
SCIENCE AND TECHNOLOGY OF
SEPARATION MEMBRANES
Tadashi Uragami
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SCIENCE AND TECHNOLOGY OF SEPARATION MEMBRANES

Science and Technology of Separation Membranes

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Functional Separation Membrane Research Center, Japan

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Preface

After reading this book, and having understood its contents, its biggest aim is to be able to contribute to new technical ideas more than existing membrane separation technologies.

At first it is essential to learn the history of the development of the separation membrane; the equilibrium phenomena of the solubility of the material and the electrochemical properties as the basic phenomena of the membrane properties of matter in the field of application, nonequilibrium phenomena such as the mass transfer, the quantitative understanding of various underlying phenomena, the problems of membrane separation technology and the solution methods for existing separation membranes are the same in all fields.

With that in mind, it is strongly wished that each researcher can suggest a new technique beyond the existing membrane separation technology with courage.

There is a membrane at all boundaries. A membrane of the thickness of the order of molecules exists even on a bare surface. Probably the only surface on which there is no membrane at all will be a solid surface newly cut under a high vacuum.

It was known for a long time that the surface of the plant cell had a cell wall. Also there is a membrane called a plasma membrane on the surface of an animal cell, and it came to be known that there is a great variety of filmy structure in the inside of the cell. It came to be recognized widely that it is the most important when the elucidation of the function pursues a life phenomenon.

In particular, from the viewpoint of saving resources, saving energy and environmental conservation, new techniques with membranes have attracted attention. For example, the development of water processing technology using an ion-exchange membrane and the reverse osmotic membrane was propelled by such a strong request. In addition, haemodialysis with a membrane, based on the artificial kidney, is at the forefront of medical technology, and has been used for the treatment of many patients. These technologies are fine examples that indicate the importance of the applied study of artificial membranes.

The principle of reverse osmosis was proposed as a new method for the desalination of seawater by Professor Breton at the University of Florida [1,2]. Today's prosperity of science and the technique of the polymer membrane are due to Professor Loeb and Sourirajan, who developed excellent semipermeable cellulose acetate membranes using their original membrane preparation method [3], and their membranes went into practical use [4]. And then Dr Kesting evaluated the remarkable developments in his book as being the 'golden age of membranology' [5]. Along with such developments has come a large number of books; commentary books have been published about the formation, structure, physical properties, function and application of polymer membranes in many countries from about 1970. Of these, a certain book establishes an important point of fundamental principle, a certain thing is main by the design of the module, and in addition, a certain one puts an important point for the function developed in as a general effect; a characteristic is devised with each book.

I engaged in the fundamentals and development study of polymer membranes and membranes that include polymers and have deepened my understanding about the basic matter that was indispensable in the study of membranes for 40-odd years.

Because the membrane exists as a partition of phases, the barrier characteristics, material permeability or separability, are the most important physical properties. The driving force of the material transportation through such membranes can involve a difference in chemical potential, a difference in electrical potential, a difference in pressure and a difference in temperature; and depending on the particular membrane, the naming of the material transportation is different, too. At first it is an important thing that we unify these and can look. Furthermore, these properties of matter may be modified in response to external stimulation, in this case not only the simple physical properties, but also the function of the membranes.

When a membrane caught some kind of outside stimulation, a fact to produce replies to support is defined as the function of the membrane. The permeability and separability are polymer responses that are brought about by a concentration gradient or a pressure gradient due to an external stimulation, but because they may not bring about a structural change of the polymer itself, a membrane function and way of speaking that it is said are usually done, but are the place where it is difficult whether it may be said that it is a polymer function.

However, in the biomembrane, membrane structure changes, for example, by outbreak of the specific material transmission and electric potential depending on stimulation like excitement phenomena and develops a chemical reaction. It may be said that this is a function enough. There is a thing indicating the behavior very similar to a reaction to participate in the function in the biomembrane with the heterogeneity structure of the artificial membrane as the inanimate object.

These permeability, separability and membrane functions are expressed by an index for the membrane as a whole, but they actually consist of a combination of some basic phenomena. To develop and improve a membrane it is necessary to understand these basic phenomena exactly. Furthermore, for an accurate understanding, quantification of the phenomenon must be accomplished.

In this book, we first describe the history and necessity for membrane science and technology. Thereafter, the structural design of the membrane, the relationship between the membrane formation conditions and the membrane structure are discussed in detail. Furthermore, various membrane preparation methods, shapes of membranes and membrane modules are introduced. And then the analyses of membrane characteristics by various methods are described. The thermodynamic basics of membrane transport phenomena and various transport models are discussed, and then the phenomena during membrane permeation in various kinds of membrane transport method and their solution methods are discussed. After the description of these basic matters, the principles of the various membrane permeation separation methods, fundamental analyses and applied technology are described from different angles. In addition, hybrid systems of membrane separation processes are discussed with interest.

