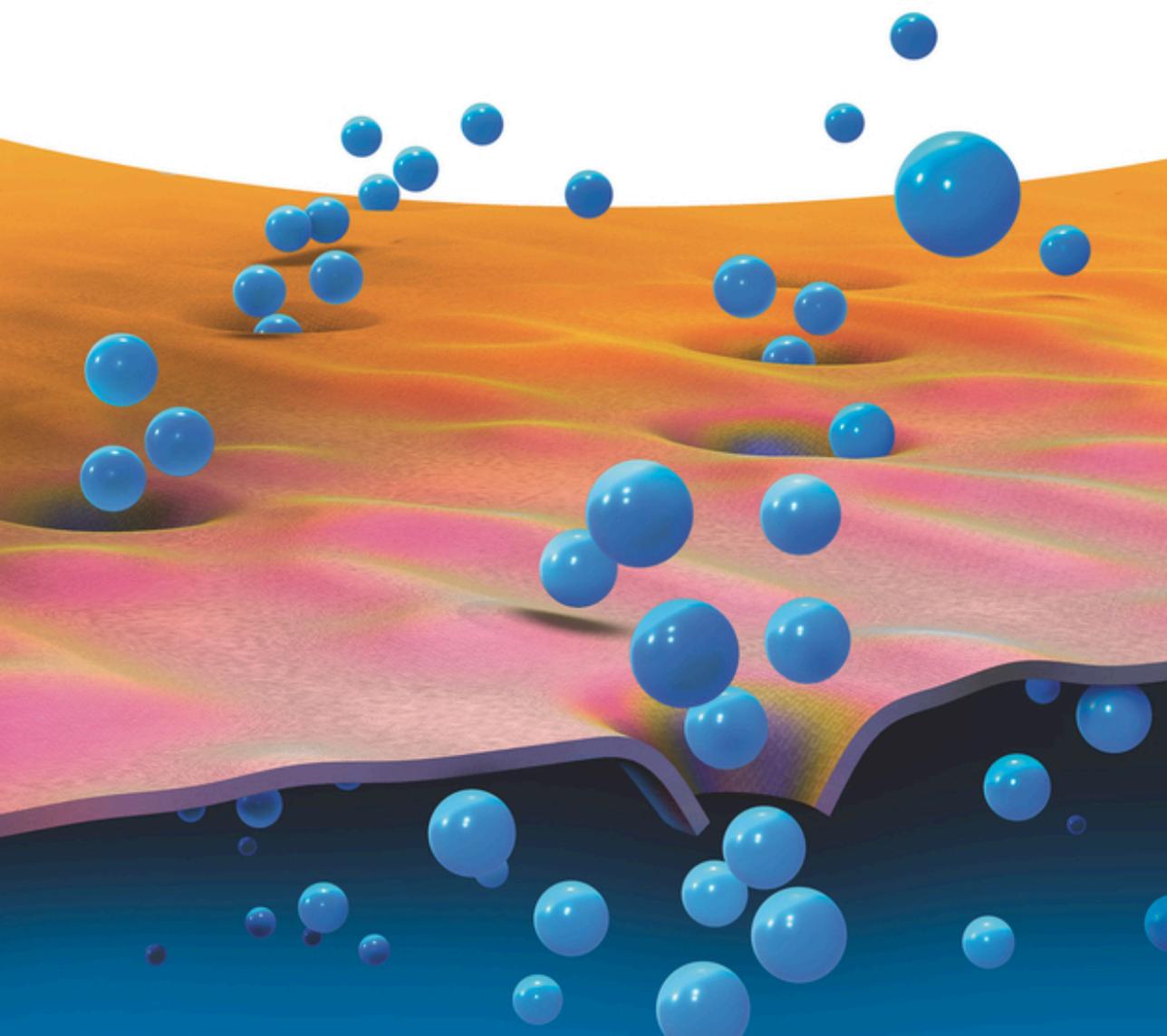


Edited by Andrea Iris Schäfer and Anthony G. Fane

# Nanofiltration

Principles, Applications, and New Materials

Second Edition





## **Nanofiltration**



# **Nanofiltration**

Principles, Applications, and New Materials

Volume 1

*Edited by*

*Andrea Iris Schäfer*

*Anthony G. Fane*

*Second Edition*

**WILEY-VCH**

# **Nanofiltration**

Principles, Applications, and New Materials

Volume 2

*Edited by*

*Andrea Iris Schäfer*

*Anthony G. Fane*

*Second Edition*

**WILEY-VCH**

## Editors

### **Prof. Dr. Andrea Iris Schäfer**

Karlsruhe Institute of Technology (KIT)  
Institute for Advanced Membrane  
Technology (IAMT)  
Hermann-von-Helmholtz-Platz 1  
76344 Eggenstein-Leopoldshafen  
Germany

### **Prof. Anthony G. Fane**

University of New South Wales  
School of Chemical Engineering  
Chemical Sciences Bldg. (F10)  
1712 Blue Water Lane  
2052 Sydney  
Australia

All books published by **WILEY-VCH** are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

**Library of Congress Card No.:**  
applied for

### **British Library Cataloguing-in-Publication Data**

A catalogue record for this book is available from the British Library.

### **Bibliographic information published by the Deutsche Nationalbibliothek**

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <<http://dnb.d-nb.de>>.

© 2021 WILEY-VCH GmbH, Boschstr.  
12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

**Print ISBN:** 978-3-527-34690-5

**ePDF ISBN:** 978-3-527-82496-0

**ePub ISBN:** 978-3-527-82497-7

**oBook ISBN:** 978-3-527-82498-4

**Cover Design** Formgeber, Mannheim, Germany

**Typesetting** Straive, Chennai, India

**Printing and Binding**

Printed on acid-free paper

10 9 8 7 6 5 4 3 2 1

## Contents

### Volume 1

**Foreword (Second Edition, 2020)** *xiii*

**Foreword (First Edition, 2005)** *xv*

**Acknowledgements** *xvii*

**Dedication** *xxi*

**Introduction** *xxiii*

### Part I Principles 1

<b>1</b>	<b>History of Nanofiltration Membranes from 1960 to 1990</b>	<b>3</b>
	<i>Charles Linder and Ora Kedem</i>	
1.1	Overview	3
1.2	Introduction	4
1.3	First-Generation NF Membranes	5
1.3.1	Cellulose Acetate Asymmetric Membranes	5
1.3.2	Deficiencies in Cellulosic Membranes	8
1.3.3	Polyelectrolyte Complexes	8
1.3.4	Polyamide Membranes	9
1.3.5	Polysulfones and Other Polymer Membranes	9
1.4	Early Studies of Charged Reverse Osmosis (Hyperfiltration) Membranes	10
1.4.1	Dynamic Membranes	10
1.4.2	Polyelectrolyte Membranes	10
1.5	Early Models of NF Selectivity	10
1.6	Negative Salt Rejection	13
1.6.1	Solutions of One Electrolyte	13
1.6.2	Separation by Negative Salt Rejection	13
1.7	Early Development of Industrial NF: Ionic Modification of Asymmetric Cellulose Acetate	13
1.8	Early NF Composites	15
1.8.1	General	15

1.8.2	Plasma Polymerization	18
1.8.3	Graft Polymerization	18
1.9	NF Composites of the 1980s	18
1.9.1	Piperazineamide Membranes	18
1.9.2	Other NF Interfacially Produced Composites	20
1.9.3	Modification of RO Membrane Composites to Bring Them into the NF Range	20
1.10	Composites Produced by Noninterfacial Cross-linking	21
1.10.1	Polyvinyl Alcohol Composites	21
1.10.2	Sulfonated Engineering Plastics as Selective Barriers	22
1.10.3	Polyethyleneimine	22
1.11	Chemically Stable NF Membranes	23
1.11.1	Chemically Stable Polymeric Asymmetric Membranes	23
1.11.2	Oxidant and pH-Stable Composite Membranes	23
1.11.3	Solvent-Stable NF Composites	24
1.11.4	Chemically Stable Inorganic NF and Polymeric/Inorganic Hybrids	26
1.12	Conclusions	27
	Abbreviations	28
	References	28
<b>2</b>	<b>Nanofiltration Membrane Materials and Preparation</b>	<b>35</b>
	<i>Hanne Mariën, Rhea Verbeke, and Ivo F.J. Vankelecom</i>	
2.1	General Introduction	35
2.2	Phase Inversion	36
2.2.1	Introduction	36
2.2.2	Basic Principles	37
2.2.3	Polymer Type	40
2.2.4	Casting Solution	40
2.2.5	Postcasting Evaporation	44
2.2.6	Coagulation Bath	45
2.2.7	Post-treatment	46
2.3	Interfacial Polymerization	47
2.3.1	Introduction	47
2.3.2	Support Materials	48
2.3.3	Monomers	49
2.3.4	Monomer Concentrations and Reaction Time	58
2.3.5	Solvent	58
2.3.6	Additives	59
2.3.7	New Approaches	60
2.3.8	Post-treatment	61
2.4	Coating	61
2.4.1	Introduction	61
2.4.2	Examples	62
2.5	Surface Modification	63
2.5.1	Introduction	63
2.5.2	Plasma Treatment	63
2.5.3	Organic Reactions	63
2.5.4	Polymer Grafting	64

2.5.5	Photochemical Modification	65
2.6	Ceramic Membranes	65
2.6.1	Introduction	65
2.6.2	General Synthesis Procedure	65
2.6.3	Membrane Types	67
2.6.4	Supports	69
2.6.5	Surface Modification	69
2.7	Hollow Fiber Preparation	71
2.7.1	Introduction	71
2.7.2	General Synthesis Procedure	71
2.7.3	Composite Hollow Fiber Membranes	72
2.8	Commercial and Novel (SR)NF Membranes	72
2.8.1	Commercial (SR)NF Membranes	72
2.8.2	Novel (SR)NF Membranes	76
2.9	Outlook	77
	Acknowledgements	78
	Abbreviations	78
	References	79
<b>3</b>	<b>Nanofiltration Module Design and Operation</b>	<b>95</b>
	<i>Tzyy Haur Chong and Anthony G. Fane</i>	
3.1	Introduction	95
3.1.1	Role of the Module	95
3.1.2	Concentration Polarization and Cross-Flow	96
3.1.3	Fouling	101
3.2	Module Types and Characteristics	102
3.2.1	Plate and Frame	102
3.2.2	Spiral Wound	103
3.2.3	Tubular	104
3.2.4	Hollow Fiber and Capillary	105
3.2.5	Others	106
3.2.6	Module Characteristics	108
3.3	Spiral Wound Module (SWM) – Design Features	110
3.3.1	Feed Channel Spacers	110
3.3.2	Modeling and Optimization	112
3.4	Strategies to Improve Control of Concentration Polarization	116
3.4.1	Process Limitation by Concentration Polarization	116
3.4.2	High Shear – Vibrating the Membrane	117
3.4.3	High Shear – Rotor/Stator Modules	119
3.4.4	Two-Phase Flow	119
3.4.5	Unsteady Shear Comparison	120
3.5	System Design and Operation	120
3.5.1	System Configurations	121
3.5.2	Diafiltration	124
3.5.3	Reflux-Recycle Cascade (Combining RO and NF)	124
3.5.4	Batch Operation – Energy Saving (Closed Circuit)	126
3.6	Conclusions	128
	Nomenclature	130
	Subscripts	131

	Greek Symbols	131
	Abbreviations	131
	References	131
<b>4</b>	<b>Nanofiltration Membrane Characterization</b>	<b>137</b>
	<i>Anthony Szymczyk and Viatcheslav Freger</i>	
4.1	Introduction	137
4.2	Structural Characteristics	139
4.2.1	Microscopy	139
4.2.2	Pore Size	141
4.2.3	Thickness and Morphology of the Active Layer	146
4.2.4	Surface Characteristics	147
4.2.5	Membrane Swelling and Solvent Uptake	149
4.2.6	Chemical Structure	150
4.2.7	Mechanical Properties	153
4.3	Charge Related Parameters	154
4.3.1	Electrokinetic Measurements	154
4.3.2	Titration and Ion Exchange	159
4.3.3	Membrane Potential	160
4.3.4	Electrochemical Impedance Spectroscopy	160
4.4	Nanofiltration Membranes for Nonaqueous Systems	163
4.5	Conclusions	165
	Nomenclature	166
	Greek Symbols	167
	Abbreviations	168
	References	168
<b>5</b>	<b>Modeling Nanofiltration of Electrolyte Solutions</b>	<b>183</b>
	<i>Andriy Yaroshchuk, Merlin L. Bruening, and Emiliy Zholkovskiy</i>	
5.1	Introduction	183
5.2	Basic Equations and Concepts	185
5.2.1	Derivation of Equations	185
5.2.2	Solution of Transport Equations for Macroscopically Homogeneous Membranes: Single Salts and Trace Ions	191
5.2.3	Specification of Phenomenological Coefficients Within the Scope of a Model of Straight, Narrow Capillaries	196
5.3	Nanopore Models of NF	197
5.3.1	Steric Exclusion and Hindrance	197
5.3.2	Local Equilibrium Partitioning Mechanisms	200
5.4	Solution-Diffusion-Electromigration Models of Nanofiltration	215
5.4.1	An Analytical Solution to Transport of Three Ions with Different Charges	215
5.4.2	Determining Single-Ion Permeances Using NF with Trace Ions	220
5.4.3	“Under-Osmotic” Operation	222
5.4.4	Deviations from Local Electrical Neutrality in Ultrathin Barrier Layers	223
5.5	Conclusions	228
	Acknowledgements	230
	Nomenclature	231

Greek Symbols	233
Abbreviations	234
References	234

<b>6</b>	<b>Chemical Speciation Effects in Nanofiltration Separation</b>	<b>243</b>
	<i>T. David Waite</i>	
6.1	Introduction	243
6.2	Chemical Speciation	243
6.2.1	Effect of Ionic Strength on Chemical Speciation	245
6.2.2	Effects of Temperature and Pressure on Chemical Speciation	247
6.3	Review of Effects of Solute Size, Charge, and Concentration on Rejection by NF Membranes	249
6.4	Solution Processes Influencing Speciation and Rejection	249
6.4.1	Acid–Base Transformations	250
6.4.2	Complexation	257
6.4.3	Precipitation	260
6.4.4	Oxidation–Reduction	264
6.4.5	Adsorption	265
6.5	Effect of Concentration Polarization on Speciation and Rejection	267
6.5.1	Exceedance of Solubility Product and Precipitation of Solids	268
6.5.2	Aggregation of Macromolecules and Precipitated Solids	268
6.5.3	Formation of Alternative Complexes and Multinuclear Species	268
6.6	Conclusions	269
	Nomenclature and Symbols	270
	Abbreviations	270
	References	271
<b>7</b>	<b>Fouling in Nanofiltration</b>	<b>273</b>
	<i>Andrea I. Schäfer, Nikolaos Andritsos, Anastasios J. Karabelas, Eric M.V. Hoek, René Schneider, and Marianne Nyström</i>	
7.1	Introduction	273
7.2	Fouling Characterization	277
7.2.1	Flux Measurement and Fouling Protocols	277
7.2.2	Normalization of Membrane Performance	279
7.2.3	Water Fouling Potential	280
7.2.4	Membrane Autopsy	284
7.3	Fouling Mechanisms	286
7.3.1	Concentration Polarization (CP)	288
7.3.2	Osmotic Pressure	290
7.3.3	Solute Adsorption	291
7.3.4	Gel Layer Formation	292
7.3.5	Cake Formation and Pore Blocking	293
7.3.6	Critical Flux and Operating Conditions	295
7.3.7	Additional Fouling Mechanisms	296
7.4	Organic Fouling	299
7.4.1	Introduction and Definition of Organic Fouling	299
7.4.2	Common Organic Foulants	299
7.4.3	Adsorption of Organic Matter	301

7.4.4	Gel Layer Formation	304
7.4.5	Cake Formation	304
7.4.6	Pore Blocking/Plugging	305
7.4.7	Impact of Solute–Solute Interactions and Salts	306
7.4.8	Impact of Fouling on Retention	308
7.5	Scaling	309
7.5.1	Introduction and Definition of Scaling	309
7.5.2	Solubility and Supersaturation of Salts	312
7.5.3	Common Scalants	314
7.5.4	Characterization of Scales	317
7.5.5	Mechanisms of Scale Formation	317
7.6	Colloidal and Particulate Fouling	319
7.6.1	Introduction and Definition of Colloidal and Particulate Fouling	319
7.6.2	Colloid Properties	321
7.6.3	NF Membrane Properties	322
7.6.4	Colloid Transport and Deposition	323
7.7	Biofouling	327
7.7.1	Introduction and Definition of Biofouling	327
7.7.2	Biofilm Formation in NF Plants	328
7.7.3	Biofilm Structure	333
7.7.4	Growth of Microbes in Biofilms	333
7.7.5	Sites for Biofouling in Membrane Systems	335
7.7.6	Measuring Microbial Load in Feedwaters and Detecting Biofilms in Membrane Systems	336
7.7.7	Biofouling Management in Membrane Systems	338
7.8	Fouling Prevention and Cleaning	339
7.8.1	Pretreatment as Fouling Prevention	339
7.8.2	Membrane Modification for Fouling Prevention	339
7.8.3	Cleaning Methods	341
7.8.4	Determination of Cleaning Effectiveness	346
7.8.5	Examples of Cleaning Applications and Cleaning Process Protocols	351
7.8.6	Regeneration of Cleaning Solutions	353
7.9	Conclusions	353
	Acknowledgements	353
	Nomenclature	354
	Greek Symbols	355
	Abbreviations	355
	References	357
<b>8</b>	<b>Pretreatment and Hybrid Processes</b>	<b>381</b>
	<i>Jack Gilron, Marianne Nyström, Jukka Tanninen, and Lena Kamppinen</i>	
8.1	Introduction	381
8.2	Pretreatment – An Overview	382
8.2.1	Importance of Pretreatment in NF	382
8.3	Non-membrane Pretreatment Methods	383
8.3.1	Control of Inorganic Precipitation (Scaling)	383

8.3.2	Removal of Colloids and Solids	387
8.3.3	Removal of Organic Substances	387
8.3.4	Biological Fouling Prevention	388
8.3.5	Biological Pretreatment	389
8.4	Pretreatment Methods Using Filter Media	391
8.4.1	Conventional Filtration	391
8.4.2	Microfiltration (MF)	391
8.4.3	Ultrafiltration (UF)	393
8.5	Nanofiltration as a Pretreatment	395
8.5.1	Pretreatment Before Reverse Osmosis (RO)	395
8.5.2	Pretreatment Before Electrodialysis (ED)	396
8.5.3	Pretreatment Before Ion Exchange (IX)	397
8.5.4	Pretreatment Before Evaporation	398
8.6	NF in Hybrids Related to Seawater Desalination	398
8.7	NF as Post-treatment and Polishing Technology	403
8.7.1	Purification	403
8.7.2	Fractionation	404
8.8	Conclusions	407
	Acknowledgements	408
	Abbreviations	408
	References	409

## Volume 2

**Foreword (Second Edition, 2020)** *xvii*

**Foreword (First Edition, 2005)** *xix*

**Acknowledgements** *xxi*

**Dedication** *xxv*

**Introduction** *xxvii*

**Part II Applications** *419*

9	<b>Water Treatment</b>	<i>421</i>
	<i>Erich Wittmann, Edvard Sivertsen, and Thor Thorsen</i>	
10	<b>Water Reclamation, Remediation, and Cleaner Production with Nanofiltration</b>	<i>451</i>
	<i>Yoram Cohen, Jin Y. Choi, and Anditya Rahardianto</i>	
11	<b>Nanofiltration in the Food Industry</b>	<i>499</i>
	<i>Marie-Pierre Belleville, José Sanchez-Marcano, Gerrald Bargeman, and Martin Timmer</i>	
12	<b>Nanofiltration in the Chemical Processing Industry</b>	<i>543</i>
	<i>Markus Kyburz, G. Wytze Meindersma, and Gerrald Bargeman</i>	
13	<b>Nanofiltration in the Pulp and Paper Industry</b>	<i>599</i>
	<i>Mika Mänttari, Marianne Nyström, Jutta Nuortila-Jokinen, and Mari Kallioinen</i>	

- 14      **Nanofiltration of Textile Dye Effluent** 621  
*Chidambaram Thamaraiselvan and Woei-Jye Lau*
- 15      **Nanofiltration in Landfill Leachate Treatment** 663  
*Johannes Meier, Kirsten Remmen, Thomas Wintgens, and Thomas Melin*
- 16      **Nanofiltration Bioreactors** 691  
*Luong N. Nguyen and Long D. Nghiem*
- 17      **Photocatalytic Nanofiltration Reactors** 707  
*Raffaele Molinari, Pietro Argurio, Lidieta Giorno, Leonardo Palmisano, and Enrico Drioli*
- 18      **Nanofiltration in Hydrometallurgy** 759  
*Adrian A. Manis, Karin H. Solden hoff, Elizabeth M. Ho, and Peter D. Macintosh*
- 19      **Trace Contaminant Removal by Nanofiltration** 805  
*Alessandra Imbrogno, Youssef-Amine Boussouga, Long D. Nghiem, and Andrea I. Schäfer*
- 20      **Organic Solvent Nanofiltration** 889  
*Torsten Brinkmann and Volkan Filiz*
- 21      **Nanofiltration Retentate Treatment** 933  
*Bart Van der Bruggen*
- 22      **Renewable Energy-Powered Nanofiltration** 961  
*Bryce S. Richards and Andrea I. Schäfer*
- Part III      Future Nanofiltration Materials** 1021
- 23      **Carbon Nanotube Composite Materials for Nanofiltration** 1023  
*Francesco Fornasiero*
- 24      **Biomimetic Nanofiltration Materials** 1057  
*Mihail Barboiu*
- 25      **Novel Polymer-Based Materials for Nanofiltration** 1081  
*Mathias Ulbricht*
- 26      **Graphene-Based Membranes for Nanofiltration** 1125  
*Wanqin Jin*
- Conclusions and Future Developments** 1165  
*Andrea I. Schäfer*
- Index** 1171

## Contents

### Volume 1

**Foreword (Second Edition, 2020)** *xv*

**Foreword (First Edition, 2005)** *xvii*

**Acknowledgements** *xix*

**Dedication** *xxiii*

**Introduction** *xxv*

### **Part I Principles** *1*

- 1 History of Nanofiltration Membranes from 1960 to 1990** *3*  
*Charles Linder and Ora Kedem*
- 2 Nanofiltration Membrane Materials and Preparation** *35*  
*Hanne Mariën, Rhea Verbeke, and Ivo F.J. Vankelecom*
- 3 Nanofiltration Module Design and Operation** *95*  
*Tzyy Haur Chong and Anthony G. Fane*
- 4 Nanofiltration Membrane Characterization** *137*  
*Anthony Szymczyk and Viatcheslav Freger*
- 5 Modeling Nanofiltration of Electrolyte Solutions** *183*  
*Andriy Yaroshchuk, Merlin L. Bruening, and Emiliy Zholkovskiy*
- 6 Chemical Speciation Effects in Nanofiltration Separation** *243*  
*T. David Waite*
- 7 Fouling in Nanofiltration** *273*  
*Andrea I. Schäfer, Nikolaos Andritsos, Anastasios J. Karabelas, Eric M.V. Hoek, René Schneider, and Marianne Nyström*
- 8 Pretreatment and Hybrid Processes** *381*  
*Jack Gilron, Marianne Nyström, Jukka Tanninen, and Lena Kamppinen*

**Volume 2****Foreword (Second Edition, 2020)** *xvii***Foreword (First Edition, 2005)** *xix***Acknowledgements** *xxi***Dedication** *xxv***Introduction** *xxvii***Part II Applications** *419*

<b>9</b>	<b>Water Treatment</b> <i>421</i>
	<i>Erich Wittmann, Edvard Sivertsen, and Thor Thorsen</i>
9.1	Introduction <i>421</i>
9.2	Overview of Nanofiltration Applications in Drinking Water <i>421</i>
9.3	Plant Design <i>423</i>
9.3.1	Membrane Selection <i>423</i>
9.3.2	Nanofiltration Treatment Systems <i>425</i>
9.3.3	Configurations with Spiral Wound Membranes <i>425</i>
9.3.4	Configurations with Tubular Membranes <i>427</i>
9.3.5	Pretreatment for Spiral Wound Membranes <i>427</i>
9.3.6	Post-treatment <i>428</i>
9.3.7	Residual Disposal <i>429</i>
9.4	Plant Operation and Monitoring <i>429</i>
9.5	Case Studies <i>430</i>
9.5.1	Case Study 1: Méry-sur-Oise <i>430</i>
9.5.2	Case Study 2: Sulfate Removal – Jarny <i>436</i>
9.5.3	Case Study 3: Pesticide Removal and Softening of a Borehole Water – Debden Road <i>438</i>
9.6	Plants Treating Highly Colored Water <i>438</i>
9.6.1	Color Removal Using Tubular Membranes <i>440</i>
9.6.2	Color Removal Using Spiral Wound Membranes <i>440</i>
9.7	Conclusions <i>446</i>
	Abbreviations <i>446</i>
	References <i>447</i>
<b>10</b>	<b>Water Reclamation, Remediation, and Cleaner Production with Nanofiltration</b> <i>451</i>
	<i>Yoram Cohen, Jin Y. Choi, and Anditya Rahardianto</i>
10.1	Introduction <i>451</i>
10.2	Reclamation of Municipal Effluent <i>452</i>
10.2.1	Project Drivers – Water Reclamation <i>452</i>
10.2.2	Advantages of NF in Municipal Reclamation Applications <i>458</i>
10.2.3	Process Fundamentals <i>458</i>
10.2.4	Process Limitations <i>460</i>
10.2.5	Conclusions <i>467</i>
10.3	Groundwater Remediation <i>469</i>

10.3.1	Project Drivers – Recovery of Industrial By-product	469
10.3.2	Project Drivers – Removal of Groundwater Contaminants	474
10.3.3	Conclusions	477
10.4	Agricultural Drainage Water	478
10.4.1	Project Drivers – Reduction of Agricultural Drainage Water Salinity	478
10.4.2	Advantages of Low-Pressure RO/NF	478
10.4.3	Process Feature and Fundamentals	478
10.4.4	Process Limitations and Progress	481
10.4.5	Conclusions	483
10.5	Industrial Reuse and Cleaner Production	484
10.5.1	Project Drivers – Water Reuse	484
10.5.2	Advantages of NF	484
10.5.3	Process Features and Fundamentals	485
10.5.4	Limitations	488
10.5.5	Conclusions	489
10.6	Closure	489
	Acknowledgements	490
	Abbreviations	490
	References	491
<b>11</b>	<b>Nanofiltration in the Food Industry</b>	<b>499</b>
	<i>Marie-Pierre Belleville, José Sanchez-Marcano, Gerrald Bargeman, and Martin Timmer</i>	
11.1	Introduction	499
11.2	Applications in the Milk Industry and Whey Processing	502
11.2.1	General	502
11.2.2	Production of Partially Demineralized Whey Concentrate	502
11.2.3	Production of Lactose from Whey Permeate	506
11.3	Applications in the Beverage Processing	507
11.3.1	General	507
11.3.2	Concentration of Fruit Juices	508
11.3.3	Production of Beverage with Low Alcohol Content	509
11.3.4	Concentration of Coffee Extract and Decaffeination of Coffee	511
11.4	Applications in Sugar Production	511
11.4.1	General	511
11.4.2	Concentration of Dextrose Syrup	511
11.4.3	Concentration of Thin Juice	513
11.5	Applications in the Edible Oil Industry	514
11.5.1	General	514
11.5.2	Solvent-Based Degumming	516
11.5.3	Direct Degumming	517
11.5.4	Deacidification	517
11.6	Production of Food Ingredients and Nutraceuticals	518
11.6.1	General	518
11.6.2	NF for Production of Peptides and Amino Acids	520
11.6.3	NF for Production of Oligosaccharides and Sweeteners	521

11.6.4	NF for Production of Phenolic Compounds	523
11.7	Process Water Treatment	525
11.7.1	General	525
11.7.2	Treatment of Ion Exchange Resin Regenerate	526
11.7.3	Filtration and Reuse of CIP Solutions	528
11.7.4	Demineralization of Colored Brine from Anion Exchange Resin Elution Solutions	530
11.7.5	Filtration and Recycling of Process Water	531
11.8	Conclusions	531
	Abbreviations	532
	Nomenclature	532
	References	532
<b>12</b>	<b>Nanofiltration in the Chemical Processing Industry</b>	<b>543</b>
	<i>Markus Kyburz, G. Wytze Meindersma, and Gerrald Bargeman</i>	
12.1	Introduction	543
12.2	Inorganic Chemical Industry	543
12.2.1	Characterization of the Industry	543
12.2.2	NF of Processing of Sodium Chloride Brines	544
12.2.3	Pollution Treatment in the Inorganic Chemical Industry, MLD and ZLD	554
12.3	Organic Chemical Industry	558
12.3.1	Characterization of the Industry	558
12.3.2	Potential and Actual Applications for NF in the Organic Chemical Industry	559
12.4	Pharmaceutical and Biotechnology Industry	569
12.4.1	Research and Development of Bench Test Technology	569
12.4.2	General Industrial Process Description	571
12.4.3	NF Applications in the Pharmaceutical and Biotechnology Industry	571
12.5	Petrochemical Industry	581
12.5.1	Solvent Lube Dewaxing	581
12.5.2	Removal of Contaminants	584
12.5.3	Deacidifying Crude Oil	585
12.5.4	Tertiary Oil Production: SAGD (Steam-Assisted Gravity Drainage)	586
12.5.5	DeSO <sub>x</sub> /Bio-deNO <sub>x</sub> Processes	588
12.6	Conclusions	590
	Acknowledgements	590
	Abbreviations	590
	References	591
<b>13</b>	<b>Nanofiltration in the Pulp and Paper Industry</b>	<b>599</b>
	<i>Mika Mänttari, Marianne Nyström, Jutta Nuortila-Jokinen, and Mari Kallioinen</i>	
13.1	Introduction	599
13.2	Streams that could be Processed with NF Membranes	600

13.3	NF Modules and Demands in the Pulp and Paper Industry	605
13.4	Examples of Mill-Stage NF Plants	607
13.4.1	Nanofiltration in Upgrading Effluent Quality	608
13.4.2	Nanofiltration in Recirculation of Water at Paper Mill	608
13.4.3	Zero Discharge Mill with Membrane Technologies	609
13.4.4	Reduction of Concentrate Volume with Nanofiltration	609
13.4.5	Recirculation of Waste Streams in Medium Density Fiber Board Mill	609
13.5	Pilot and Bench-Scale Systems	610
13.5.1	Purification of Bleaching Effluents	610
13.5.2	Purification of Mechanical Pulp Mill Process Waters	611
13.5.3	Purification of Paper Mill Process Waters	611
13.5.4	NF as Polishing Stage after Biological Wastewater Treatment	613
13.5.5	NF in Recovering Side Products from Spent Cooking Liquors	613
13.6	Conclusions and Future Prospects	615
	Abbreviations	615
	References	616
<b>14</b>	<b>Nanofiltration of Textile Dye Effluent</b>	<b>621</b>
	<i>Chidambaram Thamaraiselvan and Woei-Jye Lau</i>	
14.1	Introduction	621
14.2	Textile Wastewater Treatment Overview	623
14.3	Membrane-Based Technologies for Textile Wastewater Treatment	630
14.3.1	Ultrafiltration	630
14.3.2	Membrane Bioreactor (MBR)	631
14.3.3	Nanofiltration (NF)	633
14.3.4	Reverse Osmosis (RO)	633
14.4	Advances in Nanofiltration Fabrication and Modification	634
14.4.1	TFC Flat Sheet Membranes	634
14.4.2	TFC and Asymmetric Hollow Fiber Membranes	635
14.4.3	Positively and Negatively Charged Membranes	636
14.5	Factors Affecting NF Performance	639
14.5.1	Influence of Feed Properties	639
14.5.2	Influence of Membrane Properties	641
14.5.3	Influence of Hydrodynamic Conditions	642
14.6	Fouling Control Approaches	644
14.7	Integrated Process Involving Nanofiltration	646
14.8	Economic Evaluation on Nanofiltration Hybrid Process	651
14.9	Conclusions	653
	Abbreviations	653
	References	653
<b>15</b>	<b>Nanofiltration in Landfill Leachate Treatment</b>	<b>663</b>
	<i>Johannes Meier, Kirsten Remmen, Thomas Wintgens, and Thomas Melin</i>	
15.1	Introduction	663
15.2	Landfill Leachate	664

