Membrane Technology and Applications

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Richard W. Baker

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MEMBRANE TECHNOLOGY AND APPLICATIONS

PREFACE

My introduction to membranes was as a graduate student in 1963. At that time membrane permeation was a sub-study of materials science. What is now called membrane technology did not exist, nor did any large industrial applications of membranes. Since then, sales of membranes and membrane equipment have increased more than 100-fold and several tens of millions of square meters of membrane are produced each year—a membrane industry has been created.

This membrane industry is very fragmented. Industrial applications are divided into six main sub-groups: reverse osmosis; ultrafiltration; microfiltration; gas separation; pervaporation and electrodialysis. Medical applications are divided into three more: artificial kidneys; blood oxygenators; and controlled release pharmaceuticals. Few companies are involved in more than one sub-group of the industry. Because of these divisions it is difficult to obtain an overview of membrane science and technology; this book is an attempt to give such an overview.

The book starts with a series of general chapters on membrane preparation, transport theory, and concentration polarization. Thereafter, each major membrane application is treated in a single 20-to-40-page chapter. In a book of this size it is impossible to describe every membrane process in detail, but the major processes are covered. However, medical applications have been short-changed somewhat and some applications—fuel cell and battery separators and membrane sensors, for example—are not covered at all.

Each application chapter starts with a short historical background to acknowledge the developers of the technology. I am conscious that my views of what was important in the past differ from those of many of my academic colleagues. In this book I have given more credit than is usual to the engineers who actually made the processes work.

Readers of the theoretical section (Chapter 2) and elsewhere in the book will see that membrane permeation is described using simple phenomenological equations, most commonly, Fick's law. There is no mention of irreversible thermodynamics. The irreversible thermodynamic approach to permeation was very fashionable when I began to work with membranes in the 1960s. This approach has the appearance of rigor but hides the physical reality of even simple processes behind a fog of tough equations. As a student and young researcher, I struggled with irreversible thermodynamics for more than 15 years before finally giving up in the 1970s. I have lived happily ever after.

ACKNOWLEDGMENTS FOR THE FIRST EDITION

As a school boy I once received a mark of $\frac{1}{2}$ out of a possible 20 in an end-of-term spelling test. My spelling is still weak, and the only punctuation I ever really mastered was the period. This made the preparation of a polished final draft from my yellow notepads a major undertaking. This effort was headed by Tessa Ennals and Cindi Wieselman. Cindi typed and retyped the manuscript with amazing speed, through its numerous revisions, without complaint. Tessa corrected my English, clarified my language, unsplit my infinitives and added every semicolon found in this book. She also chased down a source for all of the illustrations used and worked with David Lehmann, our graphics artist, to prepare the figures. It is a pleasure to acknowledge my debt to these people. This book would have been far weaker without the many hours they spent working on it. I also received help from other friends and colleagues at MTR. Hans Wijmans read, corrected and made numerous suggestions on the theoretical section of the book (Chapter 2). Ingo Pinnau also provided data, references and many valuable suggestions in the area of membrane preparation and membrane material sciences. I am also grateful to Kenji Matsumoto, who read the section on Reverse Osmosis and made corrections, and to Heiner Strathmann, who did the same for Electrodialysis. The assistance of Marcia Patten, who proofed the manuscript, and Vivian Tran, who checked many of the references, is also appreciated.

ACKNOWLEDGMENTS FOR THE SECOND EDITION

Eighteen months after the first edition of this book appeared, it was out of print. Fortunately, John Wiley & Sons, Ltd agreed to publish a second edition, and I have taken the opportunity to update and revise a number of sections. Tessa Ennals, long-time editor at Membrane Technology and Research, postponed her retirement to help me finish the new edition. Tessa has the standards of an earlier time, and here, as in the past, she gave the task nothing but her best effort. I am indebted to her, and wish her a long and happy retirement. Marcia Patten, Eric Peterson, David Lehmann, Cindy Dunnegan and Janet Farrant assisted Tessa by typing new sections, revising and adding figures, and checking references, as well as helping with proofing the manuscript. I am grateful to all of these colleagues for their help.

CONTENTS

1 OVERVIEW OF MEMBRANE SCIENCE AND TECHNOLOGY

Introduction

Membranes have gained an important place in chemical technology and are used in a broad range of applications. The key property that is exploited is the ability of a membrane to control the permeation rate of a chemical species through the membrane. In controlled drug delivery, the goal is to moderate the permeation rate of a drug from a reservoir to the body. In separation applications, the goal is to allow one component of a mixture to permeate the membrane freely, while hindering permeation of other components.

