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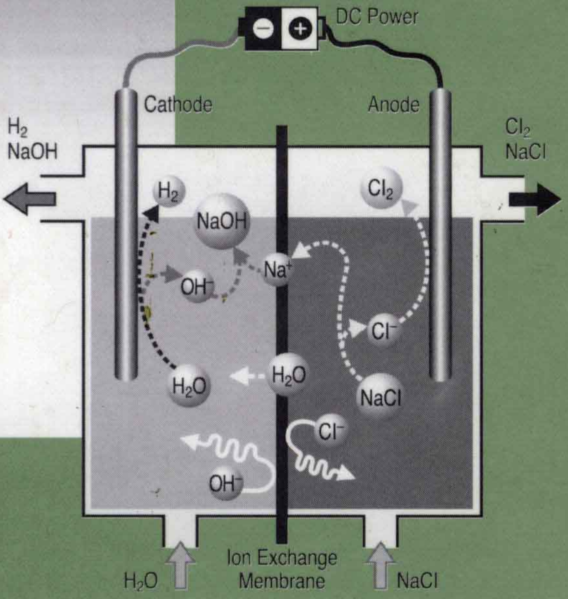

Ion Exchange Membranes

PREPARATION, CHARACTERIZATION, MODIFICATION and APPLICATION

TOSHIKATSU SATA

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Preface

Various separation membranes have been developed and contribute to industry and human life: microfiltration membranes, nanofiltration membranes, ultrafiltration membranes, membranes for reverse osmosis process, ion exchange membranes, membranes for pervaporation, liquid membranes, gas separation membranes, membranes for artificial kidneys, *etc.* In addition, new membranes are still being developed. Among these, the ion exchange membrane is one of the most advanced separation membranes. It can have a charged, positive and/or negative, porous or non-porous structure. However, in general, it is recognized that the ion exchange membrane is a dense, non-porous membrane, which is impermeable to ions, solvents and gases in the presence of ordinary hydraulic pressure.

About half a century has passed since the publication of the first paper on the ion exchange membrane. To establish a theoretical explanation of membrane phenomena, to develop industrially usable ion exchange membranes and establish their application technology, much effort has been made by many researchers and engineers in universities, institutes and companies, etc. The author is one such contributor to ion exchange membranes during that half century. The author joined the research and development of ion exchange membranes at Tokuyama Soda Co., Ltd. (Tokuyama Corporation; located in Tokuyama City, Yamaguchi Prefecture, Japan) in 1963 after graduation from Kyushu University and studied the membranes for about 30 years at the company; he then worked in Yamaguchi University as a professor from 1992 to 1997 to carry out further basic research and to educate young researchers.

During the long research life the author has met many excellent leaders, the late Mr Reiichi Yamane, Dr Yukio Mizutani, Dr Yasuharu Onoue, and excellent coworkers, Mr Ryuji Izuo, Mr Fumio Hanada, Dr Kuniaki Takata, Dr Koji Kusumoto, Dr Masakatsu Nishimura, Mr Yasuhiro Kagiyama and others, who were employees of Tokuyama Soda Co., Ltd.

At Yamaguchi University many excellent students have studied ion exchange membranes together with the author: 'Students learn from a professor and the professor learns much more from the students'. The author sincerely thanks them for their cooperation in his study. Also, the author sincerely thanks his wife, Mrs Takako Sata, who has assisted his work in every aspect, and thanks his son, Mr.

Tomoaki Sata, who is also an employee of Sumitomo Chemical Co., Ltd., for assistance in the preparation of this book.

Recently, the author has felt it necessity to record his research experience and knowledge of the ion exchange membrane for the benefit of a younger generation. Mrs Janet Freshwater who is a Commissioning Editor at the Royal Society of Chemistry was therefore timely in asking the author to write this book on ion exchange membranes. In this he was fortunate.

Concerning the content of the book, because the author has spent most of his working life in the laboratory of a company or university, where the study of membranes and products is related to commercialization, the book mainly consists of his practical experiences or knowledge, and is not theoretical.

Again, on finishing writing this book, the author sincerely thanks his coworkers, students and wife and son, and also Mrs Janet Freshwater, Commissioning Editor at the Royal Society of Chemistry, for her assistance in completing this book.

