Inamuddin · Mohammad Luqman
Editors

Ion Exchange Technology I

Theory and Materials

Springer

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Preface

Ion exchange is a process of exchanging ions between stationary and mobile phases. It is a natural process and has been in practice for ages. Since commercial development took place in the last century, both academic and industrial research have been improving technology to find new applications.

This edition covers the introduction, principle, instrumental and theoretical fundamentals, structure, synthesis and characterization, kinetic and equilibrium, simulation and computer modeling studies of ion exchange materials in addition to the preparation and properties of ion exchange membranes for electrodialysis and fuel cells.

Chapter 1 covers the basic fundamentals of ion exchange kinetics and equilibrium and discusses the various applications that utilize ion exchange processes. Chapter 2 reviews the selectivity coefficient as well as the exchange isotherm diffusion and transport in terms of thermodynamics, equilibria and ion exchange kinetics. Chapter 3 examines the various conditions of ion exchange equilibrium with important theories developed in literature and reviews ion exchange kinetics and mass transport processes based on semi empirical models, Fick's law and derived expressions. Chap. 4, presents fundamentals of ion exchange fixed bed operations. Chapter 5 deals with the performance of ion exchange membrane electrodialysis for saline water desalination. The desalination performance of a practical-scale electrodialyzer is discussed using computer simulation. Chapter 6 is devoted to the structure, synthesis and properties of organic ion exchange materials. Preparation, properties and application of ion exchange membranes are discussed in Chap. 7. Chapter 8 focuses on the synthesis, structure, properties and applications of synthetic ion exchange materials. Chapter 9 reviews the most important aspects such as: synthesis, physical and chemical properties, equilibria and kinetics, as well as of sorption processes, possible and real field applications of fibrous ion exchangers. Fibrous catalysts, color-changing sorbents and hybrid fibrous sorbents impregnated with nanoparticles of inorganic substances are also described. The structure, coordination chemistry and applications of most commonly employed chelating ion exchangers are discussed in Chap. 10. Chapter 11 focuses on the recent advances in the field of ion exchanger–based voltammetric sensors, whose widespread use has instigated a new electroanalytical technique named ion exchange voltammetry. Chapter 12 discusses the properties of sulfonated poly(ether ether ketone) (SPEEK) as a promising membrane material for polymer electrolyte fuel cell. Chapter 13 reviews the preparation and use of organic–inorganic hybrid ion exchangers in organic reaction catalysis. An introduction to the ion exchange technique in solid matter, mainly optical glasses, to fabricate wave guides telecommunications is reviewed in Chap. 14. Network simulation of electrical response using Nernst–Planck and Poisson equations is used to describe the ionic transport processes through a cation-exchange membrane and two diffusion boundary layers on both sides of the membrane in Chap. 15. Chapter 16 reviews the authors' work on the mathematical and computer modeling of ion exchangers on styrene–divinylbenzene matrix, a mathematical model based on the concept of the influence of neighbouring exchange sites on the properties of each other. Such a model allowed to explain the dependence of selectivity and additive properties of the ion exchange system on the degree of ion exchange.

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We are most indebted to the grace of the Almighty "One Universal Being," who inspires entire Humanity to knowledge, and who blessed us with the needed favor to complete this work.

This book gathers the remarkable contributions from international leading experts in the field of ion exchange technology and provides a comprehensive review and research work. We are thankful to all the authors for their esteemed contribution to this book. We would also like to thank all the publishers and authors who granted us permission to use their copyright material. Although sincere efforts were made to obtain copyright permissions from the respective owners and to include citations with the reproduced materials, we would like to offer our sincere apologies to any copyright holder whose rights may have been unknowingly infringed.

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Last but not least, we would like to express our heartfelt gratitude to our family members for their constant inspiration and gracious support.

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Editors' Bios

Dr. Inamuddin is currently working as Assistant Professor in the Department of Applied Chemistry, Aligarh Muslim University (AMU), India. He received his Master of Science degree in Organic Chemistry from Chaudhry Charan Singh (CCS) University, Meerut, India, in 2002 and his Master of Philosophy and Doctor of Philosophy degrees in Applied Chemistry from AMU in 2004 and 2007, respectively. He has extensive research experience in the multidisciplinary fields of Analytical Chemistry, Material Chemistry, and Electrochemistry and, more specifically, Renewable Energy and Environment. He has worked in different projects funded by the University Grants Commission (UGC), Government of India, and Council of Scientific and Industrial Research (CSIR), Government of India. He has received Fast Track Young Scientist Award of Science and Technology, Government of India, to work in the area of bending actuators and artificial muscles. He has published 30 research articles and 4 book chapters of international repute. Recently, he has edited the book entitled *Advanced Organic–inorganic Composites: Materials, Devices and Allied Applications* and co-edited the books entitled *Green Solvents I: Properties and Applications in Chemistry* and *Green Solvents II: Properties and Applications of Ionic Liquids* published by Nova Science Publishers, Inc, and Springer, United Kingdom, respectively. He is presently working as editor in chief of the Journal of Chemical and Environmental Research published from The Muslim Association for the Advancement of Science (MAAS), India. He has worked as a Postdoctoral Fellow, leading a research team at Creative Research Initiative Center for Bio-Artificial Muscle, Hanyang University, South Korea, in the field of renewable energy, especially biofuel cells. He has also worked as Postdoctoral Fellow at Center of Research Excellence in Renewable Energy, King Fahd University of Petroleum and Minerals, Saudi Arabia, in the field of polymer electrolyte membrane fuel cells and computer fluid dynamics of polymer electrolyte membrane fuel cells. He is a life member of the *Journal of the Indian Chemical Society*.

