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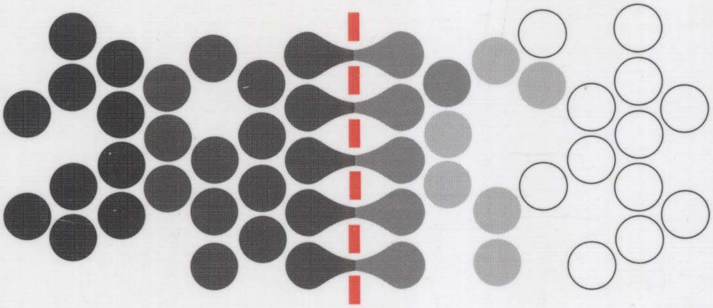

ION EXCHANGE MEMBRANES
FUNDAMENTALS AND APPLICATIONS

Yoshinobu Tanaka

Membrane Science and Technology Series, 12

ION EXCHANGE MEMBRANES: FUNDAMENTALS AND APPLICATIONS

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Preface

Ion exchange membranes function as concentrating or desalting electrolyte solutions. Paying attention to this phenomenon in 1940, Meyers and Straus electrodialyzed a 0.01 M KCl solution using a cellophane cation exchange membrane and an artificial intestinal wall anion exchange membrane and realized doubled KCl concentration (Meyer and Straus, 1940). In 1950, Juda and McRae synthesized ion exchange membrane (Juda and McRae, 1950) and this invention started the industrial application of ion exchange membranes. In 1952, Ionics Inc. developed a test electrodialyzer integrated with the synthesized ion exchange membranes for desalting a salt solution, and further in 1954, operated the practical scale desalting plant. Ion exchange membrane technology was applied afterward in the fields of desalination and concentration of electrolyte solutions. The largest scale application in the desalting fields is the demineralization of salt solutions. Other applications are desalination and reuse of sewage or industrial waste, treatment of radioactive waste, refining of amino acid solutions and desalination of milk, whey and sugar liquor etc. The applications in the concentrating fields are recovery of useful components from industrial waste or a metal surface treatment process, seawater concentration, production of inorganic chemicals and organic acid concentration etc. Electrodialysis (ED) is assumed to be the fundamental technology based on the ion exchange membrane, and it is applied thereafter to the succeeding technology such as electrodialysis reversal (EDR), bipolar membrane electrodialysis (BP), electrodeionization (EDI), electrolysis (EL), diffusion dialysis (DID), redox flow battery (RFB), fuel cell (FC) etc.

This book interprets the ion exchange membrane technologies dividing them into the volume of Fundamentals and that of Applications. The author tried to discuss the various phenomena exhibited by ion exchange membranes in the Fundamentals and review the applications of ion exchange membranes in ED, EDR, BP, EDI, EL etc., in the Applications. However, such a volume classification is extremely audacious, so that the author excuse beforehand that some instances in applications are discussed in the volume of Fundamentals, and other ones in fundamentals are reviewed in the volume of Applications.

In the Fundamentals, Chapter 1 introduces general procedures to prepare the ion exchange membranes. Chapter 2 comments on the membrane property measurement processes definitely. Chapter 3 discusses the ionic transport and permselectivity across the membranes. Both Chapters 4 (Theory of Teorell, Meyer and Sievers) and 5 (Irreversible thermodynamics) are classical basic theories of the transport phenomena across the ion exchange membrane. Chapter 6 (overall mass transport) describes the practical concept on the transport phenomena based on the irreversible thermodynamics and it is applicable to analyze electrodialysis phenomena. Chapter 7 is about concentration polorization arising in a boundary layer formed on the membrane surface and investigated widely. Chapter 8 discusses water dissociation caused by the concentration polarization. However, the mechanism of this phenomenon has not been cleared. Current density distribution (Chapter 9) is an inevitable phenomenon occurring in a practical apparatus. However, the investigation on this phenomenon is relatively few. Hydrodynamics (Chapter 10) is an extremely important phenomenon, in spite of the fact that the discussion in this field is also few. Limiting current density (Chapter 11) has been discussed widely so far. This phenomenon is discussed in this book paying attention to the effect of distribution of circumstances in the operating apparatus. Chapter 12 consists of electric current leakage and solution leakage and they are unavoidable phenomena in the apparatus. The latter is discussed using the overall mass transport in Chapter 6. Chapter 13 is a simplified explanation of the energy consumption computation (ED program) based on Chapters 6, 9, 10 and 11. The concept in this chapter must be developed further. Chapter 14 consists of membrane characteristic deterioration, surface fouling and organic fouling. Industrial application of ion exchange membranes started at first in the field of electrodialysis and it induced the development of the fundamental theory. Because of this fact, many phenomena explained in the Fundamentals are described taking the electrodialysis into account. The author gives several opinions in the Fundamentals based on his investigations. It is grateful for reviewing the opinions.