This book provides a general introduction to membrane science and technology. Chapters 2 to 4 cover membrane science, that is, topics that are basic to all membrane processes, such as transport mechanisms, membrane preparation, and boundary layer effects. The next six chapters cover the industrial membrane separation processes, which represent the heart of current membrane technology. Carrier facilitated transport is covered next, followed by a chapter reviewing the medical applications of membranes. The book closes with a chapter that describes various minor or yet-to-be-developed membrane processes, including membrane reactors, membrane contactors and piezodialysis.

Historical Development of Membranes

Systematic studies of membrane phenomena can be traced to the eighteenth century philosopher scientists. For example, Abbé Nolet coined the word 'osmosis' to describe permeation of water through a diaphragm in 1748. Through the nineteenth and early twentieth centuries, membranes had no industrial or commercial uses, but were used as laboratory tools to develop physical/chemical theories. For example, the measurements of solution osmotic pressure made with membranes by Traube and Pfeffer were used by van't Hoff in 1887 to develop his limit law, which explains the behavior of ideal dilute solutions; this work led directly to the

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van't Hoff equation. At about the same time, the concept of a perfectly selective semipermeable membrane was used by Maxwell and others in developing the kinetic theory of gases.

Early membrane investigators experimented with every type of diaphragm available to them, such as bladders of pigs, cattle or fish and sausage casings made of animal gut. Later, collodion (nitrocellulose) membranes were preferred, because they could be made reproducibly. In 1907, Bechhold devised a technique to prepare nitrocellulose membranes of graded pore size, which he determined by a bubble test [1]. Other early workers, particularly Elford [2], Zsigmondy and Bachmann [3] and Ferry [4] improved on Bechhold's technique, and by the early 1930s microporous collodion membranes were commercially available. During the next 20 years, this early microfiltration membrane technology was expanded to other polymers, notably cellulose acetate. Membranes found their first significant application in the testing of drinking water at the end of World War II. Drinking water supplies serving large communities in Germany and elsewhere in Europe had broken down, and filters to test for water safety were needed urgently. The research effort to develop these filters, sponsored by the US Army, was later exploited by the Millipore Corporation, the first and still the largest US microfiltration membrane producer.

By 1960, the elements of modern membrane science had been developed, but membranes were used in only a few laboratory and small, specialized industrial applications. No significant membrane industry existed, and total annual sales of membranes for all industrial applications probably did not exceed US$20 million in 2003 dollars. Membranes suffered from four problems that prohibited their widespread use as a separation process: They were too unreliable, too slow, too unselective, and too expensive. Solutions to each of these problems have been developed during the last 30 years, and membrane-based separation processes are now commonplace.

The seminal discovery that transformed membrane separation from a laboratory to an industrial process was the development, in the early 1960s, of the Loeb–Sourirajan process for making defect-free, high-flux, anisotropic reverse osmosis membranes [5]. These membranes consist of an ultrathin, selective surface film on a much thicker but much more permeable microporous support, which provides the mechanical strength. The flux of the first Loeb–Sourirajan reverse osmosis membrane was 10 times higher than that of any membrane then available and made reverse osmosis a potentially practical method of desalting water. The work of Loeb and Sourirajan, and the timely infusion of large sums of research and development dollars from the US Department of Interior, Office of Saline Water (OSW), resulted in the commercialization of reverse osmosis and was a major factor in the development of ultrafiltration and microfiltration. The development of electrodialysis was also aided by OSW funding.

Concurrently with the development of these industrial applications of membranes was the independent development of membranes for medical separation processes, in particular, the artificial kidney. W.J. Kolf [6] had demonstrated the first successful artificial kidney in The Netherlands in 1945. It took almost 20 years to refine the technology for use on a large scale, but these developments were complete by the early 1960s. Since then, the use of membranes in artificial organs has become a major life-saving procedure. More than 800 000 people are now sustained by artificial kidneys and a further million people undergo open-heart surgery each year, a procedure made possible by development of the membrane blood oxygenator. The sales of these devices comfortably exceed the total industrial membrane separation market. Another important medical application of membranes is for controlled drug delivery systems. A key figure in this area was Alex Zaffaroni, who founded Alza, a company dedicated to developing these products in 1966. The membrane techniques developed by Alza and its competitors are widely used in the pharmaceutical industry to improve the efficiency and safety of drug delivery.