15.2.1	Generation of Landfill Leachate	664
15.2.2	Characteristics of Landfill Leachate	665
15.2.3	Legal Standards for Treated Landfill Leachate	668
15.3	Overview of Currently Employed Processes	669
15.3.1	Biological Treatment	670
15.3.2	Adsorption	670
15.3.3	Oxidation/Reduction	671
15.3.4	Membrane Processes	672
15.3.5	Concentrate Removal	673
15.3.6	Process Combinations	674
15.4	Landfill Leachate Treatment by Nanofiltration	674
15.4.1	General Features of NF in Landfill Leachate Treatment	676
15.4.2	NF as Single Process	676
15.4.3	Biology and NF	677
15.4.4	Biology and NF with Concentrate Treatment by Adsorption/Oxidation	679
15.4.5	RO with Concentrate Treatment by NF, Crystallization, and High Pressure RO	682
15.4.6	Biology, NF, and Adsorption on Powdered Activated Carbon	684
15.4.7	Economics of the Described Processes	686
15.5	Conclusions	687
	Acknowledgements	688
	Abbreviations	688
	References	688
<b>16</b>	<b>Nanofiltration Bioreactors</b>	<b>691</b>
	<i>Luong N. Nguyen and Long D. Nghiem</i>	
16.1	Introduction	691
16.2	NF-MBR Configurations	692
16.3	Wastewater Treatment Applications	693
16.4	Removal of Organic Matter and Nutrients	693
16.5	Removal of Trace Organic Contaminants	695
16.6	Operational Challenges	696
16.6.1	Salinity Build-up	696
16.6.2	Membrane Fouling and Degradation	697
16.7	Nutrient Recovery Opportunities	698
16.8	Bioprocessing	698
16.8.1	Bioethanol Production	698
16.8.2	Raw Chemical Precursor Production	699
16.9	Conclusions	701
	Abbreviations	702
	References	702
<b>17</b>	<b>Photocatalytic Nanofiltration Reactors</b>	<b>707</b>
	<i>Raffaele Molinari, Pietro Argurio, Lidieta Giorno, Leonardo Palmisano, and Enrico Drioli</i>	
17.1	Introduction	707

17.2	Background	708
17.2.1	Basic Principles of Heterogeneous Photocatalysis	709
17.2.2	Factors Affecting the Performance of PMRs	714
17.3	Possible System Configurations	718
17.3.1	Membranes as TiO <sub>2</sub> Particle Separator: PMRs with Suspended Photocatalyst	719
17.3.2	Membranes as TiO <sub>2</sub> Confinement or Carrier: PMRs with Immobilized Photocatalyst	723
17.3.3	Irradiation of Immobilized and Suspended Catalyst in the Photoreactors	725
17.3.4	Investigation on General NF Membranes Behavior	727
17.4	Some Applications from Laboratory to Industrial Scale	728
17.4.1	Examples of Contaminant Removal in Pressure-Driven Membrane Photoreactors	728
17.4.2	Examples of Contaminant Removal in Submerged NF Membrane Photoreactors	736
17.4.3	NF Wastewater Treatment in Photocatalytic Membrane Reactors	740
17.4.4	Hint on Processes Alternative to NF in Water Treatment	743
17.5	Conclusions	744
	Abbreviations	745
	References	746
<b>18</b>	<b>Nanofiltration in Hydrometallurgy</b>	<b>759</b>
	<i>Adrian A. Manis, Karin H. Soldenhoff, Elizabeth M. Ho, and Peter D. Macintosh</i>	
18.1	Introduction	759
18.2	Challenges in the Application of Nanofiltration to Hydrometallurgy	760
18.3	Nanofiltration in Copper Hydrometallurgical Processing	762
18.3.1	Nanofiltration of Copper Pregnant Leach Solution	762
18.3.2	Nanofiltration of Copper Electrowinning Bleed	764
18.3.3	Nanofiltration of Tailings Pond Water	764
18.3.4	Application of Nanofiltration in a Copper Smelting Plant	765
18.4	Nanofiltration in Uranium Processing	765
18.4.1	Nanofiltration of Uranium In Situ Leach and Heap Leach Solutions	767
18.4.2	Sodium Bicarbonate Recovery from Ion Exchange Eluate	769
18.4.3	Acid Recovery from Ion Exchange/Resin-in-Pulp Eluate	769
18.4.4	Acid Recovery from Solvent Extraction Strong Acid Strip Liquor	772
18.4.5	Sodium Chloride Recovery from Ion Exchange Eluate or Solvent Extraction Strip Liquor	773
18.4.6	Uranium Recovery by Ion Exchange and Nanofiltration from Alkaline Leach Liquor	774
18.5	Nanofiltration in Processing of Lithium Brines	776
18.5.1	Nanofiltration of Raw Brine	777

18.5.2	Nanofiltration After Dilution of Evaporated Brine	779
18.5.3	Treatment of Salt Lake Brine by a Combined Nanofiltration and Membrane Distillation Process	779
18.5.4	Treatment of Geothermal Brines	780
18.5.5	Research into New Membranes	780
18.6	Nanofiltration in Zinc Processing	780
18.6.1	Nanofiltration in Waelz Oxide Processing	780
18.6.2	Nanofiltration to Concentrate Bioleach Liquor and Recover Indium	782
18.6.3	Nanofiltration to Remove Boron	782
18.7	Nanofiltration in Gold Processing	783
18.7.1	Nanofiltration of Gold Cyanide Leach Liquor	783
18.7.2	Nanofiltration Integrated with Activated Carbon Elution and Electrowinning	784
18.7.3	Pressure Oxidation of Gold Ore	784
18.7.4	Treatment of Hypersaline Process Water	785
18.8	Other Processing Applications	785
18.8.1	Nanofiltration in Vanadium Processing	785
18.8.2	Nanofiltration of Bayer Process Liquors (Alumina Production)	787
18.8.3	Nanofiltration in Tungsten Processing	788
18.8.4	Nanofiltration in Treatment of Spent Nickel Electrolyte	790
18.8.5	Metal Separation from Phosphoric Acid by Nanofiltration	790
18.9	Nanofiltration for Recovery of Critical Materials from Secondary Sources	793
18.9.1	Scandium	793
18.9.2	Rare Earths	794
18.9.3	Germanium and Rhenium	794
18.10	Conclusions	794
	Acknowledgements	795
	Abbreviations	795
	References	796
<b>19</b>	<b>Trace Contaminant Removal by Nanofiltration</b>	<b>805</b>
	<i>Alessandra Imbrogno, Youssef-Amine Boussouga, Long D. Nghiem, and Andrea I. Schäfer</i>	
19.1	Introduction	805
19.2	Occurrence of Trace Contaminants and their Effect on Health and Environment	806
19.2.1	Water Sources	808
19.2.2	Current Regulations and Water Guidelines	810
19.2.3	Endocrine-Disrupting Chemicals (EDCs)	811
19.2.4	Pharmaceutically Active Compounds (PhACs)	815
19.2.5	Pesticides	816
19.2.6	Disinfection By-products (DBPs)	818
19.2.7	Perfluorochemicals (PFCs)	819
19.2.8	Arsenic	820
19.2.9	Fluoride	821

19.2.10	Uranium	822
19.2.11	Boron	823
19.2.12	Nitrate	824
19.3	Nanofiltration in Water and Wastewater Treatment	825
19.3.1	Removal of Trace Contaminants by Nanofiltration	825
19.3.2	Application of NF for Organic Trace Contaminant Removal in Prospect with Water Guidelines	826
19.3.3	Application of NF for Inorganic Trace Contaminant Removal with Respect to Water Guidelines	831
19.4	Removal Mechanisms of Trace Contaminants by Nanofiltration	832
19.4.1	Organic Contaminants	833
19.4.2	Inorganic Contaminants	848
19.5	Fouling, Chemical Cleaning, and Aging	857
19.5.1	Impact of Membrane Fouling on Trace Contaminant Removal	857
19.5.2	Impact of Chemical Cleaning on Trace Contaminant Removal and Desorption	859
19.5.3	Impact of Membrane Aging and Defects on Trace Contaminant Removal	861
19.6	Conclusions	862
	Acknowledgements	863
	Nomenclature	863
	Abbreviations	864
	References	865
<b>20</b>	<b>Organic Solvent Nanofiltration</b>	<b>889</b>
	<i>Torsten Brinkmann and Volkan Filiz</i>	
20.1	Introduction	889
20.2	Membrane Materials	890
20.2.1	Introduction	890
20.2.2	Membrane Preparation and Fabrication	892
20.2.3	Membranes	893
20.3	Membrane Modules for Organic Solvent Nanofiltration	903
20.4	Modeling and Simulation of the Membrane Module Performance	906
20.5	Models for the Description of the Permeation Behavior	907
20.6	Process Examples	911
20.6.1	Pharmaceuticals	911
20.6.2	Base Chemicals	912
20.6.3	Organic Solvent Nanofiltration in Combination with Catalytic Processes	913
20.7	Conclusions	915
	Nomenclature	917
	Greek Symbols	918
	Superscripts	918
	Subscripts	918
	Abbreviations	919
	References	920

<b>21</b>	<b>Nanofiltration Retentate Treatment</b>	<b>933</b>
	<i>Bart Van der Bruggen</i>	
21.1	Introduction	933
21.2	Disposal Strategies	934
21.3	Further Treatment	937
21.4	Volume Reduction	942
21.5	Resource Recovery Strategies	946
21.6	Concentrates as the Target Fraction	949
21.7	Conclusions	953
	Abbreviations	953
	References	954
<b>22</b>	<b>Renewable Energy-Powered Nanofiltration</b>	<b>961</b>
	<i>Bryce S. Richards and Andrea I. Schäfer</i>	
22.1	Introduction	961
22.1.1	Water as a Global Challenge	961
22.1.2	Water Quality Issues	962
22.1.3	Water Energy Nexus	965
22.1.4	Decentralized Treatment Systems	966
22.1.5	Robust Systems for Harsh Environments	967
22.2	Renewable Energy-Powered Nanofiltration (RE-NF) Systems	967
22.2.1	Renewable Energy	967
22.2.2	Concept of Renewable Energy-Powered Systems	970
22.2.3	Impact of Membrane Choice	973
22.2.4	Energy Storage and Buffering	973
22.2.5	Overview of Commercially Available RE Membrane Systems	974
22.3	Performance of Small-Scale RE-NF Systems	976
22.3.1	System Design	977
22.3.2	Constant Power	977
22.3.3	Safe Operating Window (SOW)	980
22.3.4	Directly Connected Solar-Powered RE Membrane System	982
22.3.5	Directly Connected Wind-Powered RE Membrane System	986
22.3.6	Energy Storage and Buffering for Small-Scale RE Membrane Systems	990
22.4	System Performance in Terms of Water Quality	995
22.4.1	Salinity	998
22.4.2	Variation of pH and Speciation	1000
22.4.3	Removal of Trace Contaminants	1002
22.4.4	Removal of Organic Matter	1004
22.4.5	Fouling and Scaling	1006
22.4.6	Water Distribution	1007
22.5	Conclusions and Outlook	1008
	Acknowledgements	1010
	Abbreviations	1011
	References	1011

**Part III Future Nanofiltration Materials 1021**

- 23 Carbon Nanotube Composite Materials for Nanofiltration 1023**  
*Francesco Fornasiero*
- 23.1 Carbon Nanotube Membranes 1023
    - 23.1.1 Introduction 1023
    - 23.1.2 Basic Properties of Carbon Nanotubes 1024
    - 23.1.3 Principles: Modeling of CNT Transport 1024
    - 23.1.4 Fabrication of Carbon Nanotube Membranes 1029
    - 23.1.5 Functionalization 1035
    - 23.1.6 Water Permeability 1037
    - 23.1.7 Solute Transport and Retention Properties 1039
    - 23.1.8 Antifouling Properties 1043
    - 23.1.9 Challenges for Fabricating Industrially Viable Membranes 1044
    - 23.1.10 CNT Membrane Potential for Water Purification and Desalination 1046
  - Acknowledgements 1047
  - Nomenclature 1047
  - Greek Symbols 1048
  - Abbreviations 1048
  - References 1049
- 24 Biomimetic Nanofiltration Materials 1057**  
*Mihail Barboiu*
- 24.1 Introduction 1057
  - 24.2 Self-organized Hybrid Membranes 1059
    - 24.2.1 Directional Nanochannels for Facilitated Ionic Conduction 1059
    - 24.2.2 Nanochannels for Proton Conduction 1060
    - 24.2.3 Chiral Nanochannels 1064
  - 24.3 Adaptive Constitutional Membranes 1066
  - 24.4 Artificial Water Channels (AWCs) 1069
    - 24.4.1 Artificial Water Channels in Bilayer Membranes 1069
    - 24.4.2 Biomimetic Membranes Using Aquaporins and Artificial Water Channels 1073
  - 24.5 Conclusions 1075
  - Acknowledgements 1076
  - References 1076
- 25 Novel Polymer-Based Materials for Nanofiltration 1081**  
*Mathias Ulbricht*
- 25.1 Motivation and Scope 1081
  - 25.2 Overview on Fabrication Methods and Building Blocks 1084
  - 25.3 Alternative Membrane Polymers in Established Fabrication Processes 1089
    - 25.3.1 Cross-linked Hydrophilic Neutral Polymers 1090

25.3.2	Biopolymers	1091
25.3.3	Polymers with Intrinsic Microporosity (PIMs)	1092
25.3.4	Ion Exchange Polymers	1092
25.3.5	Amphiphilic Copolymers	1093
25.3.6	Well-Defined Amphiphilic Di- and Triblock Copolymers	1094
25.4	Alternative Fabrication Processes Based on Macromolecules and Nanoparticles	1096
25.4.1	Layer-by-Layer Deposition with Linear Polymers	1097
25.4.2	Deposition of Star Polymers or Nanoparticles	1098
25.5	Alternative Monomers in Established Interfacial Polymerization Fabrication Processes	1102
25.6	Alternative Fabrication Processes Based on Small Molecules	1103
25.6.1	Surface Grafting/Pore Filling Polymerization	1105
25.6.2	Molecular Layer-by-Layer Reactive Assembly Toward Polyamide Layers	1106
25.6.3	Synthesis of Covalent Organic Frameworks (COFs)	1107
25.6.4	Assembly and Cross-linking of Amphiphiles to Liquid Crystalline Microporous Phases	1108
25.6.5	Peptide Channels in Self-assembled Diblock Copolymers	1109
25.7	Mixed Matrix Composite Membranes	1109
25.8	Postmodification	1111
25.9	Approaches to Stimuli-Responsive Nanofiltration Membranes	1113
25.10	Conclusions	1114
	Nomenclature	1116
	Abbreviations	1116
	References	1117
<b>26</b>	<b>Graphene-Based Membranes for Nanofiltration</b>	<b>1125</b>
	<i>Wanqin Jin</i>	
26.1	Introduction	1125
26.2	Porous Graphene Layer	1127
26.3	Assembled Graphene Laminates	1131
26.3.1	Fabrication Methods	1131
26.3.2	Controlling Membrane Nanostructure	1139
26.4	Graphene-Based Composites	1148
26.5	Transport Mechanisms	1150
26.6	Organic Solvent Nanofiltration	1156
26.7	Conclusions and Perspectives	1157
	Nomenclature	1158
	Abbreviations	1158
	References	1160
	<b>Conclusions and Future Developments</b>	<b>1165</b>
	<i>Andrea I. Schäfer</i>	
	<b>Index</b>	<b>1171</b>

## Foreword (Second Edition, 2020)

In the foreword to the first edition of this book, Robert J. (Bob) Petersen wrote a masterful commentary on the beginning of the nanofiltration era. Little did we know then that this terminology would become so widespread in its use today. It is a testament to the wide breadth of applications for the technology.

In its infancy, when it was still called “loose membranes,” companies sought applications with higher valued end products. The “single stage seawater reverse osmosis” membrane was an elusive goal of nearly all companies and the government agency Office of Water Research Technology. It was, after all, highlighted in a much publicized speech made by President John F. Kennedy. Many companies fell by the wayside when they could not achieve this sought-after goal.

One of the secondary goals was the separation of sugar and salt. We thought this was a plausible separation considering the difference in size and stereochemistry of the disaccharide sucrose and sodium chloride. In those early days, cellulose (both di- and tri-acetate) was the polymer of choice. The techniques employed hearkened of alchemy more than polymer science. The additives were referred to as “pore formers” rather than surface charge modifiers or other more sophisticated techniques used today. The initial attempts were technically successful, but not economically competitive with existing sugar purification techniques, but they did spawn new applications for membranes.

One of the early successful applications was the concentration of cheese whey followed by drum drying, made necessary by the need to alleviate river and surface water pollution. Along the way, successful applications such as separation of enzymes from mother liquor and extraction of proteins from cheese whey became commonplace. The successful removal of proteins from whey made it possible to recover water-soluble protein instead of denatured protein using thermal methods.

The development of these applications also kick-started the use of more sophisticated hardware for the systems – clean-in-place, for example, was essential for food-grade and bio-pharma processing. Tubular membranes were very expensive and energy intensive but the recycling of recovered water-soluble paint in the automotive industry was a well-known exception. Smaller diameter multiple tubular module configurations resulted, which improved energy consumption

but were still costly. The advent of hollow fibers greatly improved surface area to volume ratio and spawned a huge application of membranes for wastewater reuse.

The expanded use of nanofiltration for commercial applications and industrial/domestic wastewater treatment has been nothing short of amazing. It now appears possible to solve age old problems such as produced water disposal by combining new membrane science with more conventional processes. Ceramic membranes, once considered overly expensive, are now more frequently included for difficult applications.

I have been encouraged by the sophisticated advances in polymer chemistry in recent years. Perhaps today's bright young minds can delve into the intricacies of polymer click chemistry and develop unique new nanofiltration membranes through bioconjugation science. This may afford a pathway to the solution of the 'big elephant in the room,' which is membrane fouling.

The future for nanofiltration continues to be promising, challenging, and ever-changing.

10 February 2020  
Poway, CA, USA

*David H. Furukawa*  
Consultant to Filmtec from 1978, VP Marketing from 1983  
(David attended the meeting with Bob Petersen and  
John Cadotte when the term, Nanofiltration, was first used.)

## Foreword (First Edition, 2005)

It was around the end of 1984. A few of us were gathered in the office of FilmTec's advertising manager to tackle a problem of terminology. What does one call a reverse osmosis process that selectively and purposely allows some ionic solutes in a feed water to permeate through? The phrase "loose RO" had been used, but it connoted the idea of leaky membranes. FilmTec had moved on to the expression "hybrid RO-UF," planning to name some products as hybrid RO-UF membranes. However, neither "loose RO" nor "hybrid" translated well into Japanese. According to FilmTec's Japanese distributor, the latter term carried objectionable overtones in Japanese.

The source of this naming problem was NS-300, a membrane discovered at North Star Research Institute. In 1976, John Cadotte combined piperazine with trimesoyl chloride, alone and blended with isophthaloyl chloride, to produce a series of thin-film-composite membranes with surprisingly high flux. These membranes also exhibited high permeability to aqueous chloride ions but high rejection of aqueous sulfate ions. The membrane was an orphan. The U.S. government's Office of Water Research and Technology, which sponsored the research, did not see any particular usefulness of the membrane for its purposes, which were primarily the development of national water resources. But FilmTec took an interest in it, with industrial applications in mind. Among these were salt whey concentration, pulp and paper effluent treatment, and preparation of sulfate-free seawater on oil platforms for secondary oil recovery operations in barium-containing oilfield strata. FilmTec had named its version of the membrane as FT40. Naming the membrane was not an issue. Naming the process was the problem!

I remember suggesting that FilmTec adopt the term "nanofiltration" for such processes. The term had at least some logical basis. First, Sourirajan and Matsuura had calculated the size of a hypothetical capillary pore in annealed cellulose acetate membranes to be about  $9 \text{ \AA}$  to  $0.9 \text{ nm}$  – in their development of the surface force/capillary flow model of reverse osmosis. Our "loose" membranes would correspondingly have hypothetical capillary pores slightly larger, presumably in the  $1.0\text{--}1.2 \text{ nm}$  range. Second, hyperfiltration was a term often used in early research on reverse osmosis membranes, and was deemed synonymous with reverse osmosis. Why not simply connect "nano" to

“filtration”? This, “nanograde” solvents were in wide use, and a term incorporating “nano” would connote goodness, purity, quality (That’s a suggestion designed to carry great influence with an advertising man!). One of the advantages of working in a small company was the ability to make instant decisions. We left that meeting with a mandate to use nanofiltration in our trade literature and publications. And two of FilmTec’s “FT” membranes were immediately recast as “NF” membranes.

It did not occur to me at the time that the term nanofiltration could be easily transliterated into foreign languages. That is, nanofiltration could be used without modification in some languages, and easily adopted into others by minor changes in spelling. Further, nanofiltration as a descriptor carried no “baggage” with it. As a new word, it referred to a particular membrane process for which it was coined, and to no other. Within a few years, other membrane scientists began using the word nanofiltration. Its widespread use today is testament to the need for just such a descriptor in the membrane lexicon.

As the body of literature on nanofiltration membranes and processes has expanded, the meaning of the term has necessarily been stretched to accommodate the wide range of features. It is appropriate that this book begins with an effort to define the term. An interesting aspect of nanofiltration membranes is the fact that so many parameters can come into play, when one tries to model and characterize the pressure-driven selectivities of such membranes. Parameters may include, for example, ionic interactions such as Donnan ion repulsion, site sharing phenomena by polyvalent ions in charged membranes, solute–membrane adsorption affinities, and steric size interactions. Compared to modeling of nanofiltration membrane behavior, modeling the behavior of high rejection reverse osmosis membranes was a comparatively simpler task.

Standard reverse osmosis for water purification has matured in many respects, and has become in large part the domain of engineers engaged in issues of yield, consistency, quality, and manufacturing efficiency. The objective is always the same – make a pure water permeate with the lowest cost. But nanofiltration, in my opinion, remains the most fascinating extension of reverse osmosis technology. Nanofiltration offers to the membrane scientist a variety of membrane possibilities and a plethora of fascinating applications. Reverse osmosis is like the main course of a dinner, like a beefsteak that can be prepared in only a limited number of ways, but satisfies the hunger. Nanofiltration, on the other hand, is like the wine menu accompanying the meal – an opportunity for creativity and exploration. As you explore this book, enjoy the wonderful variety it provides on the subject of nanofiltration.

23 December 2002  
Minneapolis, MN, USA

*Robert J. Petersen*  
Director of Research (from 1978), Filmtec Corp

## Acknowledgements

This book has been on a 20-year journey that started with an idea in 2000 based on the realization that nanofiltration was not covered in its own right by membrane books existing at the time. The first edition “Nanofiltration: Principles and Applications” was eventually published by Elsevier in 2005. Fifteen years on, the second edition “Nanofiltration: Principles, Applications, and New Materials” is about to appear with Wiley-VCH.

Editing the first book was a challenge for a then very young scientist, while the excitement of working with so many much more established colleagues was immense, providing the driving force. Repeating this effort two decades later brought new challenges. Time and time again we wondered where the energy should come from to complete this task that appeared to be delaying into the infinite. But, we made it! We are deeply indebted to our contributors for their patience and for giving in to our incessant reminders and ultimately delivering the goods. Many of the original authors from the first edition had since retired or changed research direction, which left us with material too good to discard, yet also needing new caretakers to honor these efforts and produce new updated chapters. This was managed on a very individual chapter-by-chapter basis and we have communicated the wishes of those involved carefully. This new edition has been enriched with several new chapters, as well as an entire new section looking at new materials relevant for nanofiltration.

While the foundations of the second edition lie firmly grounded in the original work, several key transitions have transpired. Thus, we would like to thank Professor David Waite (UNSW, Australia) for his initial contributions as an editor of the first edition, and our previous publisher Kostas Marinakis (Elsevier, Netherlands) for the long cooperation and handing over to Wiley-VCH in the most cooperative manner. Warm thanks go to Dr. Frank Weinreich (Wiley-VCH) for being available, effective, and a pleasure to deal with, even concerning the most challenging difficulties. Hopefully we can meet in person soon!

The highlight for this second edition was to be the book launch in the form of an international conference “Nanofiltration 2020” at the Achalm, Germany, in July 2020. Given the global COVID-19 pandemic this event was postponed to July 2021 and again to June 2022, and it appears we may have needed the extra time to finally get published. The generosity of our publisher (Dr. Frank Weinreich, Wiley-VCH) with sponsoring the wine for the event dinner is gratefully acknowledged. We are, of course, looking forward to this event in a very special environment and to celebrate the joint effort of the book, hopefully in person.

The foreword of the first edition was kindly provided by Robert J. (Bob) Petersen, while David H. Furukawa has provided the foreword for the current edition. Both are included in this book. Bob Petersen and David Furukawa are witnesses to the birth of the term nanofiltration. David H. Furukawa was a consultant to Filmtec from 1978, and VP Marketing from 1983, while Robert J. Petersen was the Director of Research (from 1978), Filmtec Corp. Both attended the meeting with John Cadotte when the term, Nanofiltration, was first used. It is a great privilege to have this moment of history present through the forewords of both editions.

Most importantly of course, about 70 authors from 16 countries have contributed to this new edition and put up with our requests, reviews, comments, formatting requirements, revising proofs, and (well, at least to an extent!) the deadlines some well into their retirement – all in return for a token honorarium. It has been a great pleasure to be in touch with you over the last several years, many of you several decades now, and we are especially grateful to those who agreed at the last minute to fill in for those who could no longer contribute so that the book could still proceed.

Reviewing book chapters is an enormous task and we appreciate the time taken and contributions made by the scientific reviewers in assisting the editors, with the challenge to peer review each chapter by two to three international experts. Great appreciation goes to colleagues and friends, some of whom have reviewed several chapters, some at very short notice, and most generously giving time and ideas.

Sadly, our co-author Dr. Martin Timmer and our reviewer Dr. Darrel Alec Patterson passed away – both far too early – during the preparation of the second edition. We will keep both in our memory. Darrel wrote to us in 2006 very poignantly “I very much enjoyed your excellent book “Nanofiltration – Principles and Applications.” It is great to have works from so many well regarded experts in one volume! Just one comment – the quote by anonymous in the Acknowledgements section can be attributed to the late and great Douglas Adams (author of among other things, “The Hitchhikers Guide to the Galaxy’ in its various forms) who was quite well known for his lack of regard for deadlines (to the chagrin of his publishers!).” Reading Darrel’s words once again, we realized that the tempo was more sedate in the second edition, and the deadlines seemed to make less of a whooshing sound ... or maybe they did, but we did not notice them above the background noise.

Thank You to the scientific reviewers;

---

Professor Dr. Mathias Ulbricht	University of Duisburg Essen, Germany
Professor Suzana Nunes	KAUST, Saudi Arabia
Professor Dr. Ing. Thomas Wintgens	RWTH Aachen, Germany
Professor Bart Van der Bruggen	KU Leuven, Belgium
Dr. Anita Buekenhoudt	VITO, Belgium
Professor Long Nghiem	UTS, Australia
Professor Andrew Zydney	The Pennsylvania State University, USA
Professor Viatcheslav Freger	Technion, Israel
Professor Anthony Szymczyk	University of Rennes, France
Professor Menachem Elimelech	Yale University, USA
Professor Alberto Tiraferri	Politecnico di Torino, Italy
Professor Dr. Stefan Panglisch	University of Duisburg Essen, Germany
Professor Maxime Pontie	University of Angers, France
Professor Dr. Ing. Wilhelm Urban	University of Darmstadt, Germany
Dr. Harry Seah	PUB, Singapore
Professor Jack Gilron	Ben Gurion University, Israel
Professor Darrell Alec Patterson <sup>†</sup>	Bath University, UK
Professor Dr. Jörg Hinrichs	University of Hohenheim, Germany
Michael Wunsch	Hager + Elsässer Water, Germany
Professor Dr. Steffen Schuetz	Mann + Hummel, Germany
Andreas Flach	MFT, Germany
Professor Abdelhadi Lhassani	Université Sidi Mohamed Ben Abdellah, Morocco
Professor HariKrishnan Ramanan	IIT Tirupati, India
Professor Seungkwon Hong	Korea University, South Korea
Professor Emile Cornelissen	KWR, Netherlands
Professor Benoit Teychene	University of Poitiers, France
Professor Katsuki Kimura	Hokkaido University, Japan
Dr. Filicia Wicaksana	University of Auckland, New Zealand
Professor Dr. Bryce Richards	Karlsruhe Institute of Technology, Germany
Professor Chuanfang (Ted) Yang	Chinese Academy of Sciences, China
Professor Sylwia Mozia	West Pomeranian University of Technology Szezecin, Poland
Professor Ivo Vankelekom	KU Leuven, Belgium
Professor Murielle Rabiller-Baudry	University of Rennes, France
Professor John Pellegrino	University of Colorado Boulder, USA
Professor Berrin Tansel	Florida International University, USA
Dr. Pia Lipp	TZW, Germany
Dr. Michael Hirtz	Karlsruhe Institute of Technology, Germany
Professor Chuyang Tang	The University of Hong Kong, Hong Kong
Dr. Frank Biedermann	Karlsruhe Institute of Technology, Germany
Dr. Francesco Fornasiero	Lawrence Livermore National Laboratory, USA
Professor Tony Fane	UNSW, Australia

---

We trust the effort will inform many new readers interested in nanofiltration while also providing a comprehensive work to the ever-increasing number of nanofiltration experts. We are grateful (in advance) for any comments, discussions, translation requests, and feedback on the book and the topic in general. With the tremendous interest in nanofiltration, from materials development through transport mechanisms to applications, it promises to remain an exciting field. We are looking forward to the next 20 years of nanofiltration and to welcoming many more to the nanofiltration family. There is a lot to be done with and discovered about nanofiltration yet.

Enjoy the read!

*Unfortunately, there is no such membrane that can separate Happiness and Sorrow of our life*

(Professor Takeshi Matsuura)

## Dedication

This book is dedicated to two very special ladies of the broader membrane family

### **Ora Kedem and Miriam Balaban**

Ora Kedem is an author in this book and a brilliant scientist with an incredible career in membranes – focusing on transport processes as well as desalination technologies.

Miriam Balaban is the most successful disseminator and pioneer in publishing in the area of water and desalination – with a passion for reconciliation.

Thank you for being an incredible inspiration with a life that achieved tremendous success despite – or because – of the very challenges that life happens to provide.

Their lives tell stories of commitment and resilience. These strong women are an inspiration to everyone privileged enough to meet them – whether discussing science or life matters – both remaining active well into their nineties. WOW!

An inspiration to keep going – no matter what – and to be incredibly grateful for what life has already provided. Not perfect – but a lot better than the conditions of our foremothers, such as Marie Curie and Lise Meitner.

Women remain underrepresented in membrane technology – including as authors in this nanofiltration book – as well as in the water industry and in leadership positions as a whole, yet role models like Ora and Miriam clearly show what women are able to achieve when given the opportunity and are brave enough to rise to the challenge.

THANK YOU and SHALOM!



*(Tel Aviv, May 2017)*

*(Toulouse, June 2019)*



## Introduction

*Andrea I. Schäfer*

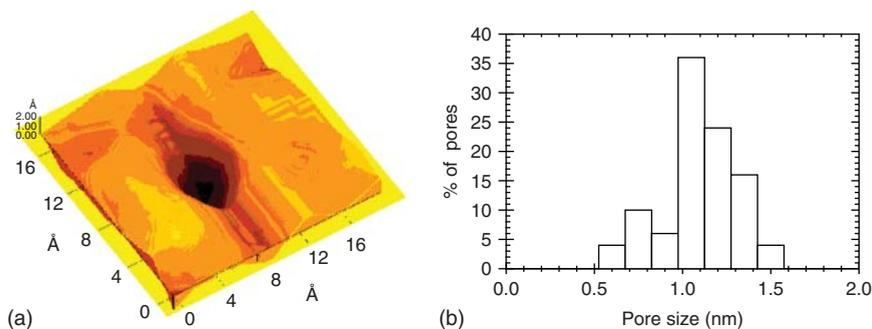
Nanofiltration (NF) is a liquid-phase pressure-driven membrane process with separation properties that overlap with both ultrafiltration (UF) and reverse osmosis (RO). Figure 1 indicates the approximate range of solute sizes relevant to the family of liquid-phase, pressure-driven membrane processes from RO to MF in comparison with other membrane processes, where the boundaries between the various processes are not precisely defined. Here, NF can be seen to fill an important gap between UF and RO, where it is able to fractionate ions and retain relatively low molecular weight organic solutes. These are important separations that have commercially significant applications. Notably, as defined in Figure 1 as “micros” and “macros,” NF can retain typical water contaminants such as humic substances almost completely, “micros” such as micropollutants to a significant extent while the retention of salt can be tuned to a great extent with the choice of membrane between loose and tight NF.

In the Introduction section to the first edition “Nanofiltration – Principles and Applications” (2005) [1], the question of whether NF deserved to be considered a process in its own right or whether it was really very loose reverse osmosis (RO) or very tight ultrafiltration (UF) was discussed. At that time, this was a moot point, even though NF had just caught up with the volume of publications of reverse osmosis. However, given the unique properties of NF membranes, the separation mechanisms identified, and the application niches that have developed, it is evident that NF fits into a special category. The first edition of this book helped to define the domain of nanofiltration, and the subsequent decade has confirmed the unique attributes of NF.

It is now widely accepted that NF membranes have individual pores, unlike RO membranes that have dynamic “free volume” between polymer domains. Figure 2a shows an atomic force microscopy (AFM) image, possibly the first, of a pore in a NF membrane and Figure 2b shows the measured pore size distribution of that particular membrane [2, 3]. The nanometer-scale pores allow passage of solvent water (approximate diameter is 0.275 nm) but retain dissolved species – very close to the size of water – on the basis of steric hindrance, electrostatic and dielectric interactions, as well as interactions with the membrane polymer. For example, differences in hydrated ion size and charge

Contaminant size	Ionic range		Molecular range		Macromolecular range	Microparticle range	
Pore size (μm)	0.001		0.01		0.1	1	10
Molecular weight (g/mol)	100	200	1000	100 000	500 000		
Solutes	Aqueous salt		Virus		Bacteria		
	Inorganic contaminants		Proteins		Micro plastics		
	MICROS (<1 nm) Pharmaceuticals, steroid hormones, personal care products, pesticides, low molecular weight acids and neutrals, etc.		Microsolutes		Humic acids		
			MACROS (>1 nm) Proteins, humic substances, natural organic matter, biopolymers, nanoparticles, viruses				
Membrane separation processes	Electrodialysis		Membrane bioreactor				
	Reverse osmosis		Membrane distillation				
	Nanofiltration			Microfiltration			
	Pervaporation		Ultrafiltration				

**Figure 1** Liquid-phase pressure-driven membrane processes – typical solute separations at the 1 nm solute scale distinguishing ultrafiltration from reverse osmosis.