In the Application, Chapter 1 consists of various applications of desalination, concentration and separation technologies in electrodialysis. Many descriptions refer to the information presented in the Meeting of the Research Group of Electrodialysis and Membrane Separation Technology. Chapter 2 explains an improved electrodialysis technology (electrodialysis reversal) to prevent scale formation by means of intermittent polarity reverse. The information was offered by Ionic Incorporation. Chapter 3 explains bipolar membrane electrodialysis, which is functioned by a bilayered membrane consisting of a cation exchange layer and an anion exchange layer and available to recovering or producing acids or hydroxides, etc. Chapter 4 describes an electrodeionization system including ion exchange membranes and ion exchange resins, which is also used to produce pure water. The descriptions refer to the information discussed in the Meeting of the EDI Workshop in the said Research Group. Chapter 5 focuses on sodium chloride electrolysis to produce chlorine and caustic soda using perfluorinated cation exchange membranes. This process is the basic technology in the chlor-alkali industry. Chapter 6 discusses diffusion dialysis, which is applied to recover acid from an electrolyte solution applying high mobility of H^+ ions across an anion exchange membrane. Chapter 7 explains a unique process (Donnan dialysis) caused by ionic diffusion and electro-neutrality. It is applied to recovering, extracting or removing ionic spices in a solution. Chapter 8 consists of dialysis battery, redox flow battery and fuel cell. Technology of fuel cells and redox flow batteries is now developing progressively for generating or storing electric power. The author appreciates the persons concerned offering the above information.

The ion exchange membrane phenomena are very often expressed using equations. Equations facilitate the explanation, but some times they make understanding difficult. In order to avoid such a trouble, in this book, the phenomena are explained using the figures and tables as much as possible. Accordingly, the readers can understand the events explained in this book by skipping the equations and reading only the text with figures and tables. We pay attention to the experiments and make efforts to explain the phenomena using the experimental results. Further we tried to explain plant operating performance and economical evaluation of the technology.

Application of ion exchange membranes is extending widely and spreading even now. Accordingly the fundamental studies are assumed to develop further in many fields. In spite of broadly expanding fields in which ion exchange membranes are applied, published textbooks of the ion exchange membrane might be relatively few. The author feels that it is very difficult to explain such an ion exchange membrane technology inclusively. So, the content of this book is insufficient but it must be supplemented in future. The references are cited on author's personal preference. It must be noticed that there are many excellent investigations not being cited.

In writing this book, the author thanks deeply to the colleagues in Japan Tobacco & Salt Public Corporation (formerly Japan Monopoly Corporation) for cooperating in the investigation. The author expresses his appreciation to persons concerned in the Research Group of Electrodialysis and Membrane Separation Technology in the Society of Sea Water Science Japan, Asahi Chemical Company, Tokuyama Incorporation and Asahi Glass Company for offering information and discussing. This book is written on the basis of author's experience with ion exchange membranes during 40 years. I'm grateful to Elsevier B.V. for proofreading, checking and publishing the book. Finally, I thank my wife Satsuko for supporting my research life.

REFERENCES

Meyer, K. H., Straus, W., 1940, La permeabilite des membranes VI. Sur le passage du courant electrique a travers des membranes selectives, Helv. Chim. Acta, 23, 795–800.

Juda, W., McRae, W. A., 1950, Coherent ion-exchange gels and membranes, J. Am. Chem. Soc., 72, 1044.

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Fundamentals

Chapter 1

Preparation of Ion Exchange Membranes

1.1. INVENTION OF AN ION EXCHANGE MEMBRANE

In 1953, W. Juda and W. A. MacRae in Ionics Inc. applied for a patent of "ion-exchange materials and method of making and using the same" (Juda and MacRae, 1953). This patent attracted a great deal of attention, and contributed to the succeeding development of membrane synthesis technology. Here, we glance over the following practicing example: "preparation of membranes of phenol sulfonic acid–formaldehyde" in the patent at first.