Mohammad Luqman, Ph.D., is serving as an Assistant Professor in Chemical Engineering Department, King Saud University (KSU), Saudi Arabia. He teaches Polymer/Material Science and Engineering courses. Before joining the KSU, he served as an Assistant Manager in Samsung Cheil Industries, Korea. He worked on the development of heat-resistant polymers, organic glass, and block copolymers as impact modifiers and compatibilizers for engineering alloys. He served as a post-doctoral fellow at Artificial Muscle Research Center, Konkuk University, Korea, in the field of Ionic Polymer Metal Composites. He was awarded the Ph.D. degree in 2007, in the field of Ionomers, by Chosun University, Korea. Dr. Luqman has published numerous papers and book chapters in the field of Ionomers, Ion-exchange Polymers, and Polymer Nanocomposites. One of his papers, published in "*Polymer*", Elsevier, was Ranked the "first" among the "Top 25 Hottest Articles" in "all" chemistry journals during April–June 2008. Dr. Luqman is acting as a Regional (Middle East) Editor of the International Journal *Chemical and Environmental Research*, Published from MAAS, India. He also serves as a Section Editor of *Journal of Industrial Research & Technology* by HATAM Publishers, Malaysia. He has delivered few invited lectures at International podiums and very recently, has served as an Invited Editor of a reference book entitled *Recent Advances in Plasticizers*.

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Abbreviations

α_B^A	Separation factor
12MR	Twelve-membered ring
4MR	Four-membered ring
4-VP	4-Vinylpyridine
6MR	Six-membered ring
8MR	Eight-membered ring
a_{Az}^{b}, a_{Bs}^{a}	Activities
APAS	Aminophosphonic acid silica
ASV	Anodic stripping voltammetry
BEA	Zeolite *Be*t*a*
BT	Breakthrough
BV	Bed volumes
CD	Cyclodextrin
CEC	Cation-exchange capacity
CMX	Cation exchange membranes
CPE	Carbon paste electrode
CsEBS	Cesium salts of ethylbenzenesulfoacid
CSV	Cathodic stripping voltammetry
CV	Cyclic voltammetry
Cyt *c*	Cytochrome *c*
D	Diffusion coefficient
D4R	Double four-membered ring
D6R	Double six-membered ring
D_{app}	Apparent diffusion coefficient
DEA	Diethylamine
DEAPA	Diethylaminopropylamine
DETA	Diethylenetriamine

DFs	Decontamination factors
DL	Detection limit
DMAPA	Dimethylaminopropylamine
DMFC	Direct methanol fuel cell
DMG	Dimethylglyoxime
DP-ASV	Differential pulse anodic stripping voltammetry
DPV	Differential pulse voltammetry
DS	Degree of sulfonation
D_s	Diffusion coefficient in the solution phase
DVB	Di-vinyl benzene
E(OC)	Open circuit electrochemical potential
$E_{1/2}$	Half-wave potential
E_{appl}	Applied potential
ECL	Electrochemiluminescence
ED	Electrodialysis
EDA	Ethylenediamine
EDR	Electrodialysis reversal
EDTA	Ethylenediaminetetraacetic acid
E_i	Initial potential
EIS	Electrochemical impedance spectroscopy
ENM	Electrospin nano-fiber membrane
Ep_b	Backward peak potential
EPBI(DMG)	Epoxidized polybenzimidazole(Dimethylglyoxime)
Ep_f	Forward peak potential
ETSS	Ethyl styrene sulfonate
EW	Equivalent weight
F	Faraday constant
FAU	*Fau*jasite
Fc	Ferrocene
Fc^+	Ferricinium cation
FCC	Fluid catalytic cracking
FS	Full scale
GCE	Glassy carbon electrode
GIS	*Gis*mondine
GME	*Gme*linite
HASB	Hard soft acid base
HPA	Hydrated tungstophosphoric acid
HPCIC	High performance chelation ion chromatography
IDA	Iminodiacetic acid
IEC	Ion exchange capacity
IEV	Ion-exchange voltammetry
IO	Integrated-optic