**Figure 2** Pores in NF membranes: (a) AFM image and (b) pore size distribution. Source: Adapted from [2, 3].

provide the mechanisms for the separation of monovalent and multivalent ions that is typical of NF. More generally, the unique separation properties for typical nanofiltration membranes with negative surface charge have been identified previously [1] and characterized by the following:

1. rejection of ions with more than one negative charge (multivalent anions), such as sulfate ( $\text{SO}_4^{2-}$ ) and phosphate ( $\text{PO}_4^{3-}$ ), being virtually complete;
2. rejection of sodium chloride (NaCl) varying from about 70% down to 0%, while even a negative rejection may be observed in mixed systems with multivalent cations;

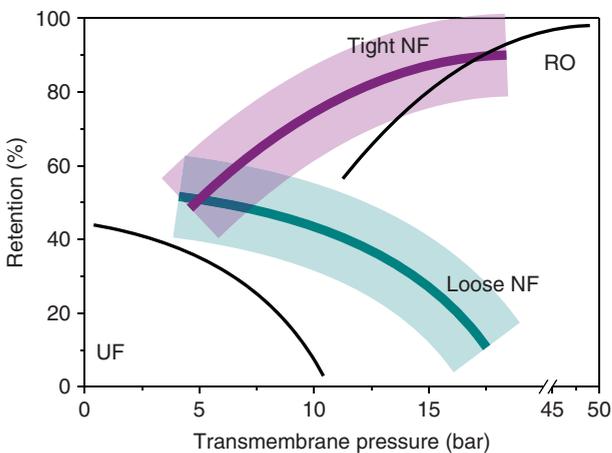
3. rejection of uncharged, dissolved materials and also of positively charged ions in solutions to relate mostly to the size and shape of the molecule in question; and the
4. molecular weight cutoff (MWCO) to be in the range of 150–300 Da.

In addition, NF has a growing role in nonaqueous separations that are largely based on size exclusion mechanisms, modified by membrane solute interactions such as swelling.

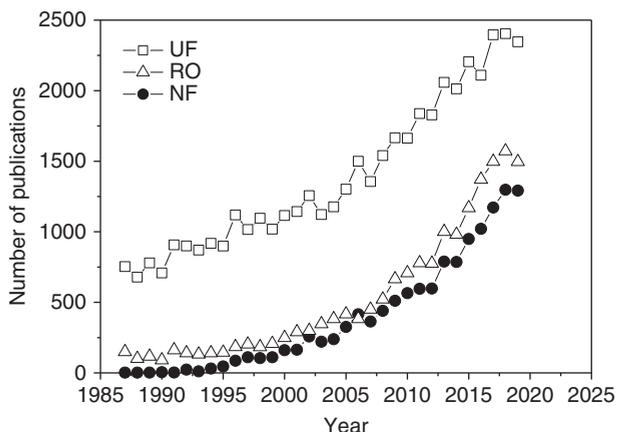
In terms of performance, NF membranes can exhibit water permeabilities,  $A$ , in the range of about  $5\text{--}15\text{ l/m}^2\text{ h bar}$ , which are up to an order of magnitude higher than RO, but 1 or 2 orders of magnitude less than typical UF. This offers, at appropriate rejection, a significant energy saving compared to RO. This is a major advantage in many applications.

The retention behavior vs. pressure can reflect both the behavior of UF and RO (Figure 3), depending on the membrane and solute. A solute with a loose membrane with partial retention will show a more typical UF behavior where retention may decrease with pressure. For partially retentive UF membranes, and in the absence of fouling, the effect of increased pressure is typically a reduction in the observed retention (Figure 3). In the UF process, solutes are convected through the pores by solvent flow, and this solute transport is exacerbated by concentration polarization (CP), which tends to be much more significant in UF, whereas CP increases with flux and solute size. The same is true for NF, albeit for different solutes to UF. Tight membranes are typically showing an increase toward an asymptote as in RO. This trend can be explained in terms of the solution–diffusion transport mechanism applied to “nonporous” RO membranes, which assumes that solute and solvent transport are uncoupled; pressure increases solvent water flow, and “dilutes” the solute in the permeate.

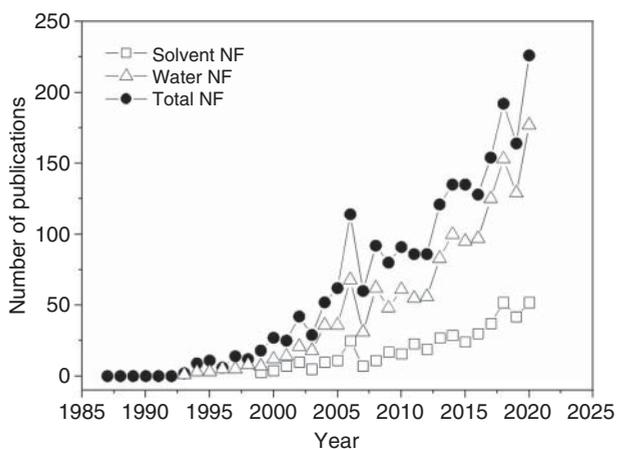
The “RO-like” behavior of tight NF is likely a combination of the effect of restricted convection in confined pores and the modest level of CP in typical



**Figure 3** Schematic trends of solute retention vs. pressure for ultrafiltration, loose/tight nanofiltration, and reverse osmosis (lines are indicative only).



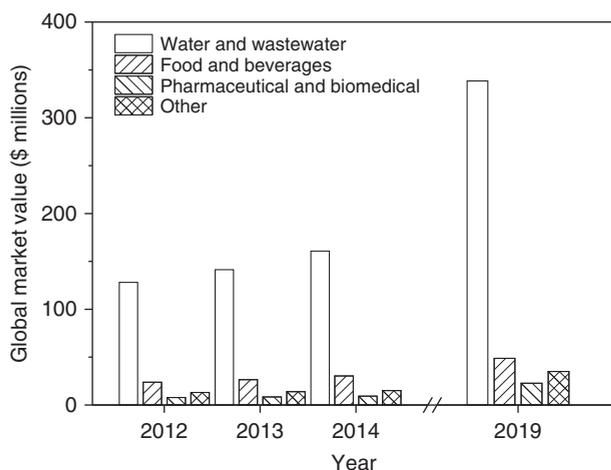
**Figure 4** Publication trends for ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO).



**Figure 5** Publications in Journal of Membrane Science (Elsevier) for nanofiltration (NF) and both Solvent and Water NF.

NF applications, whereas in loose NF, the behavior is much more “UF-like” for certain solutes.

The growing interest in NF is evidenced by research outputs (number of publications) and commercial activity (global market value). Figure 4 shows publication trends from 1987 based on the topic “Nanofiltration” from the Web of Science database, while Figure 5 shows the same trend in the Journal of Membrane Science. Since the first edition (2005), the annual output of NF-related publications has increased by a factor of >4, from about 300 to about 1300 (in 2019). Publications in the Journal of Membrane Science (JMS) reflect these trends with NF (in topic) rising from about 60 in 2005 to about 160 in 2019. Unsurprisingly, the majority of these papers relate to water treatment, which reflects that hardness removal, organic matter (humic substances and



**Figure 6** Global Market for Nanofiltration Membranes, 2012–2019 (US\$ millions). Source: Data from BCC Research [4].

**Table 1** Global Market for Nanofiltration Membranes with Market Segments (CAGR is the compound annual growth rate [CAGR] with a constant rate of return).

Market segment	2012	2013	2014	2019	CAGR% 2014–2019
Water and wastewater treatment	128.1	141.4	160.8	338.5	16.1
Food and beverages	23.8	26.5	30.4	48.8	9.9
Pharmaceutical and biomedical	7.8	8.4	9.3	22.7	19.5
Others	13.1	13.9	15.1	35.1	18.4
<b>Total</b>	<b>172.8</b>	<b>190.2</b>	<b>215.6</b>	<b>445.1</b>	<b>15.6</b>

Source: Data from BCC Research [4].

disinfection by-product precursors) removal, and trace contaminants are major concerns in the water industry and NF can remove many of these effectively. An increasing number relate to NF of organic solvents, and this research interest may anticipate a future growth area for NF applications.

Commercially, NF is experiencing an equally significant growth in applications reflected in global market value and compound annual growth rate (CAGR). The data in Figure 6 and Table 1 were sourced from a BCC Research report [4] and show

- a predicted CAGR from 2014 to 2019 to be >15.0%;
- a global market of nearly US\$0.5 billion by 2019, of which ~75% is for the water industry;
- steady growth in applications in the food and beverage sector and the pharmaceutical and biomedical sector.

A more recent BCC report [5] predicts a CAGR from 2019 to 2024 of 18.2% and a market of US\$518 million in 2019 growing to US\$1.2 billion in 2024, of which

~75% is for the water industry. Since the first edition in 2005, the NF market has probably grown from 2.5 to 4-fold, and the data provided in Figure 6 and Table 1 predict a very strong future for nanofiltration indeed.

Such a promising outlook raises the question what impact this NF “boom” will have. Savings in energy compared to RO will make a positive contribution to carbon emissions, the treatment of wastewaters in particular will reduce pollution and enable the recovery of previous resources, and the development of decentralized water treatment systems can alleviate much water-related illness and death in developing countries.

On the other hand, the increase in NF application will cost energy and cause CO<sub>2</sub> emissions, will produce concentrates that are to be treated (zero liquid discharge technologies are to date not yet available and/or economical), and, ultimately, the vast nanofiltration market will result in mountains of spent membrane modules to be disposed of. These negative features maybe offset by the use of renewable energy-driven NF (see Chapter 22), development of zero liquid discharge technologies (including resource recovery) [6], and strategies to reuse or recycle RO and NF membrane modules [7, 8].

One can only wish that the enormous market and inevitably profits made will be reinvested into meaningful research to develop more efficient technologies that have less of an impact and create a net positive benefit to our environment. A new generation of engineers and researchers may indeed be driven more by environmental impact than financial gain.

May this book provide a contribution to teach about nanofiltration and inspire a new generation of exciting applications and developments beyond nanofiltration as we currently know it.

The book is divided into three parts – a fundamental section on principles, an applications section, and a new materials section. The overview layout for the new book is presented in Figure 7.

From a history of nanofiltration chapter (Chapter 1), the book takes the reader to membrane preparation and materials (Chapter 2), module design and operation (Chapter 3), membrane characterization (Chapter 4), NF membrane performance modeling (Chapter 5), solute speciation effects in NF (Chapter 6), and an overview of current understanding of fouling (Chapter 7) to pretreatment processes and process combinations with NF (Chapter 8), which concludes Part 1: Nanofiltration Principles.

In Part 2, Nanofiltration Applications, the contents reflect the major, and in some cases potential, applications of nanofiltration. This takes the reader from NF in water treatment (Chapter 9) and water reclamation (Chapter 10) via NF in the food industry (Chapter 11), chemical processing (Chapter 12), pulp and paper (Chapter 13), and textiles (Chapter 14) to landfill leachates (Chapter 15), nanofiltration bioreactors (Chapter 16), photocatalytic reactors (Chapter 17), metal and acid recovery (Chapter 18), trace contaminant removal (Chapter 19), the growing area of nonaqueous applications (Chapter 20), issues of NF retentate treatment (Chapter 21, new), and use of renewable energy to provide power to NF (Chapter 22, new).

## PART 1: Nanofiltration Principles

- Chapter 1: History of Nanofiltration Membranes 1960 to 1990
- Chapter 2: Nanofiltration Membrane Materials and Preparation
- Chapter 3: Nanofiltration Module Design and Operation
- Chapter 4: Nanofiltration Membrane Characterization
- Chapter 5: Modeling Nanofiltration of Electrolyte Solutions
- Chapter 6: Chemical Speciation Effects in Nanofiltration Separation
- Chapter 7: Fouling in Nanofiltration
- Chapter 8: Pretreatment and Hybrid Processes

## PART 2: Nanofiltration Applications

- Chapter 9: Water Treatment
- Chapter 10: Water Reclamation, Remediation and Cleaner Production with Nanofiltration
- Chapter 11: Nanofiltration in the Food Industry
- Chapter 12: Nanofiltration in the Chemical Processing Industry
- Chapter 13: Nanofiltration in the Pulp and Paper Industry
- Chapter 14: Nanofiltration of Textile Dye Effluent
- Chapter 15: Nanofiltration in Landfill Leachate Treatment
- Chapter 16: Nanofiltration Bioreactors
- Chapter 17: Photocatalytic Nanofiltration Reactors
- Chapter 18: Nanofiltration in Hydrometallurgy
- Chapter 19: Trace Contaminant Removal with Nanofiltration
- Chapter 20: Organic Solvent Nanofiltration
- Chapter 21: Nanofiltration Retentate Treatment
- Chapter 22: Renewable Energy Powered Nanofiltration

## PART 3: Nanofiltration New Materials

- Chapter 23: Carbon Nanotube Composite Materials for Nanofiltration
- Chapter 24: Biomimetic Nanofiltration Materials
- Chapter 25: Novel polymer-based materials for nanofiltration
- Chapter 26: Graphene based nanofiltration

**Figure 7** Nanofiltration – Principles, Applications, and New Materials book structure.

In Part 3, New Nanofiltration Materials, four new chapters enrich the book in terms of carbon nanotube composite materials (Chapter 23, new), artificial ion and water channels (Chapter 24, new), novel polymer-based materials (Chapter 25, new), and graphene-based nanofiltration (Chapter 26, new). This leaves the question – what really is nanofiltration?

In the foreword of the first edition (see earlier pages), Bob Petersen (former CEO of Filmtec) concluded that “*NF offers the membrane scientist a variety of*

*membrane possibilities and a plethora of fascinating applications.*” It is the aim of this second edition of “Nanofiltration – Principles, Applications, and New Materials” to update the science and engineering of NF membrane technology, summarize the advances over the past decade or two, and look at how this exciting field may change in the coming decades.

**Enjoy the new and revised journey into Nanofiltration!**

## References

- 1 Schäfer, A.I., Fane, A.G., and Waite, T.D. (2005). *Nanofiltration: Principles and Applications*. Oxford: Elsevier.
- 2 Bowen, W.R. and Doneva, T.A. (2000). Atomic force microscopy studies of nanofiltration membranes: surface morphology, pore size distribution and adhesion. *Desalination* 129: 163–172.
- 3 Bowen, W.R. and Welfoot, J.S. (2002). Modelling of membrane nanofiltration – pore size distribution effects. *Chem. Eng. Sci.* 57: 1393–1407.
- 4 BCC Research LLC (2014). Global Markets and Technologies for Nanofiltration. *Report NAN045B*.
- 5 BCC Research LLC (2019). Global Markets and Technologies for Nanofiltration. *Report NAN045C*.
- 6 Lu, K.J., Cheng, Z.L., Chang, J. et al. (2019). Design of zero liquid discharge desalination (ZLDD) systems consisting of freeze desalination, membrane distillation, and crystallization powered by green energies. *Desalination* 458: 66–75.
- 7 Lejarazu-Larrañaga, A., Molina, S., Ortiz, J.M. et al. (2020). Circular economy in membrane technology: using end-of-life reverse osmosis modules for preparation of recycled anion exchange membranes and validation in electro dialysis. *J. Membr. Sci.* 593: 117423.
- 8 Lawler, W., Bradford-Hartke, Z., Cran, M.J. et al. (2012). Towards new opportunities for reuse, recycling and disposal of used reverse osmosis membranes. *Desalination* 299: 103–112.

**Part I**

**Principles**



## 1

## History of Nanofiltration Membranes from 1960 to 1990

*Charles Linder and Ora Kedem*

*Ben-Gurion University of the Negev, Zuckerberg Institute for Water Research, The Jacob Blaustein Institutes for Desert Research, Sede Boqer Campus, Laboratory for Desalination and Water Treatment Research, P.O. Box 653, Beer-Sheva 84990, Israel*

### 1.1 Overview

This chapter describes the developments in nanofiltration (NF) membranes from the 1960s to the early 1990s that brought NF technology to its current status. NF began as a spin-off of reverse osmosis (RO) and ultrafiltration (UF) and was thus originally known as open RO, loose RO, or tight UF. The origin of NF membranes – and indeed of most pressure-driven membranes – can be traced back to the late 1950s and the development of the Loeb–Sourirajan (L–S) anisotropic or asymmetric cellulose acetate (CA) membranes for seawater desalination. These membranes constituted the basis for modern membrane development in RO and UF. Within a few years, RO composites comprising a submicron coating of a selective film on an asymmetric UF support were developed. Progress in RO and UF technology gave birth to yet another discipline – NF. This R&D effort spanned a remarkably short period of time of about 15 years, starting in 1960. In addition, by the early 1970s, a full range of CA asymmetric (or anisotropic) membranes spanning the entire spectrum, from RO through NF to UF, were available. In the search for improved water treatment economics and for other commercial applications, the limitations of CA as a membrane material were, however, quickly revealed. These limitations restricted the range of applications and impeded efforts to expand NF into new areas. One approach to overcoming this problem was the development of integrally skinned asymmetric membranes from materials other than CA, such as polyamides, polyethersulfone (PES), polysulfones, chlorinated polyvinyl chloride (PVC), and polyvinylidene fluoride (PVDF). Although open NF membranes could be made by this approach, the selectivity/flux combination needed for many applications could not be achieved. The breakthrough in NF took place with the invention of noncellulosic composites based on coating UF supports with a submicron selective barrier by various methods such as interfacial polymerization. The work on composites started in the 1970s, but composite NF membranes were not widely available until the second half of the 1980s. Another approach, which followed later, was

the development of NF ceramic and inorganic membranes. Today, NF has the power to solve many separation problems, but such actual applications are small in number compared to the potential applications that still await improvements in membrane stability, flux, and selectivity. Ongoing developments in NF membrane preparation and materials are described in Chapter 2.

## 1.2 Introduction

Typically, separations of monovalent and divalent salts and organic solutes of molecular weights up to 1000 characterize membrane selectivity between the RO and UF regions. The range of membrane separation characteristics that are covered by this definition are currently known as NF. This term was not coined until the second half of 1980s, but in reality, such membranes already existed in the 1960s, being categorized as open RO, loose RO, intermediate RO/UF, selective RO, or tight UF membranes.

The beginnings of NF are intertwined with the early days of RO, which are vividly described by Loeb in his “Reminiscences and Recollections” [1]. Production of potable water from saline solutions was first demonstrated by Reid and Breton [2], working with Breton, at the University of Florida. They accomplished desalination at a low flux with a cellulose acetate (CA) membrane. The desalination program at UCLA arrived at the use of commercially available CA membranes from a different starting point: they had been looking for the manifestation of the negative salt adsorption near the water/air interface predicted by the Gibbs equation. In 1959, Loeb and Sourirajan experimented with porous CA membranes obtained from Schleicher and Schuell (S&S), which after being heated under water acted as desalination membranes only if installed in the experimentally determined “right direction.” Loeb considered this behavior as “...the seminal feature leading to the success of RO desalination and (to the) surge of interest in...membrane separation processes.” The big step forward was the dramatic increase in desalination flux with the development of the Loeb–Sourirajan (L–S) membranes. They developed casting solutions resulting in anisotropic RO membranes with fluxes 10 times higher than those of the S&S membranes, with equivalent desalination. This development was based on the 1936 work of Dobry, who cast CA membranes from an aqueous, saturated solution of magnesium perchlorate [3]. The mechanism of membrane formation was later termed by Kesting as phase inversion [4]. It was shown by the electron micrograph studies of Riley et al. [5, 6] that such membranes consisted of a thin (less than 1- $\mu\text{m}$ ) layer on top of a much thicker porous sublayer.

The degree of desalting obtained with CA membranes depended on the conditions of heat treatment used to anneal and further densify the top dense layer. It was realized that the limited rejection observed with partial annealing could be exploited in various applications, later to be called NF.

In the early 1970s, CA and other cellulose esters were the standard materials used for making NF membranes, but it rapidly became evident that their lack of chemical and biological stability severely limited the range of water and industrial

applications. Thus, developments after 1975 concentrated on other materials and other membrane fabrication processes, resulting in a second generation of membranes based on noncellulosic NF composites.

In the second half of the 1980s, improvements in the stability, selectivity, and flux of NF membranes were reflected in a growing number of applications. NF was then being accepted as a useful unit operation for the water treatment, dairy, and chemical industries. At that time, the term nanofiltration (NF) was introduced by FilmTec; it was derived from the membrane's selectivity toward non-charged solutes of approximately 10 Å or 1 nm cutoff.

Today, NF membranes are produced in spiral wound, plate and frame, hollow fiber, capillary, and tubular configurations from a range of materials, including cellulose derivatives, synthetic polymers, inorganic materials, and organic/inorganic hybrids. A short history of the developments that have brought us to the present state of art follows. Emphasis is placed on membrane materials, chemistry, and separation mechanisms, with implicit, but full, recognition of the developments in module design and membrane fabrication and applications that have made commercial NF possible.

## 1.3 First-Generation NF Membranes

Remarkably, in the early 1970s, a whole range of membranes including what we now call NF were commercially available. A list of such commercially available membranes taken from a 1972 review chapter by Lonsdale [7] is given in Table 1.1, covering a range of selectivity between RO and UF. As implied by the Table and article, NF membranes were not a distinct group but rather classified as either open RO or tight UF. In addition, the membranes were either asymmetric (anisotropic) or symmetric (isotropic), and the RO or NF membranes were either based on cellulose or polyelectrolyte complex membranes.

### 1.3.1 Cellulose Acetate Asymmetric Membranes

The 1964 U.S. patent of Loeb and Sourirajan describes in addition to membranes with 95+% rejection, open RO membranes with rejections in the range of 20–80% [8]. As pointed out in these patents and others, a wide range of open RO selectivities could be achieved by variation of casting solution composition, evaporation period, and annealing (Table 1.2) [9]. Subsequently, other workers also found that, by incorporating additives into the casting solution, CA membranes could be formed over a wide range of molecular weight cutoffs (MWCs) that extended from tight RO up to UF, including the intermediate NF range [7]. For example, Cohen and Loeb [10] showed how CA membranes could be cast and modified by heat treatment to form either membranes that retain sucrose and multivalent ions with sodium chloride passage or membranes that pass sucrose but retain multivalent inorganic or organic ions. A transmission electron micrograph of a Loeb–Sourirajan asymmetric cellulose acetate membrane shows the characteristic integrally skinned layered upper surface on a porous support

**Table 1.1** Commercially available loose RO (NF) membranes in 1973.

Membrane:	Manufacturer	Chemical	Net pressure	Water flux	Solute	Rejection
Type		composition	psi	l/m <sup>2</sup> d		%
Loeb–Sourirajan: anisotropic, unannealed	Several	Cellulose acetate	150	20 gfd	NaCl	25
Gel cellophane	DuPont, Union Carbide	Homogeneous	100	1.5	Sucrose	15
Polyelectrolyte: anisotropic (Diaflo UM-3)	Amicon	Sodium polystyrene sulfonate-polyvinylbenzyl triethylammonium chloride	100	25	Sucrose	90
Polyelectrolyte: Anisotropic (Diaflo UM-2)	Amicon	Sodium polystyrene sulfonate-polyvinylbenzyl triethylammonium chloride	100	60	Sucrose	50
Anisotropic: Pellicon PSAC	Millipore	Cellulose ester	100	120	Sucrose	40–60

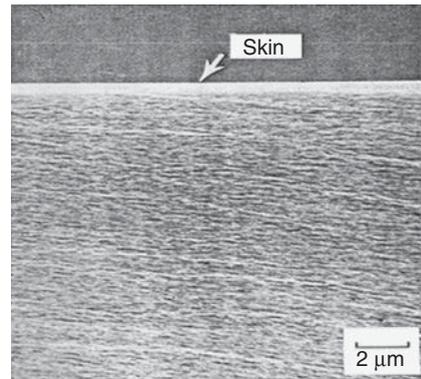
Source: From Lonsdale 1972 [7], Table 8, p. 160 with permission from the John Wiley and Sons.

**Table 1.2** Influence of evaporation and annealing temperature on flux/rejection of Loeb–Sourirajan membranes.

Membrane casting solution	Evaporation time (min)	Annealing temperature (°C)	Flux (GFD)	Rejection (%)
Acetone 45%, formamide 30%, 25% CA	1	23	97	25.2
Acetone 45%, formamide 30%, 25% CA	1	68.5	44	79
Acetone 45%, formamide 30%, 25% CA	1	71	25.6	88
Acetone 45%, formamide 30%, 25% CA	1	74	30	92
DMF75%/CA 25%	8	87.2	55.6	63
DMF75%/CA 25%	8	93	10.8	97
Acetone 64%/ DMF 21% CA 14%	3.5	Unheated	12.4	89

Membrane casting and evaporation step are carried out under ambient conditions. Membrane testing: 600 psi, RT, and 5000 ppm NaCl.

**Figure 1.1** Transmission electron micrograph cross section of the skin and upper porous layer of a Loeb–Sourirajan cellulose acetate membrane. *Source:* McKinney and Rhode [11]. Reproduced with permission of ACS Publications.



(Figure 1.1) [12]. This new method of phase inversion was found to be a very versatile tool for forming multilayered membrane structures with a controllable wide variety of morphologies and porosities [4].

Thus, in the early 1970s, membranes based on asymmetric CA, covering the NF range, became commercially available [13] from different suppliers, including Patterson Candy International Ltd. (PCI), Westinghouse Electric Corporation, Millipore, and De Danske Sukkerfabrikker (DDS), among others. These companies offered a range of asymmetric CA with cutoffs of, for example, 80%, 50%, 20%, and 0% rejection to NaCl and 95+% for 1000 MW dextran. The proposed uses were in water softening, fractionation of pharmaceutical fermentation liquors, whey desalting with lactose retention, skim milk concentration, fractionation of sugars, and concentration of antibiotics. One of the first applications was the

treatment of drinking water sources with membranes that were relatively non-fouling and had some chlorine resistance. In Florida, they were used for water softening as long ago as 1976 [14]. Commercial NF membranes based on CA, alone or in blends, were subsequently put into a variety of uses for water treatment, especially water softening and color removal from surface water. Although asymmetric CA had certain desirable characteristics, such as low fouling for some water sources, relative ease of cleaning, and chlorine resistance, the limitations of this membrane material were quickly revealed when improved water treatment economics and other commercial applications were sought.

### 1.3.2 Deficiencies in Cellulosic Membranes

The limitations of cellulosic membranes were primarily their poor biological and chemical stability (e.g. hydrolysis of the acetate groups), resulting in continual changes in rejection and flux loss because of compaction. In addition, although it was possible to cast a membrane with any given rejection within the NF range, initial fluxes were often not sufficiently high for many applications. It was quickly realized that while NF had the potential for application in a large number of processes, especially in the chemical industry, fulfilling this potential would, however, require membranes other than CA or polyelectrolyte complexes. To realize the full market potential of NF, the development catch phrase of the second half of the 1970s became stable noncellulosic membranes (produced at least in part by the powerful tool of asymmetric casting). From 1975, membranes with the following characteristics were sought:

- Improved solvent, oxidant, pH, biological, and mechanical stability.
- Selectivities and fluxes that would facilitate economically favorable replacement of two or more processes with a single process, e.g. the simultaneous concentration and purification of product streams.
- Very high retention to organic solutes (e.g. 99+%), low rejections of inorganic salts, and high water flux.
- For water softening and purification, higher rejections of divalent salts and organic solutes, monovalent salt passage, high fluxes with good compaction resistance, and chlorine resistance.

### 1.3.3 Polyelectrolyte Complexes

During the heyday of CA membrane development, Amicon Co. offered, in the 1960s, NF-type anisotropic membranes of polyelectrolyte complexes made by electrostatic interaction between strongly acidic and basic polyanions and polycations, respectively [15]. Invented by Michaels, membranes covering the whole range between RO and UF could be made by this approach. A series of membranes with MWCOs of 1000, 500, and 380 (sucrose) were commercialized for use in the concentration and demineralization of proteins and organic solutes. These membranes never achieved the same widespread application as asymmetric CA NF membranes, possibly because of their relatively low mechanical strength, flux loss because of compaction, and variable separation characteristics in high ionic strength solutions [7].

### 1.3.4 Polyamide Membranes

Starting in the 1960s, DuPont and Monsanto began using their extensive fiber technology to develop asymmetric hollow fibers of aromatic polyamides for RO seawater desalination [11, 16]. These polyamide membranes could also be made in the NF range by adjustment of the properties of the casting solution [17]. Although relatively hydrophobic, polyamide membranes gave good rejection, but they could not achieve the fluxes needed for many applications, and their chlorine resistance was poor. When more hydrophilic polyamides were used, higher flux was achieved, but it declined steadily under pressure because of compaction. In addition, the selectivities of the more hydrophilic polyamides were often too low. The introduction of ionic groups into the polymeric structures, for making membranes from aromatic polyamides (which originally gave good selectivity but low flux), improved the permeability but lowered the rejection. In general, casting of asymmetric membranes from polyamides could not be optimized to compete with existing separation processes or with the new technology of composite membranes.

### 1.3.5 Polysulfones and Other Polymer Membranes

Many other polymeric materials were investigated to make asymmetric RO and NF with improved chemical stability. This effort was guided by the electron micrograph studies of Riley et al. [5, 6] on the ultrastructure of anisotropic membranes and by the extensive work carried out on the phase inversion process by Kesting et al. It was shown that almost any polymer that forms a homogeneous solution in a solvent and a homogeneous precipitate could form asymmetric skin structures [4, 18–21]. Asymmetric membranes could be made from polycarbonates, chlorinated PVC, polyamides, polysulfone, PES, polyphenylene oxide, PVDF, polyacrylonitrile (PAN), copolymers of PAN/PVC, polyacetals, polyacrylates, polyelectrolyte complexes, and cross-linked polyvinyl alcohol (PVA). To a certain extent, the performance of the above-mentioned polymers as membrane-forming materials could be correlated with their hydrophobic/hydrophilic balance. Based on this classification, it was rapidly discovered that for asymmetric NF membranes, many hydrophobic polymers had too low flux or lacked selectivity, while hydrophilic polymers lost flux because of compaction. Achieving the optimum degree of cross-linking to prevent the swelling of hydrophilic polymers was also difficult.

Open asymmetric NF membranes with a MWCO of 1000 could, however, be made with some hydrophobic polymers such as polysulfone and PES; these membranes demonstrated good chemical and mechanical stability and reasonable flux [22]. They could not, however, be cast into selective NF membranes with lower MWCOs, such as for sucrose, without losing flux. Increasing the hydrophilicity of polyarylether sulfones by sulfonation [23] to improve flux did not work because to achieve the desired flux, the degree of sulfonation had to be increased to the point that reduced rejection. Carboxylation of polysulfone was tried by Guiver et al. [24] as a substitute for sulfonation to give high flux and selectivity with limited swelling. Model et al. [25] used the hydrophilic polymer

polybenzimidazole, which could be cast into NF asymmetric membranes with a range of MWCO as a function of casting solution and coagulation bath formulations. In a similar approach, Bayer developed sulfonated polybenzoxazindione membranes with an MWCO of 300. These membranes were, however, not developed commercially for NF, possibly because of the high cost of polymeric materials and/or because membranes with sufficiently high flux could not be made due to compaction.

## 1.4 Early Studies of Charged Reverse Osmosis (Hyperfiltration) Membranes

### 1.4.1 Dynamic Membranes

An inexpensive route to producing membranes rejecting salt by Donnan exclusion was envisioned by Kraus and his group working at the Oak Ridge National Laboratory [26]. By depositing polyelectrolytes on a robust support, a charged membrane could be formed. If the membrane became damaged or clogged, it could be removed or regenerated, hence the term dynamic membrane. Salt rejections of 25–85% could be achieved by circulating low concentrations of polymeric electrolytes, such as vinylbenzyl trimethylammonium chloride or polystyrene sulfonic acid, and depositing the polymers on a porous support [26]. As a transport barrier, this type of membrane was classified as NF in terms of its specific water permeability and MWCO [27]. Dynamic membranes were used to recover dyes and sizing materials in the textile industry [28].

### 1.4.2 Polyelectrolyte Membranes

Salt exclusion by membranes carrying fixed charges and the general properties of such polyelectrolyte membranes have been well known to physiologists for many decades; such membranes have been discussed by Meyer and Sievers [29] in the 1930s and by Teorell [30] in 1953. The salt rejection expected in hyperfiltration through collodion membranes, chemically modified for carrying a fixed charge, was later calculated from the Teorell–Meyer–Siever model by Hoffer and Kedem [31, 32]. The expected dependence of rejection on fixed charge density, salt concentration, and valency of the ions was subsequently confirmed experimentally [33, 34]. It was thought that separation between ions of different salt valencies might be a useful concept for water treatment, but this idea was not carried out in practice for a long time. Instead, the development of charged porous membranes resulted in an early industrial application for NF [35].

## 1.5 Early Models of NF Selectivity

Models to interpret NF selectivity performance were proposed and analyzed from the very beginnings of NF applications covering processes where the rejection was dependent on charge/noncharged, molecular size, and concentration.

Th models covered a range of selective processes for membranes with an MWCO of 150–1000 (in effect between RO and UF). Membrane selectivities have been interpreted by a number of models, each suited to a particular range. Some of the models were originally developed for RO, but in reality, they were more applicable and easily adapted to NF.

