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Chapter I

INTRODUCTION

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This chapter is concerned with membranes that are used to separate materials in a great variety of applications. The growing interest in membrane processes utilized in industry, biomedical engineering, and space science is evidenced by the many publications that have appeared and continue to appear in the literature.

To treat the subject in a logical manner it is essential to cover the general scope of membrane processes and illustrate them with specific examples. On the whole, the engineering aspects of membrane technology have not received adequate attention, and therefore they will be emphasized here. To ensure satisfactory performance, the engineering and design of membrane processes are as important as the development of a new membrane of high performance characteristics.

It is interesting to speculate when the concept of using a membrane for separation was first realized. Although the phenomenon of osmosis was observed in 1748 by Abbe Nollet [1], its possible use as a separation process was not recognized until a much later date. Surely, when Fick developed his mathematical model of diffusion in 1855 (see Chapter 2, Section 1) he must have concluded that the varying rates of diffusion for different substances could be used as the basis of a separation process. As far as is known, the first reference to a separation procedure by means of a membrane is Graham’s [2] use of a dialyzer in 1854, to separate a solution into its components. Subsequently, further evidence of the separation possibilities is contained in a statement made by Graham in his pioneer paper “On the Molecular Mobility of Gases” in 1863 [3]. In this treatise, which resulted in the formulation of Graham’s law, the author mentions “the partial separation of mixed gases.” Only a few years later, in 1866, Graham published another paper [4] dealing with the use of “colloid
septa” for the separation of gases. Thus, it would appear that Graham, as “master of the mint,” deserves credit for originating the use of a membrane in separation.

The natural membranes, which are of such fundamental importance in living organisms, belong to a class all by themselves. The structure of such membranes and the transport mechanisms by which they function are totally different from those of the “dead” membranes used in separation processes. Thus, it is beyond the scope of this chapter to deal with biological membranes in depth. A survey of essential information is, however, presented in Chapter X.

1 DEFINITION OF MEMBRANE

What is a membrane? Possibly the broadest definition is: a region of discontinuity interposed between two phases. This statement implies that membranes can be gaseous, liquid, or solid, or combinations of these phases. The term “region” in the definition is used to eliminate ordinary interfaces. Thus, the interfaces of two immiscible liquids, of a gas and a liquid, or of a gas and a solid would not ordinarily be considered as membrane structures.

An elusive, but nevertheless real gaseous membrane would be the front of a shock wave. So far, at least, we are not aware of any instance where this gaseous membrane has been used successfully for a separation process. Well-known examples of membranes are filmlike solids, porous or nonporous, and the recently developed liquid membranes of Li and co-workers [5], Barrer’s authoritative book Diffusion in and through Solids [6] covers most or all of the solid membranes known to the present state of the art.

Membranes vary in their make-up from the relatively crude structure of a screen to extremely fine configurations only one molecular layer thick, as in the fatty acid spreading on liquid water. No synthetic membrane has as yet been created that can approach the performance of living membranes. The spark of life introduces factors that at present are beyond our ability to duplicate. A very informative presentation on the structure of cell membranes was published by Fox [7].

2 CLASSIFICATION OF MEMBRANES

Even a cursory examination of the variety of membranes that exist makes it evident that a single classification scheme is unlikely to permit a clear and concise presentation.

However, a rather informative picture is obtained by using multiple schemes, which can readily be interrelated. Such arrangements are represented by the following:
A. classification by nature of membrane
B. classification by structure of membrane
C. classification by application of membrane
D. classification by mechanism of membrane action

A. Classification by Nature of Membrane

*Natural membranes*
1. Living membranes
2. Natural substances — modified or regenerated

*Synthetic membranes*
1. Inorganic
   - metals
   - ceramics
   - glass
2. Organic — Polymers
   - films
   - tubing
   - hollow fibers

B. Classification by Structure of Membrane

*Porous membranes*
1. Microporous media
   - compressed powders
   - microporous glass (Corning)
   - microporous ceramics
   - AEC barrier
   - microporous silver membrane (Selas)
   - Millipore filters
   - porous polymer structures
   - cellulose acetate
   - Nuclepore (General Electric)
2. Macropores
   - filters for gases and liquids, some Millipore filters
   - ultrafilters

*Nonporous membranes*
1. Inorganic
   - metal films
   - glass
2. Polymeric structures
   - films
   - tubes
   - hollow fibers
laminated films

*Morphological distinction*

1. Crystalline
   - inorganic (metals, ceramics)
   - organic
2. Amorphous
   - glass
   - polymers

*Liquid membranes*

1. Monomolecular film
   - fatty acid spreading on water
2. Liquid drop surrounded by stable liquid film, Li’s work [5]

**C. Classification by Application of Membrane**

Here, a membrane, gaseous, liquid, or solid, is interspersed between phases, as, for instance, gas-membrane-gas.