Ip_p	Peak current for analytes n the polymer phase
Ip_s	Peak current for analytes in the solution phase
IS	Iontosorb salicyl
ITO	Indium thin oxide
K_a	Equilibrium constant
k_D	Distribution coefficient
k_{ex}	Site to site electron exchange rate constant
$K_X{}^M$	Selectivity coefficient
LB	Langmuir-Blodgett
LBL	Layer-by-layer
LDPE	Low density polyethylene
LS	Lab scale
LTA	*L*inde *T*ype *A*
m- DVB	metha-Divinylbenzene
M_{As}, M_{Bs}	Molarities
m_{Az}, m_{Bz}	Molalities
MEL	Maximum exchange level
MFI	ZS*M*-5 (*fi*ve)
MHL	Metal proton ligand
MINI, MIDI(d), 3-21G*	Basis sets for non-empirical calculations.
MMT	Montmorillonite
MOR	*Mor*denite
MP2/3-21G* and MP2/MIDI(d)	Level of theory of non-empirical calculations with using basis sets 3-21G* and MIDI(d) and with accounting for electronic correlation in the frame of the second order Moeller-Plesset perturbation theory.
MSWV	Multiple square wave voltammetry
MTA	Methylthriamyl ether
MTB	Methylthributhyl ether
MV	Methyl viologen
MWW	*M*CM-22 (t*w*enty-t*w*o)
N	Noise
N-DC	N, N′ di(caroxymethyl)dithiocarbamate
NMP	N-methyl-2-pyrrolidinon
NMR	Nuclear magnetic resonance
PA	Polyamide
PAMAM	Polyamidoamine
PAN	Polyacrylonitrile
PBI	Poly(benzimidazole)
PBI	Polybenzimidazole
PC	Polycarbonate
PDDMACl	Poly(diallyldimethylammonium chloride)
PDDPCl	Poly(1,1-dimethyl-3,5-dimethylenepiperidinium chloride)

PEEK	Poly(ether ether ketone)
PEI	Poly(ether imine)
PEK	Poly ether ketone
PEKEKK	Poly(ether ketone ether ketone ketone)
PEM	Proton exchange membrane
PEMFC	Polymer electrolyte membrane fuel cell
PES	Polyether sulphone
PET	Poly(ethyleneterphthalate)
PFSA	Perfluorosulfonic acid
PI	Polyimides
PILC	Pillared clay
PLE's	Polymeric ligand exchangers
PMA	Poly mtharcylate
PMeT	Poly(3-methylthiophene)
PP	Polypropylene
PPO	poly(phenylene oxide)
PP-ST-DVB	Polypropylene with grafted polystyrene with divinylbenzene
PPy	Polypyrrole
PS-DVB copolymer	PSDC
PS-DVB	Polystyrene divinylbenzene
PSS	Poly(4-styrene sulfonate)
PSSH	Poly(styrenesulfonic acid)
PSSNa	Poly(sodium styrenesulfonate)
PSU	Polysulphone udel
PSU-NH_2	Aminated polysulfone udel
PTFE	Poly(tetrafluoroethylene)
PV	Pervaporation
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
PVP	Polyvinyl pyrollidone
Q	Ion exchange capacity
R	Gas constant
REC	Real exchange level
RHF	Restricted Hartree-Fock method for closed shalls.
RO	Reverse osmosis
ROHF	Restricted open shall Hartree-Fock method.
S	Signal
SCF MO LCAO	Model, in which a molecular orbital (MO) is represented as a linear combination of atomic orbitals (LCAO), are examined in light of ab initio self-consistent field (SCF) computations with bases of various sizes.

s-IPNs	Semi-interpenetrating polymer networks
SMM	Surface modifying macromolecules
SPE	Screen printed electrode
SPEEK	Sulfonated poly(ether ether ketone)
SPI	Sulfonated polyimide
SPME	Solid phase microextraction
SPSU	Ortho-sulfonesulfonated poly (ethersulfone)
ST	Polystyrene
ST-DVB Matrix	Styrene – divinylbenzene matrix
ST-DVB	Styrene–divinylbenzene
SWV	Square wave voltammetry
T	Temperature
t	Time
TCB	Phenol-trichlorobenzene
TEC	Theoretical exchange level
TETA	Triethylenetetraamine
T_g	Glass transition temperature
THF	Tetrahydrofuran
TMFE	Thin mercury film electrode
TPA	Tripropylamine
TPABr	Tetrapropylammonium bromide
UF	Ultra filtration
v	Scan rate
WKB method	Wentzel-Kramers-Brillouin method
XAD	Commercial polystrene divinylbenzene resin
Z_A, Z_B, S_A, S_B	Equivalent fractions
ZrP	Zirconium phosphate
ΔG^0	Free energy change
ΔH	Enthalpy change
ΔS	Entropy change