The impregnating, low molecular weight polymer was prepared as follows:

Aqueous phenol sulfonic acid (65%)–50 parts
Aqueous formaldehyde (35.4%)–24.7 parts

The acid and the formaldehyde are shaken together and partially polymerized at 50°C in a closed container (to retain the moisture and formaldehyde). This pre-curing requires 1.5 to 2 h, after which the viscous mixture was used to impregnate reinforcing webs such as Saran, vinyon, glass cloth and similar materials resistant to strong acid. It was poured into a mold to form the cast disks. The curing (until the polymer turned dark brown or black) was carried out at 100°C, in a closed system and in the presence of moisture. This process requires 2 h to two days depending upon the quantity and geometry of polymerizing mass. It was found that the specific conductivity ($1.4 \times 10^{-2}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) of the membrane in equilibrium with 1 N hydrochloric acid was greater than that in the 1 N hydrochloric acid ($0.36 \times 10^{-1}\ \Omega^{-1}\ \mathrm{cm}^{-1}$) itself.

1.2. SANDWICH METHOD

This method is developed by Ionics Inc. and the following practicing instance is found in the patent (MacDonald et al., 1992). Referring to Figs. 1.1 and 1.2, the numerical 10 indicates a continuous substrate, which is played out from substrate roll 10A. Substrate 10 passes over roll 10B and continues downwardly in a vertical direction between horizontal rolls 11B and 11′B. Numerous 11 and 11′ represent pliable films having compositions which are not soluble or swollen in the polymerizable liquid. In addition they should release easily from the finished polymer sheet.

Liquid is prepared from the mixture of the following components to form polymer, 54.6% divinylbenzene (16.6 l), vinyl toluene (5.5 l) and dixylyl ethane

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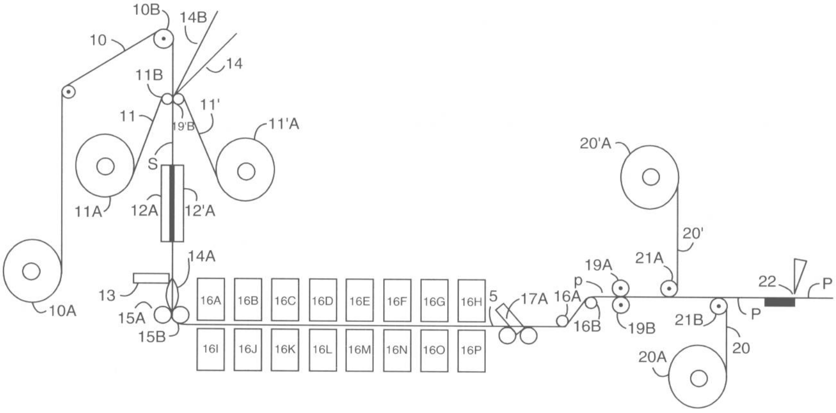

Figure 1.1 Membrane synthesizing apparatus (Ionics, Inc.) (MacDonald et al., 1992).

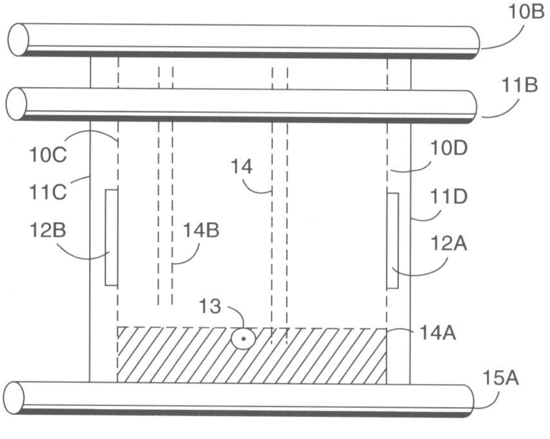

Figure 1.2 Membrane synthesizing apparatus (Ionics, Inc.) (MacDonald et al., 1992).

(18.9 l), with the following polymerization initiators: bis (4-tertiary-butylcyclohexyl)peroxyl dicarbonate (650 g), dilauroyl peroxide (410 g) and dibenzoyl peroxide (410 g). The mixture is thoroughly deoxygenated and is fed to an apparatus as shown in Fig. 1.1 through conduit means 14. Films 11 and 11′ are Mylar (3 mils thick and 24 inches wide). Substrate 10 is an acrylic plain weave fabric (20 inches wide and 19 mils thick). The linear velocity is adjusted to give polymerization time of about 25 min. Element 16A is inert and exerts a pressure of about 4 g cm^{-2} on sandwich S. Element 16B and D are fan, regulated manually to control the temperature of sandwich S. Element 16C and E are inert and exert a pressure of about 0.6 g cm^{-2} on sandwich S. Element 16I through N are heated electrically to cause the temperature of sandwich S to increase from about 60°C, at element 16I to about 110°C at element N. Elements 16A through E and I through 16 M are separated from sandwich S by Kapton adherent film anchored to the apparatus.

