MEMBRANE SEPARATION TECHNOLOGIES

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Contents

Summary

An attempt was made in this chapter to outline industrial membrane separation processes within a rather limited space, which inevitably narrowed the scope of the chapter. For example, medical applications, such as artificial organs, hemodialysis, blood-oxygenation and drug release, could not be included, although the author is fully aware of their importance as another branch of membrane technologies. As well, no mention was made to membrane as battery separator. Very little space was given to inorganic membranes even though commercial ceramic membranes such as alumina and zirconia membranes are more suitable than polymeric membranes for the treatment of aggressive effluents and high-temperature fluids. Their important applications are also in pharmaceutical and dairy industries where heat sterilization is required. Moreover, a large amount of research work has been carried out during the past ten years for the development of zeolite and other ceramic membranes for commercial purposes. As a result, zeolite membrane has become available for pervaporation applications in commercial scale. Despite enormous potential of inorganic membranes, the main stream of membrane material is still polymer, since inorganic membranes have inherent disadvantages of being brittle and more expensive than polymeric membranes. This chapter is also focused on separation processes where pressure is the major driving force, since the author believes that most of progresses made in the past forty years were in this field. The chapter however includes some membrane separation processes where electrical potential difference is the driving force. Other new membrane applications that are currently under development were also included. Thus, membrane separation processes that have been dealt with in this chapter are: reverse osmosis, nanofiltration, ultrafiltration, microfiltration, membrane gas separation, membrane vapor separation, pervaporation, electrodialysis, bipolar membrane, membrane distillation, membrane extraction, membrane reactor and hybrid separation processes. For each process, focus was more on fundamentals, although some application examples were given.

1. History

In the beginning was Gibbs Adsorption Isotherm,

$$\Gamma = -\frac{1}{RT}\frac{\partial \sigma}{\partial \ln a} \qquad (1)$$

where is surface excess of solute, R is universal gas constant, T is temperature, is interfacial tension and a is activity of solute. It is known that the surface tension (interfacial tension at solution/ air interface) of sodium chloride solution will increase when sodium chloride concentration (and also activity) increases. In equation (1) the derivative $\frac{\partial \sigma}{\partial \ln a}$ is therefore positive and hence is negative. This means that there is deficiency of solute at a sodium chloride solution/air interface. Thus, Gibbs Adsorption Isotherm predicts the presence of a thin water layer at the surface of a sodium chloride solution. The thickness of the pure water layer can be calculated to be 3 to 6 x 10^{-10} m. A similar water layer should, most likely, exist at a sodium chloride solution/solid interface. Suppose there is a pore in a solid film whose radius is equal to or smaller than the thickness of the interfacial pure water layer, t, pure water can be collected by letting it flow through the pore under a pressure differential. (see Figure 1) Hence it will be possible to produce pure water from sodium chloride solution (or potable water from seawater).

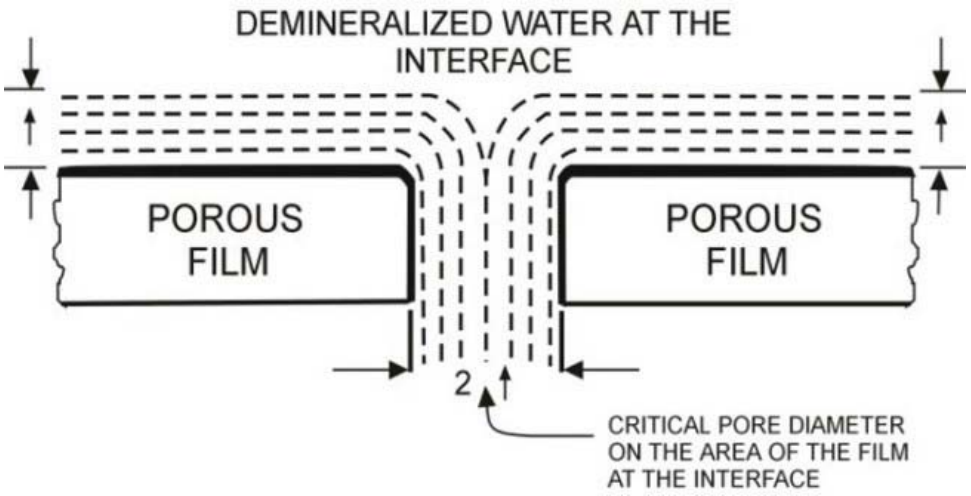

Figure 1. Preferential Sorption-Capillary Flow Mechanism

This mechanism, called Preferential Sorption-Capillary Flow Mechanism, was the fundamental principle underlying Sourirajan's work to develop a membrane for seawater desalination. His work led to the historic announcement of cellulose acetate membrane for seawater desalination together with his coinventor Loeb in 1960. The history of industrial membrane separation technologies began in this year.