Nomenclature

a	Minimum approximation distance between ions
A	External particle surface area
A_γ	Debye-Huckel constant
$A'_{\mathrm{ij}}, A'_{\mathrm{ji}}$	Margules parameters
$A^{z_{\mathrm{A}}}, B^{z_{\mathrm{B}}}, C^{z_{\mathrm{C}}}$	Counter ions with valences $z_{\mathrm{A}}, z_{\mathrm{B}}, z_{\mathrm{C}}$
$\bar{A}^{z_{\mathrm{A}}}, \bar{B}^{z_{\mathrm{B}}}$	Counter ions with valences $z_{\mathrm{A}}, z_{\mathrm{B}}$ inside the exchanger
a_{i}	Activity of species *i* in solution
$\bar{a}_{\mathrm{i}}$	Activity of species *i* in exchanger
$A_{\mathrm{i}}^{z_{\mathrm{i}}}$	Generic counter ion *i* with valence z_i
a_{p}	External surface area per unit particle volume
B	Second Virial coefficient
$B_{\mathrm{j,i}}$	Langmuir constant

C_{b}	Solute concentration at breakthrough time
$C_{\mathrm{ef,i}}$	Concentration of sorbate in the effluent
$C_{\mathrm{F,i}}$	Concentration of species *i* in the feed
C_{i}	Molar concentration of species *i* in solution
C_{i}^{*}	Molar concentration of species *i* at the exchanger/film interface
$C_{\mathrm{N,i}}$	Normality of species *i*
$C_{\mathrm{N,t}}$	Total normality of solution
$C_{\mathrm{p,i}}$	Molar concentration of species *i* inside the pores
$\bar{C}_{\mathrm{p,i}}$	Average concentration of species *i* inside the pores
C_{sat}	Saturation concentration
C_{t}	Total molar concentration of ionic species in solution
d	Particle diameter
$D_{\mathrm{A}}, D_{\mathrm{B}}$	Self-diffusion coefficients of species *A* and *B*
D_{AB}	Interdiffusion coefficient
$D_{\mathrm{eff,p,i}}$	Effective diffusion coefficient of species *i* in macropores
$D_{\mathrm{eff,s,i}}$	Effective diffusion coefficient of species *i* in micropores
D_{f}	Diffusion coefficient in the film
D_{i}	Diffusion coefficient of species *i*
	MS surface diffusivity of the pair *i–j*
	MS surface diffusivity corresponding to the interaction between *i* and the fixed ionic charges
D_{L}	Axial dispersion coefficient
e	Electron charge
$E_{\mathrm{i,j}}$	Energy of adsorption of ion *i* on site *j*
$\bar{E}_{\mathrm{i}}$	Average adsorption of ion *i*
F	Faraday constant
F_{i}	Fractional attainment of equilibrium of species *i*
g_{ij}	Energy parameter characteristic of the $i-j$ interaction
I	Ionic strength
J_{i}	Diffusion flux of species *i*
k	Boltzmann's constant
k_1	Rate constant of the first order sorption
k_2	Rate constant of the second order sorption
$K_{\mathrm{aB}}^{\mathrm{A}}$	Corrected selectivity coefficient
k_{AB}	Bohart and Adams rate constant
$K_{\mathrm{B}}^{\mathrm{A}}$	Thermodynamic (equilibrium) constant
K_{C}	Selectivity coefficient
K_{D}	Distribution coefficient
k_f	Convective mass transfer coefficient
K_{LDF}	Linear driving force coefficient
$K_{\mathrm{S}}^{\mathrm{M_xM_m}}$	Stability constant
k_{Th}	Thomas rate constant
k_{YN}	Yoon-Nelson rate constant
L	Column length

M^{m+}	Cation
m_i	Molality of species *i*
m_t	Total molality of ionic species
n	Freundlich constant, number of ionic species in solution
N_0	Avogadro's constant
n_c	Number of counter ions
n_f	Number of functional groups
N_i	Molar flux of species *i*
$N_{p,i}$	Diffusion fluxes of species *i* through the macropores
$N_{s,i}$	Diffusion fluxes of species *i* through the micropores
n_w	Number of water molecules in the zeolite
$n_x + n_y$	Total number of tetrahedral in the unit cell of zeolite
q_i	Molar concentration of ionic species *i* in exchanger
p	Parameter in binomial distribution
p_j	Equivalent fraction of exchanger site of type *j*
$\bar{q}_i$	Average loading of ionic species *i* in exchanger
q_i^*	Resinate concentration in equilibrium with the fluid concentration
Q_i	Equivalent ionic concentration of species *i* in exchanger
Q_i^e	Surface excess of ion *i*
$Q_{j,i}$	Equivalent ionic concentration of species *i* on exchanger site *j*
q_M	Kusik-Meissner parameter
q_{max}	Maximum sorbate concentration in the solid phase
q_s	Molar concentration of ionic fixed groups in exchanger
q_t	Total molar concentration of ionic species in exchanger
Q_t	Ion exchange capacity (in equivalents)
r	Radial position
R	Particle radius
$\Re$	Universal gas constant
t	Time
T	Absolute temperature
$t_{1/2}$	Time required for 50% sorbate breakthrough; stoichiometric time
t_b	Breakthrough time
U_0	Superficial velocity
u_i	Electrochemical mobility of species *i*, velocity of diffusing species *i*
V_{ef}	Volume of effluent
V_L	Volume of fluid phase
V_s	Volume of solid phase
V_{ZLC}	Volume of the ZLC column
W_{exch}	Mass of exchanger
W_{ij}	Weighting factor
x_i	Ionic fraction of species *i* in solution
X_i	Equivalent ionic fraction of species *i* in solution
X^{x-}	Anion
y_i	Ionic fraction of species *i* in exchanger