Toshikatsu Sata

Contents

CHAPTER 1

Introduction

1.1 Background

The separation of substances by membranes is essential in industry and human life. Of the various separation membranes, the ion exchange membrane is one of the most advanced and is widely used in various industrial fields: electrodialysis, diffusion dialysis, separator and solid polymer electrolyte in electrolysis, separator and solid polymer electrolyte of various batteries, sensing materials, medical use, a part of analytical chemistry, *etc.*

The ion exchange membrane originated from two different sources: the finding of ion exchange phenomena in soil and in explaining biological phenomena in cell membranes. The ion exchange phenomenon was found by the English agriculturist, H.P. Thompson[1] and the chemist J.T. Way[2] in 1850, who noted the adsorption of ammonium sulfate on soil as follows,

$$\text{Ca–Soil} + (NH_4)_2SO_4 = 2NH_4\text{–Soil} + CaSO_4$$

Their finding led to the synthesis of inorganic ion exchangers (aluminosilicate compounds).[3,4] Subsequently, the English chemists, B.A. Adams and E.L. Holmes synthesized organic cation and anion exchange resins by the condensation reaction of phenolic compounds having ionic groups and formaldehyde.[5] D'Alelio developed polymerization type ion exchange resins and laid the basis of today's ion exchange resins.[6]

Studies on ion permeable membranes, collodion type membranes, were carried out by L. Michaelis.[7] He recognized the effect of charge in the membrane on ion permeation through the membrane.[8] In 1939, K.H. Meyer, J.F. Sievers[9] and T. Teorell[10] proposed a theory of membrane potential. The modified collodion membrane was the first charged artificial membrane.[11] In 1949, Sollner published a paper concerning bi-ionic potential, which is a measure of permselectivity between ions with the same charge through the membrane.[12] They and many other researchers established the basis of studies on electrochemical properties of the ion exchange membrane.

M.R.J. Wyllie,[13] W. Juda and M.R.C. McRae[14] reported the synthesis of cation and anion exchange membranes around 1950. The former membrane is prepared by using a powdery ion exchange resin and binding polymer and the latter is composed of ionic condensation type polymers. After these works, studies on the ion exchange membranes, synthetic methods, theoretical explanation of membrane phenomena and trials for industrial applications became very active. Though the main purpose of the studies on ion exchange membranes in the USA and European countries was the electrodialytic desalination of saline water, in Japan the aim was to produce sodium chloride by electrodialytic concentration of seawater. An ion exchange membrane for seawater concentration has to meet severe requirements compared with desalination of saline water: high permselectivity at high concentration of the solution (seawater), high electrical conductivity and permselectivity for specific ions due to selective concentration of sodium chloride from seawater. In 1972, the production of edible salt in Japan was completely converted to the electrodialytic concentration of seawater and evaporation of the concentrated solution, instead of a salt field method.

It was proposed in 1950 that the ion exchange membrane could act as a separator in the electrolysis of sodium chloride solution to produce chlorine gas, hydrogen gas and caustic soda.[15] However, there was no membrane for such a purpose. After the development of perfluorocarbon carboxylic acid membranes in around 1974 in Japan, electrolysis in Japan was totally converted from the mercury method to the process using the ion exchange membrane by 1986, to avoid mercury pollution. The process is the most energy-saving among other processes, the mercury method and diaphragm method, and produces highly pure caustic soda without pollution. The process is now replacing other processes worldwide. This technology is based on the development of perfluorocarbon ion exchange membranes, Nafion®, by E.I. du Pont de Nomours & Co. (Inc), which also diversifies new and practical applications of the ion exchange membrane.

The ion exchange membrane, a non-porous, membranous polymer having ionic groups, is a typical functional polymer. The characteristics of the membrane are: (1) ion conductivity, (2) hydrophilicity and (3) the existence of fixed carrier (ion exchange groups). According to these characteristics, various applications have arisen. Table 1.1 shows example applications.

