PEG5 and PS/PA–PEG25 membranes are shown in Figure 2.5b and 2.5c, where the effect of the asymmetric structure on the impedance (Nyquist) plot is indicated, but the differences depending on the PEG concentration are also evident. The equivalent circuit for the total membrane system, $(R_eC_e) - (R_mQ_m)$, is also indicated in Figure 2.5b; the depressed semicircle, attributed to the nonconstant phase circuit element (Q_m), is due to the porous structure of these membranes and the mixture of the relaxation times associated with their electrical response (polymeric matrix and solution).

The analysis of the impedance plots also allows the determination of R_m for the different concentrations studied. Figure 2.6a shows the decrease in the membrane electrical resistance with the increase in the salt concentration, where the differences

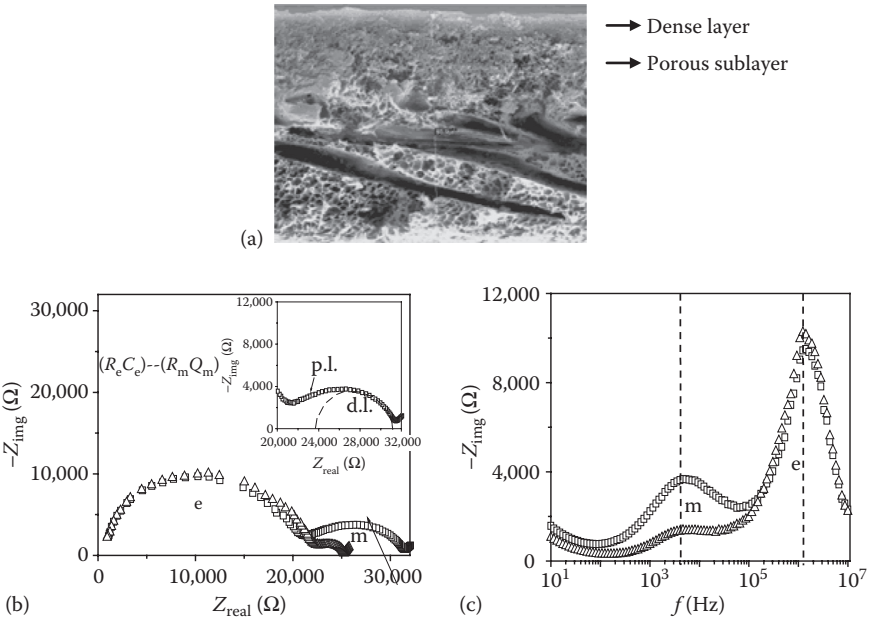

FIGURE 2.5 (a) Cross section SEM micrograph of the polyethylene glycol–sulfonated polysulfone–supported membrane. (b) Nyquist and (c) Bode plots for the electrode/NaCl solution/membrane/NaCl solution/electrode system. (□) PS/PA–PEG5 membrane and (Δ) PS/PA–PEG25 membrane.