Water flow with retention of various solutes has been studied by generations of physiologists because it is a vital function in living organisms. Developed in the early 1950s, models for exclusion by size, such as that elaborated by the group of Renkin [36, 37], may be used for analysis of transport phenomena in synthetic membranes, including those in the upper limit of the NF range. In this type of model, an effective membrane area is defined, depending on the ratio between the molecular radius of the permeant and the pore radius. Th size of the solutes limits both the probability of entrance into the pore – even if the pore radius is larger than the molecular radius – and the rate of movement through the pore.

Selective ion transport is another physiological function that is also an important NF characteristic. As already mentioned, Meyer and Sievers [29] and Teorell [30] sought to understand this phenomenon through their fixed charge model. It is clear today that this was a gross oversimplification for biomembranes, but in NF technology, salt exclusion from the membrane as a consequence of fixed charges, the well-known Donnan exclusion, is a basic mechanism of selectivity. The quantitatively predictable features of Donnan exclusion enabled the preparation of charged-ion-rejecting membranes in the early 1970s [34]. It was possible to relate the rejection of ions of different valencies to the known thermodynamic properties of polyelectrolyte solutions, assuming a homogeneous distribution of ions in the pore volume [32]. This assumption is justified for narrow pores having a pore radius smaller than the thickness of the diffuse double layer.

As long ago as 1965, Dresner [38] calculated nonhomogeneous ion distribution in wider charged pores. In 1973, Simons and Kedem [39] performed a detailed calculation of rejection in an assembly of rectangular slits in an ion exchange matrix, taking into consideration both the velocity profile and the ion distribution in the pore. Rejection of ions from a mixed electrolyte feed, which was different from the rejection of each salt separately – now a major application of NF – was predicted by Dresner [40].

A major source of basic ideas in membrane development was classic colloid and interfacial science. Th surface tension of salt solutions is higher than that of pure water, and thus, the Gibbs equation relating the interfacial concentration to surface tension predicts a salt-poor region at the air/water interface [41]. With the aim of carrying out surface skimming, the UCLA group on seawater desalination initiated their research effort with the exploitation of this phenomenon in mind. In the 1977 book edited by Sourirajan [12], the performance of the L–S CA membrane and its interpretation are discussed in detail. The well-known preferential sorption capillary flow mechanism is described by Sourirajan in the first chapter (referring to his work of the 1960s): in this work-up, the surface membrane is microporous and heterogeneous; “pore” or “capillary” refers to any connecting void space, regardless of its origin or size; preferential sorption,

positive or negative, takes place at the pore wall/fluid interface and the desalted layer is continually removed under pressure.

The Sourirajan concept was subsequently modified by Glueckauf [42], working together with Russel and coworker [43]. In a model calculation presented at the First International Symposium on Water Desalination in 1965, Glueckauf [42] showed that salt exclusion from the interface with a medium having a low dielectric constant is more pronounced in a narrow cylindrical pore than near a flat surface. The  $\epsilon$  must then be an optimal pore size that is small enough to lead to dielectric exclusion of ions but large enough to allow water flow. His estimate of the optimal pore diameter was less than 6 Å. Water would enter such a narrow space only if the matrix was sufficiently hydrophilic. Glueckauf thus concluded that the special combination of properties of CA that makes it suitable for hyperfiltration is a low dielectric constant and sufficient hydrophilicity. Salt rejection by dielectric exclusion was further elaborated by Bean [44], and his overestimate of rejection was probably because of his neglecting of the screening by the salt itself.

Yet another approach was taken by Kraus et al. [45] who considered the membrane as a continuous organic phase that dissolves water but does not dissolve salt. To back up this idea, they measured salt and water distribution with solvents closely related to CA used to make L–S anisotropic RO membranes. In their paper of 1964, when the existence of a thin dense selective layer was “almost certain,” they concluded from their data and theory that “the effective thickness of such a membrane is presumably of the order of 0.1  $\mu\text{m}$ .”

The models described above are basically related to one another far more closely than is apparent from their formal presentation. The phenomena of salt-free layers close to the polymer and of low solubility of salt in the membrane phase are both related to a low dielectric constant of the polymer. The distinction between the pore model and the solution/diffusion model becomes blurred if pores are of molecular dimensions [46, 47].

None of these models explain the unexpected specificity of seawater RO salt rejection. After all the intense efforts of polymer chemists, only very few polymers show the high salt rejection needed. NF membranes can, however, be prepared from a variety of materials. The nonspecific pore models developed for RO do, in fact, work for NF, and similarly, the Spiegler/Kedem flux equations developed for RO are applicable to NF [48]. Moreover, just as NF is a process lying between UF and RO, models from both these areas and their combinations can be used to represent NF performance. Early NF membranes used to separate salts from dyes were based on a combination of size exclusion and fixed charge exclusion (unlike the salts, the large charged dye ions cannot be drawn into the center of the pores). In thin layer polyamide NF membranes with partial salt rejection, dielectric exclusion is probably the major factor enabling separation. More porous NF relies on Donnan exclusion. The currently accepted theory for ion transport in NF membranes seeks to combine the effects of the dielectric constant of the medium and of fixed charges as a function of pore size (see Chapters 4–6 for a more extensive description of NF selectivity models and mechanisms).

## 1.6 Negative Salt Rejection

### 1.6.1 Solutions of One Electrolyte

As mentioned above, the salt rejection of charged membranes can be described by the model (TMS) based on Donnan exclusion. It was, however, realized that salt rejection depends not only on salt distribution but also on the ratios between the mobilities of the ions. For the extreme case of some acid filtered through positively charged membranes, negative rejection, i.e. enrichment in the product solution, was predicted and obtained experimentally [33]. Negative salt rejection is closely related to the so-called anomalous osmosis, leading to volume flow from the concentrate into the dilute solution in the absence of a pressure gradient. This was observed by the pioneers of membrane science, Sollner and coworker [49] and Schloegl [50].

Negative rejection of a single salt-comprising cations and anions of similar mobilities is obtained in “mosaic” membranes containing small regions of anion and cation elements. It was considered for some time that this effect could serve for desalting [51]. The considerable efforts devoted to these systems have been reviewed by Leitz [52].

### 1.6.2 Separation by Negative Salt Rejection

The salt exclusion originally described by Donnan is obtained when a membrane separates a solution containing charged macromolecules and salt from a solution of salt only. At equilibrium, the salt concentration in the mixed “inside” solution is smaller than that in the outside. When the solutions are separated by an ultrafiltration membrane and pressure is applied, salt will be enriched in the product. Such negative salt rejection was predicted and observed by Lonsdale et al. [53] in the hyperfiltration of citrate and chloride and by Akred et al. [54] in the ultrafiltration of gelatin solutions containing calcium or sodium salts. The principle of negative rejection is illustrated in Figure 1.2.

The technically important negative salt rejection from mixtures containing charged molecules of medium molecular weight (200–1000 Da) can be achieved with nanofiltration membranes of suitable cutoff. This is feasible in principle with any type of NF membrane – charged or neutral.

## 1.7 Early Development of Industrial NF: Ionic Modification of Asymmetric Cellulose Acetate

By about 1972, ecological issues were beginning to become a cause for concern to industry, especially industrial entities in Europe that found themselves in heavily populated areas. In activities such as dye production, large quantities of salty dyed polluted water were being discharged into waterbeds and rivers. One solution to this problem was to apply the new membrane technology that was becoming successful in RO applications such as water desalination and in UF applications such as protein separations. However, many industrial waste

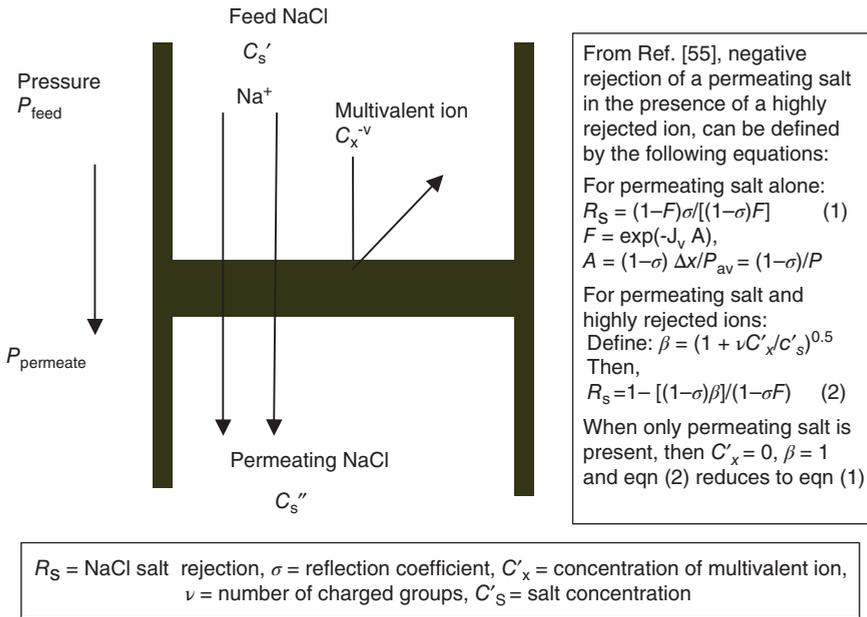


Figure 1.2 Principle of negative salt rejection in the presence of highly rejected ions [55].

streams presented special problems for the new membrane technology: In RO, the salt concentrations were so high that any concentration effort was doomed by uneconomically low flux because of the osmotic forces of the rejected salt. UF was not efficient, as both the dye and the salt permeated through the membrane.

One of the efforts to overcome these difficulties led to the founding of a small company – known as RPR – in the early 1970s by Bloch and Kedem, which used open NF asymmetric cellulosic membranes modified with reactive dyes. This approach to membrane modification was an early example of how existing membranes could be chemically modified to achieve valuable separation characteristics. The modification in this case formed charged groups on the pore walls and at the same time stabilized the membrane structure by cross-linking. With these modified membranes, 99% dye rejection was achieved.

It was found that these membranes could be advantageously applied not only to wastewater treatment but also to dye production because of the then-amazingly effective purification effect by negative salt rejection. This was explained to be a consequence of Donnan equilibrium, as described in Section 1.6. The salt passed through the membrane easily and was, in practice, equilibrated between the feed and permeate. The feed contained the large impermeable dye anions, small sodium counterions, and a high concentration of salt, while the permeate contained only small ions, which had been pushed into the permeate by the highly rejected dye counterions.

Thus, in the late 1970s, a single-unit operation could be used for both concentration and purification. The first tubular pilot units based on modified cellulosic membranes very rapidly became the core of production machines that

concentrated and desalted simultaneously, thus saving vast quantities of the salt need to precipitate the dye and solving the original development problem of reducing salty/dyed discharge. The membranes were used on an industrial scale by dye manufacturers to desalt and concentrate dye solutions. In one process, both a production and an ecology problem had been solved!

A formal description of this Donnan effect in dye solutions was published only much later (1989) after it had long been understood and put into practice [55]. The incorporation of a Donnan distribution term into the flux equations of Spiegler and Kedem [48] defined earlier could explain the strong negative salt rejection found in dye processing (shown schematically in Figure 1.2) and its concentration dependence. Negative salt rejection because of the Donnan effect may be observed for any type of NF membrane, whether charged or uncharged.

Cellulosic membranes were, however, not chemically stable and suffered from flux decline after short periods. As experience was gained, it was realized that there were still some significant drawbacks associated with the modified CA membranes: they allowed relatively large quantities of dye to pass through them, which constituted an economic loss, and membrane lifetime was not sufficiently long. It was also realized that tighter membranes, which could operate at higher and lower pH values, would have many other uses. Starting in late 1970s, tighter noncellulosic membranes were developed in RPR's manufacturing company, Membrane Products Kiryat Weizmann (MPW).

## 1.8 Early NF Composites

### 1.8.1 General

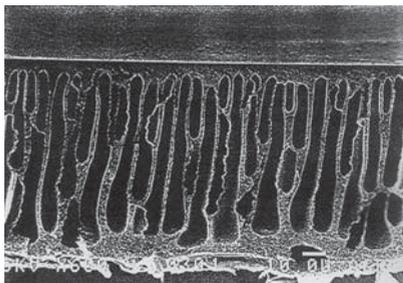
By 1975, it became apparent that asymmetric NF membranes from a single polymer or polymer mixtures could not give the characteristics of selectivity and flux needed to compete with standard technologies in many applications. Attempts to make asymmetric NF membranes by casting polymers with the hydrophilic/hydrophobic balance of CA did not produce membranes with sufficient flux or rejection if they were too hydrophobic or with flux stability if they were too hydrophilic.

Workers such as Rozelle, Cadotte, and Riley and their colleagues had resolved a similar dilemma for RO in the early 1970s with the development of composite membranes [56, 57]. They produced high-salt-rejecting membranes by placing a very thin selective layer over one surface of a finely porous asymmetric UF membrane. Such a composite membrane was produced either by coating the UF membrane with a thin CA film or by carrying out interfacial cross-linking of polyamines (for example, polyethyleneimine [PEI]) with isophthaloyl chloride (IPC), toluene diisocyanate (TDI), or other aromatic cross-linkers. The latter approach appeared to be the key breakthrough. These composite membranes exhibited important advantages over integrally skinned asymmetric membranes in that the selective barrier film and the support could be optimized independently. With this process, a variety of chemical combinations and methods could be used to form thin barrier coatings, including the use of linear and cross-linked

polymers, whereas asymmetric membrane formation was limited to processable stiff linear polymers. In Cadotte's patent of 1977 [58] and NTIS report 1968 of Rozelle et al. [59] on composite membranes, comparison examples were given of other composites made by different cross-linking reagents, which showed significantly lower salt rejections compared to the claimed RO membranes. These more open membranes were, however, what we would now term composite NF.

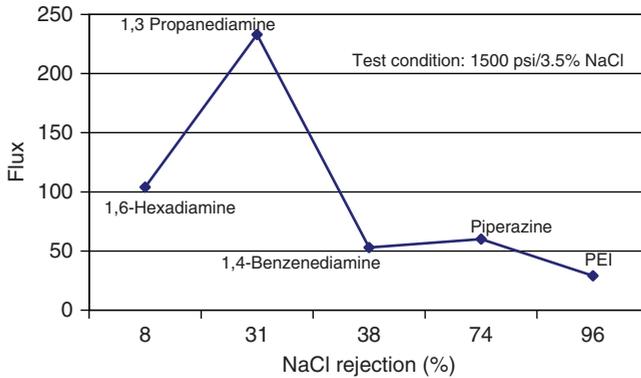
In general, it may be said that the composite approach is applied to form a selective layer that is both thin and sufficiently hydrophilic to give high water flux but at the same time cross-linked to the extent required for NF selectivity. In addition to the original method of interfacial cross-linking of polymers for forming composites, other methods have included interfacial polymerization (Section 1.9), plasma polymerization (Section 1.8.2), polymer coating and curing, and surface modification (see Section 1.8.3).

The first composites – RO composites – were based on cellulose nitrate UF supports, but they suffered from the same lack of biological, chemical, and mechanical stability that had limited CA in RO and UF applications. Very early in the 1970s, polysulfone was recognized as the material of choice for UF porous supports because such membranes combined high surface porosity with minimal pore diameter and high chemical and mechanical stability. They could be readily cast and optimized (high degree of porosity and controlled pore size distribution) to give the asymmetric structures for commercially valuable RO or NF composites [56, 57]. A number of other polymeric materials were also investigated [58], such as polycarbonate, chlorinated PVC [56], polyamide, PVDF, PAN and styrene/acrylonitrile copolymers, polyacetals, and polyacrylates. From these investigations, it was found that polymer molecules making stable compaction-resistant supports are inherently stiff chains capable of hydrogen bonding or polar and hydrophobic bonding, giving networks with low chain mobility. UF membranes based on chemically stable aromatic engineering plastics, such as polysulfone or PES, have currently become the standard supports for composite RO and NF membranes. Different UF membrane morphologies could be used for making composites; however, a typical asymmetric polysulfone is shown in Figure 1.3. The membrane comprises an integral “tight” skin layer of about 0.1–0.7  $\mu\text{m}$ , a larger pore intermediate sponge layer of 1–5  $\mu\text{m}$ , and a 80–100  $\mu\text{m}$  thick, open support layer with large finger-like pores. Other UF supports have a sponge-like structure instead of fingers in the porous layer.

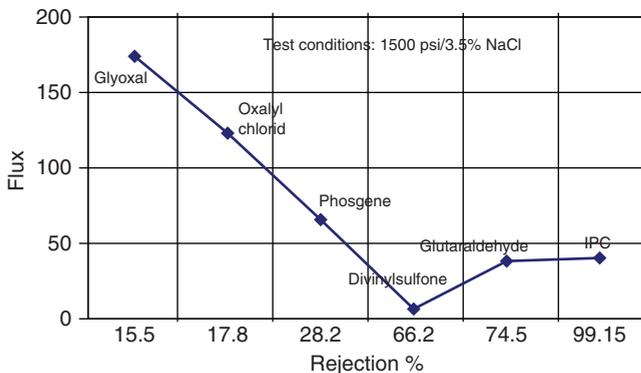


**Figure 1.3** Scanning electron micrograph of UF PES membrane used for making NF composites.

If 1960 marked the beginning of the development of asymmetric membranes, then about 1969 marked the beginning of the use of asymmetric UF membranes for making composites. From 1969, Cadotte and Rozelle [58, 60] and then Wrasildo, Riley, and coworkers [61, 62] showed that high-rejection RO composites could be made by interfacial cross-linking of coated hydrophilic polymers such as PEI or polyepiamine with IPC or TDI on polysulfone or chlorinated PVC UF membranes. As a spin-off of this development on single-pass water desalination membranes, Cadotte and others also described open RO or NF membranes. For example, in 1972, open RO (NF) composite membranes were made from the interfacial reaction of low molecular weight polyamines and teraphthaloyl chloride (Figure 1.4) [60]. Similar membranes were also made from mixtures of PEI with different cross-linkers, as described in a 1977 patent (Figure 1.5) [58]. These membranes were not, however, commercially viable and were superseded by the piperazineamide composites described below.



**Figure 1.4** Flux (gallons/ft<sup>2</sup> d) vs. salt rejection (%) for early open RO membranes (NF) prepared by interfacial polymerization of teraphthaloyl chloride with different polyamines (NTIS report No. PB-229337, November 1972) [60].



**Figure 1.5** Flux (gallons/ft<sup>2</sup>-d) vs rejection (%NaCl) for different interfacial membranes from US Patent 4, 039, 440 (1977) [58].

### 1.8.2 Plasma Polymerization

Another approach to the preparation of composites, which first appeared in the 1960s, was plasma polymerization of coated films on a microporous support. In his 1977 review of the subject, Yasuda [63] reported the use of plasma polymerization of different monomers (e.g. 4-vinylpyridine, *N*-vinyl pyrrolidinone, pyridine 1-methyl-2-pyrrolidinone, thiophene, and thiazole) on polysulfone supports to produce very thin selective membranes. Although the main goal was the production of RO membranes, NF membranes produced from a variety of monomers were also prepared.

Plasma processes were also used to modify the surfaces of UF membranes to bring them into the NF range. For example, Sano [64] used plasma polymerization with He and H<sub>2</sub> on UF PAN to produce commercial RO membranes by sealing and hydrophilizing the membrane surface. This method can be adapted to give NF membranes; for example, Lai and Chao [65] modified Nylon 4 microporous membranes with gas plasma to produce membranes with 74% rejection to NaCl. Polyarylsulfone UF membranes were also plasma-treated by Sano and his coworkers to give 96.3% rejection, where the original membrane had exhibited 0% rejection. Such membranes could also be expected to give NF under different preparation conditions.

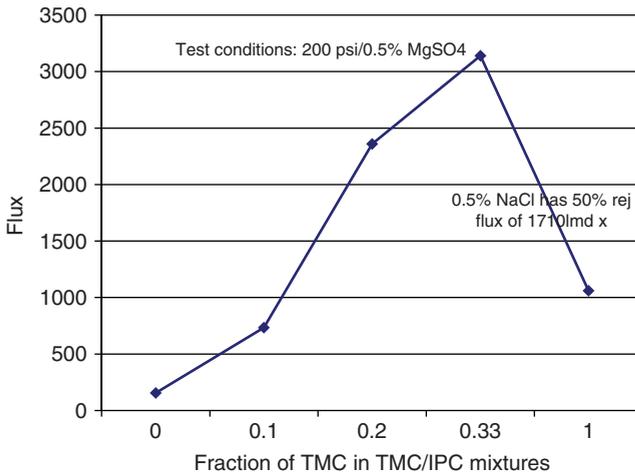
### 1.8.3 Graft Polymerization

Graft polymerization of nonionic or ionic vinyl monomers by a variety of methods, i.e. with ionizing radiation such as gamma rays from <sup>60</sup>Co, by photochemical means, or by chemical initiation on asymmetric membranes has been carried out in an effort to improve RO performance. In the 1960s and 1970s, Stannett et al. [66] grafted styrene on CA membranes. Although the results were not encouraging for RO, they did give, in some cases, membranes with NF properties. The fluxes were, however, too low for the membranes to be of commercial value. In another study, Kesting and Stannett [67] showed that the attachment of acrylic monomers could be used to increase the starting membrane permeability to salt and possibly to bring RO membranes into the NF range. In yet another study, double grafting of PVC films with 2-vinylpyridine and acrylic acid gave membranes with a high flux per unit thickness with NF salt rejections of 65% [68]. However, the absolute flux in the dense films was low, and only by casting asymmetric membranes could this approach be of practical value.

## 1.9 NF Composites of the 1980s

### 1.9.1 Piperazineamide Membranes

Commercial NF composites were not generally available until the second half of the 1980s, even though their development began in the late 1970s [28]. One of the first successful approaches was based on the interfacial polymerization of an aqueous piperazine film on a polysulfone UF support by hydrophobic aromatic



**Figure 1.6** Flux (l/m<sup>2</sup> d) vs TMC/IPC ratio of piperazineamide interfacial membranes with 99 + % rejection to MgSO<sub>4</sub> (US Patent 4, 259, 183 (1981)) [69].

cross-linkers. Many such NF products were made by a number of different companies. Polypiperazineamide NF composites were prepared when Cadotte et al. [69] replaced IPC with trimesoyl chloride (TMC), making NF membranes with high MgSO<sub>4</sub> rejection (99%) and low NaCl retention (<60%) (Figure 1.6).

Starting in the 1980s, FilmTec marketed variations of these membranes with 40–50% NaCl rejections [70]. Other companies also developed and commercialized NF composite membranes based on the interfacial polymerization of piperazine and its derivatives on UF PES and polysulfone supports. Examples of these membranes are (i) PCI's polypiperazineamide membranes in tubular form [71] having 30–70% NaCl passage and a MWCO to organics of 350 and (ii) Toray also commercialized NF polypiperazineamide-based barrier layer membranes [72]. These membranes found application in the desalting of whey, water softening, removal of organics from surface waters, removal of sulfate from seawater, recycling of waste dye streams, recycling of melamine-based anionic electrophoretic paints for aluminum surface finishing, removal of color from bleach effluents, wood pulping, and removal of radium from well waters [73].

An important commercial variation of polypiperazineamide membranes is the inclusion of a polymer that simultaneously undergoes interfacial cross-linking during the interfacial polymerization of piperazine. Because the polymer cannot readily diffuse into the interfacial layer, the piperazine monomer accumulates on the surface to form a thin polypiperazineamide layer on the cross-linked polymer, which is supported by the UF membrane. For example, Nitto Denko NTR 7199 is a polyamide [74] formed by the interfacial reaction of TMC with an aqueous solution containing both piperazine and PVA with subsequent curing at 110 °C. Their process produces a selective bilayer consisting of cross-linked PVA covered with a surface layer of polypiperazineamide, which is supported by an asymmetric UF membrane. In this membrane, chlorine stability is supposedly improved because of the presence of PVA.

In another type of commercial product, a thin coating of one polymer is first placed on a UF support, followed by interfacial polymerization of piperazine. It is thought that Desalination Engineers' Desal 5 membranes (now Osmonics Corporation) comprise a polysulfone UF support coated with a layer of sulfonated polysulfone upon which is an ultrathin layer of polypiperazineamide [75]. This type of membrane can be made to give glucose rejections of 82–98% and a sucrose rejection of 99%. Although the Desal 5 membrane is negatively charged, its characteristics are different from those of other negatively charged sulfonated polysulfone membranes and are more similar to those of piperazine composites of FilmTec (e.g. NF40).

### 1.9.2 Other NF Interfacially Produced Composites

Commercial NF membranes have also been prepared via interfacial polymerization with monomers other than piperazine. In 1985, FilmTec introduced fully aromatic cross-linked polyamide NF membranes, NF70 (70% rejection to NaCl), with an MWCO of 400 [75]. These membranes are typical of NF membranes used in drinking water purification and softening. McCray et al. [75–77], at Bend Research, developed chlorine-resistant membranes, with 20% and 60% salt rejection, respectively; these membranes were made by the interfacial polymerization of tetrakis-(*N*-methyl-amino-methyl) methane with IPC and TMC, respectively.

Multilayered NF membranes have been prepared by Linder et al. by the interfacial polymerization/cross-linking of PEI and diaminobenzene sulfonic acid with TMC [78]. In this interfacial reaction, the monomeric amine diffuses through a PEI layer that has previously undergone thermal cross-linking, reacts with TMC, and deposits a layer of diaminobenzene sulfonic acid polymer on the cross-linked PEI. According to the patent literature, these membranes have 95+% rejection to glucose and sucrose, low NaCl rejection, and sodium sulfate rejections of 90+%.

### 1.9.3 Modification of RO Membrane Composites to Bring Them into the NF Range

In the 1980s and early 1990s, patents were taken out on processes to produce NF membranes by modification treatment of RO polyamide composites with various reagents, such as acids, bases, and oxidants, with the aim of lowering rejection and increasing fluxes. For example, Strantz and Brehm [79] described a process for treating polyamide RO membranes to make NF membranes with acidic solutions of permanganate salts to open the selective barrier, followed by sodium bisulfite or hydrogen peroxide treatment to chemically stabilize the new membrane. In another example, Cadotte and Walker [80] used hot phosphoric acid/sulfuric acid mixtures to open up a polyamide composite to decrease salt rejection and increase flux. The resultant open membrane was further modified to increase  $\text{MgSO}_4$  rejection to 90+%. These rejection-enhancing agents may be colloids such as tannic acid or water-dispersible polymers.

## 1.10 Composites Produced by Noninterfacial Cross-linking

In the latter half of the 1970s, work started on developing composites by non-interfacial cross-linking methods. This resulted in the production of a class of commercial NF membranes formed by coating and curing thin selective films on asymmetric UF supports. There are two possible methods of preparation:

1. Coating of a polymer solution on a UF support, followed by a curing step to activate cross-linking via self-condensation or by a latent cross-linker in the coating solution;
2. Coating the UF support with a polymer solution, washing and/or draining the support, and then immersing it in another bath containing cross-linker(s) that diffuse into the wet film, followed by a curing step.

The curing steps may comprise a temperature increase, a change of pH, or ionizing radiation. Commonly used coating polymers are PVA, PEI, polyallylamines, and sulfonated engineering plastics such as polysulfone, PES, and polyetheretherketone.

### 1.10.1 Polyvinyl Alcohol Composites

Because of its hydrophilicity, water solubility, and ready availability in different molecular weights, PVA has always been an attractive candidate for making composites. It has generally been found that NF PVA composites made by thermal cross-linking exhibit low flux and tend to compact under high pressure. This is due to chain flexibility and hydrogen bonding, resulting in tight packing and crystallization before cross-linking, and a nonuniform distribution of cross-links, all of which give a film that compacts under pressure [81]. To make membranes with sufficiently high flux, tight packing and crystallization should be avoided.

NF composites have been made by coating a mixture of PVA with a reactive dye on microporous supports (such as microporous polypropylene), followed by cross-linking by immersion of the membrane in hot sodium sulfate, according to the 1980 patent of Linder et al. [82]. These membranes have basic pH stability to pH 12 at 60 °C and give typical rejections and fluxes of 98% to ionic dyes with an MWCO of 700+ at 20–30 bars. They can be used in various industrial applications, such as the desalting of dye solutions. Cadotte [83] developed PVA membranes from thin PVA films cross-linked on a porous support by acetylation with a dialdehyde catalyzed by phosphoric acid at 110 °C. Phosphoric acid was used both as a cross-linking catalyst and a pore former. The membrane (XP20) had 20% rejection to NaCl, 85% to MgSO<sub>4</sub>, 99% to EDTA, and pH stability up to pH 13. This membrane found use in the concentration of copper EDTA, for which it had 99% rejection, in an alkaline electroless plating bath. Other NF composites have been developed on the basis of films made with PVA and different cross-linkers such as hexahydroxycyclohexane [84] and divinylsulfone [85].

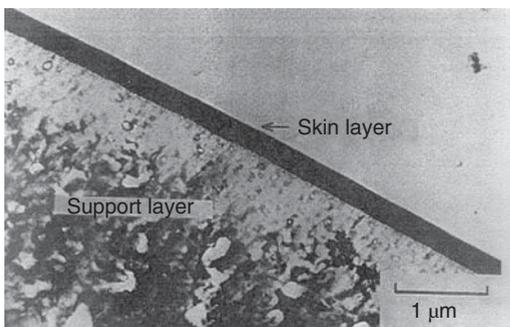
### 1.10.2 Sulfonated Engineering Plastics as Selective Barriers

Asymmetric membranes cast from solutions of sulfonated polysulfones or other engineering polymers were not successful because the degree of sulfonation needed for sufficient flux resulted in low rejection and in compaction under pressure and hence in flux loss. Sulfonated aromatic polymers were, however, used to make commercial composites by coating the polymer on a UF support, generally followed by a curing and cross-linking step.

In the second half of the 1980s, Nitto Denko commercialized NF composite membranes based on sulfonated polysulfone membranes. This series of membranes, designated NTR-7400, exhibits high flux and low salt rejection with excellent chlorine resistance [86, 87]. Their performance depends on the degree of sulfonation; for example, a membrane with a 3000-Å thick film (Figure 1.7) having a capacity of 1.92 meq./g gave 35–50% rejection to NaCl and 35% to sucrose, with lower capacity films giving higher rejections and lower fluxes. A phenomenon observed with loose-charged membranes of this type was the production of a permeate enriched in a particular anion relative to the feed [88], giving a negative rejection of an ion with mixed salt solutions.

### 1.10.3 Polyethyleneimine

NF membranes based on a cross-linked coating of PEI on UF polysulfone were described as part of the original work of Cadotte in the early 1970s [58], but these membranes were never commercialized. Linder, Nemas, and their coworkers, citing the use of hydrophilic polymers such as PEI, also extensively patented NF membranes, starting from 1980. The patents describe processes of immersing a UF membrane in a sequence of different solutions containing polymers and cross-linkers. According to the patent literature, this process comprises the following steps: the support is coated by immersion in a polymer solution; drained and immersed in an aqueous suspension or solution of cross-linkers, such as polyepoxides, reactive dyes, divinylsulfones, and polyaldehyde; drained; and finally cured in solution or by drying. Different supports have been modified by this procedure to give a range of NF membranes with different acid/base stabilities. According to the patents, the UF supports may be cellulosic [89], PAN, [90], or polysulfone [91]. These membranes have varying degrees of stability, depending on the support and the polymer cross-linking reaction. For example,



**Figure 1.7** Scanning electron micrograph cross section of a cross-linked sulfonated polyethersulfone skin on a UF polysulfone support. *Source:* Taken from Figure 1 of Ikeda et al. 1986 [86] with permission from the Elsevier .

the CA NF is limited to pH 4.0–8.0, while membranes based on polysulfone can be used between pH 2 and 12 at 60 °C. Depending on the degree of cross-linking, the membranes can have rejections to glucose that vary from 20% to 95+%, and pure salt rejection of 0–75% as a function of the selective barrier and the salt concentration. Fluxes at 20 bars can vary from 50 to 150 l/m<sup>2</sup> h as a function of the membrane type. Other membranes having rejections to organic molecules such as glucose of 95+% and ionic dye molecules of 99+% with salt passage have also been patented. In mixtures of monovalent salt, and highly rejected organic ions, large negative salt rejections were reported by Perry and Linder [55].

## 1.11 Chemically Stable NF Membranes

### 1.11.1 Chemically Stable Polymeric Asymmetric Membranes

By the early 1980s, asymmetric chemically stable NF (in effect acid-, base-, and chlorine-resistant) could be made by casting polysulfone or polyether sulfone into asymmetric membranes with an MWCO of 1000–2000. These membranes have a pH stability of 0–14 at temperatures up to 60 or 80 °C and good chlorine stability. In some cases, however, the nonwoven and module materials rather than the membrane limited performance. Asymmetric membranes with lower MWCO selectivity and good flux cannot, however, be readily made by this approach. Such relatively open membranes cannot be used effectively for applications needing high rejections to low molecular weight solutes such as sucrose. Experience in different industrial applications has shown that these membranes compacted and fouled easily, with loss of flux. To overcome fouling and to increase flux, the surfaces of these asymmetric membranes were hydrophilized by various methods [92, 93]. One procedure was to cast the membrane with a compatible hydrophilic polymer, such as polyvinylpyrrolidone, which was subsequently cross-linked by heating.