The period from 1960 to 1980 produced a significant change in the status of membrane technology. Building on the original Loeb–Sourirajan technique, other membrane formation processes, including interfacial polymerization and multilayer composite casting and coating, were developed for making high-performance membranes. Using these processes, membranes with selective layers as thin as 0.1 μm or less are now being produced by a number of companies. Methods of packaging membranes into large-membrane-area spiral-wound, hollow-fine-fiber, capillary, and plate-and-frame modules were also developed, and advances were made in improving membrane stability. By 1980, microfiltration, ultrafiltration, reverse osmosis and electrodialysis were all established processes with large plants installed worldwide.

The principal development in the 1980s was the emergence of industrial membrane gas separation processes. The first major development was the Monsanto Prism® membrane for hydrogen separation, introduced in 1980 [7]. Within a few years, Dow was producing systems to separate nitrogen from air, and Cynara and Separex were producing systems to separate carbon dioxide from natural gas. Gas separation technology is evolving and expanding rapidly; further substantial growth will be seen in the coming years. The final development of the 1980s was the introduction by GFT, a small German engineering company, of the first commercial pervaporation systems for dehydration of alcohol. More than 100 ethanol and isopropanol pervaporation dehydration plants have now been installed. Other pervaporation applications are at the early commercial stage.

Types of Membranes

This book is limited to synthetic membranes, excluding all biological structures, but the topic is still large enough to include a wide variety of membranes that differ in chemical and physical composition and in the way they operate. In essence, a membrane is nothing more than a discrete, thin interface that moderates the

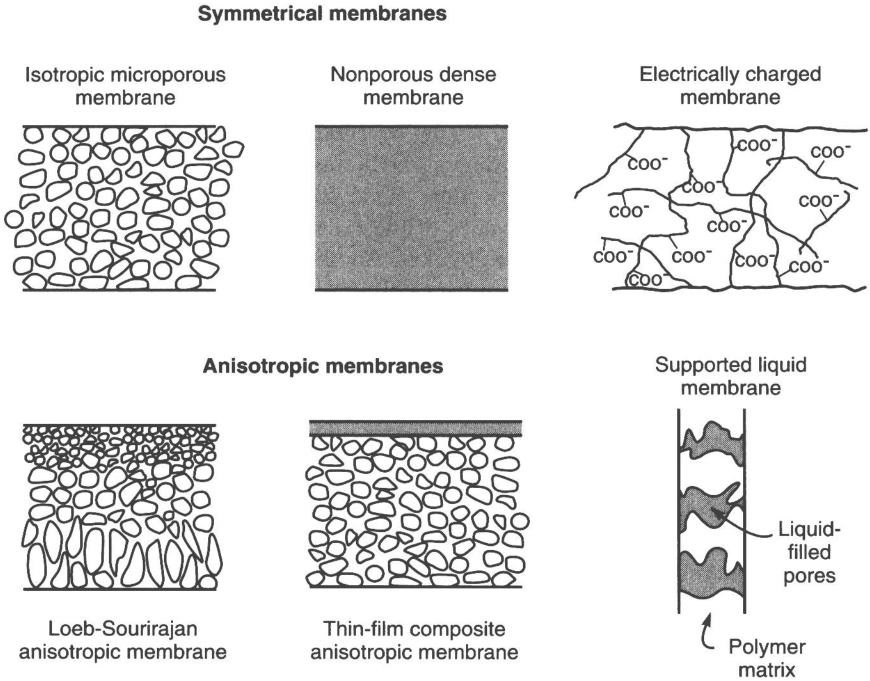

Figure 1.1 Schematic diagrams of the principal types of membranes

permeation of chemical species in contact with it. This interface may be molecularly homogeneous, that is, completely uniform in composition and structure, or it may be chemically or physically heterogeneous, for example, containing holes or pores of finite dimensions or consisting of some form of layered structure. A normal filter meets this definition of a membrane, but, by convention, the term filter is usually limited to structures that separate particulate suspensions larger than 1 to 10 μm. The principal types of membrane are shown schematically in Figure 1.1 and are described briefly below.

Isotropic Membranes

Microporous Membranes

A microporous membrane is very similar in structure and function to a conventional filter. It has a rigid, highly voided structure with randomly distributed, interconnected pores. However, these pores differ from those in a conventional filter by being extremely small, on the order of 0.01 to 10 μm in diameter. All particles larger than the largest pores are completely rejected by the membrane.

