Synthetic Membranes: Science, Engineering and Applications

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PREFACE

The chapters in this book are based upon lectures given at the NATO Advanced Study Institute on Synthetic Membranes (June 26–July 8, 1983, Alcabideche, Portugal), which provided an integrated presentation of synthetic membrane science and technology in three broad areas.

Currently available *membrane formation* mechanisms are reviewed, as well as the manner in which synthesis conditions can be controlled to achieve desired membrane structures. Membrane performance in a specific separation process involves complex phenomena, the understanding of which requires a multidisciplinary approach encompassing polymer chemistry, physical chemistry, and chemical engineering. Progress toward a global understanding of membrane phenomena is described in chapters on the *principles of membrane transport*. The chapters on *membrane processes and applications* highlight both established and emerging membrane processes, and elucidate their myriad applications.

It is our hope that this book will be an enduring, comprehensive compendium of the state of knowledge in the field of synthetic membranes. We have been encouraged in that hope by numerous expressions of interest in the book, coming from a variety of potential users.

At this time, we wish to acknowledge several individuals and groups whose contributions were essential to the success of this venture: Dr. Craig Sinclair and the NATO Science Committee; Ms. Aida de Sousa, Ms. Judite Fialho and their colleagues at SERV-INTERNACIONAL, Lisbon, Portugal; Dr. Murray Eden, Dr. Robert Dedrick, Ms. Leisa Lyles, and Ms. Inyoung Kwon, of the Biomedical Engineering and Instrumentation Branch, National Institutes of Health; the Department of Chemical Engineering, Instituto Superior Técnico, Lisbon, Portugal; and in particular, the members of the Advanced Study Institute faculty. Corporate sponsors of the ASI in 1983, as well as sponsors of the book, are listed separately; their valued assistance is gratefully acknowledged.

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SYMBOLS

The following symbols constitute a common nomenclature for the book. Symbols given specialized meanings in a particular chapter may be found at the end of that chapter. Units are first indicated in terms of base physical quantities: length (L), mass (M), time (t), temperature (T), amount of substance (mol) and electric current (A, ampere). Alternative expressions for units contain derived quantities: energy ($E = ML^2/t^2$), pressure ($p = M/Lt^2$) and electric potential (V, volt).

a	activity, mol/L^3
A	area, L^2
A_V	solvent permeation coefficient (volume), L^2t/M or L/tp
A_w	solvent permeation coefficient (mass), t/L or M/L^2tp
b	radius of spherical particle, L
B_i	solute permeation coefficient, L/t
c	concentration, M/L^3 or mol/L^3
C	heat capacity, L^2/t^2T or E/MT
d	differential operator
d	diameter (with subscript), L
d_h	hydraulic diameter, L
d_i	molecular diameter of species i, L
d_p	pore diameter, L
d_t	tube diameter, L
D	diffusion coefficient, L^2/t
D_T	thermodynamic diffusion coefficient, L^2/t
e	base of natural logarithms
E	energy, ML^2/t^2 or E
$\Delta\tilde{E}_a$	activation energy, ML^2/t^2 mol or E/mol
$\dot{E}$	rate of energy consumption, ML^2/t^3 or E/t
f	number of degrees of freedom
f_{ij}	friction coefficient, M/t mol or Et/L^2mol
F	Faraday constant, At/mol
g	gravitational acceleration, L/t^2
g_{ij}	Flory-Huggins interaction parameter of species i and j, ML^2/t^2 mol or E/mol
G	Gibbs free energy, ML^2/t^2 or E
h	membrane thickness, L

H	enthalpy, ML^2/t^2 or E
$\Delta\hat{H}_v$	latent heat of vaporization, ML^2/t^2 or E
i	electric current density, A/L^2
i_{lim}	limiting current density, A/L^2
I	electric current, A
J_i	flux of species i, M/L^2t or mol/L^2t
J_V	volumetric flux, L/t
k	thermal conductivity, ML/t^3T or E/LtT
κ	Boltzmann constant, ML^2/t^2T or E/T
k_f	forward reaction rate constant, $(mol/L^3)^{1-n}/t$, n = order of reaction
k_i	mass transfer coefficient for species i, L/t
k_r	reverse reaction rate constant, $(mol/L^3)^{1-n}/t$, n = order of reaction
K_{eq}	equilibrium coefficient, various units
K_i	distribution coefficient for species i, a_i/a_i', dimensionless
K_s	solubility product, various units
L	membrane length, L
L_p	hydraulic permeability, hydraulic conductivity or filtration coefficient, L^2t/M or L/tp, L^3t/M or L^2/tp
L_{ij}	phenomenological conductance coefficient, various units
m	molal concentration, mol/M
M	mass, M
$\bar{M}$	molecular weight, M/mol
n	number of moles
$\bar{N}$	Avogadro constant, $(mol)^{-1}$
Δp	pressure drop or loss, M/Lt^2 or p
p	pressure or partial pressure (with subscript), M/Lt^2 or p
P	permeability coefficient, various units
Pe	Peclet number, vd/D, dimensionless
q	heat flux, M/t^3 or E/L^2t
$\mathcal{Q}$	heat, ML^2/t^2 or E
$\dot{\mathcal{Q}}$	heat consumption rate, ML^2/t^3 or E/t
Q	volumetric flow rate, L^3/t
r	radial coordinate, radial position, or radius (with subscript), L
r_p	pore radius, L
r_t	tube radius, L
r_{ij}	phenomenological resistance coefficient, various units
$\mathcal{R}$	rejection or retention, dimensionless
R	gas constant, ML^2/t^2Tmol
R	resistance coefficient (with subscript), various units
R_c	cake resistance, M/L^2t or pt/L
R_e	electrical resistance, V/A
R_m	membrane resistance, M/L^2t or pt/L
Re	Reynolds number, vd/ν, dimensionless
s_i	solubility coefficient of gaseous species i, various units

