Basic Principles of Membrane Technology

second edition

Marcel Mulder

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by

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Preface

Membranes play a central role in our daily life, or as indicated by one of my foreign colleagues, Richard Bowen, 'If you are tired of membranes, you are tired of life'. Biological membranes are hardly used in industrial applications, but separations with synthetic membranes have become increasingly important. Today, membrane processes are used in a wide range of applications and their numbers will certainly increase. Therefore, there is a need for well educated and qualified engineers, chemists, scientists and technicians who have been taught the basic principles of membrane technology. However, despite the growing importance of membrane processes, there are only a few universities that include membrane technology in their regular curricula. One of the reasons for this may be the lack of a comprehensive textbook. For me, this was one of the driving forces for writing a textbook on the basic principles of membrane technology which provides a broad view on the various aspects of membrane technology. I realise that membrane technology covers a broad field but nevertheless I have tried to describe the basic principles of the various disciplines. Although the book was written with the student in mind it can also serve as a first introduction for engineers, chemists, and technicians in all kind of industries who wish to learn the basics of membrane technology.
The book is divided into eight chapters, each covering a basic topic:
Chapter 1 is an introduction to the field and gives some definitions and the historical development. Chapter 2 is a survey of polymers used as membrane material and describes the factors that determine the material properties. Chapter 3 gives an overview of various preparation techniques. Most of the commercial available membranes are prepared by phase-inversion and this technique will be described in detail. Chapter 4 describes all kind of characterisation techniques, both for porous membranes as well as for nonporous membranes. Transport across a membrane occurs when a driving force is applied. Different types of driving forces can be applied and are described in chapter 5. Also membrane transport is described in this chapter. Chapter 6 gives a survey of various technical membrane processes. These processes are classified according to their driving forces. Concentration polarisation is a phenomenon which is inherently related to membrane separation. Description of this phenomenon and of fouling are given in chapter 7. Finally, in chapter 8 the basic aspects of module and process design are described. At the end of this chapter some process calculations are given.

Let me conclude by acknowledging the many who helped me writing this book. I am pleased to say that they are all (former) members of our membrane research group at the University of Twente. My first experience with membrane technology was in 1974 when I entered this university. Membrane research had just started at that time initiated by the promising expectations from the activities of the Office of Saline Water in the USA. Since then, the research activities have grown and at this moment membrane technology is one of the main research topics in our faculty, with more than 70 researchers being active in various fields.
In 1980, we started a graduate course on membrane technology for chemical engineering students. Since then, the course has been extended and improved. All my colleagues who contributed to the course also contributed directly or indirectly to helping me write this book. I am specially indebted to Kees Smolders, the driving force behind membrane research at our

University, who is always very dynamic, enthusiastic and stimulating. Other colleagues of the beginning period were Frank Altena and Maarten van der Waal. Since then a number of people have been involved in the membrane course: Hans Wijmans, Hans van den Berg, Hans Wesselingh, Matthias Wessling, Heiner Strathmann, Thonie van den Boomgaard, and Gert van den Berg. I would like to thank all these colleagues who added substantially to this book. Furthermore, I wish to thank Zandrie Borneman who made a number of the scanning electron micrographs and Ingo Blume, who has critically read the manuscript and suggested corrections. Errors that remain are my fault. It was also Ingo Blume who designed the cover and Willem Puper who drew the Maxwell demon. Especially, I wish to acknowledge my wife Jos for her patience and understanding during the many hours in the evenings when I was writing the book. Finally, I wish to express my warm feelings to my sons Ivo and Joris for just being there.

Marcel Mulder, April 1991

Preface to second edition

Membrane technology is increasingly expanding and the number of people dealing with membranes is growing rapidly. Most applications refer to concentration, purification and fractionation. However, in the last decade much research has been devoted to membrane reactors (and membrane bioreactors), the combination of a chemical reaction with a membrane separation process to shift the equilibrium or to provide in a better way the reactants that a higher productivity is obtained. New materials and membranes are required in which catalytic activity has been incorporated but there is still a long way to go. Some aspects of membrane reactors are described in chapter VI. Also membrane contactors, in which the membrane acts as an interphase, are described now, at least some basic principles. The major difference with the first edition is the incorporation of problems. It was said in one of the book reviews, 'problems should be a part of a (any) textbook' and I agree with that.
I want to thank all the people from all places around the world for their comments, considerations and positive reactions. This makes it worth to put so many hours in writing and up-dating the book and it helped me to finalize the second edition.