### 1.11.2 Oxidant and pH-Stable Composite Membranes

In the early development of noncellulosic NF membranes with hydrolytic stability, good selectivity, and high flux, polyamide and polyurea composites were made. The stability of these membranes to chlorine was, however, found to be lower than that of CA membranes. The chlorine tolerance of the Desal 5 membrane is about 1000 ppm-h, while other polypiperazineamide membranes can typically operate at constant chlorine exposure levels of 0.1 < ppm. Dechlorination is, however, generally recommended for most polypiperazineamide and polyaromatic amide membranes. In comparison, PVA and CA NF membranes can operate continuously at 0.5 ppm of chlorine (up to a maximum of 1.0 ppm). High chlorine stability can be achieved in sulfonated polysulfone composites; for example, the NTR-7400 series, having high flux and low salt rejection (50%), are stable in 10 000 ppm chlorine for at least 30 days. These oxidant-stable membranes are, however, open NF membranes, and as such cannot be used for many of the applications requiring better selectivity. NF membranes with

a combination of high flux, selectivity to low molecular weight solutes, and chlorine resistance are still to be developed.

One of the first goals of membrane development in the 1970s was improvement of the pH stability of CA membranes, which were limited to a pH range of 4–8. Polyamide and polyurea composite membranes offered by many companies such as Desalination Engineers (now Osmonics) (Desal 5) and Dow FilmTec (NF40, 45, 50, and 70) can be operated continuously at room temperature at pH values between 1 and 11, but under more acidic or basic conditions or at high temperatures, they lose rejection ability. Asymmetric membranes cast from sulfonated polybenzoxazindione with an MWCO of 300 stable from pH 2 to 12 were developed by Bayer but were never commercialized [94]. The Nitto membrane of sulfonated polyether sulfone on a polysulfone support (NTR-7400 series) showed stability in the pH range of 0.5–13 in immersion tests at 80 °C [86]. This class of membranes has a high MWCO, with sucrose rejections of 50% in the tightest membrane.

There are many potential applications for NF at the pH extremes of 0–14 and at elevated temperatures that require selectivities to low molecular weight solutes, such as glucose, sucrose, aluminates, and sodium carbonate, while freely passing acids and bases. For example, aqueous acid and base streams are used on a large scale as reaction media, as catalysts in fine chemicals, in the mining, petrochemical, and pharmaceutical industries and for daily cleaning in the dairy, food, beverage, and pharmaceutical industries. The ability to carry out selective separations of acids, bases and solvents from low molecular weight organics (150+) and salts (e.g. carbonates) present in production and waste stream would enable these recycling chemicals, the concentration and purification of products, and the recovery of valuable materials from waste streams.

During the 1980s, a series of patents by Linder et al. [91, 95, 96] described acid/base-stable NF membranes with good selectivity based on the chemical modification of polysulfone. It is claimed in these patents that the membranes are stable in the pH range from 2 to 12 at temperatures up to 80 °C and that the membranes can be made with an MWCO of 200 with fluxes from 50 to 150 l/m<sup>2</sup> h at 20 bars. According to the patent literature, the modification was carried by a sequence of immersion steps, which, for example, resulted in a cross-linked selective layer of PEI on a polysulfone or PES UF support. In 1989, Perry and Linder described NF membranes with 95+% rejection to sucrose and stability at pH 0.5–12 [55], and in 1991, Perry and Linder described NF membranes with an MWCO of 200 and pH stability from 0 to 14 at 80 °C [97, 98].

### 1.11.3 Solvent-Stable NF Composites

The use of solvents is particularly prevalent in the fine chemical, pharmaceutical, food, and petrochemical industries as described in Chapters 12 and 20.

The ability to carry out selective separations with solvent-containing solutions would enable the recycling of solvents, the concentration and purification of products, and the recovery of valuable materials. Many such applications require the rejection of low molecular weight solutes (down to 150) and the free passage of the solvents. There are, however, a number of problems in developing

solvent-stable NF membranes for solvent applications, i.e. the need to provide (i) support stability, (ii) economically favorable fluxes by optimizing a different membrane for each solvent class, and (iii) membrane selectivities that vary from one solvent to another and in solvent mixtures. The origin of the flux/selectivity problems lies in solvent/support interactions, the solution–diffusion transport mechanism, and the many different solvents with a wide range of hydrophobicity/hydrophilicity balances, viscosities, and surface tensions. Solvent stability can be measured as a function of the degree of swelling of a membrane in a particular solvent. For constant performance in a particular application, the membrane, including the support, should be essentially nonswelling in that application's solvent. Many claimed solvent-resistant supports are nonswelling for one category of solvents but swell in others. A general solvent-stable UF support is one that is nonswelling in many solvent categories.

The potential of the new membrane technology for solvent applications was recognized in the 1960s by Sourirajan [99] and others on a condition that both the necessary selectivity and stability could be developed. The membranes used in early studies were based on CA and cross-linked rubbery materials [100]. NF membranes based on CA or polyamide composites on polysulfone supports could be used with solvents that do not swell the support (e.g. hexane) [101]. Most commercial NF membranes, including CA and polyamides, swell or dissolve in many solvent classes and are therefore not considered to have general solvent stability.

Most work on solvent separations involves pervaporation. There are, however, patents on pressure-driven processes for treating solutions of organic solvents. For example, Black [102] prepared composite membranes formed on solvent-stable supports (e.g. nylon, cellulose, polyester, Teflon, and polypropylene) by the interfacial polymerization and cross-linking of polyamines with polyfunctional agents. The proposed use was the separation of aromatic extraction solvents, such as 1-methyl-2-pyrrolidinone (NMP), furfural, phenols, and ketones, from oils and aromatic hydrocarbons under RO conditions. Composites on a microporous nylon support (0.04  $\mu\text{m}$ ) with oil rejections of 98% and NMP fluxes of 103 l/m<sup>2</sup> d were achieved at 500 psig. It does not appear that the membranes or the applications have been developed into commercial processes, possibly because of the lack of long-term stability or uneconomically low fluxes.

In another approach to NF operating at 20–80 bars, Bitter et al. developed membranes, which retained the solvents but passed the hydrocarbon oil [103]. Their membranes were based on dense selective silicone layers (1–10  $\mu\text{m}$  thick), coated onto microporous supports (e.g. polypropylene with rectangular 0.2 by 0.02  $\mu\text{m}$  pores). Apparently, the oil was transported by a solution diffusion mechanism through the silicone barrier while the more polar solvent was rejected. These membranes were not, however, applied in actual practice. The thickness of the selective layer and support size are quite different from the thin selective barriers placed on UF supports for most NF membranes.

In the 1980s and early 1990s, MPW commercialized general solvent-stable NF membrane composites, designated as MPT 42, MPT 50, and MPT 60, which had MWCOs of 200, 700, and 400, respectively, and were stable to pH values of 2–10 and nonswelling in a broad range of solvents [97]. The patent literature cites

**Table 1.3** SelRO™ acid/base/solvent-resistant membranes.

Membrane	Acid/base stability	Solvent stability	Typical % rejections					
			MWCO	NaCl 5% (MW 58)	Ampicillin (MW 349)	Murexide (MW 284)	Remazole Blue (510)	Lactose (360)
MPT-11	Yes			31	99	95	99.9	99.5
MPT 20		Yes	600	0		90	99.9	97
MPT 30	Yes		500	10	98	90	99.9	96
MPT 40		Yes	300	15		95	99.9	90
					Glucose (MW 186)	Sucrose (MW 342)	Raffinose (MW 504)	Aspartame (MW 294)
MPT 42		Yes	150		93	98	99	99

Source: Adapted from Ref. [98].

stable NF membranes prepared by Linder et al. [104–106] based on cross-linked PAN and polysulfone, with the composites being made by coating and curing or interfacial polymerization. To achieve sufficient flux, the selective layer was optimized for a particular solvent category. The patent literature shows that hydrophobic solvents, such as hexane, were treated with solvent-stable composites with polysiloxane layers, giving good fluxes. For polar solvents, such as ethanol, esters, dimethyl formamide, and NMP, more hydrophilic composites with selective layers of polyamines or polyphenyleneoxide derivatives are required. The membranes cited in the above-described patents have MWCOs down to 150 and solvent fluxes that vary according to the particular membrane and solvent (Table 1.3).

A more detailed account of NF membranes in solvent applications is given in Chapter 20.

#### 1.11.4 Chemically Stable Inorganic NF and Polymeric/Inorganic Hybrids

The development of inorganic NF membranes, which are generally ceramic materials, is motivated by superior thermal and solvent stability characteristics compared to organic polymers. Typically, the porous support for the selective NF layer is composed of Al<sub>2</sub>O<sub>3</sub>, carbon, SiC, or a metal made by sintering large particles of these materials. The substrate is then coated with a thin layer of small particles of zirconia, alumina, or titania to form a microporous membrane. A third layer of still finer particles or a colloidal dispersion is then applied to form a UF membrane. On these UF membranes, an NF film is coated. Each stage of the ceramic membrane composite is formed by sintering particles or by a sol–gel technique.

In the early 1990s, ceramic NF membranes were developed by two different approaches: (i) All-inorganic membranes were made by coating a ceramic UF membrane with nanoparticles, followed by sintering or by a sol–gel process, or (ii) hybrid NF membranes were produced by coating the ceramic UF membrane with organic polymers or organic–inorganic polymers.

NF ceramic membranes can be made with high rejection to charged organic solutes with molecular weights as low as 400. For example, Larbot et al. [107] prepared  $\alpha$ -alumina NF membranes having rejections to NaCl of 10% and to sucrose of 70%. The ceramic route to NF has not yet been able to produce NF membranes with selective separations of noncharged solutes such as glucose and sucrose from salt. There are also indications of changing rejection characteristics under pressure because of fusion of the nanosized particles that make up the selective layer. In the early 1990s, NF membranes comprising a porous ceramic support coated with a thin polymeric layer were developed. For example, Guizard and his group [108, 109] coated a porous ceramic support with polyphosphazenes or heteropolysiloxanes to give NF membranes with 50% rejection to sucrose and low rejections (10%) to NaCl. Bardot et al. [110] coated other polymeric barriers, such as sulfonated polysulfone, polybenzimidazolone-grafted PVDF, or Nafion, on inorganic supports to make RO and NF membranes.

## 1.12 Conclusions

CA membranes were the first membranes to be used for NF applications. They demonstrated the potential of selective separations within the molecular weight range up to 1000. One of the major drawbacks of these membranes was their lack of stability, which resulted in a rapid loss of rejection ability and/or of flux in many industrial applications. With each successive improvement in stability, there was a widening of the range of applications. The first improvements were made in pH stability and then in stability to solvents and oxidants. Improvements in selectivity and flux were made together with improvements in stability. The number of NF applications could be greatly widened if stability and selectivity could be refined further. This chapter covered NF developments of the first three decades (1960–1990). Improvements in NF performance continued in the 1990s, until the present, and are described in subsequent chapters (Chapters 2 and 3).

In the fine chemical and pharmaceutical industries, there is still a need for improved solvent stability with better selectivity in the molecular weight range below 500. In the mining and sugar industries, there is a need for high-flux selective membranes with improved acid stability at values as low as pH 0. In other industries, improved flux together with better stability and selectivity would open many new applications; in particular, base stability at concentrations of 10–50% at temperatures up to 80 °C with 150–200 MWCO would have many applications. In the petrochemical industry, solvent separations and purifications are extremely important but require solvent-stable membranes with selectivity properties optimized for each solvent class. Work in this area has only just begun with ceramic and solvent-stable polymeric membranes.

Another important industrial application relates to the widespread use of sulfuric acid as a solvent catalyst and pH adjuster. This results in the production of waste streams with high concentrations of sodium sulfate. NF membranes that could selectively pass sulfate with less than 20% rejection while retaining low molecular weight organics, such as sucrose and glucose, would find many applications.

Separation between molecules with molecular weights up to 1000 is needed in many aspects of water and industrial activity. Achieving such separations economically is becoming important in terms of ecological and energy considerations. NF membranes have made significant contributions to this activity, and as progress is made in stability, selectivity, and flux, even more applications will be found.

## Abbreviations

CA	Cellulose acetate
IPC	Isophthaloyl chloride
L-S	Loeb–Sourirajan
MPW	Products Kiryat Weizmann
MWCO	Molecular weight cutoffs
NF	Nanofiltration
PAN	Polyacrylonitrile
PCI	Patterson Candy International Ltd.
PEI	Polyethyleneimine
PES	Polyethersulfone
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
RO	Reverse osmosis
S&S	Schleicher and Schuell
TMC	Trimesoyl chloride
UF	Ultrafiltration

## References

- 1 Loeb, S. (1994). Reminiscences and Recollections. NAMS Membrane Quart.
- 2 Reid, C.E. and Breton, E. (1959). Water and ion flow across cellulosic membranes. *J. Appl. Polym. Sci.* 1: 133.
- 3 Dobry, A. (1936). The perchlorates as solvents of cellulose and its derivatives. *Bull. Soc. Chem. Fr.* 3: 312–318.
- 4 Kesting, R. (1971). *Synthetic Polymeric Membranes*. New York: McGraw-Hill.
- 5 Riley, R.L., Gardner, J.O., and Merten, U. (1964). Cellulose acetate membranes: electron microscopy of structure. *Science* 143: 801–803.
- 6 Riley, R.L., Merten, U., and Gardner, J.O. (1966). Replication electron microscopy of cellulose acetate osmotic membranes. *Desalination* 1: 30–34.
- 7 Lonsdale, H.K. (1972). Theory and practice of reverse osmosis ultrafiltration. In: *Industrial Processing with Membranes*, Chapter VIII (eds. R.E. Lacey and S. Loeb), 123–178. NY: Wiley Interscience.
- 8 (a) Loeb, S. and Sourirajan, S. (1964). High flow semipermeable membrane for separation of water from saline solutions. US Patent 3, 133, 132, May 12, 1964; (b) Loeb, S., Sourirajan, S., and Weaver, D. (1964). High flow

- semipermeable membrane for separation of water from saline solutions. US Patent 3, 133, 137.
- 9 Th Regents of the University of California of Berkeley (1967). State of California, United States of America. Desalination Membrane. GB 1, 056, 636, Jan. 25, 1967.
  - 10 Cohen, H. and Loeb, S. (1977). Industrial waste treatment by means of RO membranes. In: *Reverse Osmosis and Synthetic Membranes* (ed. S. Sourirajan), 511–525. National Research Council Canada.
  - 11 McKinney, R. Jr., and Rhode, J.H. (1971). Aromatic polyamide membranes for RO separations. *Macromolecular* 4: 633.
  - 12 Lonsdale, H.K. (1982). The growth of membrane technology. *J. Membr. Sci.* 10: 81–181.
  - 13 Sourirajan, S. (ed.) (1977). *Reverse Osmosis and Synthetic Membranes*. National Research Council Canada.
  - 14 Conlon, W.J. and McClellan, S.A. (1989). Membrane softening: a treatment process comes of age. *J. Am. Waterworks Assoc.* 81 (11): 47.
  - 15 Michaels, A.S. (1965). Polyelectrolyte complexes. *Ind. Eng. Chem.* 57 (10): 32.
  - 16 Richter, J.W. and Hoehn, H.H. (1971). Permselective polymer membranes. US Patent 356, 632.
  - 17 Blais, P. (1977). Polyamide membranes. In: *Reverse Osmosis and Synthetic Membranes* (ed. S. Sourirajan), 167–208. National Research Council Canada.
  - 18 Michaels, A.S. (1971). High flow membranes for ultrafiltration or reverse osmosis. US Patent 3, 651, 024.
  - 19 Frommer, M.A., Feiner, I., Kedem, O., and Bloch, R. (1970). Mechanism for formation of skinned membranes. II Equilibrium properties and osmotic flow. *Desalination* 7: 39.
  - 20 Strathmann, H., Scheible, P., and Baker, R.W. (1971). A rationale for the preparation of Loeb-Sourirajan-type cellulose acetate membranes. *J. Appl. Polym. Sci.* 15: 811.
  - 21 Broens, L., Altena, F.W., Smolders, C.A., and Koenhen, D.M. (1980). Asymmetric membrane structures as a result of phase separation phenomena. *Desalination* 32: 33.
  - 22 Cabasso, I., Klein, E., and Smith, J.K. (1976). Polysulfone hollow fibers. I Spinning and properties. *J. Appl. Polym. Sci.* 20: 2377.
  - 23 Bourganel, J. (1973). Process for the preparation of anisotropic semipermeable membranes of polyarylether sulfones. US Patent 3, 855, 122, Dec. 17, 1973.
  - 24 Guiver, M.D., Tremblay, A.Y., and Tam, C.N. (1989). Reverse osmosis membranes from novel hydrophilic polysulfones. In: *Advances in Reverse Osmosis and Ultrafiltration* (eds. T. Matsuura and S. Sourirajan), 53. National Research Council Canada.
  - 25 Model, F.S., Davis, H.J., Boom, A.A. et al. (1971). The Influence of the Hydroxyl Ratio on the Performance of Reverse Osmosis Desalination Membranes. *Research and Development Progress Report No 657*. Washington, DC: U.S. Department of the Interior, Office of Saline Water.

- 26 Kraus, K.A., Phillips, H.O., Marcinowsky, A.E. et al. (1966). Hyperfiltration studies. VI. Salt rejection by dynamically formed polyelectrolyte membranes. *Desalination* 1: 225.
- 27 Altman, M. and Hasson, D. (1999). Review of dynamic membranes. *Rev. Chem. Eng.* 15 (1): 1–40.
- 28 Lonsdale, H.K. (1987). The evolution of ultrathin synthetic membranes. *J. Membr. Sci.* 33: 121–136.
- 29 Meyer, K.H. and Sievers, J.F. (1936). La perme'abilite' des Membranes I. Th orie de la perme'abilite' ionique. *Helv. Chim. Acta* 19: 649, *ibid*" La perme'abilite' des Membranes II. Essais avec des membrane se'lectives artificielles" p665, *ibid* " La perme'abilite' des Membranes IV. Analyse de la structure de membranes vege'tales at animals" p987.
- 30 Teorell, T. (1953). Transport processes and electrical phenomena in ionic membranes. *Progr. Biophys. Biophys. Chem.* 3: 305.
- 31 Hoffer, E. and Kedem, O. (1967). Hyperfiltration in charged membranes: the fixed charge model. *Desalination* 2: 25.
- 32 Hoffer, E. and Kedem, O. (1972). Hyperfiltration in charged membranes: prediction of salt rejection from equilibrium measurements. *J. Phys. Chem.* 76: 3638.
- 33 Hoffer, E. and Kedem, O. (1968). Negative rejections of acids and separation of ions by hyperfiltration. *Desalination* 5: 167.
- 34 Hoffer, E. and Kedem, O. (1972). Ion separation by hyperfiltration through charged membranes. II. Separation performance of collodion-polybase membranes. *I&EC Process Des. Dev.* 11: 226.
- 35 Linder, C., Aviv, G., and Perry, M. (1983). Proceedings of Ashkelon Conference Separation Sciences May 30, –June 1, 1983. Robust industrial membranes for reverse osmosis and ultrafiltration.
- 36 Pappenheimer, J.R., Renkin, E.M., and Borrero, L.M. (1951). Filtration diffusion and molecular sieving through peripheral capillary membranes. *Am. J. Physiol.* 167: 13.
- 37 Renkin, E.M. (1954). Filtration diffusion and molecular sieving through porous cellulose membranes. *J. Gen. Physiol.* 38: 225.
- 38 Dresner, L. (1965). The exclusion of ions from charged microporous structures. *J. Phys. Chem.* 69: 2230.
- 39 Simons, R. and Kedem, O. (1973). Hyperfiltration in porous fixed charged membranes. *Desalination* 13: 1.
- 40 Dresner, L. (1972). Some remarks on the integration of the extended Nernst-Planck equations in the hyperfiltration of multicomponent solutions. *Desalination* 10: 27, *ibid* "Geometric effects in piezodialysis through charged mosaic membranes" p47.
- 41 Scatchard, G. (1976). *Equilibrium in Solutions. Surface and Colloid Chemistry*. Cambridge, MA: Harvard University Press.
- 42 Glueckauf, E. (1965). *1st International Symposium on Water Desalination*, 1, 145. Washington, DC: Office of Saline Water, U. S. Department of the Interior.
- 43 Glueckauf, E. and Russel, P.J. (1976). The distribution of electrolytes between cellulose acetate membranes and aqueous solutions. *Desalination* 18: 155.

- 44 Bean, C.P. (1972). *Membranes, Macroscopic Systems and Models*, Chapter 1 (ed. G. Eisenman). New York: Dekker.
- 45 Kraus, K.A., Raridon, R.J., and Baldwin, W.H. (1964). Properties of organic-water mixtures: I Activity coefficients of sodium chloride, potassium chloride, and barium nitrate in saturated water mixtures of glycol, glycerol and their acetates. Model solutions for hyperfiltration membranes. *J. Am. Chem. Soc.* 86: 2571.
- 46 Th u, G., Bloch, R., and Kedem, O. (1966). Water transport in porous and nonporous membranes. *Desalination* 1: 129.
- 47 Glueckauf, E. and Russel, P.J. (1970). The equivalent pore radius of dense cellulose acetate membranes. *Desalination* 8: 351.
- 48 (a) Spiegler, K.S. and Kedem, O. (1966). Thermodynamics of hyperfiltration (reverse osmosis) criteria for efficient membranes. *Desalination* 1: 311–326. (b) Jagur-Grodzinsky, J. and Kedem, O. (1966). Transport coefficients and salt rejection in uncharged hyperfiltration. *Desalination* 1: 327.
- 49 Grimm, E. and Sollner, K. (1957). The contributions of normal and anomalous osmosis to the osmotic effects arising across charged membranes with solutions of electrolytes. *J. Gen. Physiol.* 40: 887.
- 50 Schloegl, R. (1955). Theory of anomalous osmosis. *Z. Phys. Chem.* 3: 73.
- 51 Merten, U. (1966). Desalination by pressure osmosis. *Desalination* 1: 297.
- 52 Leitz, F.B. Piezodialysis. In: *Membrane Separation Processes*, Chapter 7 (ed. P. Mears), 261–294. Amsterdam: Elsevier Scientific Publishing Co.
- 53 Lonsdale, H.K., Pusch, W., and Walch, A. (1975). Donnan membrane effects in hyperfiltration of ternary systems. *J. Chem. Soc., Faraday Trans.* 71: 501.
- 54 Akred, A.K., Fane, A.J., and Field, J.P. (1980). Negative rejections of cations in the ultrafiltration of gelatin and salt solutions. *Polym. Sci. Technol.* 13: 353.
- 55 Perry, M. and Linder, C. (1989). Intermediate reverse osmosis ultrafiltration membranes for the concentrations and desalting of low molecular weight organic species. *Desalination* 71: 233–245.
- 56 Rozelle, L.T., Cadotte, J.E., King, W.L. et al. (1973). Development of Ultrathin Reverse Osmosis Membranes for Desalination. *Research & Development Progress Report, No. 659*. Office of Saline Water OSW.
- 57 (a) Riley, R.L., Lonsdale, H.K., and Lyons, C.R. (1970). *Proceedings of the 3rd International Symposium on Fresh Water from the Sea*, vol. 2 (eds. A.A. Delyannis and E.E. Delyannis), 551. Athens, GA. (b) Riley, R.L., Lonsdale, H.K., and Lyons, C.R. (1971). Composite membranes for sea water desalination by reverse osmosis. *J. Appl. Polym. Sci.* 15: 1267.
- 58 Cadotte, J.E. (1977). Reverse osmosis membranes. US Patent 4, 039, 440 Aug. 2, 1977.
- 59 Rozelle, L.T., Cadotte, J.E., Corneliussen, R.D., and Erickson, E.E. (1968). Final Report on development of new reverse osmosis membranes. *NTIS Report no. PB-206329*. National Technical Information Service (NTIS).
- 60 Cadotte, J.E. and Rozelle, L.T. (1972). In Situ-Formed Condensation Polymers for Reverse Osmosis Membranes. *NTIS Report No. PB-229337*. National Technical Information Service (NTIS).

- 61 Wrasildo, W.J. (1977). Semipermeable membranes and method for the preparation thereof. UP Patent 4, 005, 012; Jan. 25 1977.
- 62 (a) Riley, R.L., Fox, R.L., Lyons, C.R. et al. (1977). Spiral wound thin film composite membrane systems for brackish and seawater desalination by reverse osmosis. *Desalination* 23: 331. (b) See also Riley, R.L., Milstead, C.E., Wrasildo, W.J. et al. (1973). Research and Development on a Spiral-Wound Membrane System for Single-Stage Water Desalination. Annual Report of January 1, 1973 –December 31 1973, Contract 14-30-3191 for the Office of Saline Water US Department of the Interior.
- 63 Yasuda, H. (1977). Composite reverse osmosis membranes prepared by plasma polymerization. In: *Reverse Osmosis and Synthetic Membranes* (ed. S. Sourirajan), 263–294. National Research Council Canada.
- 64 Sano, T. (1980). A new reverse osmosis membrane made of polyacrylonitrile. *Chem. Econ. Eng. Rev.* 12 (5): 22.
- 65 Lai, J.Y. and Chao, Y.C. (1990). Plasma modified Nylon 4 membranes for reverse osmosis desalination. *J. Appl. Polym. Sci.* 39: 2293.
- 66 Stannett, V., Hopenberg, H.B., Bittencourt, E., and Haider, M.I. (1977). Grafted membranes for reverse osmosis. In: *Reverse Osmosis and Synthetic Membranes* (ed. S. Sourirajan), 153. National Research Council of Canada.
- 67 Kesting, R. and Stannett, V. (1963). The grafting of styrene to cellulose by mutual and preirradiated techniques. *Makromol. Chem.* 65: 248.
- 68 Jendrychowska-Bonanour, A.M. (1973). Semipermeable membranes synthesized by grafting poly(tetrafluorethylene) films: synthesis and study of properties I Anionic and cationic monografted membranes. *J. Chim. Phys.* 70: 8–15.
- 69 Cadotte, J.E., Steuck, M.F., and Petersen, R.J. (1981). Research on in situ-formed condensation polymers for reverse osmosis membranes. NTIS 1978, and US Patent 4, 259, 183.
- 70 Cadotte, J., Forester, R., Kim, M. et al. (1988). Nanofiltration membranes broaden the use of membrane separation technology. *Desalination* 70: 77–88.
- 71 Pepper, D. (1988). RO-fractionation membranes. *Desalination* 70: 89–93.
- 72 Kurihara, M., Uemura, T., Nakagawa, Y., and Tonomura, T. (1985). Thin film composite low pressure reverse osmosis membranes. *Desalination* 54: 75.
- 73 Comstock, D.L. (1989). Desal-5 membrane for water softening. *Desalination* 76: 61.
- 74 (a) Kuzuse, N., Shintani, T., and Iwana, A. (1981). Composite semi-permeable membranes. Jpn. Kokai Tokkyo Koho JP 61 93,806 12 May 1981 [Chem Abstract 105: 174043t]; (b) Ohya, H. (1985). Reverse osmosis separation of aqueous solutions. *Membrane* 10: 101.
- 75 Petersen, R.J. (1993). Composite reverse osmosis and nanofiltration. *J. Membr. Sci.* 83: 81–150.
- 76 McCray, S.B., Friesen, D.T., and Ray, R. (1992). Novel reverse osmosis membranes made by interfacial polymerisation. *5th Annual Meeting North American Membrane Society*, Lexington (17–20 May 1992).

- 77 McCray, S.B. (1989). Composite RO membranes of a microporous polymeric support and a polyamide reaction product of a tetrakis-aminomethyl compound and a polyacrylhalide are disclosed, said membranes exhibiting high flux and good chlorine resistance. US Patent 4, 876, 009; Oct. 24, 1989.
- 78 Linder, C., Aviv, G., Perry, M., and Katrarro, R. (1988). Composite amphoteric membranes useful for the separation of organic compounds of low molecular weight solutes from inorganic salt streams. US Patent 4, 767, 645; Aug. 30, 1988.
- 79 Strantz, J. Jr., and Brehm, W.J. (1990). Treatment for reverse osmosis membranes. US Patent 4, 938, 872; July 3, 1990.
- 80 Cadotte, J.E. and Walker, D.R. (1989). Novel water softening membranes. US Patent 4, 812, 270; Mar. 14, 1989.
- 81 Cadotte, J.E., Cobian, K.E., Forester, R.H., and Petersen, R.J. (1976). Continued Evaluation of in situ-Formed Condensation Polymers for Reverse Osmosis Membranes. *NTIS report No. PB-253193*. Midwest Research Inst., Minneapolis, Minn. North Star Research Div.; Office of Water Research and technology, Washington, D.C.
- 82 Linder, C., Perry, M., and Katrarro, R. (1980). Semipermeable composite membranes, their manufacture and use. Modified polyvinyl alcohol membranes. US Patent 4, 753, 725, Sept. 16, 1980.
- 83 Cadotte, J.E. (1990). Alkali resistant hyperfiltration membrane. US Patent 4, 895, 661; Jan. 23, 1990.
- 84 Fujimaki, H., Kurihara, M., and Uemura, T. (1990). Japan Kokai, Tokkyo Koho Japan 60,183,009 (Chemical Abstract 104:21033u).
- 85 Himeshima, Y. and Uemura, T. (1989). Japan Kokai, Tokyo Koho Japan 01,254,203 (Chemical Abstract 112: 1409148).
- 86 Ikeda, K., Nakano, T., Ito, H. et al. (1986). New composite charged membrane. *Desalination* 68: 109–119.
- 87 Ikeda, K., Yamamoto, S., and Ito, H. Eur. Pat. Appl. EP 165, 077.
- 88 Tsura, T., Urairi, M., Nakao, S., and Kimura, S. (1991). Negative rejection of anions in the loose reverse osmosis separation of mono- and divalent ion mixtures. *Desalination* 81: 219.
- 89 Linder, C. and Perry, M. (1986). Porous, semipermeable membranes of chemically modified cellulose acetate. US Patent 4, 604, 204; Aug. 5, 1986.
- 90 Linder, C., Aviv, G., Perry, M., and Katrarro, R. (1984). Modified acrylonitrile polymers containing semipermeable membranes. US Patent 4, 477, 634; Oct. 16, 1984.
- 91 Linder, C., Aviv, G., Perry, M., and Katrarro, R. (1987). Chemically modified semipermeable polysulfone membranes and their use in reverse osmosis and ultrafiltration. US Patent 4, 690, 766; Sept. 1, 1987.
- 92 Wrasildo, W.J. and Mysels, K.S. (1983). Hydrophilic surfaces and processes for making them. US Patent 4, 413, 074; Nov. 1 1983.
- 93 Roesink, H.D.W., Smolders, C.A., Mulders, M.H.V., and Koenhen, D.M. (1989). Process for the preparation of hydrophilic membranes and such membranes. US Patent 4, 797, 847; Jan. 17, 1989.
- 94 Pusch, W. and Walch, A. (1982). Synthetic membranes - preparation, structure, and application. *Angew. Chem. Int. Ed. Engl.* 21: 660–685.

- 95 Linder, C., Aviv, G., Perry, M., and Katrarro, R. (1988). Semipermeable encapsulated membranes. US Patent 4, 778, 596; Oct. 18, 1988.
- 96 Linder, C., Aviv, G., Perry, M., and Katrarro, R. (1987). Chemically modified semipermeable membranes and their use in reverse osmosis and ultrafiltration. US Patent 4, 690, 765.
- 97 Perry, M., Yacubowicz, J., Linder, C., and Shavit, R. (1993). Novel chemically stable SelRO™ nanofiltration membranes and modules for applications in chemical processes and treatment of waste streams, Aachener Membran Kolloquium Preprints, 9–11.3.93, 213–229.
- 98 Perry, M. and Linder, C. (1991). Advanced nanofiltration membranes possessing high chemical and solvent stability, Aachener Membran Kolloquium Preprints, 19.-21.3.91
- 99 Sourirajan, S. (1964). Separation of hydrocarbon liquids by flow under pressure through porous membranes. *Nature* 203: 1348–1349.
- 100 Kopecek, J. and Sourirajan, S. (1970). Performance of porous cellulose acetate membranes for RO separation of mixtures of organic liquids. *Ind. Eng. Chem. Process Des. Dev.* 9 (1): 5–12.
- 101 Paul, D.R. (1976). The solution diffusion model for swollen membranes. *Sep. Purif. Methods* 5 (1): 33–50.
- 102 Black, L. (1991). Interfacial polymerized membranes for the reverse osmosis separation of organic solvent solutions. Canadian Patent application 2,026,054 1990/09/24.
- 103 (a) Bitter, J.G.A., Haan, J.P., and Rijkens, H.C. (1988). Process for the separation of solvents from hydrocarbons dissolved in the solvents. US Patent 4, 748, 288; May 13, 1988; (b) Bitter, J.G.A. and Haan, J.P. (1989). Process for the separating a fluid feed mixture containing hydrocarbon oil and an organic solvent. US Patent 4, 810, 366; Mar. 7, 1989.
- 104 Linder, C., Nemas, M., Perry, M., and Katrarro, R. (1991). Solvent stable membranes. US patent 5, 039, 421; Aug. 13, 1991.
- 105 Perry, M., Yacubowicz, H., Linder, C. et al. (1992). Polyphenylene oxide-derived membranes for separation in organic solvents. US Patent 5, 151, 18; Sept. 29, 1992.
- 106 Linder, C., Nemas, M., Perry, M., and Katrarro, R. (1993). Silicone derived solvent stable membranes. US Patent 5, 265, 734; Nov. 30, 1993.
- 107 Larbot, S., Alami-Younssi, M., Persin, J. et al. (1992). Alumina nanofiltration membrane; application to metal removal. *5th Annual Meeting of the North American Membrane Society*, Lexington (17–20 May 1992).
- 108 Guizard, C., Larbot, A., and Cot, L. (1990). A new generation of membranes based on organic inorganic polymers. *Proceedings International Conference Inorganic Membranes*, Montpellier (3–6 July 1990).
- 109 Boye, A., Grangeon, A., and Guizard, C. (1992). Composite nanofiltration membrane. US Patent 5, 266, 207; Assigned to Techsep; filed April 30, 1992.
- 110 Bardot, C., Carles, M., Desplantes, R., and Shrive, L. (1993). Reverse osmosis or NF membrane and its production process. US Patent 5, 342, 521; April 21, 1993.