Over the past forty years, membrane separation processes have been adopted by various industries, displacing conventional separation processes due to the following inherent advantages.

a. Membrane separation processes require less capital investment.
b. Membrane separation processes are energy efficient.
c. Membrane devices are simple, compact and modular.

2. Definition and classification

In every membrane separation process there is a membrane that is placed between two phases. One phase is called feed and the other is called permeate.

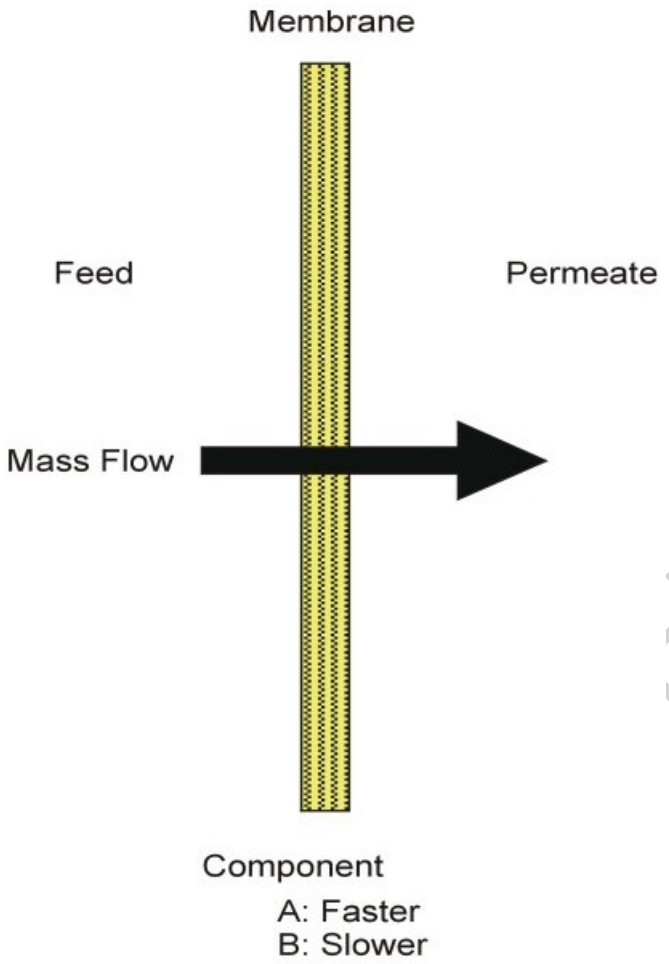

Figure 2. Schematic representation of membrane separation

(See Figure 2) A flow of mass is induced from feed to permeate by applying a driving force. When the feed consists of equal to or more than two components, and some of those components flow faster than others through the membrane, separation of the feed mixture takes place. Different driving forces can be conceived, but the difference in pressure, concentration and electrical potential between the feed and the permeate phase are by far the most popular in industrial applications.

Membrane separation processes can be classified according to their driving forces as follows.

a. Pressure is the driving force.
   Reverse osmosis
   Nanofiltration
   Ultrafiltration
   Microfiltration
b. Partial pressure is the driving force.
   Gas separation
   Vapor permeation
   Pervaporation
c. Concentration is the driving force.

Dialysis
Membrane extraction

d. Electrical potential is the driving force.
Electrodialysis
Membrane electrolysis

In this chapter focus is on membrane separation processes where the driving forces are either pressure or partial pressure, since most of progresses made during the last forty years are in this area.

3. Performance parameters

Membrane performance is characterized always by flux and selectivity. Flux is volume of permeate passing through a membrane per unit area and time. Using SI units this is given as m^3/m^2 s, but other units such as L/m^2 h, L/m^2 day and gal/ft^2 day are often used in the literature. For flux of gas and vapor, mol/m^2 s, is the most appropriate unit, but $cm^3(STP)/cm^2$ s is also often used.

Separation, f, defined as

$$f = 1 - \frac{c_{permeate}}{c_{feed}} \tag{2}$$

where c_{permeate} and c_{feed} are concentration of solute in the permeate and in the feed, respectively, is often used as a measure of selectivity when a solute is separated from a solution.