Means 12A and B (Fig. 1.2) and 12′A and B (Fig. 1.2) are heat welding elements (12′B lies behind 12′A in Fig. 1.1 and behind 12B in Fig. 1.2). Element 13 is a capacitative sensor. Roll 15A and 19A are covered with 30 durometer rubber to a depth at least 1 cm. Roll 15B and 19B are chrome steel. The edges of the sandwich are slit by element 17A and B and films 20 and 20′ (i.e., 11 and 11′) taken up by rolls 20A and 20′A, respectively. Polymer sheet P is cut by shear 22 into lengths of about 40 inches each. The resulting sheets are leached in methylene dichloride to remove the dioxyl ethane and sulfonated. The resulting cation exchange membranes have ion exchange capacities of about 2.8 meq g^{-1} dry membrane and water contents of about 50% of wet membrane. The membranes are useful in the electrodialytic production of potable water from brackish water.

1.3. LATEX METHOD

This method is for producing a styrene–butadiene membrane practiced by Asahi Glass Co. (Hani et al., 1960). Threads (grass fiber, reinforcement) are immersed into styrene–butadiene rubber latex for 1 h, then pulled up and dried at 80°C for 6 h to obtain a film. The film is sulfonated and cross-linked in a 96.5% sulfuric acid solution. A cation exchange membrane is obtained by immersing it into 80%, 60% and 30% sulfuric acid solutions for 30 min, respectively, in sequence, and finally washing with water. In order to produce an anion exchange membrane, the film described above is cross-linked and ring-linked by immersing it into 30°C titanium tetrachloride (bridging agent) for 1 h, and washed by methanol (solvent). It is dried, chloromethylated in a 30°C chloromethyl ether solution containing titanium tetrachloride (catalyst) and tetrachloroethane (expansive agent) for 5 h, and is washed with methanol (solvent). Consecutively, dried, chloromethylated (chloromethyl ether, titanium tetrachloride catalyst, tetrachloroethane expansive agent, 30°C, 5 h) and washed by methanol (solvent), and further, aminated (0.5 N trimethylamine–methanol solution) and washed. Finally, an anion exchange membrane is obtained by converting the form of functional groups into Cl^- type in a NaCl solution.

Synthetic reaction of styrene–butadiene membrane is shown in Figs. 1.3 and 1.4. An excellent characteristic of this membrane is owing to the stretching performance of long-chain hydrocarbons existing between benzene rings allowing dimensional change of polymer structure and preventing the cracking of the membrane body. On the other hand, the method has a weak point such that after the completion of the reaction, double bonds are remained and apt to be

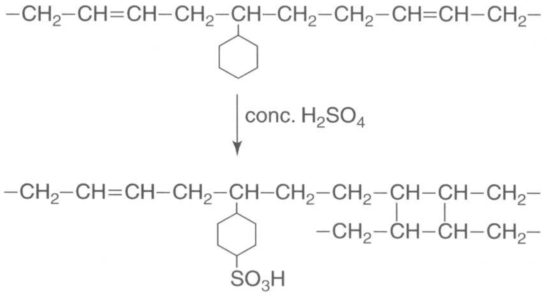

Figure 1.3 Styrene–butadiene cation exchange membrane.

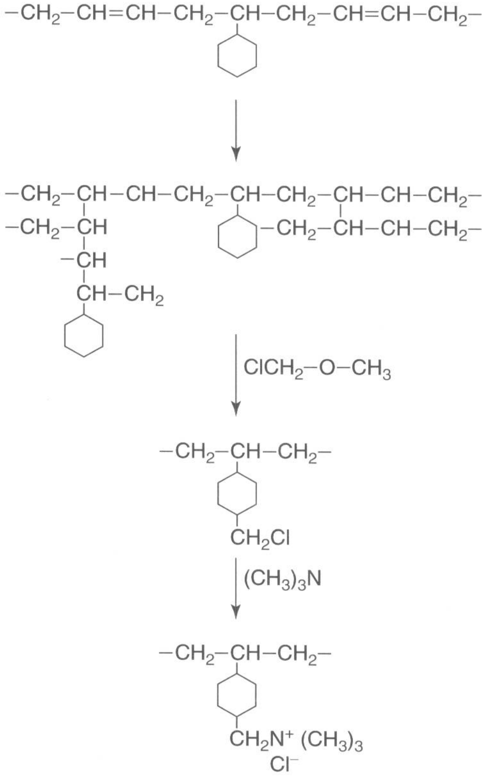

Figure 1.4 Styrene–butadiene anion exchange membrane.