Marcel Mulder, May 1996

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I Introduction

II Materials and material properties

III Preparation of synthetic membranes

VI Membrane processes

I INTRODUCTION

I.1. Separation processes

In 1861, at about the time that Graham reported his first dialysis experiments using synthetic membranes [1], Maxwell created the 'sorting demon', "a being whose faculties are so sharpened that he can follow every molecule in its course and would be able to what is at present impossible to us" [2]. In other words, the demon is able to discriminate between molecules. Suppose that a vessel is divided into two parts A and B by a division in which there is a small hole and that Maxwell's demon sits at the hole which he can open and close at will (see figure I - 1).

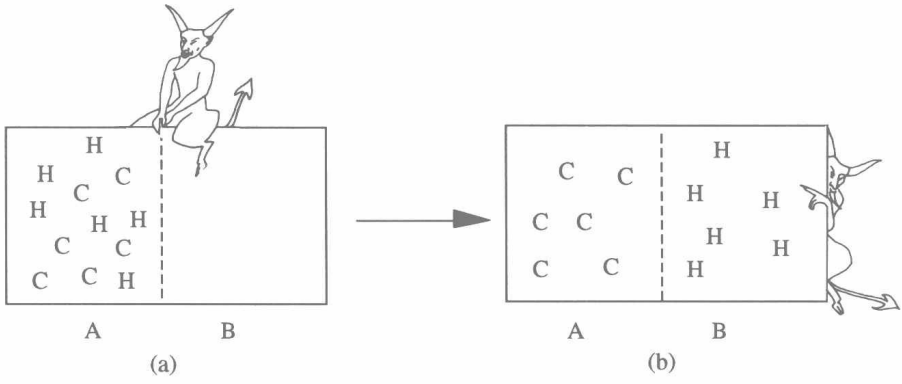

Figure I - 1. The 'sorting demon' has ensured that a random situation (a) has been transformed into an ordered one (b).

Part A is filled with a gas consisting of hot (H) and cold (C) molecules (i.e. H and C differ in average speed) and the demon allows only the hot molecules (H) to pass. After he has been doing this for a while, the hot (H) and cold (C) molecules will be separated completely (figure 1b). Hence, starting from a random situation, an ordered one is attained which is against the second law of thermodynamics. This law states that a system tends to maximise its entropy, i.e. when left alone, the system tries to reach a situation of maximum disorder. Suppose now we have a membrane that separates the two parts of the vessel, with part A being filled with an isomeric mixture. Now, instead of employing a demon, we exert a driving force on both isomers. The membrane may discriminate between the two types of molecules because of differences in size, shape or chemical structure, and again separation will be achieved, but only to a limited extent: the membrane will never do the job as well as the demon, i.e. the membrane will not be able to separate the mixture completely. Of

course, these two examples are not quite comparable, irrespective of the fact that such a demon does not exist, for in the case of the membrane we put energy (work or heat) into the system while the demon is assumed to do the job without the expenditure of work.

The separation of substances which mix spontaneously can be accomplished either via a demon or some device which consumes energy supplied in the form of heat or mechanical work. The basic principle of any separation process is that a certain amount of energy is required to accomplish the separation. Hence, two substances A and B will mix spontaneously when the free enthalpy of the product (the mixture) is smaller than the sum of the free enthalpies of the pure substances. The minimum amount of energy (W_{min}), necessary to accomplish complete separation is at least equal to or larger than the free enthalpy of mixing.

$$W_{min} \geq \Delta G_m = \Delta H_m - T\Delta S_m \qquad (I - 1)$$

In practice, the energy requirement for separation will be many times greater than this minimum value W_{min}. Different types of separation processes exist and each requires a different amount of energy. Thus, the production of fresh water from the sea, which is a very practical problem, can be performed by several commercially available separation processes:

i) distillation: heat is supplied to the solution in such a way that water distils off;
ii) freezing: the solution is cooled and pure ice is obtained;
iii) reverse osmosis : the solution is pressurised allowing water molecules to pass through the membrane while salt molecules are retained;
iv) electrodialysis: an electric field is applied to a salt solution between a number of charged membranes, and ions are forced into certain compartments leaving water molecules in other compartments; and
v) membrane distillation: heat is supplied to a salt solution causing the transport of water vapour through non-wetted the membrane.