Y_i	Equivalent ionic fraction of species *i* in exchanger
y_s	Mole fraction of ionic fixed groups in exchanger
z_i	Valence of ionic species *i*

Subscripts

0	Initial condition
e	Equilibrium
f	Free
s	Solid, fixed ionic groups of the exchanger
t	Total
intra	Intraparticle

Greek Letters

$\alpha_\mathrm{B}^\mathrm{A}$	Separation factor
$\bar{\alpha}_\mathrm{j}^\mathrm{i}$	Average separation factor
δ	Film thickness
ε	Dielectric constant
ε_b	Bed porosity
ε_p	Particle porosity
φ	Electric potential
γ_i	Activity coefficient of species *i* in solution
$\bar{\gamma}_\mathrm{i}$	Activity coefficient of species *i* in exchanger
Γ_ij	Thermodynamic factor
Γ	Reduced activity coefficient of Meissner and Kusik
λ_i	Distribution coefficient of species *i*
$\Lambda_\mathrm{ij}, \Lambda_\mathrm{ji}$	Wilson parameters
μ_i	Chemical potential of species *i* in solution
$\bar{\mu}_\mathrm{i}$	Surface chemical potential of species *i*
v	Volumetric flow rate, number of site types
v_c	Number of cations per electrolyte
v_i	Pure-component molar volume
v_a	Number of anions per electrolyte
ρ_w	Density of pure solvent
σ_i	Standard deviation of energy distribution
τ_d	Time constant for intraparticle diffusion
$\tau_\mathrm{d,m}$	Maximum value of τ_d
$\tau_\mathrm{d,i}$	Minimum value of τ_d

Chapter 1
Introduction to Ion Exchange Processes

Mohamed Mahmoud Nasef and Zaini Ujang

Abstract Ion exchange technology remains the workhorse of various chemical, petrochemical, food, power, and pharmaceutical industries. The success of ion exchange process depends literally on understanding of its basic principles and applying them in a way suiting the nature of the treated feed. This chapter reviews the basic fundamentals and key components of ion exchange process taking into consideration the latest progress taking place in the field. The variation in the ion exchange materials, their nature, forms, and functions are reviewed. The kinetics, sorption equilibrium, operating modes, and engineering configurations for ion exchange processes are also discussed. A brief encounter for the various applications utilizing ion exchange processes is also presented.

1.1 Introduction

Ion exchange is a technology that has been ever receiving growing attention in various industries for several decades. This technology is commonly used to purify solutions by removing the dissolved ions by electrostatic sorption into ion exchange materials of various physical forms. The removed ions are replaced with equivalent amounts of other ions of the same charge in the solutions. The use of ion exchange reaction allows either all ions to be removed from a solution or particular ions to be selectively separated. Therefore, both selective removal of ionic contamination and

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complete deionization can be distinguished. The selection between both depends mainly on the composition of the solution and the extent of decontamination required [1].

The applications of ion exchange are numerous and cover wide ranges of industries and households. These applications mainly cover purification purposes; however, ion exchange is also widely implemented in the separation and extraction of valuable substances such as uranium and plutonium from the nuclear industry waste [2]. Deionization (demineralization) of water and water softening are known to be the most common applications. However, the spectrum of other applications varies from large-scale extraction of metals in hydrometallurgical and metal finishing processes to recovery of precious metals [3, 4]. The applications of ion exchange are also extended to food and beverages, petrochemical and chemical, pharmaceutical, sugar and sweeteners, industrial wastewater, ground and potable water, semiconductor, production power soil remedy, and pulp and paper industry.