*Gaseous-phase systems*

1. Molecular flow — size of pores and molecular velocity determine separation
2. Molecular flow with surface flow (surface or diffusive flow results from adsorptive properties of microporous media)
3. Sweep gas diffusion — use of carrier gas
4. Diffusive solubility flow of polymeric structures — solubility of diffusing gases or vapors is controlling parameter
5. Diffusive flow in solvated polymers — occurs with liquids or vapors that swell or modify membrane properties

*Gas-liquid systems*

1. Macropore structure
   - removal of liquid entrainment in gas stream
   - introduction of gas into liquid phase
2. Microporous structure
   - ultrafine filters
3. Polymeric structures
   - gas diffusion from or into liquid, that is, blood oxygenation (oxygenation and CO₂ removal)

*Liquid-liquid systems*

1. Gas transport from one phase to another liquid phase
   - organ preservation devices, blood oxygenation
2. Osmotic processes
   - reverse osmosis
   - gel permeation
3. Liquid membranes
selective flow through liquid film

*Gas-solid systems*
1. Removal of particulate matter in gas by filter

*Liquid-solid systems*
1. Filtration of slurry with macroporous media
2. Biological waste treatment
3. Emulsion breaking

*Solid-solid systems*
1. Screening of solids on basis of particle size

D. Classification by Mechanism of Membrane Action

*Adsorptive membranes*
1. Microporous membranes
   porous Vycor
   activated charcoal, silica gel, and the like (as compressed powders)
2. Reactive membranes
   a chemically reactive material is contained in the membrane and
   reacts with one of the permeating constituents

*Diffusive membranes*
1. Polymeric membranes
   diffusive solubility flow
2. Metallic
   atomic-state diffusion
3. Glass
   molecular state or affinity phenomena

*Ion-exchange membranes*
1. Cation-exchange resins
2. Anion-exchange resins

*Osmotic membranes*
1. Regular osmotic membranes
2. Reverse osmotic membranes
3. Electro-osmotic membranes

*Nonselective membranes* (Inert behavior)
1. fritted glass
2. filters, screens

3 MEMBRANES IN SEPARATIONS

The role of a membrane in a separation process is to act as a selective barrier. It should permit preferred passage of a certain component out of the mixture. Macroscopic processes, like filtration, do not rely on the molecular properties of a membrane. However, microscopic processes, which constitute the majority
of the membrane processes, are mostly due to molecular interactions between membranes and fluids. By virtue of the differences in their degree of affinity, the transmission rate through a membrane is expected to be different for each component. Thus, separation becomes possible.

For example, permeation through a polymeric membrane usually involves both diffusivity and solubility of the permeant species, and these properties are the result of molecular interactions. The sole exception would be the case of gaseous diffusion through a microporous membrane which proceeds strictly on the basis of free molecular or Knudsen diffusion. If surface diffusion is absent, or if it is so small that it can be ignored, bulk flow would not depend on the molecular characteristics of the membrane. As long as the pores are small enough to ensure Knudsen flow, it does not make any difference what kind of membrane is used. In actual practice, however, the adsorptive behavior of gases may not be negligible, depending on temperature and pressure of operation, and the phenomenon of surface flow will enter the picture.

In general, separation takes place on the surface of the membrane, or in the membrane, itself, where the molecular interactions compete with one another. Thus, it is necessary to understand what goes on in the vicinity and inside the membrane. The respective mechanism of permeation is the key.

In order to improve the separation efficiency, two factors should be examined thoroughly. One is selectivity, and the other is total flow for a given membrane. Both of these factors can be studied only after one has knowledge of the actual transport mechanism through the membrane. Taking the above example of the polymeric membrane, one is bound to seek higher solubility and diffusivity for a preferred component and lower solubilities and diffusivities for the other components. When such a membrane can be found it will give a high degree of separation.

References

General References