The minimum amount of energy necessary for the desalination of sea water can be obtained by simple thermodynamic calculations. When 1 mol of solvent (in this case water) passes through the membrane, the minimum work done when the process is carried out reversibly is:

$$W_{min} = \pi \, . \, V_w = 25. \, 10^5 \, (N \, m^{-2}). \;\; 18. \, 10^{-6} \, (m^3 \, mol^{-1}) = 45 \, J \, mol^{-1} = 2.5 \, MJ \, m^{-3}$$

where π is the osmotic pressure of seawater ($\approx$ 25 bar) and V_w is the molar volume of water (0.018 l mol^{-1}). However, separation processes consume more energy than this minimum amount, with reverse osmosis having the lowest energy consumption of those mentioned above. Also the mechanisms necessary to achieve separation are quite different among these processes, with distillation and membrane distillation being based on differences in (partial) vapour pressure, the freezing or crystallisation process on differences in freezing tendencies, reverse osmosis on differences in solubility and on the diffusivity of water and

salt in the membrane and electrodialysis on ion transport in charge selective ion-exchange membranes. Freezing and distillation involve a phase transition, which means that a heat of vaporisation has to be supplied. Membrane processes such as reverse osmosis and electrodialysis occur without a phase transition, and involve a lower energy consumption. Membrane distillation, which is also a membrane process, involves no net phase transition although two transitions, vaporisation (on the feed side) and condensation (on the permeate side) occur in fact.
Desalination of (sea)water is an illustrative example of a separation problem for which competitive separation processes, based on different separation principles and consuming different amounts of energy, can be used.

A classification of some separation processes in terms of the physical or chemical properties of the components to be separated is given in table I.1. This table is far from complete and a more detailed description of separation processes can be found in a number of excellent textbooks (see e.g.[3]).

Table I.1 Separation processes based on physical/chemical properties

physical/chemical property	separation process
size	filtration, microfiltration, ultrafiltration, dialysis, gas separation, gel permeation chromatography
vapour pressure	distillation, membrane distillation
freezing point	crystallisation
affinity	extraction, adsorption, absorption, reverse osmosis, gas separation, pervaporation, affinity chromatography
charge	ion exchange, electrodialysis, electrophoresis, diffusion dialysis
density	centrifugation
chemical nature	complexation, carrier mediated transport

It can be seen from table I.1 that differences in the size, vapour pressure, affinity, charge or chemical nature of molecules facilitate membrane separation. The number of possible separation principles, some of which are used in combination, distinguish this technique from other separation processes and also provide an indication of the number of situations in which membrane processes can be applied. It should be noted that competitive separation processes are not necessarily based on the same separation mechanism. This has already been demonstrated in the example given above on water desalination. However, this example did not indicate which of the separation processes mentioned is to be preferred.

How can a separation process be selected to solve a given problem? Since several factors influence the choice of the separation process but are not generally applicable specific criteria often have to be met. However, two general criteria apply to all separation

processes:

i) the separation must be feasible technically; and

ii) the separation must be feasible economically.

The first criterion is not surprising since the separation process must be capable of accomplishing the desired separation and achieve a quality product. Sometimes a combination of two or more separation processes is necessary to attain these requirements. However, economical feasibility depends strongly on the value of the products isolated. This is often related to the concentration of the raw material. A decreasing concentration generally leads to an enhanced price for the pure product, as expressed by a so-called 'Sherwood-plot' [4,5].