In principle, ion exchange is a process involving an exchange of ions between an electrolyte solution (aqueous phase) and similarly charged ions immobilized in an ion exchange material (solid phase), which takes place through a stoichiometric reversible ion exchange reaction. Ion exchange materials represent the heart of ion exchange processes that fall into various categories: polymeric and mineral, cationic and anionic, and resins and membranes depending on their classification. Engineering systems of various configurations meeting the requirements for industrial application are available and vary depending on the morphology of the ion exchange materials. Batch and column systems are the most common configurations to accomplish ion exchange processes using resins, whereas plate and frame modules/cells are favored upon using membrane/sheet forms. Currently, a large number of commercial resins and membranes are available giving high possibility for more than one technically effective solution that allows the utilization of custom-designed ion exchange process. However, having a robust system design requires a thorough knowledge of all available resin types along with a clear understanding of basic fundamentals and economics of ion exchange to ensure highly efficient and cost-effective operations.

This chapter provides an intensive review for the basic fundamentals of ion exchange process covering its essential ion exchange materials, reaction kinetics and sorption equilibrium, operating modes, system configurations, process economy, and industrial applications.

1.2 Historical Perspective

Ion exchange phenomena have been known for many years. The first examples of this phenomena were discovered by Thompson and Way (1850) [5, 6] during their investigations concerning the way in which soluble manures were retained for long periods in the soil, instead of being washed out by rainwater. The importance of this discovery (in ion exchange terms) was not fully understood until later in that decade

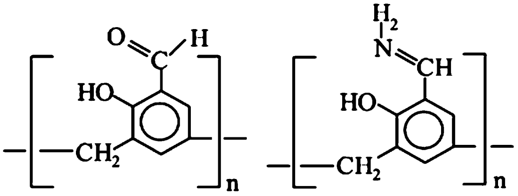

Fig. 1.1 Phenol formaldehyde ion exchange resins

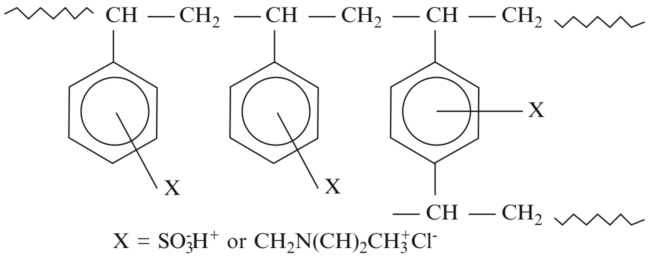

Fig. 1.2 Strong cation- and anion-exchange resins based on polystyrene divinylbenzene copolymer resins

when this reaction was found to be reversible. This phenomenon was caused by certain minerals in the soil as released in the latter half of the nineteenth century. These minerals, called resins, are based on tetrahedron structure of silicon and aluminum compounds called zeolites. In 1905, synthetic zeolites were manufactured and utilized for water treatment in a form of water-softening agent ever since [7]. Synthetic cation-exchange resins were developed during the 1930s using certain types of coal treated with sulfuric acid [8, 9]. This was an important evolution due to the fact that the sulfonated coal would operate in a greater pH range, 1–10. This made the sulfonated coal more versatile for the use in many more industrial applications. However, these resins were found to have serious deficiency caused by their lower exchange capacity compared to the zeolites. A few years later, the phenol formaldehyde polymer resin from the type shown in Fig. 1.1 was synthesized [10]. This polymer was sulfonated forming strong acid ion exchange resin. Using the same base polymer only functionalized with an amine (NH_2) produced the first weak base ion exchange resins. The major development for the power industry came in USA in 1944 when strong acid and strong base resins from the types shown in Fig. 1.2 were produced based on divinylbenzene cross-linked polystyrene, which was treated with sulfuric acid to make a strongly acidic resins or chloromethylated and subsequently aminated to produce strongly basic resins [11–13]. These resins possess much better characteristics than earlier phenol/formaldehyde resins. These new resins are now used almost exclusively in water demineralization plants for high pressure boilers. By the year 1950, weakly acidic ion exchange resins shown in Fig. 1.3 based on polymerization of methacrylic acid and divinylbenzene were developed. Eventually, the macroporous methyl methacrylate and divinylbenzene resins were synthesized with various functionalities (weakly basic, strongly basic,

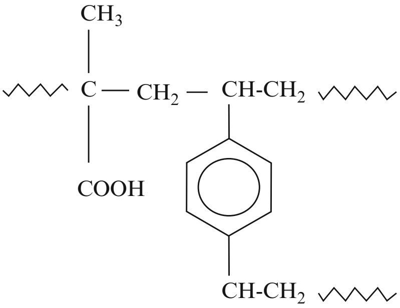

Fig. 1.3 Weak cation-exchange resins based on polymethylmethacrylate divinylbenzene copolymer resins

Table 1.1 The most important milestones in the development of ion exchange resins