## 2

## Nanofiltration Membrane Materials and Preparation

Hanne Mariën, Rhea Verbeke, and Ivo F.J. Vankelecom

*KU Leuven, Membrane Technology Group (MTG), cMACS, Department of Microbial and Molecular Systems, Faculty of Bioscience Engineering, Celestijnenlaan 200F, PO Box 2545, 3001 Leuven, Belgium*

### 2.1 General Introduction

This chapter will cover the literature in which the synthesized membranes were applied both in nanofiltration (NF) as in reverse osmosis (RO) experiments. The difference between aqueous NF and RO is generally made on an application base and, more specifically, on the applied pressure (5–20 bar for NF and 10–100 bar for RO) or the nature of the compounds to be separated (200–1000 Da and divalent salts for NF, <200 Da and monovalent salts for RO). However, this is already a rather vague split; the distinction at the level of membrane synthesis becomes extremely imprecise. Indeed, loose RO membranes used in the separation of ions and tight NF membranes used to filter organic compounds at lower pressures can have exactly the same chemical composition and membrane preparation method. Besides aqueous NF, this chapter also includes the preparation of solvent-resistant nanofiltration (SRNF) membranes. The cited literature was further restricted to the synthesis of membranes that had actually been applied already in (SR)NF or RO experiments. This means that other rather tight membranes, which were not (yet) tested in NF, were not considered, even though these membranes could possibly show an interesting NF potential.

The main class of NF and RO membranes is thin film composite (TFC) membranes. Also for SRNF applications, the TFC membrane market is growing [1]. By far, the most important type herein are the membranes prepared via interfacial polymerization (IP), originally presented in 1965 [2], followed by membranes prepared via coating. TFC membranes consist of a thick, porous, nonselective support covered with an ultrathin barrier layer. The support is sometimes supported itself by a woven or nonwoven fabric, most commonly a polyester or polypropylene/polyethylene, to facilitate the handling of the membranes. The multilayer approach allows a more flexible optimization of each layer. The support layer should offer a maximal mechanical strength and compression resistance, combined with a minimal resistance to permeation. The top layer on the other hand should show the desired combination of solvent flux and solute rejection.

Integrally skinned asymmetric membranes form the second important group of (SR)NF/RO membranes. Based on the pioneering work of Loeb and Sourirajan in 1963 [3], they are prepared via the phase inversion process and possess a dense surface skin on top of a porous sublayer, both having the same composition. These membranes are prepared in one step, which makes them generally cheaper and thus more appropriate for low-cost applications, such as water treatment. Cellulose acetate (CA) membranes, for example, can only be prepared via this method. Together with polyamides (PAs), which can be prepared via both phase inversion and IP, CA dominates the field of commercial (mostly aqueous) NF/RO applications, even though the CA market share has been declining substantially in the last years.

Compared with polymeric NF membranes, the use of NF membranes based on ceramics is less widespread, even though significant progress in this field has been made in the last years. Ceramic membranes generally show a higher chemical, structural, and thermal stability. They do not deform under pressure, do not swell, and can be cleaned easily. However, they tend to be more brittle and more expensive than polymeric membranes [4, 5].

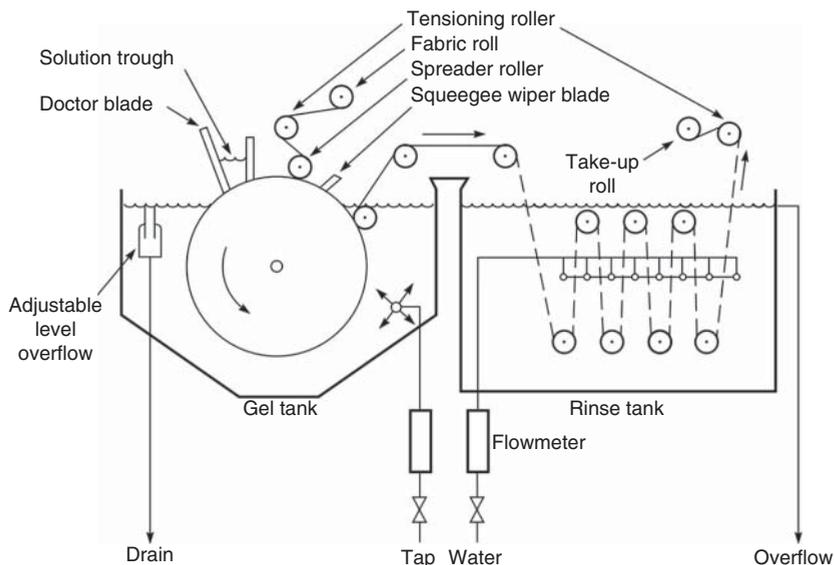
This chapter will cover the preparation techniques of all these different types of membranes, starting with a concise description of the underlying fundamental background when needed, before describing the more specific examples. Whenever the reported membrane synthesis parameters are linked to molecular weight cutoffs (MWCs) and pore diameters, care should be taken in interpreting these numbers as they might have been determined under slightly different conditions (pressures, flow mode, solute type, etc.), with different definitions (90% or 95% rejection) or obtained via slightly different calculation methods. More details on the historical membrane developments are given in Chapters 1 and 25.

## 2.2 Phase Inversion

### 2.2.1 Introduction

Phase inversion is a commonly used method to prepare NF membranes [6]. It refers to the controlled transformation of a cast polymeric solution from a liquid into a solid state [7]. During the phase inversion process, a thermodynamically stable polymer solution is mostly subjected to a controlled liquid–liquid demixing. This “phase separation” of the cast polymer solution into a polymer-rich and a polymer-lean phase can be induced by immersion in a nonsolvent bath (“immersion precipitation”), by evaporating the volatile solvent from a polymer that was dissolved in a solvent/nonsolvent mixture (“controlled evaporation”), by lowering the temperature (“thermal precipitation”), or by placing the cast film in a vapor phase that consists of a nonsolvent saturated with a solvent (“precipitation from vapor phase”) [8].

The development of integrally skinned asymmetric membranes meant a major breakthrough for NF/RO membrane synthesis [3]. Their specific structure is obtained via immersion precipitation in either a nonsolvent (Figure 2.1) [8, 9], in a sequence of two different nonsolvents (“dual bath method”) [10],



**Figure 2.1** Schematic of nonsolvent-induced phase inversion process to obtain integrally skinned asymmetric membranes. *Source:* Baker 2012 [45]. Reproduced with permission of John Wiley and Sons.

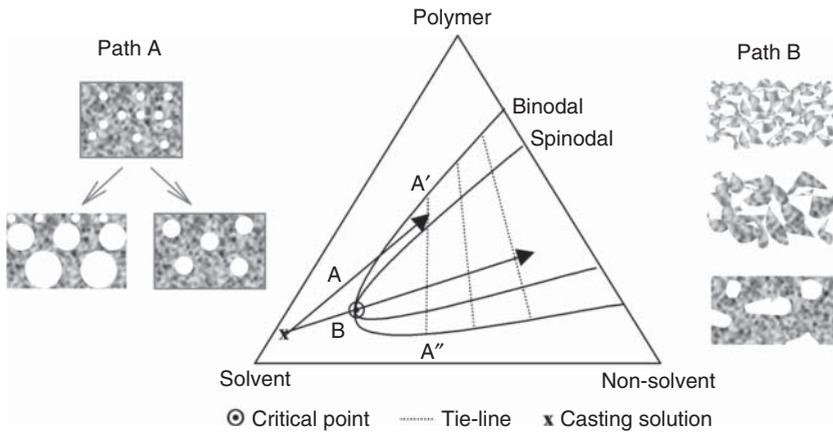
or by immersion in a nonsolvent after partial “dry” phase inversion caused by evaporation of the more volatile solvent from a solvent/nonsolvent mixture in the casting solution (“dry/wet method”) [11].

### 2.2.2 Basic Principles

The thermodynamic aspects of immersion precipitation can be best visualized by the polymer/solvent/nonsolvent phase diagram (Figure 2.2). The initial casting solution is situated in the stable region of the diagram outside the binodal. The so-called “demixing by nucleation and growth” (pathway A in Figure 2.2) is the most common way to phase separate. Polymer solutions situated in the region between the binodal and spinodal are metastable. They will phase separate into a polymer lean and a polymer-rich phase according to the nucleation and growth mechanism. The composition of both of these phases is represented by the  $A'$  and  $A''$  ends of the tie lines on the diagram. Under ideal conditions, the nuclei would just grow and mostly progress to a phase coalescence.

The second pathway B in Figure 2.2 represents “spinodal decomposition.” It occurs when the demixing path crosses the critical point, going directly into the unstable region, or when the composition passage through the metastable region is too fast. Again, following the tie lines, two separate phases appear, but instead of forming well-defined nuclei, two cocontinuous phases will be formed.

The phase diagram represents the composition of the membrane at thermodynamic equilibrium, but it does not give any information about the size and morphology of the formed phases. These membrane properties are the result of the system kinetics. Two types of demixing exist, as shown in Figure 2.2. The

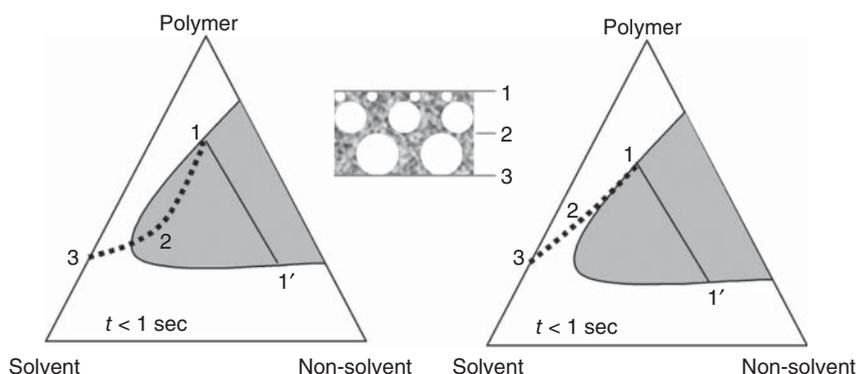


**Figure 2.2** Phase diagram of a ternary system of polymer, solvent, and nonsolvent, representing the mechanism of phase separation during immersion precipitation. *Source:* Nunes and Peinemann 2001 [215]. Reproduced with permission of John Wiley and Sons.

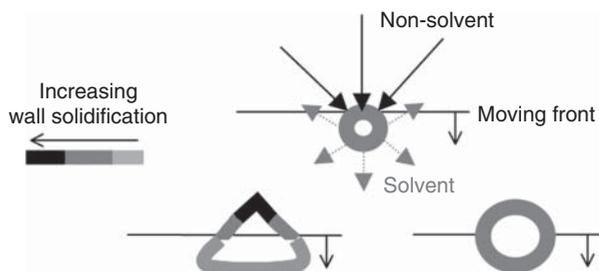
dotted line represents the composition path of the cast film (1 = top of the film; 3 = bottom) at a certain time  $t$  almost immediately after immersion. For each subsequent moment, another composition path will exist as more solvent will gradually be exchanged by more nonsolvent. In the left figure, the binodal is crossed already by the main part of the film at the time  $t$  and demixing will start directly (immediate demixing). On the right figure, a stable composition is still present at any position in the film. Demixing will only start after a while, when more nonsolvent has entered the film so that the binodal can be crossed (delayed demixing).

If the polymer system gels and solidifies soon after the first steps of phase separation, the membrane will have a fine pore structure, closely reflecting the original characteristics given by the initial demixing mechanism. Spinodal demixing favors the formation of an interconnected pore structure from the beginning. By nucleation and growth, closed cells can only be prevented when the growing nuclei grow sufficiently and eventually touch. When the demixing is immediate, these closed cells are formed close to the film surface and subsequently grow toward the bottom side, resulting in a porous membrane. However, when demixing is delayed, more solvent can be removed from the cast film, resulting in a film with a higher polymer concentration at the surface [12, 13].

Macrovoids are finger-like pores formed by means of a rapidly moving front of nonsolvent (Figures 2.3 and 2.4). Macrovoid formation is favored when the inward diffusion of nonsolvent into the polymer-poor phase exceeds that of the outward solvent diffusion and when the polymer system only starts to solidify at relatively high nonsolvent concentrations. As more nonsolvent enters, the wall will deform and expand in the form of a tear. The main driving force for the nonsolvent to enter the developing pore is the locally generated osmotic pressure. At a certain point, the pore wall will vitrificate or partially crystallize as the solvent concentration decreases: the pore wall is then completely formed. Membranes with small pore sizes (sponge-type membranes) are favored when the diffusion



**Figure 2.3** Composition of the polymer film immediately after immersion in the coagulation bath. Left: immediate demixing. Right: delayed demixing. *Source:* Nunes and Peinemann 2001 [215]. Reproduced with permission of John Wiley and Sons.



**Figure 2.4** Formation of macrovoids. *Source:* Nunes and Peinemann 2001 [215]. Reproduced with permission of John Wiley and Sons.

coefficient of the nonsolvent is low, when the osmotic pressure is low or when a lot of small, stable nuclei are formed.

The modynamic characteristics of the polymer solution combined with the kinetic aspects of diffusion thus both determine the ultimate membrane morphology [8]. The following parameters have a large impact on this morphology:

1. Type of polymer (hydrophilicity, charge density, polymer structure, molecular weight [MW], polymer dispersity, and purity)
2. Composition of the casting solution (solvent, polymer concentration, and additives)
3. Postcasting evaporation (solvent evaporation time and atmospheric conditions [temperature, humidity, air flow, composition, etc.])
4. Coagulation medium (composition and temperature)
5. Post-treatment (wet or dry annealing, exposure to concentrated mineral acids, and treatment with conditioning agents)

The following section describes how these parameters can be used to change and improve the morphology and performance of asymmetric membranes.

### 2.2.3 Polymer Type

Many types of polymers have been used to prepare membranes via phase inversion. The most common ones are polysulfone (PSf), polyethersulfone (PES), polyacrylonitrile (PAN), cellulose, poly(vinylidene fluoride) (PVDF), polyimide (PI), and PA [14]. Their structures are shown in Table 2.1.

The first important factor in the selection of a membrane material is the desired stability of the polymer. CA has a rather low chemical, mechanical, and thermal stability. Polymers such as PSf and PES are much more chemically and thermally resistant, as indicated by their high glass transition temperatures of 190 and 230 °C, respectively. However, for many SRNF applications in which harsh solvents are used, they are only suitable when cross-linked. Other highly solvent-resistant polymer types are (by preference cross-linked) poly(ether ether ketone) (PEEK) [15, 16], PI [17, 18], and poly(benzimidazole) (PBI) [19].

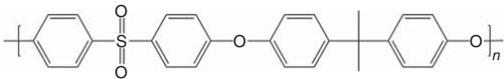
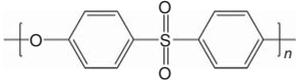
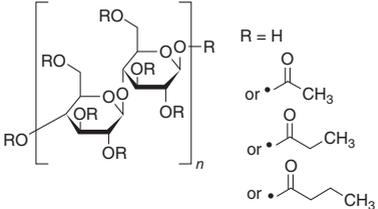
Because the chemical structure of nonporous (SR)NF and RO membranes directly influences the solution–diffusion behavior of the permeating components from the feed, the choice of the polymer determines the membrane performance [14]. Therefore, hydrophilic polymers are very suitable for aqueous applications because they generate membranes with a higher water flux than hydrophobic polymers. Moreover, they generally show a higher resistance to fouling in aqueous environments where mainly hydrophobic compounds tend to adhere to the membrane polymer [20]. Membrane hydrophilicity can be improved by introducing charged groups, e.g. via sulfonation [20] or bromination [21].

The chemical structure also determines the chain flexibility and the conformation and configuration of the polymer, thereby influencing the interaction between the polymer chains. Higher fluxes can be expected with membranes prepared from nonlinear polymers, as their interchain distance is higher. In aromatic polymers [22, 23], the linearity of the chains depends on the substitution of the groups on the benzene rings: more para-substituted rings increase the chain symmetry, thus lead to a more compact structure and a decreased flux. In the case of relatively rigid polymers, such as PAs and polyamide hydrazides (PAHs), higher MWs of the polymer chains lead to lower fluxes and higher rejections. This was explained by the higher amount of hydrogen bonds between longer polymer chains, causing an overall membrane densification [24].

### 2.2.4 Casting Solution

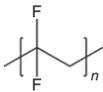
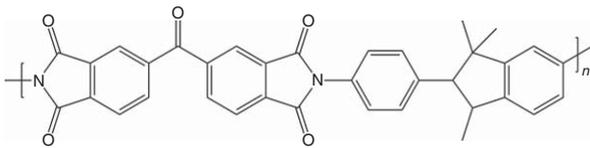
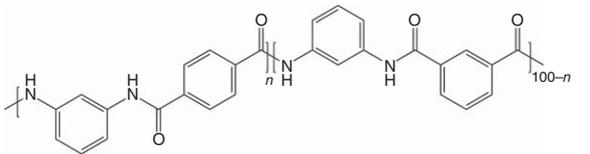
The casting solution contains at least a polymer and a solvent. Cosolvents, nonsolvents, or other additives can be added to the casting solution to influence the membrane morphology and performance. Important parameters are the polymer concentration and the interaction between the solvent in the casting solution and the nonsolvent in the coagulation bath. When the interaction is low, more sponge-like membranes will be obtained [25].

**Table 2.1** Common polymers used in the preparation of membranes via phase inversion.

Polymer	Abbreviation	Structure
Polysulfone	PSf	
Polyethersulfone	PES	
Polyacrylonitrile	PAN	
Cellulose acetate Cellulose acetate butyrate Cellulose propionate	CA CAB CP	

(Continued)

Table 2.1 (Continued)

Polymer	Abbreviation	Structure
Poly(vinylidene fluoride)	PVDF	
Polyimide	PI	
Polyamide	PA	

#### 2.2.4.1 Polymer Concentration

Because of higher viscosity, an increasing polymer concentration slows down the in-diffusion of nonsolvent and the out-diffusion of solvent, causing the demixing to be delayed. The high polymer concentration at the film surface, together with the delayed demixing, results in a membrane having a thicker and denser skin layer. Therefore, membranes prepared from higher polymer concentrations generally show higher rejections and lower permeances [7, 26–31].

#### 2.2.4.2 Addition of Volatile Cosolvents

When volatile cosolvents are added to the casting solution, an evaporation step is generally introduced between casting and phase inversion to selectively evaporate the volatile cosolvent partly (see Section 2.2.5). The effect on membrane morphology and performance depends on the cosolvent type (boiling point, interaction with the polymer, solvent, and nonsolvent), the cosolvent concentration, the evaporation time, and the atmospheric conditions (temperature, humidity, air flow, etc.). Commonly used cosolvents are tetrahydrofuran (THF) and dioxane, with respective boiling points of 66 and 101 °C. The effects of volatile cosolvent evaporation on membrane morphology and performance are discussed in Section 2.2.5.

#### 2.2.4.3 Addition of Nonsolvents

The concentration of nonsolvent that can be added to the casting solution is determined by the position of the binodal in the ternary diagram (Figure 2.2), as no demixing may occur before the immersion in the coagulation bath. The addition of nonsolvent causes the composition of the casting solution to move toward the binodal, favoring instantaneous demixing and thus promoting the formation of a more porous membrane [8]. However, other factors that are influenced by addition of a nonsolvent, such as an increasing viscosity of the casting solution and a decreasing osmotic pressure difference at the nonsolvent moving front during phase inversion, might counteract fast demixing [29]. Therefore, the effects of nonsolvent addition on membrane morphology are very dependent on the polymer–solvent system, the nonsolvent properties, concentration, etc.

By adding water, acetone, isopropanol (IPA), or hexanol as nonsolvent to a casting solution of PI, *N*-methylpyrrolidone (NMP), and THF, membrane morphology unexpectedly changed from a finger-like to a sponge-like structure, resulting in a decreased IPA permeance [29]. Moreover, the addition of water as nonsolvent to a CA solution suppressed the formation of macrovoids when the solvent was 1,4-dioxane, while it promoted macrovoid formation with acetone as solvent [13]. Also, the concentration of the nonsolvent has shown to be an important factor in the promotion or suppression of macrovoid formation [32].

#### 2.2.4.4 Addition of Other Additives

A wide range of additives, both inorganic and organic, can be added to the casting solution. Besides their specific function, general additive properties that affect membrane morphology are their concentration, viscosity, volatility, and nonsolvent power [7].

Possible inorganic additives are inorganic salts, metal oxides, and nanoparticles. Salts have an influence on the interaction between the polymer chains and on the solution quality [7]. The addition of LiCl to a PA casting solution increased the porosity of the formed membrane, said to be caused by leaching of LiCl from the membrane during phase inversion, leaving behind pores [33]. Metal oxides generally suppress macrovoid formation, as their presence increases the viscosity of the casting solution and thus slows down the exchange between solvent and nonsolvent during phase inversion, which promotes delayed demixing. This effect was shown for PI-based SRNF membranes containing TiO<sub>2</sub> [34]. Noble metal nanoparticles have been added for their photothermal heating properties, allowing them to turn light into heat [7]. When incorporated in a membrane, the nanoparticles can improve the flux without compromising the selectivity by simple light irradiation on the membrane. This beneficial effect was proven by incorporating gold nanoparticles in CA- and polydimethylsiloxane (PDMS)-based membranes and irradiating them with a laser beam during filtration [35, 36]. Later on, the technique was optimized by switching to cheaper silver nanoparticles together with a cheaper and energetically more efficient light emitting diode (LED) light source [37].

Organic additives can either be small molecules or larger polymeric structures. Examples of low MW additives are glycerol, alcohols, diols, and dicarboxylic acids. Frequently used polymeric additives are polyvinylpyrrolidone (PVP) and polyethylene glycol (PEG). Organic additives can induce or suppress macrovoid formation depending on the specific polymer/solvent system and on the used additive concentration. Therefore, the effect of an additive on membrane morphology is difficult to predict [7]. The addition of a low concentration of diethylene glycol diethyl ether (DGDE) to a PSf/NMP or polyethylene imine (PEI)/NMP casting solution did not significantly influence the size or number of macrovoids in the membrane, although a decrease in permeance and an increase in selectivity was observed. However, at high DGDE concentrations, the formation of macrovoids was totally suppressed [38, 39]. The addition of polymeric additives such as PEG has two opposite effects. On the one hand, it increases the viscosity of the casting solution, promoting delayed demixing and the formation of more dense membranes. On the other hand, hydrophilic PEG can leach out of the membrane during phase inversion, leaving voids behind [40]. Adding PEG200 to a PEI/NMP casting solution suppressed the formation of macrovoids and caused the retention of the membrane to drastically increase, while the permeance decreased [41].

### 2.2.5 Postcasting Evaporation

During the evaporation step, volatile cosolvents added to the polymer solution selectively evaporate from the cast polymer film, resulting in a skin layer with a locally increased polymer concentration. During phase inversion, this dense skin layer creates an extra resistance against diffusion of solvent and nonsolvent, which may result in delayed demixing [26]. Longer evaporation times cause the formed skin layer to be thicker [28]. At very high evaporation times, absorption of

water from the air may occur, which may lead to partial demixing of the polymer film before immersion in the coagulation bath [29].

Parameters that have been examined thoroughly in the literature are the volatile cosolvent concentration and the evaporation time. As expected, the formation of a dense skin layer results in a decreased permeance of the membrane, both at increased cosolvent concentration and at increased evaporation time [26, 28–31, 42]. However, the effect of the evaporation step on membrane selectivity can increase membrane selectivity or keep it unaffected. In some studies, an increased cosolvent concentration or evaporation time resulted in an increase in selectivity [26, 29–31], while in others, the selectivity remained constant [28, 42]. This difference could not be ascribed to the type of polymer nor cosolvent used in the studies.

Also, the evaporation temperature obviously strongly influences solvent evaporation, although less frequently investigated in detail. Lower fluxes and higher rejections at increasing evaporation temperatures were observed for PAH and PA membranes, with the rejection reaching a plateau from 120 °C onward for the PAH membranes [23, 33, 43].

A high relative humidity is mostly unwanted because water from the air can be absorbed in the polymer film, especially when hygroscopic solvents such as dimethylformamide (DMF) or NMP are used in the casting solution or when long evaporation times are applied. This water uptake can cause partial demixing of the polymer film. For PES membranes, a high relative humidity lowered the reproducibility of the preparation process [27].

### 2.2.6 Coagulation Bath

The type of nonsolvent used in the coagulation bath determines the exchange rate between solvent and nonsolvent during phase inversion and can drastically influence membrane morphology. A good solvent/nonsolvent interaction results in a high exchange rate, favoring immediate demixing and the formation of macrovoids. This is the case in a dimethylsulfoxide (DMSO)/water solvent/nonsolvent system [8].

To delay the demixing process, a solvent for the polymer or a weaker nonsolvent can be added to the coagulation bath. However, the opposite effect might occur when the solvents used in the casting solution have a better miscibility with the solvent added to the coagulation bath than with the original nonsolvent in the coagulation bath. This promotes solvent exchange and thus instantaneous demixing. When IPA is added to a water coagulation bath, delayed demixing is favored for the PI, as PI has a higher solubility in IPA than in water. However, the interaction between the solvent and the nonsolvent is also lowered as the miscibility of the solvents used in the casting solution (NMP, DMF, or dimethylacetamide) with IPA is higher than with water. This would favor instantaneous demixing. In this specific case, the former effect seemed to dominate, as the formation of a sponge-like structure with decreasing macrovoid formation at increasing IPA concentration in the coagulation bath was observed [29].

A higher coagulation bath temperature increases the solvent/nonsolvent exchange rate, leading to faster demixing. The formation of a more porous membrane with higher permeance and lower selectivity after increasing coagulation bath temperature between 0 and 25 °C was shown for PEI and CA membranes [30, 44].

## 2.2.7 Post-treatment

Several post-treatments can be applied to improve membrane performance, chemical stability, or practical handling. Membranes can be post-treated by wet or dry annealing, cross-linking, or drying by solvent exchange or by using conditioning agents.

### 2.2.7.1 Annealing

During synthesis, the presence of gas bubbles in the casting solution, dust particles on the support fabric, or imperfections in it can introduce defects in the final membrane [45]. Annealing is used to reduce the number of defects and therefore generally improves selectivity and lowers the permeance. Wet annealing is mostly performed in a water bath and optimized per polymer type but typically at 70–90 °C [7]. The densification effect of wet annealing was shown for a CA RO/NF membrane, causing a dramatic increase in NaCl rejection from 15% to 82% [44].

### 2.2.7.2 Cross-linking

Cross-linking is mainly applied to improve the chemical stability of the membrane. Possible methods are thermal, chemical, UV, or electron beam (EB) cross-linking.

Polyaniline membranes were made solvent resistant by thermal cross-linking at 180 °C, creating reactive radicals that formed interchain bonds [46]. Chemical cross-linking with diamines was intensively studied for PI membranes. After phase inversion, the membranes were placed in a diamine/methanol bath, in which the solvent acts as a swelling agent for the membrane to improve cross-linker uptake [47]. Phase inversion and cross-linking could also be performed simultaneously by adding the cross-linker to the aqueous coagulation bath, which eliminates the need for a hazardous swelling solvent [18, 48]. UV cross-linking was used in the preparation of PSf and PI membranes, where semi-interpenetrating networks were formed using polyfunctional acrylates [49, 50]. These acrylate based cross-linkers could also be applied in the EB cross-linking of PSf membranes, with the advantage that photoinitiators were no longer needed [51].

### 2.2.7.3 Drying

To preserve their surface structure and prevent pore collapse during drying, the membranes are exposed to a solvent exchange or are impregnated with conditioning agents before the drying step.

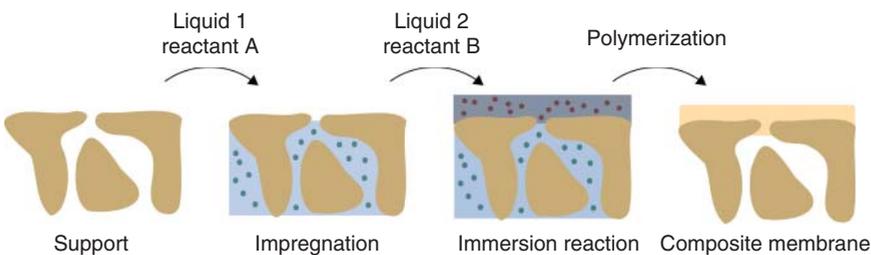
In the solvent exchange method, the nonsolvent in the membrane after phase inversion (mostly water) is exchanged with a series of more volatile solvents, making it more easy to obtain a dry membrane that retains its initial structure [52]. The solvents have to be miscible with the previous solvent and should not dissolve the membrane. A screening of several solvents to perform the exchange process has been made for PEEK membranes [53]. Mineral oils were used as conditioning agents for PI membranes, making it possible to dry the membranes without the formation of cracks [28]. Other reported conditioning agents are glycerol and hexadecane [54].

## 2.3 Interfacial Polymerization

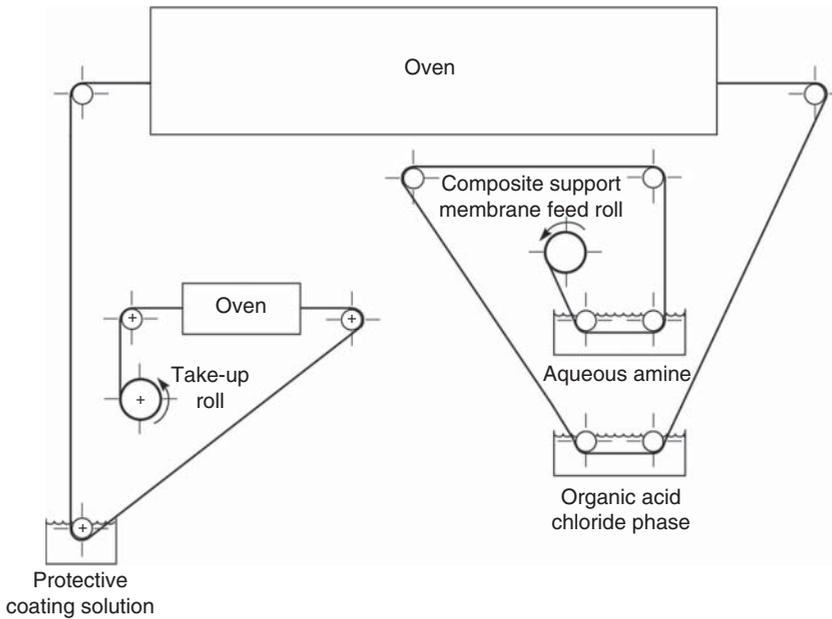
### 2.3.1 Introduction

IP is the most important technique for the synthesis of TFC RO and NF membranes [6]. In this synthesis method, a polymer film is formed via a reaction between two monomers at the interface of two immiscible solvents (Figure 2.5). A porous support is first impregnated with a (mostly) aqueous solution containing the first monomer. The excess of solution is removed and the saturated support is contacted with an organic solution containing the second monomer. At the interface between the two immiscible solvents, the monomers react to form a dense film on top of the porous support. Because the formation of this top layer inhibits further contact between the two monomers, the reaction is believed to be “self-terminating” and the formed film is typically very thin, ranging from a few tens to a few hundreds of nanometers [55]. Post-treatment steps, such as temperature curing or applying a protective coating, are often applied to further optimize the membrane performance and physicochemical properties. A schematic of industrial membrane manufacturing based on IP is shown in Figure 2.6.

PA, synthesized through IP, clearly dominates the field of TFC membranes as they can concurrently achieve high salt rejection while maintaining good water fluxes. The composition and morphology of the membranes, as well as their separation performance, depend on different parameters, such as concentration of the reactants, their partition coefficients and reactivities, kinetics and diffusion



**Figure 2.5** Schematic representation of the conventional IP procedure to synthesize composite membranes.



**Figure 2.6** Schematic representation of the IP process executed at large scale. *Source:* Baker 2012 [45]. Reproduced with permission of John Wiley and Sons.

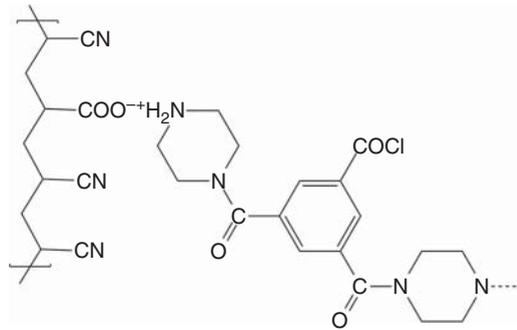
rates of the reactants, presence of by-products, competitive side reactions, cross-linking reactions, and postreaction treatment.

### 2.3.2 Support Materials

The support material provides the mechanical stability of the composite membrane. For aqueous NF and RO, PSf and PES ultrafiltration (UF) membranes are frequently mentioned supports. Because these polymers are sensitive to certain solvents, their use for SRNF applications is limited. Alternatively, other UF supports, such as PI, PAN, PEEK, and PVDF can be used, cross-linked if required, as well as inorganic membranes.