Separation factor, $_{AB}$, defined as

$$\alpha_{AB} = \frac{(c_A / c_B)_{permeate}}{(c_A / c_B)_{feed}} \tag{3}$$

where c_A and c_B are concentrations of A and B, respectively, is often used for the separation of a mixture of A and B, when it is difficult to tell which component is solute.

Molecular weight-cut off defined as molecular weight of solute whose separation is 90 % is often used as a measure of selectivity of ultrafiltration membranes.

4. Membrane separation processes where the driving force is pressure

4.1. Reverse osmosis

4.1.1. Principle of reverse osmosis

Reverse osmosis is a membrane separation process by which a solution is separated into its components. A solute, which is either a small organic molecule or an inorganic electrolyte, or a mixture of solutes, is separated from solvent, which is in most case water. Pore sizes as small as less than one nm (10^{-9} m) are required to enable the separation of such small substances. When a high pressure is applied on a feed solution that is brought into contact with one side of a membrane, water molecules, the size of which is as small as a fraction of one nm, pass through the pore. The solute molecules or electrolytes that are dissolved in water, on the other hand, can not pass, since they are either too large to enter the pore or they are rejected at the pore entrance by some forces working against their entry into the pore. (see Figure 3)

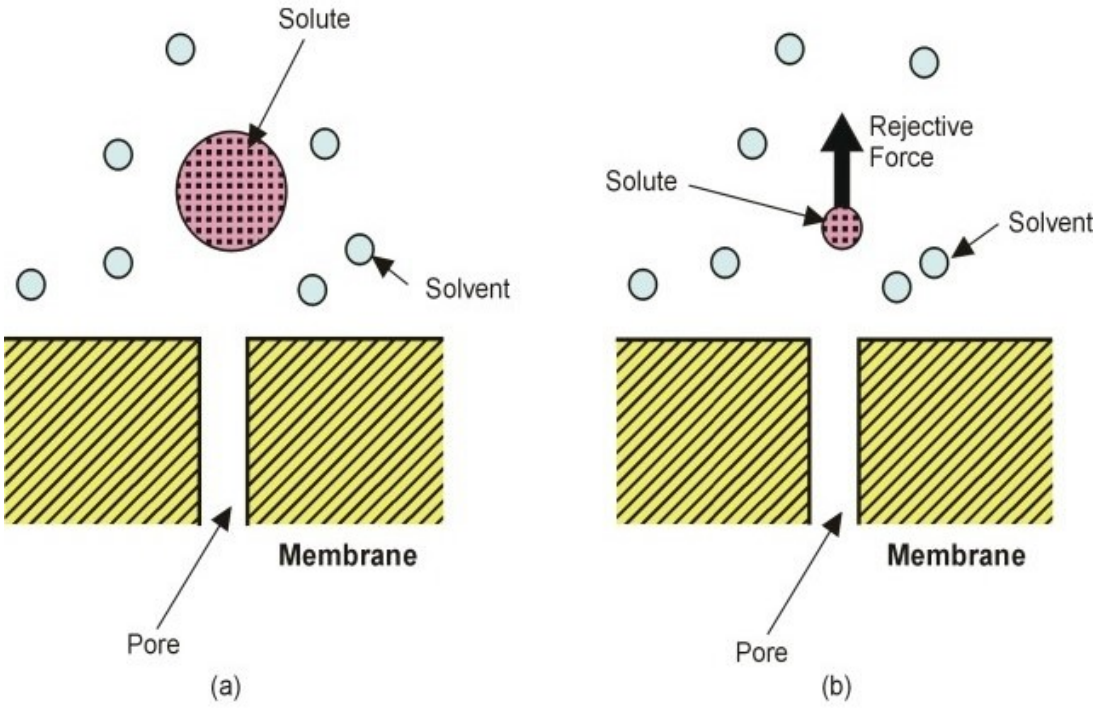

Figure 3. Mechanism of membrane separation

When a membrane with pores smaller than one nm is placed between pure water and a solution in which sodium chloride is dissolved (e.g. sea water), water starts to flow from the pure water side to the solution side. (see Figure 4) As more water flows into the solution, the level of the solution goes up until the flow of water will stop. This phenomenon is called osmosis and the difference in the levels of pure water and the solution is called osmotic pressure. When a pressure higher than the osmotic pressure is applied on the solution side, the flow of water is reversed; i.e. water starts to flow from the solution to pure water side. Sodium chloride can not flow through the pore, hence pure water can be obtained from the sodium chloride solution. Since the direction of water flow is reversed, this process is called reverse osmosis.