S	entropy, ML^2/t^2T or E/T
Sc	Schmidt number, ν/D, dimensionless
Sh	Sherwood number, k_iL/D, dimensionless
t	time, t
t	transference number (with subscript), dimensionless
$t_{1/2}$	half-life, t
T	temperature, T
T_b	normal boiling point, T
T_c	critical temperature, T
T_g	glass transition temperature, T
u_i	absolute mobility of species i, t mol/M or L^2mol/Et
v	velocity, L/t
v_m	membrane permeation rate, L/t
V	volume, L^3
$\bar{V}_i$	partial molar volume of species i, L^3/mol
w	channel width, L
w_i	mass fraction of species i, dimensionless
x, y, z	rectilinear coordinates, L
x_i	mole fraction of species i, dimensionless
X	thermodynamic force, E/mol
Y	yield, dimensionless
z_i	valency of species i (with sign)
α_{ij}	separation factor, $y_i''y_j'/y_i'y_j''$, $y = c, p, w$, etc., dimensionless
β_i	enrichment factor, y_i''/y_i', $y = c, p, w$, etc., dimensionless
γ	surface tension, M/t^2 or E/L^2
γ_i	activity coefficient of species i, a_i/c_i, dimensionless
$\gamma_\pm$	mean activity coefficient, $\sqrt{\gamma_+\gamma_-}$, dimensionless
Γ_{ij}	selectivity coefficient, D_iK_i/D_jK_j or D_is_i/D_js_j, dimensionless
δ	polarization layer thickness, L
δ	solubility parameter (with subscript), $(E/L^3)^{1/2}$
∂	partial differential operator
Δ	difference operator
ϵ	porosity, dimensionless
η	efficiency (with subscript), dimensionless
η	viscosity, M/Lt
θ	tortuosity factor, dimensionless
λ	channel height, L
μ	chemical potential, ML^2/t^2 mol or E/mol
ν	kinematic viscosity, L^2/t
ν	vibrational frequency, t^{-1}
ν_i	number of ions per molecule of electrolyte i
ξ	current utilization, dimensionless
π, Π	osmotic pressure, M/Lt^2 or p

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ρ	density or mass concentration (with subscript), M/L^3
σ	reflection coefficient, dimensionless
Σ	summation operator
τ	time constant or transition time, t
ϕ	volume fraction, dimensionless
ϕ_f	fraction free volume, dimensionless
χ	Flory-Huggins interaction parameter, dimensionless
ψ	electric potential, V
ω	solute permeability coefficient, t mol/LM, t mol/M

Diacritical Marks

˜	per mole
ˆ	per unit mass
¯	average value
˙	time rate of change

Superscripts

	value in the membrane indicated by absence of superscript
′	value in feed stream or on high pressure side of membrane; value in phase external to the membrane
″	value in extract, permeate, product or on low pressure side of membrane
°	standard reference state

Subscripts

A, B	particular components
bulk	interior of stream outside of boundary layer
i	general species index or solute species i
int	membrane-solution interface
In	inlet
j	species j
l	liquid
m	membrane or confined to membrane
obs	observed or apparent
Out	outlet
p	product, permeate, or permeant
r	retentate or reject
s	solution
t	tube
v	vapor
w	water or solvent
0	initial value

ABBREVIATIONS

Chemical Names:

CA	cellulose acetate
CE	cellulose ester
CN	cellulose nitrate
CTA	cellulose triacetate
DMAc	dimethyl acetamide
DMF	dimethyl formamide
DMSO	dimethyl sulfoxide
EDTA	ethylenediaminetetraacetic acid
NMP	N-methy-2-pyrrolidone
NR	natural rubber
PA	polyamide
PC	polycarbonate
PE	polyethylene
PI	polyimide
PS	polystyrene
PO	polyolefin
PAN	polyacrylonitrile
PBD	cis-polybutadiene
PEA	polyethylacrylate
PEI	polyethyleneimine
PEM	polyethylmethacrylate
PMA	polymethylacrylate
PPN	polyphosphonate
PPr	polypropylene
PSF	polysulfone
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
PVP	polyvinylpyrrolidone
PDMS	polydimethylsiloxane
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene flouride
SR	silicone rubber
TDI	toluene diisocyanate
THF	tetrahydrofuran
VAMA	vinylacetate/methylacrylate copolymer

Processes:

DO	direct osmosis
ED	electrodialysis
IE/IX	ion exchange
ME	multiple effect
MF	microfiltration
MSF	multistage flash evaporation
PRO	pressure-retarded osmosis
RED	reverse electrodialysis
RO	reverse osmosis
UF	ultrafiltration
VC	vapor compression

Other:

GPD	gallons per day
GSFD	gallons/ft^2/day
TDS	total dissolved solids

CONTENTS

SYNTHETIC MEMBRANES AND THEIR PREPARATION

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In recent years, separations with synthetic membranes have become increasingly important processes in the chemical industry, in food and waste-water processing, and in medical treatment. Synthetic membranes made from a variety of polymers are used in processes such as microfiltration, ultrafiltration, reverse osmosis, electrodialysis, and gas separations. In this paper, the different membrane structures, their function and application in various separation processes are described. The preparation procedures of the various membrane types are discussed with special emphasis on symmetric and asymmetric membranes obtained by the phase inversion process.

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