Support morphology (pore size and porosity) and chemical properties (hydrophilicity and reactivity with the monomers) have an influence on the IP process and the characteristics of the resulting top layer. Support hydrophilicity can be increased by adding additional hydrophilic polymers to the casting solution. The addition of hydrophilic PEG and PVP to a PSf casting solution has shown to lower the water permeability of the composite PA membrane [56]. It is assumed that the amine monomer in the support interacts with PEG and PVP through hydrogen bonding, limiting the diffusion of the amine monomer into the organic phase and causing the PA to be formed partly in the pores of the support [56]. In SRNF, the affinity between the support layer and the feed solvent is expected to affect the solvent flux, as PA membranes show a higher THF flux when formed on a hydrophilic cross-linked PI support than on a hydrophobic

**Figure 2.7** Improved interaction through ionic bonds between a modified PAN support and a PA-based top layer [58].



PEEK support, while the opposite trend is observed for the flux of hydrophobic toluene [57].

Lee and coworkers transformed part of the nitriles of the PAN support with NaOH into carboxylic acids (Figure 2.7). These were reacted with a diamine to form a bond between the support and the top layer that was prepared subsequently. It resulted in higher fluxes and a small increase in rejection [58].

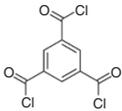
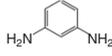
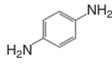
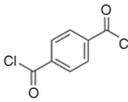
### 2.3.3 Monomers

The properties of the top layer, which performs the effective separation, are determined by the characteristics of the polymer obtained after the IP. Density, thickness, hydrophilicity, roughness, functional groups, and charge of the polymer determine the membrane performance [59]. The most widespread type of top layer for (SR)NF and RO applications is PA, formed via the reaction between an amine and an acyl chloride.

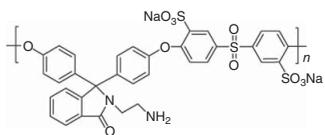
#### 2.3.3.1 Amines

In general, PA films made with aromatic diamines show better rejections but lower fluxes than those with aliphatic diamines [60]. Therefore, aromatic diamines are commonly used in the synthesis of RO membranes, while aliphatic diamines are applied for the preparation of more loose NF membranes. Typical amines are *m*- and *p*-phenylenediamine (*m*-PDA and *p*-PDA [61]) for RO and tight NF membranes and piperazine (PIP) for loose NF membranes (Table 2.2). The mutual position of the amines strongly affects these properties. Reactions of *o*-phenylenediamine (*o*-PDA), *m*-PDA, or *p*-PDA with isophthaloyl chloride (IPC) or terephthaloyl chloride (TPC) resulted in the best rejections and highest fluxes when the diamines and the diacylchlorides were located at the same position on the aromatic ring [62]. Reaction of trimesoylchloride (TMC) with *m*-PDA gave the best membrane performance (Figure 2.8) and is the commonly used combination nowadays in the synthesis of RO or tight NF membranes. TMC has a triple functionality and can thus form cross-linked polymer chains. After synthesis, the unreacted acyl chloride groups are hydrolyzed to carboxylic acid groups, causing the top layer to be negatively charged at neutral pH. The highly cross-linked top layer together with its negative charge allows the membrane to exclude salts and other solutes via both size exclusion and Donnan

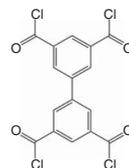
**Table 2.2** Monomers used in the synthesis of PA, polyester, and polyamine thin film composite membranes.

Aqueous monomer	Chemical structure	Organic monomer	Chemical structure
Polyamide (amine + acyl chloride) PIP		TMC	
<i>m</i> -PDA		IPC	
<i>p</i> -PDA		TPC	

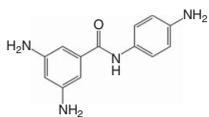
SPES-NH<sub>2</sub> [64]



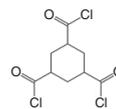
mm-BTEC [82]



DABA [65]



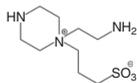
HTC [77]



PVAm [66, 67]

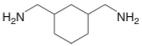
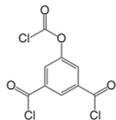
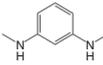
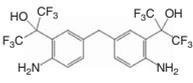
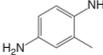


AEPPS [68]

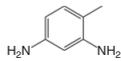


(Continued)

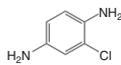
Table 2.2 (Continued)

Aqueous monomer	Chemical structure	Organic monomer	Chemical structure
CHMA [72]		Polyamide-urethane CFIC [81]	
<i>Improved chlorine resistance</i> N,N'-DMMPD [73]			
o-PDA [74]			
BHITM [75]			
M-p-PDA [76]			

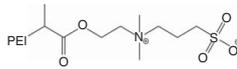
M-*m*-PDA [77]



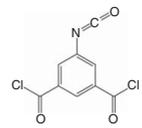
CPDA [76]



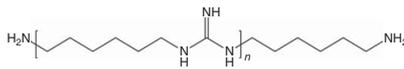
*Improved fouling resistance*  
PEI-g-SBMA [78]



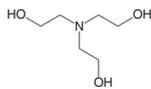
Polyamide-urea  
ICIC [83]



PHGH [79]



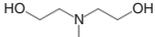
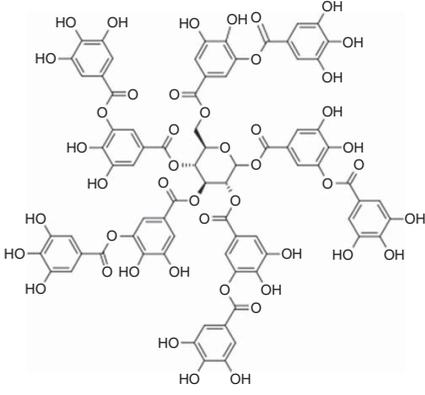
Polyester (alcohol + acyl chloride)  
TEOA [84]



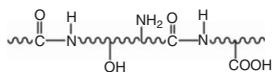
Acyl chlorides (see polyamide)

(Continued)

Table 2.2 (Continued)

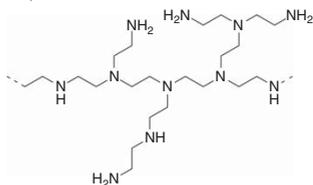
Aqueous monomer	Chemical structure	Organic monomer	Chemical structure
MDEOA [85]			
Tannic acid [86]			

Sericin [87]  
(protein)

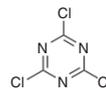


Polyamine (amine + alkyl chloride)

PEI [88]



Cyanuric chloride [88]

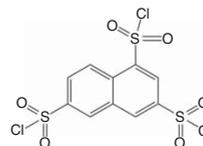


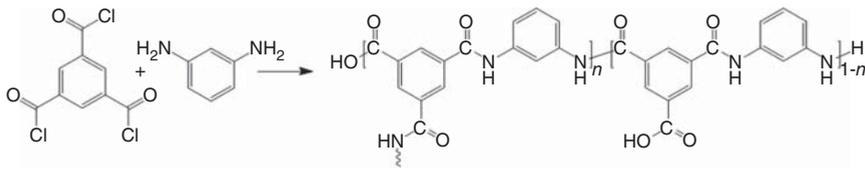
Other amines (see polyamide)

Polysulfonamide (amine + sulfonyl chloride)

Amines (see polyamide)

NTSC [89]





**Figure 2.8** Interfacial polymerization of a PA dense layer based on trimesoyl chloride (TMC) and *m*-phenylene-diamine (MPD). When  $n = 1$ , the resulting polymer is fully cross-linked. When  $n = 0$ , the resulting polymer is fully linear. The terminal carboxylic acid group will be deprotonated under normal operating conditions, causing the membrane to be negatively charged.

(electrostatic) exclusion. In NF, anions with a high charge density will be rejected more strongly by the membrane as they are affected more severely by Donnan repulsion compared to low charge density anions [63].

To further improve the properties of the top layer, new types of amine monomers were tested in the recent past (Table 2.2). Incorporation of sulfonated cardo poly(arylene ether sulfone) (SPES-NH<sub>2</sub>) in a PA top layer composed of *m*-PDA and TMC resulted in a remarkable increase in water permeance with only a slight decrease in NaCl retention [64]. Also, membranes made with a combination of *m*-PDA and 3,5-diamino-*N*-(4-aminophenyl) benzamide (DABA), a trifunctional amine, in the aqueous phase showed a similar increase in water permeance [65]. The use of polyvinylamine (PVA) as aqueous monomer resulted in the formation of a PA layer with its surface being positively charged at pH lower than 6 and negatively charged at pH higher than 7 [66, 67]. Moreover, zwitterionic amines can be used to create a PA top layer bearing positive and negative charges at the same time. The addition of the zwitterion aminoethyl piperazine propane sulfonate (AEPPS) to the aqueous PIP solution significantly increased the resulting membrane hydrophilicity, resulting in an almost doubling in water permeance with constant salt rejection [68]. The use of star-shaped poly(acryloyl hydrazide) polymer as a reagent in the aqueous phase during IP with TMC in hexane resulted in TFC membranes with permselectivity that can be tuned for both NF and RO applications [69].

The main limitation of aromatic PA composite membranes is their sensitivity for chlorine, a common disinfectant in water treatment [70]. It is assumed to be caused by the presence of N—H bonds in the PA top layer, which is chlorinated to form N—Cl [71]. This reaction also occurred when a cycloaliphatic amine, 1,3-cyclohexanebis(methylamine) (CHMA), was used to form the PA top layer [72]. It causes the hydrogen bonds between the PA chains to be destructed. However, by immersing the membrane in water, the reaction is partly reversed. In fully aromatic PA, an Orton rearrangement can take place, in which the chlorine group is irreversibly transferred from the amide bond to the aromatic ring [71]. By using secondary amines, such as *N,N'*-dimethyl-*m*-phenylenediamine (*N,N'*-DMMPD), no hydrogen was present in the formed amide bond, making the membrane more resistant to chlorine [73]. Moreover, the chlorine tolerance could be improved by using aromatic diamines having their amine groups in ortho position, such as *o*-PDA [74]. Also,

the presence of other groups, such as chlorine, methyl, or fluorine-containing groups (e.g. in 2-2'-bis(1-hydroxyl-1-trifluoromethyl-2,2,2-trifluoroethyl)-4-4'-methylenedianiline (BHTTM)[75], 2-methyl-*p*-PDA (*M-p*-DPA) [76], 4-methyl-*m*-PDA (*M-m*-PDA) [77], and 2-chloro-*p*-phenylenediamine (CPDA) [76] in ortho position to the amine group showed this beneficial effect, is caused by sterical hindrance for chlorine attack and by their influence on the basicity of the nitrogen atom of the amide bond.

Another drawback of PA composite membranes, their high fouling tendency, is attributed to the high surface roughness and surface charge of the PA layer. Fouling is mainly limited by surface modification via grafting (see Section 2.5.4). Some alternative amine monomers were reported to improve the fouling resistance of the PA top layer, such as the zwitterionic polyethyleneimine-*g*-sulfobetaine methacrylate (PEI-*g*-SBMA), which creates an electroneutral NF membrane [78], and the antibacterial polyhexamethylene guanidine hydrochloride (PHGH), which lowers the membrane biofouling tendency [79].

### 2.3.3.2 Acyl Chlorides

Just like for amines, there is a broad range of mono-, bi-, and tri-acylchlorides to select from (Table 2.2). Although the use of bifunctional acylchlorides such as IPC [66] and TPC [80] is reported occasionally, the trifunctional acylchloride TMC generally gives the best rejections and is therefore commonly used. To form a combined aromatic-cycloaliphatic PA film, TMC was replaced by cyclohexane-1,3,5-tricarbonyl chloride (HTC) [77]. In 5-chloroformyloxysophthaloyl chloride (CFIC), one of the three acylchloride groups was replaced by chloroformyloxy group, resulting in the formation of a mixed PA-urethane top layer after reaction with *m*-phenylene diamine (MPD) [81]. Furthermore, the reaction of PIP with 3,3',5,5'-biphenyl tetraacyl chloride (mm-BTEC) instead of TMC resulted in a positively charged NF membrane with increased salt rejection and water permeance [82]. The application of 5-isocyanatoisophthaloyl chloride (ICIC) with MPD improved the fouling resistance of the PA-urea RO membrane, assumed to be caused by its lower surface roughness and higher hydrophilicity [83].

### 2.3.3.3 Other Polymer Types

Besides PA, mixed PA-urethane, and PA-urea, other non-PA top layers are also formed via IP (Table 2.2). The use of triethanolamine (TEOA) or methyl-diethanolamine (MDEOA) as aqueous monomer resulted in the formation of a polyester top layer after reaction with TMC. These NF membranes were particularly useful for treating acidic feed because the water permeance increased at low pH because of the protonation of the tertiary amine group in TEOA or MDEOA, which increased its hydrophilicity [84, 85]. Other polyester top layers were formed by reacting TMC with the natural materials tannic acid and sericin. These NF membranes showed improved antifouling properties compared to the conventional PA NF membranes [86, 87]. TFC membranes with a polyamine top layer were reported as well for NF applications. This top layer, formed by reacting PEI and cyanuric chloride, showed to be significantly more stable in extreme pH conditions compared to the conventional PA top

layer [88]. Also, polysulfonamide membranes, formed via the reaction between PIP and naphthalene-1,3,6,-trisulfonyl chloride (NTSC), possess an improved pH stability compared to conventional PA [89].

### 2.3.4 Monomer Concentrations and Reaction Time

In conventional PA formation via IP, the solvent for the amine monomer is water, while the acyl chloride monomer is dissolved in an apolar solvent, mostly hexane. Because of the very low solubility of the acyl chloride in water, the PA film is assumed to be formed in the organic phase [90, 91]. The ratio of the two monomers in the reaction zone determines the degree of cross-linking of the formed film and is influenced by the transport rate of the monomers across the interface as well as their solubility and diffusion rate in the organic phase.

In the preparation of RO and tight NF membranes, commonly used concentrations are 2.0% (w/v) *m*-PDA in the aqueous phase and 0.1% (w/v) TMC in the hexane phase. An excess *m*-PDA is necessary because only a part of the monomers is transported toward the organic phase. When lowering the *m*-PDA or TMC concentration, a decreasing salt rejection and increasing water permeance indicates the less optimal *m*-PDA/TMC ratio in the reaction zone [61, 92, 93]. Lower monomer concentrations are also expected to limit the rate of top layer formation, resulting in a thinner and looser structure with lower selectivity [82, 92]. PIP is used instead of *m*-PDA to form more loose NF membranes. A similar correlation between amine concentration and membrane performance was found with an optimal PIP concentration between 0.5% and 2.5% (w/v) for a TMC concentration of 0.1–0.3% (w/v) [60, 82, 94].

Because the reaction between an amine and an acyl chloride proceeds very fast, the top layer is assumed to be formed completely within a time frame of a few seconds to a few tens of seconds, depending on the monomer structure [95]. The shortest IP time reported in the literature, using *m*-PDA and TMC as monomers and resulting in a high salt rejection, is 15 seconds. Increasing the reaction time did not further influence the water permeance and salt rejection, although opposite results have also been reported [96]. Shorter reaction times were not tested because of practical limitations of lab-scale membrane preparation [97]. It is generally assumed that IP follows a diffusion-limited growth caused by the increasing resistance against monomer diffusion by the formed PA film [98].

### 2.3.5 Solvent

Besides the conventionally used hexane as a solvent for the acyl chloride monomer, other solvents reported in the literature are heptane, dodecane, cyclohexane, benzene, 1,2-dichloroethane, isopar, and the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [81, 99–103]. While the diffusivity of the amine monomer in the organic phase is determined by the solvent viscosity, the amine solubility is determined by the molecular interactions with the solvent [81, 99]. Moreover, the interfacial tension between the aqueous and the organic phase influences the transport rate of the amine across the interface [103]. Also, the solubility of the formed PA film in the solvent

is important because it determines the speed of precipitation of the film. Fast precipitation inhibits further reaction and may result in a lower MW of the PA [100, 104].

Furthermore, the solvent temperature was investigated to optimize the membrane performance. Although only the temperature of the organic solution itself was controlled, the temperature of the whole system is expected to be altered after pouring this heated or cooled organic solution on the impregnated support. When using isopar, an increase in temperature from 10 to 50 °C resulted in a remarkable improvement in water flux, together with only a slight decrease in salt retention [81, 99]. Recently, the application of subzero temperatures of the TMC/heptane solution resulted in a nine time increase in water permeance, while the salt retention only decreased 4%. The lowest flux was achieved with a solvent temperature of 25 °C, while a further increase in temperature caused the flux to rise again [102].

### 2.3.6 Additives

Different types of additives are used in the aqueous or organic phase to improve membrane performance. Surfactants can be added to facilitate the impregnation of the support with the aqueous amine solution and to lower the water–organic interfacial tension, which promotes the transport of the amine monomers toward the organic phase [59, 97]. This mostly results in an increase in water flux of the composite membrane. Cationic (e.g. triethyl benzyl ammonium bromide [100] and cetyl trimethyl ammonium bromide [105, 106]) as well as nonionic (e.g. Triton X-100 [105, 106]) and anionic surfactants (e.g. sodium dodecyl sulfate [60, 93, 97, 105, 106]) are reported, added either to the aqueous or to the organic phase. Also, camphor sulfonic acid, applied to adjust the pH of the amine solution, is believed to improve the amine uptake in the support [99, 107]. Because hydrogen chloride (HCl) is formed during PA formation, acid acceptors (e.g. sodium hydroxide) can be added to the aqueous phase to prevent the amine monomers from being protonated by HCl and lose reactivity [60, 97]. However, a negative effect on the membrane performance was observed in some cases, which might be caused by the hydrolysis of the acyl chloride by the hydroxyl ions of the acid acceptor [97, 108]. Some acid acceptors, such as triethylamine (TEA), can also act as a catalyst for the reaction between the amine and the acyl chloride monomer. Because TEA is more nucleophilic than the amine monomer, it reacts with the carbonyl group of the acyl chloride, creating an intermediate that is more reactive toward the amine monomer than the original acyl chloride [97]. The addition of inorganic salts (e.g. CaCl<sub>2</sub> [109] and LiBr [85]) to the aqueous phase results in an increase in water flux, mostly accompanied by a decrease in selectivity. It is assumed that complexation of the Ca<sup>2+</sup> and Li<sup>+</sup> ions with the carbonyl group of TMC increases the rate of hydrolysis of the acyl chloride, resulting in a more loose PA or polyester top layer after reaction with an amine or an alcohol, respectively [85, 109]. In the final PA membrane, the complexation would also cause the N in the amide bond to be positively charged, which limits the attack of electrophilic chlorine and thus improves the chlorine resistance of the membrane [109]. The addition of a zwitterionic copolymer

(poly(aminopropyl dimethylaminoethyl methacrylate)-*co*-poly(sulfobetaine methacrylate)) to the aqueous MPD solution during IP with TMC in hexane resulted in a PA-based NF membrane having a 10 times higher water permeance with comparable dye rejection compared to commercial NF membranes [110].

Instead of adding the additives to one of the reaction phases, they can also be inserted in the pores of the support before impregnation with the first monomer. By filling the pores of a cross-linked PI support with PEG, the hydrophilicity of the support increases, improving its wetting with the aqueous amine solution. The resulting TFC membrane showed a significantly higher permeance, possibly caused by the slower transport of *m*-PDA toward the organic phase during IP. This was ascribed to hydrogen bonding of *m*-PDA with the PEG molecules in the support, causing the top layer to be thinner [57, 111]. In a similar way, the addition of linear polymer chains in the substrate, designed to participate in the IP reaction between *m*-PDA and TMC, helped reinforce the thin top layer. Increased rejection of divalent salts with improved water permeability was observed [112].

Besides additives, also cosolvents are added to the aqueous as well as the organic phase. The aim is to improve the miscibility of the aqueous and the organic phase, creating a more diffuse interface. This generally results in an improved flux of the composite membrane. Cosolvents reported are DMSO [113], *n*-propanol [100], IPA [81, 100], and hexamethyl phosphoramide [114] in the aqueous phase and acetone [115, 116], ethyl acetate [117–119], diethyl ether [117–119], and toluene [118] in the organic phase.

### 2.3.7 New Approaches

Recently, Hermans et al. presented a more efficient, time-saving, and material-saving approach to prepare interfacially polymerized membranes. Here, the amine monomer for the IP was added to the coagulation bath, making it possible to perform phase inversion and impregnation of the support with the amine monomer at the same time [93]. Moreover, a cross-linker for the support could also be added to the coagulation bath, converting a three-step synthesis (phase inversion, cross-linking, and impregnation) to a one-step process [120].

Two new approaches were developed to obtain composite membranes with extremely high permeances. In the first one, Karan et al. fixed a cadmium hydroxide nanostrand layer on a porous support before IP. After top layer formation, the nanostrand layer was removed by acid dissolution and the free floating top layer was transferred to a polymeric or alumina support. This top layer was less than 10 nm in thickness and showed, after fixation on an alumina support, an acetonitrile permeance, which was 2 orders of magnitude higher than that of commercially available membranes [121]. In the second approach, Jimenez-Solomon et al. used contorted monomers in IP to create a top layer with enhanced microporosity and higher interconnectivity of the intermolecular network voids. By reacting TMC with contorted aromatic phenols, a polyarylate (aromatic polyester) top layer with a thickness down to 20 nm was formed. The membrane showed solvent permeances up to 2 orders of magnitude higher than conventional TFC membranes [122].

Electrospraying has recently emerged as a novel technique to produce PA films, allowing full control over its roughness and thickness, two parameters that cannot be controlled in conventional IP [123, 124]. PA films synthesized through this so-called 3D printing technique are smoother and thinner than conventional PA membranes while they still exhibit good permselectivity [123, 124].

### 2.3.8 Post-treatment

To improve membrane selectivity by completing the cross-linking of the top layer and to remove residual solvent, a curing step at elevated temperature is sometimes applied. By increasing the curing temperature or time, the degree of cross-linking and membrane density is increased. However, too high temperatures can damage the membrane, which results in a decrease in selectivity. Conventional curing temperatures lie in the range of 40–120 °C [99]. The rejection of the membranes for neutral molecules, such as boron, can also be tuned postsynthesis by plugging the pores of the PA by letting it react with hydrophobic amines [125].

The application of a coating layer on top of an IP-synthesized membrane allows to modify the surface properties, adding an extra tuning possibility in membrane synthesis. Neutral hydrophilic polymers, for example, such as poly(vinyl alcohol), have been widely used to increase membrane hydrophilicity, increase membrane smoothness, and reduce surface charge [126].

Another post-treatment of TFC PA membranes is their immersion in or filtration with an activating solvent, e.g. DMF or DMSO. Although the mechanism is not fully understood yet, it was shown that this treatment causes the solvent permeance to increase drastically [111, 120, 127].

## 2.4 Coating

### 2.4.1 Introduction

A relatively simple membrane preparation technique is the coating of a solution on a support. The solution contains a polymer, a prepolymer, or a monomer that will form the selective layer of the membrane. After the coating step, the membrane is generally heated to evaporate the solvent of the coating solution and to cross-link the top layer, which improves the membrane stability and performance [128]. Different types of coating exist, e.g. dip coating, spin coating, or spray coating [8].

The polymer choice depends on many parameters, such as strength and stability of the polymer, film-forming properties, solubility in solvents, price, possibility to cross-link, etc. One or more layers can be coated on the support, the latter commonly referred to as “layer-by-layer (LbL)” deposition. An increasing number of layers increases the thickness of the selective layer and mostly lowers the flux [129, 130]. Also, the viscosity of the coating solution, which is influenced by the temperature of the solution, the polymer concentration, and the presence of additives, determines the thickness of the selective layer. A higher polymer

concentration generally results in a decreased flux and an increased rejection [128, 131]. The type of cross-linker, its concentration, reaction medium, reaction time, temperature, etc., determine the degree of cross-linking [132].

Besides the above-mentioned coating techniques, atomic layer deposition (ALD) is another technique capable of depositing a variety of thin film materials from the vapor phase and, thanks to the recent improvements made in the field, can now be applied atop polymeric materials [133, 134].

### 2.4.2 Examples

The dip coating technique was applied to fix a PEEK-selective layer on a porous support, followed by curing. Before membrane synthesis, tertiary amine groups were attached to the polymer to obtain a positively charged membrane [131]. In situ cross-linking of the PEEK top layer with bisphenol A diglycidyl ether clearly improved the salt rejection, while only a minor decrease in water flux was observed [128].

Spin coating was used to prepare a top layer from nanosized polymer particles [130] or polymers of intrinsic microporosity (PIMs) [135]. PIMs are contorted, rigid polymers having a continuous network of interconnected, intermolecular voids, which are therefore expected to show an improved solvent permeance during filtration. A high *n*-heptane permeance was indeed observed after optimizing the top layer thickness by varying the PIM concentration, being 2 orders of magnitude higher than the permeance of a commercial SRNF membrane [135]. In the coating of nanosized polymer particles, the size of the nanoparticles determined the dimensions of the interstitial spaces through which permeation occurred. An increasing nanoparticle concentration and a higher number of coating layers improved the selectivity of the membrane while flux decreased [130].

Other frequently used polymers in LbL coating are polyelectrolytes. In this method, a charged support is alternately dipped into oppositely charged polyelectrolytes, generating a multilayer film, which is stabilized by electrostatic interactions [129]. The important parameters in the synthesis are shown to be the number of bilayers deposited, the dipping and rinsing times, the coating temperature, and coating solvent. By optimizing these reaction conditions with poly(diallyldimethylammonium) chloride as a polycation and poly(vinylsulfonic acid sodium salt) or poly(sodium 4-styrenesulfonate) as a polyanion, an earlier 20–80-step synthesis was shortened to 6 steps, lowering the preparation time from 7 hours to 12 minutes without negatively influencing the membrane performance [136]. By using weak polyelectrolytes, such as poly(allylamine hydrochloride) as a polycation and poly(acrylic acid) as a polyanion, the charge density of the multilayer membrane can be tuned by changing the coating pH. As the membrane performance shown to be highly dependent on this charge density, an extra synthesis variable for optimizing the membrane performance was introduced in this method [137]. Because most polyelectrolyte multilayer membranes are stable in harsh solvents such as DMF, THF, and acetonitrile, they are highly suitable for use in SRNF [136].

Moreover, an “IP-like” LbL coating procedure was presented, in which TMC and *m*-PDA solutions were alternately deposited on the membrane surface. In

every step, only a single molecular layer was added because the stoichiometry between the monomers limits the degree of polymerization. This way, a more homogeneous PA top layer with a 70 times lower surface roughness compared to the conventional interfacially polymerized PA top layer was formed [138].

The deposition of an  $\text{Al}_2\text{O}_3$  layer atop a PA-based TFC membranes through ALD resulted in an increase in hydrophilicity of the top layer, although at the expense of salt rejection [134]. When applying ALD of  $\text{TiO}_2$  on RO and NF membranes, differences with respect to film growth kinetics, optimal ALD conditions, and depth of deposition are observed. For RO membranes, the coating is mainly located at the surface and causes an increase in surface charge, while for NF membranes, the coating is also present inside the pores [139].

## 2.5 Surface Modification

### 2.5.1 Introduction

Surface modifications of RO or (SR)NF membranes are often applied to further enhance the performance of the prepared membranes or to improve their long-term stability. The modification techniques can change the pore structure, introduce functional groups, change hydrophilicity, etc. Reported modifications are plasma treatment, classical organic reactions, polymer grafting, and photochemical modification.

### 2.5.2 Plasma Treatment

The treatment of membranes with a high-frequency discharge plasma allows to change the surface chemical composition, which can dramatically alter the surface properties [140]. An electric glow discharge plasma with ambient air as the working gas was used to modify a poly(1-trimethylsilyl-1-propyne) (PTMSP) membrane for SRNF applications. The treatment induced the formation of oxygen-containing groups and negative charges and increased the surface hydrophilicity, leading to lower alcohol fluxes [140]. Similar effects on the membrane surface properties were observed when treating a PDMS membrane with an Ar,  $\text{Ar}-\text{H}_2$ , or an  $\text{Ar}-\text{O}_2$  plasma [141] and a PA TFC membrane with a  $\text{NH}_3$  plasma [142]. The latter also showed a decreased fouling tendency for proteins and humic acid in aqueous applications.

### 2.5.3 Organic Reactions

#### 2.5.3.1 Covalent Linking of Monomers

Reactive functional groups on the membrane surface can be used to link certain monomers to the surface in order to modify the hydrophilicity and/or charge of the membrane. To improve the water flux in RO and NF applications, a PA TFC membrane was capped with 2,5-diaminobenzene sulfonic acid [143] or with TEOA [144] via a reaction of the free acyl chloride groups on the membrane surface with the amine groups or the hydroxyl groups of the monomer, respectively.

Acyl chloride quenching with ethylene glycol, ammonium hydroxide, methanol, ethanol, and *iso*-propanol was also performed to alter the surface charge and the water salt selectivity and water permeability [145]. By capping the surface of a PA TFC membrane with monomers containing hydrophobic groups, the hydrophilicity of the membrane was reduced, which greatly improved the apolar solvent flux [127].

#### 2.5.3.2 Sulfonation

The reaction of cross-linked asymmetric membranes based on PS with concentrated sulfuric acid resulted in the sulfonation of these membranes. Both water flux and salt rejection were thus increased [146].

#### 2.5.3.3 Nitration

A gas-phase nitration technique was developed to modify PSf UF membranes. The membranes were treated with a gas mixture of NO and NO<sub>2</sub>, followed by a reduction with hydrazine hydrate to form amine groups. This resulted in the transformation of the UF membrane into a NF membrane [147].

### 2.5.4 Polymer Grafting

In polymer grafting, covalent bonds are generated between the membrane surface and monomer, which is polymerized during the grafting step or a grafted polymer. Therefore, reactive sites, usually in the form of radicals, have to be generated. Radicals can be formed via UV, redox, electron beam (EB),  $\gamma$ -ray, or plasma initiation. Besides radicals, reactive functional groups on the membrane surface can also act as grafting sites.

Polymer grafting is a commonly used technique to reduce the fouling tendency of RO and aqueous NF membranes as the surface charge is altered and the membrane surface is made more hydrophilic. PA top layers can be grafted with fluorinated polyamines, which are covalently bound to the membrane surface via the reaction between their amine groups and the excess carboxylic acid groups on the PA surface [148] or with zwitterionic 3-(methacryloylamino)propyl-dimethyl-(3-sulfopropyl) ammonium hydroxide monomers, in which the graft polymerization is redox initiated with cesium(IV) [149]. Also, asymmetric NF membranes can be grafted to improve their antifouling behavior. Methacrylic acid was used as a grafting molecule for PES membranes, with potassium disulfate and potassium thiosulfate as redox initiators [150]. The UV-initiated grafting of acrylic acid and ethylenediamine dihydrochloride on a PES membrane was reported as well [151]. In all cases, polymer grafting caused the permeance of the membrane to decrease, while its selectivity and fouling resistance (mostly tested with humic acid or proteins as fouling agents) increased. To increase membrane hydrophobicity, an Ar plasma was applied to cleave the C—H bonds in a PAN membrane, which then formed reactive sites for graft polymerization with styrene. This treatment improved the membrane performance in the removal of dewaxing solvents (methyl ethyl ketone and toluene) from dewaxed lube oil [152].

Grafting through EB has also been reported, although less often compared to UV photoinitiation. Besides the low availability and more costly setup, EB does not require catalysts, photoinitiators, solvents, or other toxic reagents and can also interpenetrate the membrane, allowing functionalization of the inner surface [153]. EB-induced grafting of 2-acrylamido-2-methylpropanesulfonic acid onto a PSf-based UF membrane resulted in high removal of Cr(VI), therefore converting it into a highly permeable NF membrane [154].

### 2.5.5 Photochemical Modification

When a photochemically active group is incorporated into the membrane polymer, UV radiation can convert this active group into a wide range of functionalities.

A poly(sulfonamide) composite membrane containing a 3-diazo-4-*oxo*-3,4-hydro functionality was modified by converting the photochemically active group into a bromo-ethylester derivative by UV irradiation in the presence of 2-bromo-ethanol. The bromo-ethylester was then treated with TEA to obtain a dioxolan ring structure, through which the NaCl rejection increased by a factor of 3. The ring was later opened via an acid treatment to form a hydroxy-ethylester membrane [155].

## 2.6 Ceramic Membranes

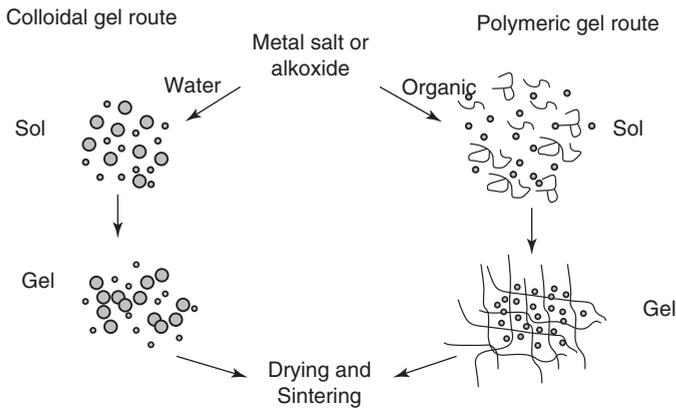
### 2.6.1 Introduction

Ceramic membranes consist of metal oxides, nitrides, or carbides. The most common membranes are made of Al, Si, Ti, or Zr oxides, with Ti and Zr oxides being more stable at extreme pHs, while Al or Si oxides are more resistant toward organic solvents [156]. In some less-frequent cases, Sn or Hf was used as base element. Each oxide has a different surface charge in solution. Other membranes can be composed of mixed oxides of two of the previous elements or are stabilized by additional compounds present in minor concentrations.