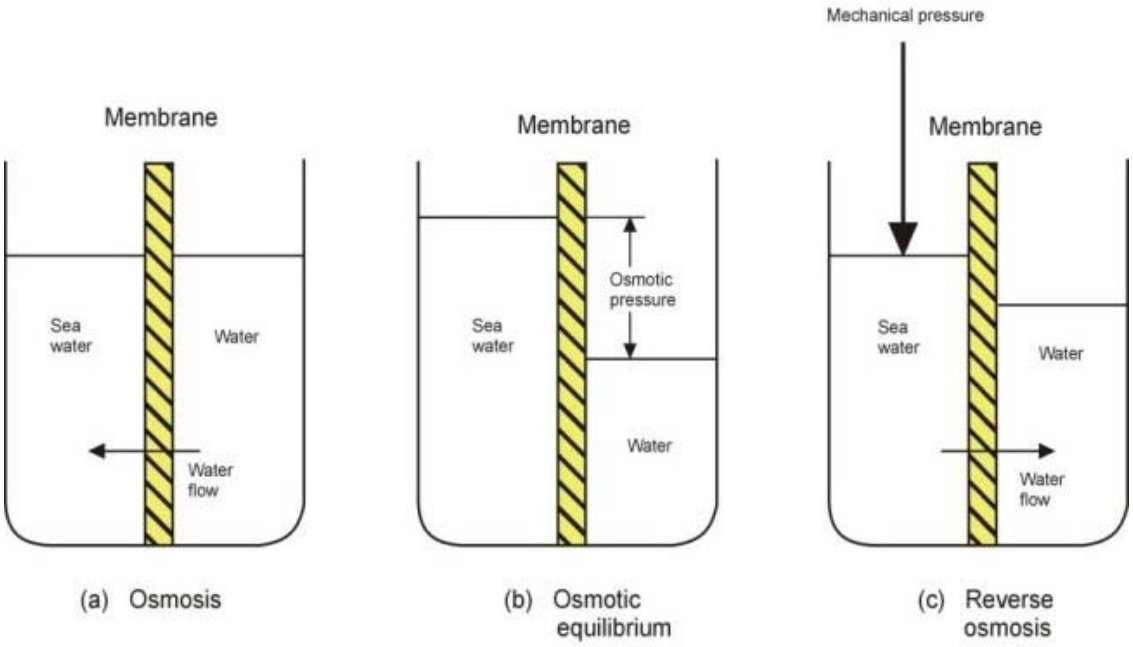

Figure 4. Principle of reverse osmosis

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Biographical Sketch

Professor Matsuura was born in Shizuoka, Japan, in 1936. He received his B.Sc. (1961) and M.Sc. (1963) degrees from the Department of Applied Chemistry at the Faculty of Engineering, University of Tokyo. He went to Germany to pursue his doctoral studies at the Institute of Chemical Technology of the Technical University of Berlin and received Doktor-Ingenieur in 1965.
After working at the Department of Synthetic Chemistry of the University of Tokyo as a staff assistant and at the Department of Chemical Engineering of the University of California, Davis, as a postdoctoral research associate, he joined the National Research Council of Canada in 1969. He came to the University of Ottawa in 1992 as a professor and the chairholder of British Gas/NSERC Industrial Research Chair. Currently, he is professor of the Department of Chemical Engineering and the director of the Industrial Membrane Research Institute (IMRI), which is affiliated to the Department of Chemical Engineering.
Dr. Matsuura received the Research Award of International Desalination and Environmental Association in 1983. He is a fellow of the Chemical Institute of Canada and a member of the North American Membrane Society and the Chemical Society of Japan. In October 1986, he was invited by the Institute of Oceanography, Hangzhou, China, to give a series of lectures on membrane separation processes at various research institutes of China. In September 1991, he was invited by Japan Industrial Technology Association to deliver a series of lectures at industry, government and universities in Japan. He was also invited to Korea in July 1996 to deliver a lecture at the 4th Workshop of the Membrane Society of Korea. He has published more than 200 papers in refereed journals, authored or co-authored three books and edited three books. A symposium for membrane gas separation was held at the Eighth Annual Meeting of the North American Membrane Society, May 18-22, 1996, Ottawa, to honour Dr. Matsuura together with Sr. Sourirjan for their life-long contribution to the membrane research. He received George S. Glinski Award for Excellence in Research from the Faculty of Engineering of the University of Ottawa in 1998.