The ion exchange membrane is ion conductive, namely, ions can permeate through the membrane together with water molecules. There are many driving forces to transport ions and solvents through the membrane. The electrochemical potential has been mostly used: electrodialysis, *e.g.*, concentration and desalination of electrolyte solutions, separation between electrolyte and non-electrolyte, acid and base production using bipolar ion exchange membranes, electrodialytic ion exchange across the membrane, electro-deionization which is a desalination method based on a combination of ion exchange resins and the ion exchange membrane,[16] electrodialytic double decomposition, *etc.* A typical application of the membrane to electrolysis is the chlor-alkali process. The ion exchange membrane is also used in electrochemical organic synthesis as a separator when anolyte and catholyte should not mix. Oxidizing agents, O_3, H_2O, *etc.* are synthesized using a composite of the membrane and electrodes.

Many separations based on differences of chemical potential have also been proposed and practiced. Diffusion dialysis simply uses differences in chemical

Table 1.1 *Characteristics and applications of ion exchange membranes*

Characteristics	*Application*	*Example*
Ion conductivity	Electrodialysis	Concentration or desalination of electrolytes, separation between electrolyte and non-electrolyte, bipolar ion exchange membrane process to produce acid and alkali, ion-exchange reaction across the membrane, electro-deionization (EDI, CDI), *etc.*
	Separator for electrolysis	Chlor-alkali production, organic synthesis by electrolysis, *etc.*, synthesis of O_3, H_2O_2, *etc.*
	Diffusion dialysis	Acid or alkali recovery from waste
	Neutralization dialysis	Separation of electrolyte and non-electrolyte, desalination of water, *etc.*
	Donnan dialysis	Recovery of precious metals, softening of hard water, preconcentration of a trace amount of metal ions for analysis, *etc.*
	Up-hill transport	Separation and recovery of ions
	Piezodialysis	Desalination or concentration, *etc.*
	Thermo-dialysis	Desalination or concentration, *etc.*
	Battery	Alkali battery, redox-flow battery, concentration cell, *etc.*
	Fuel cell	Hydrogen–oxygen, methanol–oxygen
	Actuator	Catheter for medical use
Hydrophilicity	Pervaporation	Dehydration of water miscible organic solvents
	Dehumidification	Dehumidification of air and gases
	Sensor	Gas sensor (humidity, CO, NO, O_2, *etc.*), medical (enzyme immobilization, *etc.*)
Fixed carrier (Ion exchange groups)	Facilitated transport (gas separation)	Removal of acidic gas, separation of olefins from alkanes, separation of sugars, *etc.*
	Modified electrodes	

potential as the driving force and the process is industrially used in the recovery of acid and alkali from waste.[17] Donnan dialysis[18] enables recovery of trace amounts of precious metals by proton transport through the cation exchange membrane as a driving force, to soften hard water in the presence of the concentration difference of sodium chloride solution, *etc*. Neutralization dialysis is based on the neutralization energy between acid and alkali across the membrane, which is large, being used to separate salt from non-electrolyte, *etc.*[19] Many studies on up-hill transport have been made using the ion exchange membrane. Because the concentration of the electrolyte in the membrane phase is higher than that of the solution, the electrolyte solution with higher concentration permeates through the mosaic ion exchange membrane in the presence of hydraulic pressure, which enables the desalination of salt solutions (piezodialysis).[20] Because a small amount of the concentrated solution permeates through the membrane, and a large amount of desalted solution remains in the upper stream, piezodialysis is, in principle, efficient in desalinating saline water compared with reverse osmosis. When a temperature difference exists across the ion exchange membrane, salt and solvent (water) permeate through the membrane according to the ionic species and the particular membrane (thermo-dialysis).[21]

The ion exchange membrane has been examined as a component of batteries and is now used in batteries as a separator and solid polymer electrolyte. In alkali batteries it is used as a separator instead of a porous separator. Batteries having a large capacity have been actively studied for load leveling of electricity: the zinc-chlorine battery, zinc-bromine battery, redox flow battery such as Fe–Cr system, vanadium system, *etc.*[22] These batteries, especially redox flow batteries, require the cation or anion exchange membrane to separate anolyte and catholyte. Conversely, when the ion exchange membrane separates a concentrated solution from the dilute one, a membrane potential arises, which results in a concentration cell.[23] Recently, hydrogen–oxygen and methanol–oxygen fuel cells have been actively studied as new energy generation methods, which require a proton conductive membrane or a cation exchange membrane.[24] It is important, however, that tubular-type cation exchange membranes are examined to prepare an actuator such as a catheter for medical use, in which the stimulus is an electrochemical potential.[25]