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Acknowledgements

I studied the kinetics of the formation mechanism of thermosetting resins and the theory of their gelation from 1964 to 1970 and acquired the degree of the doctor of engineering in 1970. I began the study of polymer separation membranes when I became a teacher in Kansai University in 1970. I seemed to engage in the totally different study field at first, but I noticed that it was not so different a field when I looked from the point of view of handling molecules, and so decided that I would make separation membrane study a lifetime friend, and that has been the case for 40-odd years now and has culminated in the opportunity to write this book.

First, I express great gratitude in having got much encouragement and support from many friends during the writing of this book.

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1

Introduction to Membrane Science and Technology

1.1 History of Membrane Science and Technology

The word 'osmosis' is used to describe the permeation of water through a diaphragm in contact on one side with a water–ethanol mixture and on the other side with pure water, as shown in Figure 1.1, a process discovered by Nollet in 1748 [1]. Probably, the relation between a semipermeable membrane and the osmotic pressure was recognized first by Nollet.

Graham carried out more systematic studies on mass transport in semipermeable membranes, studied the diffusion of gases through different media and, furthermore, discovered that rubber exhibits different permeabilities to different gases [2]. Membranes in the nineteenth and early twentieth centuries were not applied to industrial or commercial fields, but were used to analyse physical/chemical theories. As a good example, van't Hoff used the measurements of osmotic pressure of solutions with membranes to develop his limit law, to explain the behaviour of ideal dilute solutions, in 1887; this work led directly to the van't Hoff equation.

Most of the early studies on membrane permeation were carried out with natural membranes, such as bladders of pig, cattle, fish and sausage casings made of animal gut or gum elastics. Traube was the first to introduce an artificially prepared semipermeable membrane by precipitating cupric ferrocyanide in a thin layer of porous porcelain [3]. This type of membrane was used by Pfeffer in his fundamental studies on osmosis [4]. The theoretical treatment and much of the interpretation of osmotic phenomena and mass transport through membranes is based on the studies of Fick, who interpreted diffusion in liquids as a function of concentration gradients, and van't Hoff, who gave a thermodynamic explanation for the osmotic pressure of dilute solutions [5,6]. A little later, Nernst and Planck introduced the flux equation for electrolytes under the driving force of a concentration or electrical potential gradient [7,8]. With the classical publications of Donnan describing the theory of membrane equilibria and membrane potentials in the presence of electrolytes, the early history of membrane science ends with most of the basic phenomena satisfactorily described and theoretically interpreted [9].

Until about 1960, interest in membrane technology was mainly in the academic field. Cellulose nitrate, the first synthetic (or semisynthetic) polymer was studied by Schoenbein [10] in 1846. In 1855 Fick [11] used cellulose nitrate membranes in his classic study 'Über Diffusion'. In the same year, the concept of *solution*, that is, membrane–permeant interaction, to membrane permeation theory was proposed by L'hermite [12]. Thus, at the very outset, the cast of characters for the ongoing solution–diffusion drama was complete. In 1860, Schumacher dipped test tubes into cellulose nitrate (collodion) solutions and prepared the first tubular membranes [13]. Baranetzky [14] prepared the first

Science and Technology of Separation Membranes, First Edition. Tadashi Uragami.

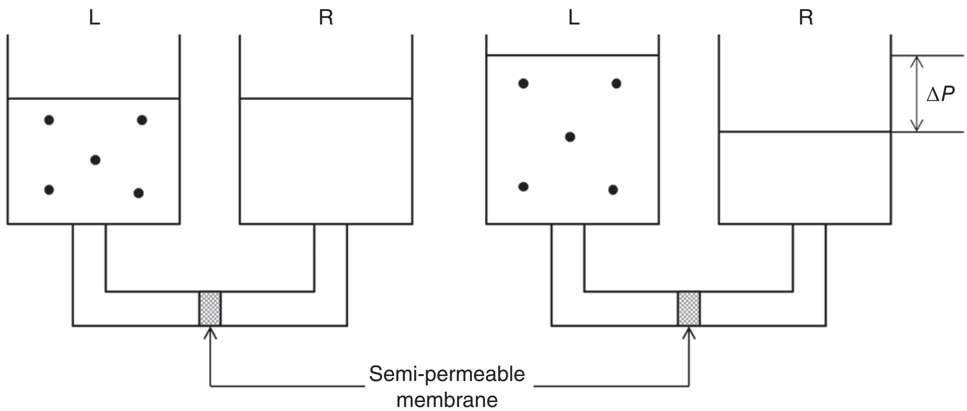

Figure 1.1 Osmosis across the semi-permeable membrane. ΔP is the hydrostatic pressure difference.