Costs can be reduced by improving the technique employed for separation. In this respect, the high-value products of biotechnology are interesting since these bioproducts must be recovered from very dilute aqueous solutions. However, other factors also determine the price besides the degree of dilution. The bioproducts are usually very fragile and hence require specific separation conditions. Furthermore, the medium from which the bioproduct are isolated usually contains a large number of low and high molecular weight materials as well as many with similar properties. To obtain high-value products the energy costs must constitute only a small fraction of the product value, whereas with low-value products the energy costs may contribute appreciably to the overall price.

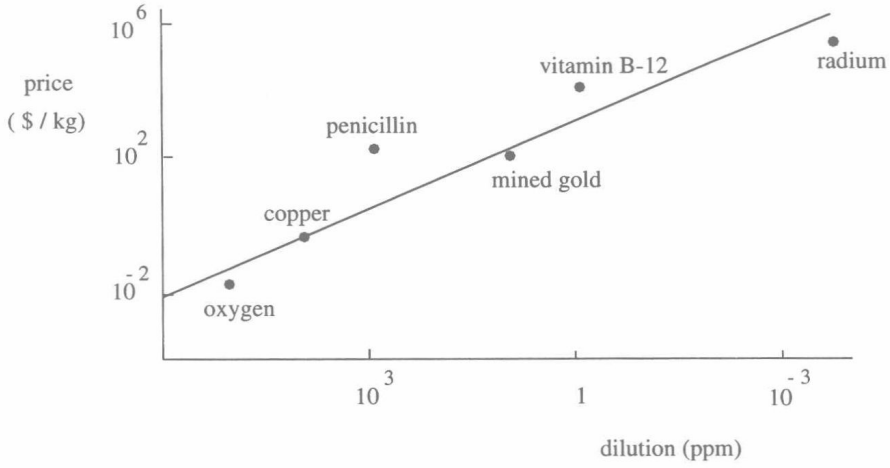

Figure I - 2. Sale price as related to the degree of dilution (expressed in parts per million) of the raw material [4,5].

Other factors can be mentioned that determine the price of low-value products. Water is a very cheap product but its price changes from location to location. Hence, potable water is a cheap product in the western world whilst energy is relative expensive. However,

in the Middle East water is much more expensive whilst energy is cheap. This implies that, because of geographic differences, different criteria are involved in selecting separation processes. Energy and investment costs become more important with decreasing product values. Other factors which can be mentioned are politics and the environment.
From an economical point of view worthless waste streams are hardly worthy of treatment, but environmental considerations and governmental regulations often determine that the separation must be carried out. In addition, political considerations often insist that a certain process be used which may not be the most advantageous from an economical point of view.

Finally, the economics of a separation process may be governed by product loss and damage. Damage to the product can occur particularly when heat-sensitive components are produced, e.g. in the pharmaceutical industry (enzymes, antibiotics, vitamins). Product loss will be especially important in the case of high-value products.

In order to achieve a given separation, a number of different processes can be used. The objectives of separation can be classified roughly as follows:

- concentration: the desired component is present in a low concentration and solvent has to be removed;
- purification: undesirable impurities have to be removed; and
- fractionation: a mixture must be separated into two or more desired components.
- reaction mediation: combination of a chemical or biochemical reaction with a contineous removal of products will increase the the reaction rate.

The membrane processes necessary to undertake these basic functions will be described in more detail in chapter VI.

Membrane processes are characterized by the fact that the feed stream is divided into two streams, i.e. into the retentate or concentrate stream and the permeate stream (figure I - 3), which implies that either the concentrate or permeate stream is the product.

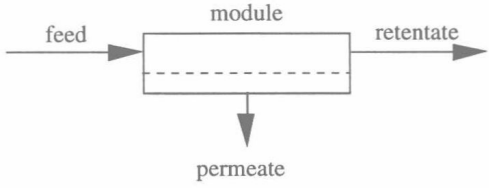

Figure I - 3. Schematic representation of a membrane process where the feed stream has been separated into a retentate and a permeate stream.

If the aim is concentration, the retentate will usually be the product stream. However, in the case of purification, both the retentate or the permeate can yield the desired product depending on the impurities that have to be removed. For example, if potable water is required from surface water containing traces of volatile organic contaminants, both reverse osmosis and pervaporation can be used for separation. With reverse osmosis the solute is