Because ion exchange membranes have ionic groups, which are hydrated, these membranes are hydrophilic. Utilization of ion exchange membrane in a pervaporation process, which dehydrates water-miscible organic solvents by evaporation across the membrane (liquid phase/vapour phase),[26] is an example application of these characteristics. Though membranes for pervaporation processes do not require ion exchange groups to exist in the membrane, the ion exchange membrane shows excellent performance in this process. These characteristics are also effective in the dehumidification of various gases.[27] Also, because the membrane adsorbs water molecules according to humidity, the membrane also shows the properties of a humidity sensor (hygrometer).[28]

The charged groups of the membrane act as a fixed carrier for various ionic materials and provide new applications of the membrane. An ion exchange membrane ion-exchanged with amines selectively permeates acidic gases, *e.g.*, carbon dioxide, by carrier transport[29] and a membrane with silver ions selectively permeates olefin gases compared with paraffin gases.[30] The membrane can also be used to prepare modified electrodes and to immobilize enzymes due to the ion exchange groups (fixed carrier). Membrane applications are spreading in analytical chemistry. The characteristics of ion conductivity, hydrophilicity and a fixed carrier provide various applications for sensing materials.

Finally, the author is thankful for studies on ion exchange membranes because he has learned physical chemistry, organic synthesis, polymer chemistry, polymer modification, electrochemisty, *etc.* while preparing the ion exchange membrane, evaluating its properties exactly and seeking its application, because studies on ion exchange membranes are typically interdisciplinary.

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CHAPTER 2

Theory of Membrane Phenomena in Ion Exchange Membranes

2.1 Introduction

Because ion exchange groups, anionic or/and cationic charged groups, exist in non-porous membranes, various interesting phenomena are observed in the ion exchange membrane: permselectivity of cations or anions through the membrane, generation of membrane potential and bi-ionic potential, ion conductivity, diffusion of electrolyte and non-electrolyte through the membrane, water transport such as osmotic water and electro-osmotic water, salt rejection in the presence of hydraulic pressure, *etc*. Studies on these membrane phenomena mainly originate from attempts to explain phenomena in biological membranes.

There are three basic concepts that explain membrane phenomena: the Nernst–Planck flux equation, the theory of absolute reaction rate processes, and the principle of irreversible thermodynamics. Explanations based on the theory of absolute reaction rate processes provide similar equations to those of the Nernst–Planck flux equation. The Nernst–Planck flux equation is based on the hypothesis that cations and anions independently migrate in the solution and membrane matrix. However, interaction among different ions and solvent is considered in irreversible thermodynamics. Consequently, an explanation of membrane phenomena based on irreversible thermodynamics is thought to be more reasonable. Non-equilibrium thermodynamics in membrane systems is covered in excellent books[1] and reviews,[2] to which the reader is referred. The present book aims to explain not theory but practical aspects, such as preparation, modification and application, of ion exchange membranes. In this chapter, a theoretical explanation of only the basic properties of ion exchange membranes is given.[3,4]

2.2 Flux Equation

The Nernst–Planck flux equation has been widely applied to explain transport phenomena in ion exchange membranes and solution systems. When ion i diffuses through the ion exchange membrane (x axis is perpendicular to membrane surface), the flux, J_i (mol cm^{-2} s^{-1}), is expressed by a product of the gradient of the chemical potential, $-(\mathrm{d}\mu_i/\mathrm{d}x)$, and the concentration of i and a constant,

$$\begin{aligned} J_{i(d)} &= \frac{D_i}{RT} C_i \left(-\frac{\mathrm{d}\mu_i}{\mathrm{d}x} \right) \\ &= -D_i C_i \frac{\mathrm{d}\ln a_i}{\mathrm{d}x} \end{aligned} \tag{2.1}$$

where D_i is the diffusion coefficient of i, R the gas constant, T the absolute temperature, a_i activity of i ($a_i = C_i\gamma_i$: C_i, the concentration of i; γ_i, activity coefficient of i).