Year	Milestones
1850	Agricultural chemists Harry Thompson and John Way discovered ion exchange phenomena
1858	German Chemist Eichom reported that ion exchange is a reversible reaction
1905	Robert Gans introduced first process to soften water using zeolite (sodium aluminosilicate)
1913	American company (Permutit) introduced first commercial zeolites
1935	English chemists Adams and Holmes prepared first synthetic polymer cation and anion exchangers (phenol formaldehyde and polyamine formaldehyde)
1944	D'Alelio developed cation-exchange resins based on polymerization of styrene and divinylbenzene
1946	Anion-exchange resins based on polymerization of styrene and divinylbenzene were developed
1950	Weakly acidic cation-exchange resins based on polymerization of methacrylic acid and divinylbenzene were developed
1965	Weakly basic resins based on polymerization of methyl methacrylate and divinylbenzene were developed
>1965	Bifunctional resins based on polymerization of methyl methacrylate and divinylbenzene were developed

and bipolar), by the year 1965 and above, with each resin having its own niche application in the water treatment industry [3]. Table 1.1 shows the most important milestones in the development of ion exchange resins. Today, hundreds of resins of various types, chemical groups, structures, and morphologies are available in the market with many more materials being researched to introduce more tolerance, cost-effectiveness, and new applications to ion exchange processes.

Ion exchange membranes are another significant class of materials that have been explored since the discovery of ion exchange phenomena. A significant development in ion exchange membranes was started by studies on ion-permeable membranes, collodion-type membranes which were carried out by Michaelis [14] who recognized the effect of membrane charge on ion permeation through the membrane. The theory of membrane potential was proposed by Meyer et al. [15]

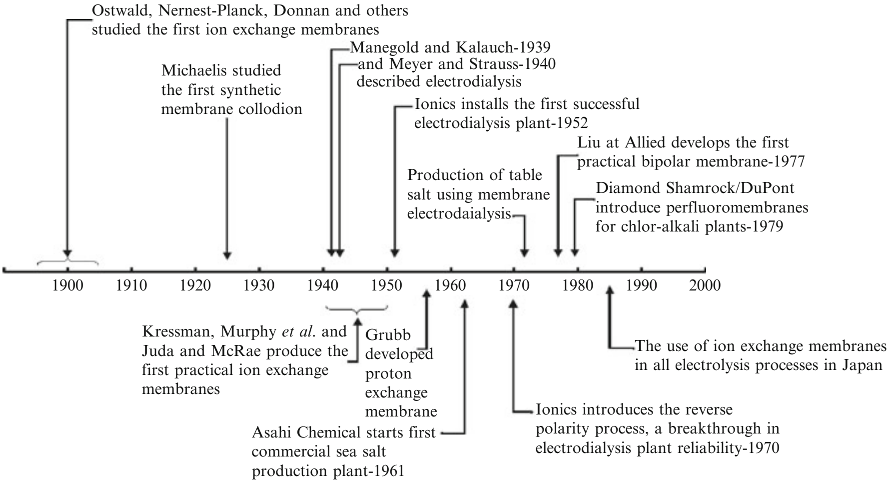

Fig. 1.4 Milestones of the development of ion exchange membranes and related processes

paving the way for the modified collodion membrane to be the first charged artificial membrane. The synthesis of ion exchange membranes was reported in 1950 by Juda and MacRae [16]. The preparation of proton exchange membrane and its use in fuel cells was first reported by Grubb in 1955. Later, in 1961 [17], Asahi Chemicals installed a membrane electrodialysis plant for the production of edible salt in Japan, and as a result, electrolysis in Japan was totally converted from the mercury method to a process using the ion exchange membranes by 1986. In 1977, the membrane chlor-alkali industry was introduced by Asahi Chemicals. This was followed by the introduction of Nafion (perfluorinated sulfonic acid membrane) for chlor-alkali industry by Diamond Shamrock and DuPont in 1979 [18]. The milestones in the development of ion exchange membranes are schematized in Fig. 1.4.

1.3 Ion Exchange Materials

Ion exchangers are a class of functional materials that display ion exchange properties owing to existence of fixed ionic sites bonded to their framework, which is held together by chemical bonds or lattice energy and can be called polyions. Oppositely charged ions move throughout the framework and can be replaced by ions of similar charge. Ion exchange materials are available in different forms and structures varying in their classifications depending on origin, physical form (morphology), immobilized functional group, and their functions, as shown in Fig. 1.5. The mechanism of ion exchange is dictated by various parameters related to the ion exchange materials such as the nature and type of fixed functional groups, the physical forms, and the origin of the ion exchange material [19].