flat membranes in 1872. Bechhold [15] prepared the first series of microfiltration membranes of graded pore size in 1907 and was also the first to define the relationship between bubble point, surface tension and pore radius, and developed a method of making the first synthetic membranes by impregnating a filter paper with a solution of nitrocellulose in glacial acetic acid [16]. These membranes could be prepared and accurately reproduced with different permeabilities by varying the ratio of acetic acid to nitrocellulose. Nitrocellulose membranes were also used in the studies of Zsigmondy and Bachmann as ultrafilters to separate macromolecules and fine particles from an aqueous solution [17]. Based on a patent of Zsigmondy, Sartorius GmbH began in 1927 the production of a series of nitrocellulose membranes with various pore sizes. These membranes were used in microbiological laboratories in analytical applications.

Early attempts to control and vary porosity were largely empirical. Bechhold observed that permeability varied inversely with the concentration of polymer in the sol. Bigelow and Gemberling [18] studied the effects of drying time on the membrane preparation process. Zsigismondy *et al.* [19] and Elford [20] developed two series of graded pore-size membranes of cellulose nitrate. The former were the basis for the first commercial microfiltration membranes, which appeared in 1927 in Germany.

The concept of pore-size distribution was developed by Karplus, cited by Erbe [21], who combined bubble point and permeability measurements. The development of the first successfully functioning haemodialyser [22] was the key to the large-scale application of membranes in the biomedical area.

Industrial interest of the membrane separation technology suddenly increased from about 1950. On the other hand, with the progress in high polymer chemistry, a large number of synthetic polymers which are excellent for the preparation of new membranes with specific transport properties, excellent mechanical and thermal stability were provided. In addition, a comprehensive theory based on the thermodynamics of irreversible processes for membrane transport properties was proposed by Staverman [23] and Kedem and Katchalsky [24]. Merten described membrane processes based on postulating certain membrane transport models, such as the model of a diffusion–solution membrane [25].

In 1960 the important paper by Maier and Scheuermann [26] provided the basic mechanism which has since been utilized by Kesting to accommodate every (wet, dry and thermal) class of *phase inversion* membranes within its general framework. The two editions of *Synthetic Polymeric Membranes* [27,28] provide comprehensive coverage of phase inversion, which is by far the most versatile and important membrane fabrication process.

The beginning of the golden age of membrane science and technology depended significantly upon both the invention of reverse osmosis by Professor Reid [29] and the development of the asymmetric cellulose acetate membrane by Loeb and Sourirajan [30,31]. The development of a reverse osmosis membrane from cellulose acetate which gave high salt rejection and high fluxes at moderate operating pressures by Loeb and Sourirajan was a major advance toward the application of reverse osmosis membranes as an effective technology for the production of potable water from sea water.

The membrane developed by them was an asymmetric structure consisting of a dense skin layer, which determines the selectivity of salt and flux of desalinated water, and a porous layer that holds the mechanical strength of the whole membrane. The preparation of asymmetric cellulose acetate membranes is based on a phase inversion process in which a homogeneous polymer solution is converted into a two-phase system, such as a solid polymer-rich phase forming the solid polymer structure and a polymer lean phase making the liquid-filled membrane pores [27,28,32]. Soon, other synthetic polymers – such as polyamides, polyacrylonitrile, polysulfone and polyethylene – were used as basic material for the preparation of synthetic membranes in reverse osmosis desalination. These polymers often showed better mechanical strength, chemical stability, thermal stability and tolerance for bacteria than the cellulose esters as semi-natural material. However, cellulose acetate remained the dominant material for the preparation of reverse osmosis membranes until the development of the interfacial-polymerized composite membrane [33,34]. These membranes showed significantly higher fluxes, higher rejection, and better chemical stability, mechanical strength, tolerance for bacteria and chlorine sterility than the cellulose acetate membranes.

Microfiltration was developed in 1918 by Richard Zsigmondy, who is a Nobel Prize in Chemistry winner, and then he developed the ultrafiltration membrane in 1922 and established the basics of membrane separation technology as one of founders of Sartorius. In medicine, dialysis (from Greek dialusis, 'διάλυσις', meaning *dissolution*, dia, meaning *through*, and lysis, meaning *loosening or splitting*) is a process for removing waste and excess water from the blood and is used primarily as an artificial replacement for lost kidney function in people with kidney failure (https://en.wikipedia.org/wiki/Dialysis). Electrodialysis (ED) is used to transport salt ions from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. This is done in a configuration called an electrodialysis cell. The cell consists of a feed (dilute) compartment and a concentrate (brine) compartment formed by an anion exchange membrane and a cation exchange membrane placed between two electrodes. (https://en.wikipedia.org/wiki/Electrodialysis). This method was proposed for the first time in 1890 by Maigrot and Sabates [35]. Reverse osmosis was proposed by Reid and Breton [29] and developed by Loeb and Sourirajan [30] for the desalination of sea water.