Particles smaller than the largest pores, but larger than the smallest pores are partially rejected, according to the pore size distribution of the membrane. Particles much smaller than the smallest pores will pass through the membrane. Thus, separation of solutes by microporous membranes is mainly a function of molecular size and pore size distribution. In general, only molecules that differ considerably in size can be separated effectively by microporous membranes, for example, in ultrafiltration and microfiltration.

Nonporous, Dense Membranes

Nonporous, dense membranes consist of a dense film through which permeants are transported by diffusion under the driving force of a pressure, concentration, or electrical potential gradient. The separation of various components of a mixture is related directly to their relative transport rate within the membrane, which is determined by their diffusivity and solubility in the membrane material. Thus, nonporous, dense membranes can separate permeants of similar size if their concentration in the membrane material (that is, their solubility) differs significantly. Most gas separation, pervaporation, and reverse osmosis membranes use dense membranes to perform the separation. Usually these membranes have an anisotropic structure to improve the flux.

Electrically Charged Membranes

Electrically charged membranes can be dense or microporous, but are most commonly very finely microporous, with the pore walls carrying fixed positively or negatively charged ions. A membrane with fixed positively charged ions is referred to as an anion-exchange membrane because it binds anions in the surrounding fluid. Similarly, a membrane containing fixed negatively charged ions is called a cation-exchange membrane. Separation with charged membranes is achieved mainly by exclusion of ions of the same charge as the fixed ions of the membrane structure, and to a much lesser extent by the pore size. The separation is affected by the charge and concentration of the ions in solution. For example, monovalent ions are excluded less effectively than divalent ions and, in solutions of high ionic strength, selectivity decreases. Electrically charged membranes are used for processing electrolyte solutions in electrodialysis.

Anisotropic Membranes

The transport rate of a species through a membrane is inversely proportional to the membrane thickness. High transport rates are desirable in membrane separation processes for economic reasons; therefore, the membrane should be as thin as possible. Conventional film fabrication technology limits manufacture of mechanically strong, defect-free films to about 20 μm thickness. The development of novel membrane fabrication techniques to produce anisotropic membrane structures was one of the major breakthroughs of membrane technology during the past 30 years. Anisotropic membranes consist of an extremely thin surface layer supported on a much thicker, porous substructure. The surface layer and its substructure may be formed in a single operation or separately. In composite membranes, the layers are usually made from different polymers. The separation properties and permeation rates of the membrane are determined exclusively by the surface layer; the substructure functions as a mechanical support. The advantages of the higher fluxes provided by anisotropic membranes are so great that almost all commercial processes use such membranes.

Ceramic, Metal and Liquid Membranes

The discussion so far implies that membrane materials are organic polymers and, in fact, the vast majority of membranes used commercially are polymer-based. However, in recent years, interest in membranes formed from less conventional materials has increased. Ceramic membranes, a special class of microporous membranes, are being used in ultrafiltration and microfiltration applications for which solvent resistance and thermal stability are required. Dense metal membranes, particularly palladium membranes, are being considered for the separation of hydrogen from gas mixtures, and supported liquid films are being developed for carrier-facilitated transport processes.

Membrane Processes

Six developed and a number of developing and yet-to-be-developed industrial membrane technologies are discussed in this book. In addition, sections are included describing the use of membranes in medical applications such as the artificial kidney, blood oxygenation, and controlled drug delivery devices. The status of all of these processes is summarized in Table 1.1.

The four developed industrial membrane separation processes are microfiltration, ultrafiltration, reverse osmosis, and electrodialysis. These processes are all well established, and the market is served by a number of experienced companies.

The range of application of the three pressure-driven membrane water separation processes—reverse osmosis, ultrafiltration and microfiltration—is illustrated in Figure 1.2. Ultrafiltration (Chapter 6) and microfiltration (Chapter 7) are basically similar in that the mode of separation is molecular sieving through increasingly fine pores. Microfiltration membranes filter colloidal particles and bacteria from 0.1 to 10 μm in diameter. Ultrafiltration membranes can be used to filter dissolved macromolecules, such as proteins, from solutions. The mechanism of separation by reverse osmosis membranes is quite different. In reverse osmosis membranes (Chapter 5), the membrane pores are so small, from 3 to 5 Å in diameter, that they are within the range of thermal motion of the polymer