$$\begin{aligned} J_{i(d)} &= -D_i C_i \left(\frac{\mathrm{d}\ln C_i}{\mathrm{d}x} + \frac{\mathrm{d}\ln \gamma_i}{\mathrm{d}x} \right) \\ J_{i(d)} &= -D_i \left(\frac{\mathrm{d}C_i}{\mathrm{d}x} + C_i \frac{\mathrm{d}\ln \gamma_i}{\mathrm{d}x} \right) \end{aligned} \tag{2.2}$$

When there is an electrical potential gradient, including diffusion potential, the flux of i, $J_{i(e)}$, is proportional to the gradient of the electrical potential, $(\mathrm{d}\Psi/\mathrm{d}x)$, the concentration, C_i, and valence, z_i, of ion i and its electrochemical mobility u_i,

$$J_{i(e)} = -u_i z_i C_i \frac{\mathrm{d}\Psi}{\mathrm{d}x} \tag{2.3}$$

The Nernst–Einstein equation is

$$u_i = D_i \frac{F}{RT} \tag{2.4}$$

where F is the Faraday constant, thus,

$$J_{i(e)} = -D_i \frac{F}{RT} z_i C_i \frac{\mathrm{d}\Psi}{\mathrm{d}x} \tag{2.5}$$

Therefore, the total flux of ion i is

$$J_i = J_{i(d)} + J_{i(e)} = -D_i \left(\frac{\mathrm{d}C_i}{\mathrm{d}x} + z_i C_i \frac{F}{RT} \frac{\mathrm{d}\Psi}{\mathrm{d}x} + C_i \frac{\mathrm{d}\ln \gamma_i}{\mathrm{d}x} \right) \tag{2.6}$$

This is known as the Nernst–Planck flux equation and is applicable to ideal systems.

Ion exchange membranes have a large number of hydrated counter-ions in the membrane phase. The counter-ions impart more momentum to the solvent than co-ions do and solvent transfer takes place to the respective electrode chamber (due to osmosis and electro-osmosis). If the membrane has an anionic charge (cation exchange membrane), solvent transfer takes place from anolyte to catholyte. The velocity of this solvent transfer is proportional to the strength of the electrical potential gradient and is inversely proportional to the resistance to flow of the membrane matrix. If the flow velocity of the solvent is ν and $\overline{C}_i$ is the concentration of i (counter-ion) in the membrane, the flux of liquid in the membrane (convection), $J_{i(\mathrm{conv})}$, is expressed as follows,

$$J_{i(\mathrm{conv})} = \overline{C}_i \nu_i \tag{2.7}$$

Thus, the total flux of i ion through the membrane is expressed as

$$\begin{aligned} J_i &= J_{i(d)} + J_{i(e)} + J_{i(\mathrm{conv})} \\ &= -\overline{D}_i \left(\frac{\mathrm{d}\overline{C}_i}{\mathrm{d}x} + z_i \overline{C}_i \frac{F}{RT} \frac{\mathrm{d}\Psi}{\mathrm{d}x} + \overline{C}_i \frac{\mathrm{d} \ln \overline{\gamma}_i}{\mathrm{d}x} \right) + \overline{C}_i \nu \end{aligned} \tag{2.8}$$

This equation can apply to all ions under the condition of electro-neutrality.

Based on electro-neutrality, we deduce the following equation for the ion exchange membrane, where X is the fixed ion concentration of the membrane, and ω is the sign of the fixed charge (-1 for negatively charged membranes, $+1$ for positively charged membranes),

$$\sum_i z_i \overline{C}_i + \omega X = 0 \tag{2.9}$$

At steady state, the concentrations are independent of time, and therefore,

$$\frac{\mathrm{d}J_i}{\mathrm{d}x} = 0$$

As the ionic species move in the presence of an electric potential gradient they give electric current I, which is related to flux, J_i,

$$I = F \sum_i z_i J_i \tag{2.10}$$

The specific conductivity, $\overline{\kappa}$, and transport number of i in the membrane, $\overline{t}_i$, may be written as

$$\overline{\kappa} = -\left[\frac{I}{(\mathrm{d}\Psi/\mathrm{d}x)} \right] \tag{2.11}$$

$$\overline{t}_i = \frac{FJ_i}{I} \tag{2.12}$$