Nanofiltration is a relatively recent membrane filtration process used most often with low total dissolved solids water, such as surface water and fresh groundwater, with the purpose of softening (polyvalent cation removal) and removal of disinfection by-product precursors, such as natural organic matter and synthetic organic matter. Nanofiltration is also becoming more widely used in food processing applications, such as dairy, for simultaneous concentration and partial (monovalent ion) demineralization (https://en.wikipedia.org/wiki/Nanofiltration). Nanofiltration was known as low-pressure reverse osmosis and came to gradually attract attention from the second half of 1980, and the first applications were reported by Eriksson [36], Colonlon and McClellan [37].

Sir Thomas Graham carried out the first membrane gas separation and obtained oxygen-enriched air containing 46.6% oxygen. He proposed that increasing the pressure of a gas mixture to be separated should be beneficial for obtaining higher fluxes. He observed that changes in the thickness of films affect the flux but not the composition of permeated gas. He noted the effect of temperature on permeation rates [38].

Pervaporation is one of the most popular areas of current membrane research, but the concept of pervaporation separation is not new. As early as 1906, Kahlenberg reported a qualitative study on the separation of a mixture of a hydrocarbon and an alcohol through a rubber membrane [39]. As early as 1917, it was recorded that water permeated through collodion films selectively, and the term pervaporation was first introduced by Kober [40]. Schwob [41] demonstrated dehydration of alcohols by using 20 μm thin membranes. However, an analysis of pervaporation literature and patents showed that most of the work in the field was done in more recent times [42]. In 1955, Hagerbaumer conducted the first quantitative investigation with a microporous Vycor glass membrane with a high-pressure drop across it, to allow for the separation of liquid–liquid mixtures [43]. It was the work by Binning and co-workers [44,45] from 1958 to 1961 that established the principles and highlighted the potential of pervaporation separation.

Later, in 1965, Binning and co-workers utilized this operation of separating a liquid–liquid mixture into a vapour mixture using a nonporous polymeric film. This research yielded a high degree of separation along with high permeation rates. The process did not come into commercial use until 1982 when Gesellchaft für Trenntechnik mbH (GFT) of Germany installed a pervaporation plant to separate water from concentrated alcohol solutions. Since then, more than 100 plants have been installed. Recently, Exxon has used pervaporation in its refineries to separate hydrocarbon mixtures containing aromatics and aliphatics. Another commercial use for pervaporation is the removal of methylene chloride from small waste streams [46].

Membrane distillation was developed more than 50 years ago. It is a thermally driven separational programme in which separation is enabled due to phase change. A hydrophobic membrane displays a barrier for the liquid phase, allowing the vapour phase (e.g. water vapour) to pass through the membrane's pores. The driving force of the process is given by a partial vapour pressure difference commonly triggered by a temperature difference (https://en.wikipedia.org/wiki/Membrane_distillation).

A membrane reactor is a physical device that combines a chemical conversion process with a membrane separation process to add reactants or remove products of the reaction. Chemical reactors making use of membranes are usually referred to as membrane reactors. The membrane can be used for different tasks, such as separation – selective extraction of reactants and retention of the catalyst, distribution/dosing of a reactant and catalyst support (often combined with distribution of reactants). Membrane reactors are an example for the combination of two unit operations in one step; for example, membrane filtration with a chemical reaction.

Uragami *et al.* [47] proposed 'evapomeation (EV)' as a new membrane separation technique method to improve a fault of pervaporation in 1988. This EV has some advantages, such as an improvement of membrane performance with the repression of swelling or shrinking of the membrane due to the feed liquids [48–53] (see detail in Chapter 16) and gives excellent dehydration, organic permselectivity of aqueous organic mixtures and separation of organic–organic liquid mixtures.

Uragami and co-workers also proposed temperature-difference controlled evapomeation (TDEV), further developing the EV method. In this TDEV method, the temperature of membrane surroundings is set less than that of the feed liquid (see detail in Chapter 17) [48–51,54–65].

The first carrier transport experiment was carried out by Osterhout, who investigated the transport of ammonia through algae cell walls [66]. Gliozzi explained biologically the couple transport mechanism in liquid membranes, as shown in Figure 1.2 [67].

About the middle of 1960s a number of couple transport systems were studied by Shean and Sollner [68]. Bloch *et al.* published the first paper on coupled transport [69], and the separation of uranium using phosphate ester carriers was later reported [70,71].

Table 1.1 summarizes the history of membrane processes and materials.