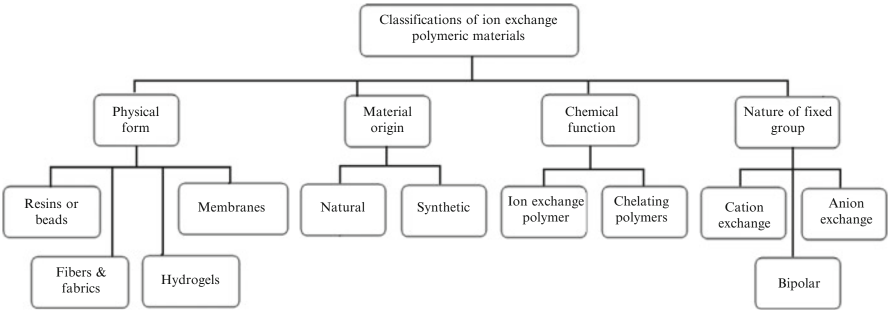

Fig. 1.5 Various classifications of ion exchange materials

1.3.1 *Classifications of Ion Exchange Materials*

On the basis of origin, there are two general types of ion exchange materials, that is, organic and minerallic; the former majority are synthetic polymers available in cationic and anionic forms whereas the latter exists in cation-exchange form only (e.g., zeolites and betonites). Thus, organic ion exchange materials can be cationic, anionic, and combined cationic/anionic (amphoteric) exchangers considering the nature of fixed ion exchange sites (functional groups).

Since ion exchangers act in a similar way to conventional acids and bases, the main classes of these materials, that is, cation and anion exchangers, can be further classified depending on the type of the functional group into several types: strongly acidic, strongly basic, weakly acidic, and weakly basic materials. Ion exchange materials containing sulfonate ($–SO_3^-$) and phosphorate acid ($–PO_3^-$) groups and those containing tetraammonium ($–NR_3^+$) basic groups are strongly acidic and strongly basic exchangers, respectively. On the other hand, materials containing phenolic (–OH) groups and primary amine ($–NH_2$) and secondary amine (–NRH) groups are weakly acidic and weakly basic exchangers, respectively. Carboxyl groups ($–COO^-$) and tertiary amine ($–NR_2$) groups take a medium position between strong and weak acidic and basic exchangers, respectively.

Practically, most strong acid exchangers contain sulfonate groups, which are active over the entire pH range. Unlikely, most weak acid exchangers have carboxylic groups, which are not active at pH values below 4–6. However, such exchangers often have higher ion exchange capacities than sulfonate exchangers together with other specific advantages [4]. Similarly, strong basic exchangers are active over the entire pH range unlike weak base exchangers which are not active at alkaline pH. A summary of the common functional groups and their negative logarithm of the dissociation constant (pK) are presented in Table 1.2. It can be clearly seen that each of these major resin classes has several physical or chemical variations within the class. Such variations impart different operating properties to the resin. Thus, the terms strong and weak in the ion exchange world do not refer to the strength of binding; it rather reflects the extent of variation of ionization with pH

Table 1.2 Common functional groups of polymeric ion exchange materials and their respective pK values

Anion-exchange materials		Cation-exchange materials	
Fixed ionic groups	pK	Fixed ionic group	pK
$\equiv N^+$	1–2	$-SO_3H$	1–2
$=N$	4–6	$-PO_3H_2$	2–5
$=NH$	6–8	$-COOH$	4–6
$-NH2$	8–10	$-OH$	9–10

of the medium solution. Each of these major resin classes has several physical or chemical variations within the class. Strongly acidic resins are commonly available in Na^+ form or H^+ form with different degrees of cross-linking to meet the requirements in various applications, whereas strongly basic resins are available in Cl^- or OH^- forms.

Physically, organic (polymeric) ion exchange materials are available in various morphologies related to the polymer framework carrying the functional groups. This includes beads, fibers, and membranes. Such variation in the physical forms brings about wide differences in chemical and physical properties of these ion exchangers. The majority of these ionic forms have synthetic polymer structures and mainly exist in a resin form represented by a wide number of commercial resins with polystyrene divinylbenzene backbone. A smaller class of biosorbents obtained from modified natural polymer sources including alginate, chitosan, and cellulose is also under development. Ion exchange resins fall into two main categories: cation- and anion-exchange forms. A combination of cation- and anion-exchange groups can be used to obtain a bipolar form of the resins that can replace mixed bed in ion exchange column. More details on the various types of ion exchange materials can be found in Refs. [4] and [20].

1.3.2 Ion Exchange Resins

Considering the separation mechanism, ion exchangers can be further classified into various categories including ion exchange resins, chelating adsorbents, hydrogels, affinity polymers, and ion exchange membranes. Among all, ion exchange resins, which are covalently cross-linked insoluble polyions supplied as spherical beads (particles), represent the major class of exchanger being commercially produced as stated earlier.

1.3.2.1 Preparation of Ion Exchange Resins

Commercial ion exchange resins that are available in market today are commonly produced by suspension polymerization, polycondensation, or polymer-analogous transformations [19]. Resins based on styrene-divinylbenzene copolymers as a building block involve the preparation of a cross-linked bead copolymer followed