Ceramic membranes normally have an asymmetrical structure composed of at least two, mostly three, but sometimes even more, different porosity levels. Before applying the active, microporous top layer in ceramic NF membranes, a mesoporous intermediate layer is often applied to reduce the surface roughness. The macroporous support ensures the mechanical resistance of the NF membrane. Most ceramic NF membranes are prepared using a sol-gel process, in which pore sizes can be easily controlled for the desired application. MWCOs between 200 and 1000 g/mol have been reported [157].

### 2.6.2 General Synthesis Procedure

Sol-gel is a very general process that converts a colloidal or polymeric solution into a gelatinous network (Figure 2.9). In the colloidal gel route, a sol is formed by mixing a metal salt with water, while in the polymeric gel route, metal-organic



**Figure 2.9** The colloidal and polymeric route in the sol–gel process. *Source:* Li 2001 [157]. Reproduced with permission of John Wiley and Sons.

precursors are mixed with an organic solvent. After coating the sols on a membrane support, they are transformed to either a colloidal or a polymeric gel via drying. By applying a thermal treatment, the membranes are then further sintered. The colloidal gel route is considered to be the most environmentally benign technique because it does not use hazardous organic solvents and is therefore preferred for industrial ceramic membrane preparation [158].

### 2.6.2.1 Sol

The sol is a solution of nanometer-sized particles, which allows an intimate mixing at molecular level of different precursors and is thus capable of yielding homogeneous multicomponent ceramics. The hydrolysis and condensation behavior of the sol is of key importance in the transformation to a gel and is determined by several process parameters, such as the type of metal, the water to alkoxide ratio, and the presence of catalysts [159]. A binder (e.g. glycerol [158, 160], polyvinyl alcohol [156, 160], hydroxypropyl cellulose [161], or glycerin [161]) is often added to control membrane thickness, limit infiltration of the sol by increasing its viscosity [160, 162], and reduce crack formation during the drying step [158].

In the colloidal gel route [158, 160, 161], the hydrolysis rate is fast and a “particulate” sol consisting of gelatinous hydroxide particles is formed. The primary colloidal particles are usually in the range of 5–15 nm. Particle size, shape, and packing are important because the final membrane pores are formed by the voids generated by the packing of the primary particles [162]. The fine colloids obtained through the colloidal sol route need to be stabilized by an acid (e.g.  $\text{HNO}_3$  or  $\text{HCl}$ ) to avoid aggregation. The acid causes the particles to peptize, creating smaller, and positively charged particles, which results in the formation of a clear sol [156, 158, 161].

A much smaller amount of water is present in the polymeric gel route [156, 163, 164]. This route actually does not go through a real “sol” state, but rather a “solution” state, in which the basic components are not really particles but more polymeric molecules. They have a mineral core surrounded by an organic shell

that prevents aggregation. The interpenetration of the polymeric structures ultimately leads to the formation of the pores [165].

#### 2.6.2.2 Coating

Deposition of the sol layer on a porous support is commonly performed via dip coating [156, 158, 161, 163]. Mostly, humidity is controlled during coating and drying, as it influences the hydrolysis and the condensation reactions [156, 160].

#### 2.6.2.3 Gel

Drying of the coated sol layer is mostly performed at moderate temperatures between 20 and 100 °C. During this process, the solvent evaporates and the sol is transformed to a gel via polycondensation of the hydroxylated metal species, creating metal-*oxo*-metal or metal-hydroxy-metal bonds [159]. The growing clusters eventually collide to form a three-dimensional network, called gel [162]. Gelling can be detected by a sharp increase in viscosity in the colloidal gel route. Viscosity increases much more gradually in the case of polymeric gels.

#### 2.6.2.4 Sintering

After formation of the gel layer, the membrane is heated to obtain the final membrane structure. The sintering (also called calcination or firing) temperature commonly ranges between 350 and 600 °C. During sintering, the particles in the gel grow, causing an increase in pore size and decrease in pore volume of the membrane [162]. This treatment thus determines the final MWCO of the membrane.

### 2.6.3 Membrane Types

#### 2.6.3.1 Titania

Titania is a very common material for the preparation of ceramic NF membranes. In the past, these membranes were mainly synthesized via the polymeric route. However, because of the easy operation and the nonvolatility and nontoxicity of water, the colloidal route is preferred for industrial membrane production and is being more intensively investigated nowadays [161].

In the synthesis of TiO<sub>2</sub> membranes via the colloidal route, the moment at which organic binders are added to the sol has shown to influence the resulting membrane morphology. When adding them before the acid-induced peptization of the sol, they tended to bind to the surface of the TiO<sub>2</sub> nanoparticles, separating them into smaller fragments. This did not take place when the binder was added after peptization. After transformation of the smaller particles to a gel, a membrane with smaller pore size and higher salt rejection was obtained [161].

#### 2.6.3.2 Zirconia

Also, zirconia is a frequently reported ceramic membrane material. ZrO<sub>2</sub> NF membranes with an MWCO of 200–300 Da were prepared via the polymeric gel route. To create a highly pH-stable membrane, the alumina mesoporous interlayer was replaced by a zirconia interlayer. The resulting membranes did not show any corrosion (no significant changes in permeance and MWCO) after a four-week filtration test with feed solutions having a pH of 1 or 13 [156].

### 2.6.3.3 Alumina

The two most important crystallographic forms of alumina are  $\alpha$ - and  $\gamma$ -alumina, of which the former is commonly used as macroporous support, while the latter is mainly applied in the formation of a microporous top layer.

$\gamma$ -Alumina membranes were formed via the colloidal gel route by using acetic acid or nitric acid as a peptizing agent and glycerol as a binder. Acetic acid is shown to be the superior peptizing agent, generating an alumina sol consisting of smaller particles with a more narrow particle size distribution. This stable sol resulted in the formation of a membrane with a higher porosity, a more narrow pore size distribution, and a smaller tortuosity, having an MWCO of 1000 Da and a high pure water permeance of more than 20 l/m<sup>2</sup> h bar [158].

Alumina-based membranes suffer deterioration and blistering under steam-containing environments at elevated temperatures. Delamination of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membrane from the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports in hot steam has also been observed, further limiting the application of these membranes in high temperature and humid conditions as encountered in food processing and medical applications. To overcome the hydrothermal instability of alumina-based membranes, doping with lanthanum, gadolinium, and calcium has been investigated. Improved adherence between the different layers of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was achieved through phosphate bonding [166]. It should also be noted that zirconia and titania are more stable over a wide pH range than  $\gamma$ -alumina [167].

### 2.6.3.4 Silica

Silica is an attractive material to form NF membranes because the pore size can be controlled in a wide range. However, the low stability of narrow-pore silica under high temperatures, especially in the presence of water vapor, causes the aqueous applications of silica membranes to be limited [168]. This is because SiO<sub>2</sub> undergoes densification through the restructuring of the silica upon exposure to water vapor at elevated temperatures, causing tremendous drops in membrane permeability [169].

A SiO<sub>2</sub> NF membrane was prepared via dip coating a silica sol on an alumina support. The membrane showed a very low water permeance and only moderate rejections of mono- and divalent salts (30–50%). However, the membrane was able to retain ibuprofen and caffeine by about 80% [170].

### 2.6.3.5 Mixed Oxides

To overcome the hydrothermal instability of silica and alumina membranes, they can be doped with other metals such as zirconia, titania, alumina, or nickel. This might also positively influence membrane performance [168]. When doping a silica sol with 5% TiO<sub>2</sub>, a membrane with a 30 times higher water permeance and increased rejection compared to the pure silica membrane was obtained. Mono- and divalent salt rejections increased from 30–50% to 50–70%, while the rejection of ibuprofen and caffeine increased from 80% to 90% [170]. A membrane prepared from equimolar concentrations of SiO<sub>2</sub> and ZrO<sub>2</sub> showed an MWCO of 200–350 Da. The water permeance decreased when increasing the firing temperature from 200 to 550 °C [168].

Also, titania is frequently mixed with other oxides. A  $\text{TiO}_2/\text{ZrO}_2$  membrane was prepared using equal molar amounts of Ti and Zr precursors. The resulting membrane showed an MWCO of 620–860 Da but with a rather low water permeance [164]. To increase the hydrophobicity of this type of membrane for use in SRNF, carbon was incorporated in the selective layer by sintering under inert atmosphere ( $\text{N}_2$ ), which causes pyrolysis of the alkoxide groups. Additional components were added to the sol to further increase the amount of carbon after pyrolysis. An MWCO of 350 Da could be obtained with these hydrophobized membranes [163].

An yttria-stabilized zirconia ( $\text{ZrO}_2/\text{Y}_2\text{O}_3$ ) membrane was prepared via the colloidal gel route with a Zr/Y molar ratio of 92/8. The size of the sol particles was influenced by the precursor concentration, the refluxing temperature, and the molar ratio of reagents. An MWCO of 800 Da together with a high water permeance of  $28 \text{ l/m}^2 \text{ h bar}$  was obtained [160].

#### 2.6.3.6 Organic Doped Ceramic Membranes

The addition of organic chelating ligands to the sol allows tuning of the pore size and the hydrophilicity of the final NF membrane [171]. When diethanolamine is added to the sol and the gel is subsequently sintered under inert atmosphere, carbon is integrated in the  $\text{TiO}_2/\text{ZrO}_2$  ceramic membrane. This causes the hydrophobicity of the membrane to increase, while achieving an MWCO of 350 g/mol for styrene in THF [163].

### 2.6.4 Supports

Even though they only give support to the top layer, which performs the actual separation, the importance of the support layers cannot be underestimated. The quality of the support often determines the final quality of the composite membrane because defects and irregularities in the support usually also produce defects in the thin top layer applied on it. For an optimal deposition of the top layer, constant and homogeneous surface characteristics, such as a small pore size, narrow pore size distribution, low roughness, and high thermal, acid–base, and/or solvent stability, are required [172]. To lower the roughness and pore size of the final support surface, intermediate layers with a gradual decrease in thickness and pore size are often applied between the ceramic support and the top layer. Common supports are disc- [156, 164, 173] or tubular-shaped [158, 160, 161, 163, 170] but also ceramic hollow fibers can be used [174].

$\alpha$ -Alumina with a pore size ranging from  $1 \mu\text{m}$  down to 100 nm is frequently used as macroporous support [156, 158, 161, 163, 164, 170, 173]. In contrast to  $\gamma$ -alumina, it cannot be produced with pores smaller than 100 nm. The mesoporous interlayer can be prepared from different materials, such as  $\gamma$ -alumina [161, 164, 170], zirconia [160], or alumina or yttrium-doped zirconia [156].

### 2.6.5 Surface Modification

Grafting is a frequently applied technique to modify the surface of ceramic NF membranes. By replacing the OH groups on the membrane surface by

other, sometimes large molecules with varying functionalities, membranes with increased hydrophobicity (for SRNF applications), narrowed pore size and improved selectivity, or lowered fouling tendency (for aqueous applications) can be obtained.

Different types of covalent bonds with the membrane surface can be formed, depending on the type of grafted molecule. The metal (M) of the membrane can be connected with the grafted molecule via oxygen (O) and a heteroelement, which is the case in silanation (M–O–Si–R), etherification (M–O–R), and phosphonic acid grafting (M–O–P–R). While the first two bond types are quite sensitive to rehydroxylation, the third one is more stable. An even more stable covalent bond can be formed when the metal is bound directly to the grafted molecule (M–R). This type of bond can be obtained when a grafting method based on Grignard chemistry is applied [175].

Silanation of commercial titania or  $\gamma$ -alumina membranes was performed by grafting the membrane surface with perfluoroalkylsilanes with different alkyl chain lengths [176] or with PDMS [173, 177]. Depending on the characteristics of the grafted macromolecule, the hydrophilicity of the membrane can be tuned. Phosphonic acid and Grignard grafting were applied to lower the fouling tendency of commercial titania membranes. Although ceramic membranes have a lower intrinsic fouling tendency than polymeric membranes, their resistance against typical fouling agents could be further increased by this grafting step. Especially, the methyl Grignard grafted membrane showed an extraordinary low degree of irreversible fouling [178]. In another study, Grignard grafting was applied to increase the hydrophobicity of commercial titania membranes. Grafting of pentyl or octyl groups on the membrane surface caused a remarkable increase in nonpolar solvent flux, together with increasing selectivity. Because the OH groups on the surface were only partially replaced by alkyl groups, the membrane obtained an amphiphilic character and the water flux remained more or less constant [175].

Surface modification of ceramic membranes (ME, UF, and NF) through ALD has recently also been reported, often with titania and alumina or silica as deposited layers. The number of ALD cycles allows to finely tune the pore size and therefore directly influences the separation performance of the membrane [179–181]. The deposition of a silica layer on porous anodic alumina membranes through ALD and the subsequent chemical functionalization with perfluorodecyldimethylchlorosilane showed enhanced NF selectivity for hydrophobic molecules over hydrophilic molecules [182]. Atmospheric pressure ALD, which is more economical and less complex than conventional ALD, has also been reported to deposit  $\text{TiO}_2$  layers on top of ceramic NF membranes [183]. These coated membranes largely outperform polymeric and pristine ceramic NF membranes of comparable MWCO. Next to ALD and chemical grafting, in situ chemical deposition [184] and chemical vapor deposition [185, 186] have also been used to convert ceramic UF membranes into NF membranes by tuning the pore size.

## 2.7 Hollow Fiber Preparation

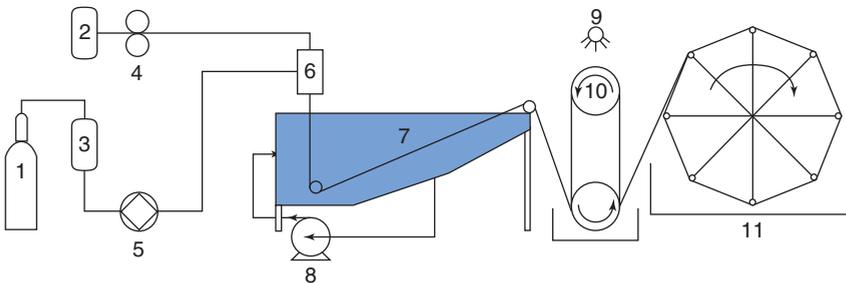
### 2.7.1 Introduction

Hollow fibers consist of cylindrical membranes with an inner diameter of less than 0.5 mm [55]. Thousands of these fibers are combined into a bundle, which forms the membrane module after applying an outer shell [187]. By applying this configuration, a high packing density and high surface/volume ratio is obtained, which allows to use relatively small devices [188]. Two module arrangements exist, an “inside-out” and an “outside-in” configuration, in which the feed or the permeate flows through the inner part (lumen-side) of the fibers [55].

Hollow fibers are used as membrane configurations for NF applications, although the industry standard is still flat sheet membranes assembled in a spiral wound configuration as they require less pretreatment and are intrinsically less prone to fouling [45, 188, 189]. Here, the general synthesis procedures of conventional and composite hollow fiber membranes are given, while the main advantages and disadvantages of the different existing membrane modules (spiral wound, plate-and-frame, hollow fiber, etc.) are discussed in Chapter 9.

### 2.7.2 General Synthesis Procedure

The general hollow fiber preparation procedure is shown in Figure 2.10. A dope solution is extruded through a spinneret with a specified inner and outer diameter, while a bore fluid, serving as an internal coagulant, is introduced via a needle into the lumen side of the dope fiber precursors. The pressure applied on the dope tank determines the flow rate of the solution through the spinneret. After going through an air gap, phase inversion of the fiber precursor occurs in a coagulation bath. Subsequently, the formed fibers are taken up by two roles and collected on a reel. The fibers are then cut, washed with water, and dried before preparing the membrane module. The dimensions of the fiber are determined by the dope flow rate, the spinneret dimensions, the length of the air gap, and the take-up speed on the roles [188].



**Figure 2.10** Hollow fiber preparation procedure. (1) N<sub>2</sub> gas cylinder, (2) bore fluid tank, (3) dope solution tank, (4) bore fluid pump, (5) dope solution pump, (6) spinneret, (7) external coagulation bath, (8) circulation pump, (9) water spray, (10) take-up roles, and (11) reel. *Source:* Darvishmanesh et al. 2001 [188]. Reproduced with permission of Elsevier.

Polymeric as well as ceramic membranes can be formed into a hollow fiber configuration. In the case of a polymeric membrane, the dope solution contains a polymer dissolved in a solvent. As phase inversion will occur, the same parameters as discussed in Section 2.2 will determine the final membrane morphology and separation capacity. Fibers preferably contain a microporous structure having a dense selective layer on either the outside or the inside surface. The dense surface layer can either be an integral part of the fiber or a separate layer coated onto the porous support fiber (see Section 2.7.3) [45]. For ceramic membranes, a stable suspension consisting of a metal oxide, a solvent, binders, and possibly other additives is used. After drying the hollow fiber ceramic membrane, a sintering step must be applied to remove the organic components and to densify the membrane structure [174, 190].

### 2.7.3 Composite Hollow Fiber Membranes

Coating of UF hollow fibers to achieve NF or even RO performance has been widely reported. Composite hollow fibers can be achieved through the LbL technology by depositing multilayer films of anionic and cationic polyelectrolytes [191, 192]. Similar to flat sheet TFC membranes, IP can also be used to deposit a thin film either on the inside or the outside of the fibers [193–195]. Both methods allow individual optimization of the top and the support layer as synthesis of both layers is decoupled. However, this multistep approach is costly and time consuming and has therefore motivated the preparation of composite hollow fiber membranes in one step. The “chemistry in a spinneret” approach simultaneously allows formation of the porous support and the selective layer by adding one monomer to the bore fluid and dissolving another monomer in the polymer solution [196, 197].

## 2.8 Commercial and Novel (SR)NF Membranes

### 2.8.1 Commercial (SR)NF Membranes

While RO and NF membranes were formerly produced through phase inversion from cellulose acetate, they are nowadays mostly TFC membranes [198]. Current commercial NF membranes are almost solely based on PIP-TMC chemistry, while for RO membranes, the basis is the reaction between MPD and TMC, also widely known as FT-30 chemistry. A noncomprehensive overview of some widely used commercial NF membranes is given in Table 2.3. Even though the core chemistry of these membranes is the same, the final membrane performance differs because of slightly different synthesis parameters, the use of additives, and the application of post-treatment steps, information, which are often trade secrets of the membrane manufacturers. Regarding commercial membranes for organic solvent nanofiltration (OSN)/SRNF, several companies are in the market. Evonik’s commonly used asymmetric membranes are produced through phase inversion from polyimide and can be used in a wide variety of solvents. The lowest MWCO is currently 150 g/mol, obviously depending on the solvent/solute combination.

**Table 2.3** Overview of widely used commercial NF membranes for aqueous and solvent applications.

Aqueous NF applications					
Type	Manufacturer	Chemistry	Specifically used in/for removal of	MgSO <sub>4</sub> rejection (2000 ppm)	Water permeance or permeability
NF90	FILMTEC™	Polyamide (MPD)	Salts, nitrates, iron, and organic compounds	97%	8.7 l/m <sup>2</sup> h bar
NF270	FILMTEC	Polyamide (PIP)	Total organic carbon (TOC) and trihalomethanes (THMs)	>97%	10.4 l/m <sup>2</sup> h bar
SR90	FILMTEC	Polyamide (PIP)	Sulfates	n.s.	n.s.
NF200	FILMTEC	Polyamide (PIP)	TOC, medium hardness removal	n.s.	n.s.
NF245	FILMTEC	Polyamide (PIP)	Organics, variable degree of monovalent salts	99%	9.9–13.6 l/m <sup>2</sup> h bar
TNE, TMNF	Toray	Polyamide (PIP)	Lactose, organic molecules	n.s.	n.s.
TS40	TriSep	Polyamide (PIP)	Divalent ions	99%	4.4 l/m <sup>2</sup> h bar
TS80	TriSep	Polyamide-TFC	Divalent ions	99%	4.54 l/m <sup>2</sup> h bar
SB90	TriSep	Cellulose acetate/triacetate blend	n.s.	97%	3.31 l/m <sup>2</sup> h bar
XN45	TriSep	Polyamide (PIP)	Divalent salts	95%	7.93 l/m <sup>2</sup> h bar
DK	GE Osmonics	Polyamide (PIP)	Divalent salts, dyes	96%	11.5 l/h bar
Duracid	GE Osmonics	Polyamide-TFC	Divalent salts	98%	0.99–2.10 l/m <sup>2</sup> h bar
DL, HL, CK	GE Osmonics	Polyamide-TFC	Divalent salts	94–98%	3.24–9.73 l/m <sup>2</sup> h bar
VNF1	Vontron	Polyamide	TOC	≥96%	5.7 l/m <sup>2</sup> h bar
NFS	Synder	Polyamide	Sulfates	99.5%	51–68 l/m <sup>2</sup> h

Table 2.3 (Continued)

Aqueous NF applications					
Type	Manufacturer	Chemistry	Specifically used in/for removal of	MgSO <sub>4</sub> rejection (2000 ppm)	Water permeance or permeability
NFX	Synder	Polyamide	Sulfates, concentration of lactose, and dyes	99%	4.49–5.49 l/m <sup>2</sup> h bar
NFG	Synder	Polyamide	Dairy industry	50%	12.48–13.60 l/m <sup>2</sup> h bar
Inopor <sup>®</sup> nano	Inopor	Ceramic TiO <sub>2</sub>	Salts, dyes, organics	MWCO of 200 g/mol	n.s.
NP010	Microdyn Nadir	PES	Acid and caustic environments	35–75% (Na <sub>2</sub> SO <sub>4</sub> )	>5 l/m <sup>2</sup> h bar
NP030	Microdyn Nadir	PES	Acid and caustic environments	35–75% (Na <sub>2</sub> SO <sub>4</sub> )	>1 l/m <sup>2</sup> h bar
OSN/SRNF applications					
Type	Manufacturer	Chemistry	Resistant in	Rejection	Solvent flux
Puramem	Evonik	Polyimide (P84)	Alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, butyl acetate, ethyl acetate, methyl-ethyl-ketone, methyl-tert-butyl-ether	90% for 280 g/mol styrene in toluene	18 l/m <sup>2</sup> h toluene at 30 barg
Duramem150	Evonik	Modified polyimide (P84)	Type1: acetone, tetrahydrofuran, methanol, ethanol, methyl-tert-butyl-ether, methyl-ethyl-letone, methyl-isobutyl-ketone, butyl acetate, ethyl acetate Type2: dimethylformamide, dimethylsulfoxide, N-methylpyrrolidone	90% for 150 g/mol styrene in toluene	n.s.

oNF-2	Borsig GmbH	Silicone polymer-based composite type	Alkanes, aromatics, alcohols, ethers, ketones, esters	350 g/mol	n.s.
NF030306	Solsep BV	Silicone-based polymer	Alcohols, esters, ketones, aromatics, chlorinated solvents, reducing atmosphere, THF, aldehydes, crude alkanes, petroleum ethers	99+% for 500 g/mol dye in ethanol	~2 l/m <sup>2</sup> h bar acetone (T = 20 °C) ~5 l/m <sup>2</sup> h bar acetone (T = 80 °C) ~2 l/m <sup>2</sup> h bar veg. Oil (T = 140 °C)
NF010206	Solsep BV	n.s.	Aldehydes, ketones, crude alkanes, acetone, (m)ethanol, IPA, hexane, petroleum ether, ethyl acetate, MEK, methylbenzol, methylchloride, chlorobenzol, tetrachloroethylene	90% for 300 g/mol FA in acetone	n.s.
NF010306	SolSep BV	n.s.	Aldehydes, ketones, crude alkanes, acetone, (m)ethanol, IPA, hexane, petroleum ether, ethyl acetate, MEK, methylbenzol, methylchloride,	99+% for 500 g/mol dye in ethanol	~2 l/m <sup>2</sup> h bar acetone (T = 20 °C) ~2 l/m <sup>2</sup> h bar veg. Oil (T = 140 °C)
NF300705	SolSep BV	n.s.	Alcohols	95+% for 500 g/mol dye in ethanol	~2 l/m <sup>2</sup> h bar hexane (T = 20 °C) 0.2–0.4 l/m <sup>2</sup> h bar heptane
NF070706	SolSep BV	n.s.	Aromatics and alkanes (e.g. toluene, hexane, heptane)	90+% for 250 g/mol sterols in heptane	~1 l/m <sup>2</sup> h bar toluene (T = 20 °C) ~1 l/m <sup>2</sup> h bar heptane
PEEK-Sep™	Porogen (air liquide)	PEEK	n.s.	n.s.	n.s.
PEEK5,20 100	Novamem™	PEEK	n.s.	n.s.	n.s.
PVDF20,100	Novamem	PVDF	n.s.	n.s.	n.s.

n.s.: not specified by manufacturer.

### 2.8.2 Novel (SR)NF Membranes

Besides tuning membrane performance through the use of novel monomers, additives or by changing reaction conditions or post-treatment steps, as discussed before for both ceramic and polymeric membranes, new generations of NF membranes are getting increased attention. Especially in the field of polymeric membranes, disruptive findings have been reported.

The embedding of (porous) nanoparticles in the thin PA top layer of thin film nanocomposite (TFN) membranes, giving rise to the so-called TFN membranes, has gained a lot of attention lately. Tremendous increases in permeance are observed, with no or only slight losses in rejection. The exact functioning of these membranes is however poorly understood, demonstrated by large variations in final membrane performance as a function of the incorporated amount of filler. It is speculated that the high water permeances are not only caused by low-resistant flow paths through the embedded porous NPs but also by intrinsic variations in the polymer structure because of the presence of the NPs during synthesis [199]. Examples of embedded NPs are ZIFs, MOFs, PIMs, zeolites, carbon (quantum) dots, COFs, graphene oxide, and silica NPs.

The incorporation of aquaporin, a biological membrane protein, into polymeric membranes has also been proposed as a new pathway to overcome the conventional permeability–selectivity trade-off. Aquaporin is intrinsically highly permeable to water and is also able to selectively reject ions, protons, and neutral solutes. One major challenge is to synthesize defect-free membranes and to overcome both membrane and protein stability [6, 200]. CNTs and other synthetic nanochannels, such as *m*-phenylene ethynylene or peptide nanotubes [201, 202] or cyclic macromolecules [203], have also been explored for NF and RO purposes as they can be functionalized for specific separations and the diameter of the channels can be customized. Even though these materials have demonstrated excellent separation capabilities, both through experiments and modeling, scale-up is still a major hurdle [200].

Novel nonpolyamide polymers for NF have also been explored. Narrow pore size distribution can be achieved through equilibrium self-assembly of lyotropic or thermotropic liquid crystalline mesophases [204] or through block copolymers [205]. Separations through liquid crystalline mesophasic membranes currently already fall into the NF range [200] and block copolymers also represent a scalable alternative to conventional NF membranes as they can be synthesized through phase inversion. However, elucidating the structure–property–performance relationships of these membranes is of paramount importance for large-scale manufacturing [205]. The use of epoxides as a novel reagent for IP has also been reported. The resulting loose NF membrane with a poly(epoxyether) top layer is chlorine and acid-resistant and has enormous tuning possibilities [206]. Coordination between tannic acid, a polyphenol, and Fe(III) can rapidly form a thin film on PES, resulting in a green TFC membrane, which is able to selectively reject endocrine-disruptive compounds and divalent salts [207]. *N*-methyl-*D*-glucamine-assisted polydopamine coating of a PES support membrane resulted in high water fluxes, high dye and divalent salt rejection, and high monovalent salt permeation. Furthermore,

chemical stability in acid and caustic conditions makes this membrane an attractive alternative for polyamide-based NF membranes [208].

An overview of reported polymers for phase inversion and reported monomers for IP used for OSN/SRNF applications is given in [187]. Solvent-resistant mixed matrix and TFN membranes can also be used in this field but are not (yet) commercialized. Recent advances with respect to novel SRNF membranes are mainly based on cross-linking existing polymers or the use of completely new chemistries. The alkyne functionalization of porous polyoxindolebiphenylene, polytriazole, and polybenzimidazole membranes, for example, allows full stability in DMF, even at 140 °C, although the performance is currently still in the UF range [209]. Examples of novel chemistries for IP are the reaction between tannic acid or morin hydrate and TPC on cross-linked PAN, resulting in NMP-resistant membranes [210, 211], or between catechin and TPC on a cellulose substrate, resulting in fully bio-derived TFC membranes stable in DMF over 30 days [212]. The coating of a microfiltration membrane with ultrathin layers of solvated reduced GO allowed ultrafast acetone transport (215 l/m<sup>2</sup> h bar), while achieving rejection in the NF range. Stability in methanol and ethanol, as well as in oxidizing, alkaline, and acidic media, was also achieved [213]. In a similar manner, highly laminated GO membranes outperformed state-of-the-art polymeric membranes with regard to methanol permeance and dye rejection [214].

## 2.9 Outlook

NF technology has become a state-of-the-art process for separations at industrial level. RO membranes reject almost all solutes, except for a few small neutral organics (e.g. 1,4-dioxanes and *N*-nitrosodimethylamine), while the rejection of NF membranes is depending on the characteristics of the solute (size, charge, charge density, etc.). In theory, this allows NF membranes to be tailor-made for a specific application; however, the lack of knowledge of the structure–property–performance of the membrane is still the limiting factor to achieve the full potential of NF. Research should therefore focus on the nano- and molecular control of materials to achieve stronger correlations between synthesis conditions and membrane performance. Additionally, a membrane separation process is traditionally seen as the removal of compound X from solvent Y. However, the selective permeation of one solute over another, which requires development of membranes with very narrow MWCO curves, would further open up the application potential of (SR)NF.

As for SRNF, its potential in the chemical, food, and pharmaceutical industry is enormous and is steadily getting more attention. As this field has been entered much more recently than the aqueous, many improvements in terms of membrane selectivity and (long-term) stability, as well as solvent permeance can still be made. Obviously, this field is much more complex because each solvent has its own specific interactions with a given solute and membrane material. This tremendously increases the level of complexity and the difficulty to fully grasp membrane structure–performance relationships as compared to aqueous applications, which take place in only one, well-understood “solvent.”

Even though many new materials have emerged as possible candidates for (SR)NF applications, their difficult and expensive large-scale synthesis is limiting scale-up. Better understanding the pitfalls that prevent defect-free membrane synthesis at large scale is therefore mandatory to transfer these technologies from academia to industry. In the same regard, more attention should be focused on module and process design, as, in the end, the membrane itself is only one part of an even more complex overall process.

## Acknowledgements

The authors are grateful for the financial support from the OT (11/061) funding from KU Leuven, the Nanomexico IWT.150474 project from IWT-STW, an FWO research project (G0D5119N), the I.A.P. – P.A.I. grant (IAP 7/05 FS2) from the Belgian Federal Government, and the long-term Methusalem (CASAS) funding by the Flemish Government. R.V. thanks Research Foundation Flanders for her SB PhD grant (1S00917N).

## Abbreviations

AEPPS	aminoethyl piperazine propane sulfonate
ALD	atomic layer deposition
BHTTM	2–2'-bis(1-hydroxyl-1-trifluoromethyl-2,2-trifluoroethyl)-4–4'-methylenedianiline
CA	cellulose acetate
CFIC	5-chloroformyloxisophthaloyl chloride
CHMA	1,3-cyclohexanebis(methylamine)
CPDA	2-chloro- <i>p</i> -phenylenediamine
DABA	3,5-diamino- <i>N</i> -(4-aminophenyl) benzamide
DGDE	diethylene glycol diethyl ether
DMF	dimethylformamide
DMSO	dimethylsulfoxide
EB	electron beam
HTC	cyclohexane-1,3,5-tricarbonyl chloride
ICIC	5-isocyanatoisophthaloyl chloride
IP	interfacial polymerization
IPA	isopropanol
IPC	isophthaloyl chloride
LbL	layer by layer
MDEOA	methyl-diethanolamine
mm-BTEC	3,3',5,5'-biphenyl tetraacyl chloride
M- <i>m</i> -PDA	4-methyl- <i>meta</i> -phenylenediamine
<i>m</i> -PDA	<i>meta</i> -phenylenediamine
M- <i>p</i> -DPA	2-methyl- <i>para</i> -phenylenediamine

MW	molecular weight
MWCO	molecular weight cut-off
NF	nanofiltration
NMP	<i>N</i> -methylpyrrolidone
<i>N,N'</i> -DMMPD	<i>N,N'</i> -dimethyl- <i>m</i> -phenylenediamine
NTSC	naphthalene-1,3,6,-trisulfonyl chloride
<i>o</i> -PDA	<i>ortho</i> -phenylenediamine
PA	polyamide
PAH	polyamide hydrazide
PAN	polyacrylonitrile
PBI	poly(benzimidazole)
PEEK	poly(ether ether ketone)
PEG	polyethylene glycol
PEI	polyethyleneimine
PEI- <i>g</i> -SBMA	polyethyleneimine- <i>g</i> -sulfobetaine methacrylate
PES	polyethersulfone
PHGH	polyhexamethylene guanidine hydrochloride
PI	polyimide
PIM	polymer of intrinsic microporosity
PIP	piperazine
<i>p</i> -PDA	<i>para</i> -phenylenediamine
PSf	polysulfone
PTMSP	poly(1-trimethylsilyl-1-propyne)
PVAm	polyvinylamine
PVDF	poly(vinylidene fluoride)
PVP	polyvinylpyrrolidone
RO	reverse osmosis
SPES-NH <sub>2</sub>	sulfonated cardo poly(arylene ether sulfone)
SRNF	solvent-resistant nanofiltration
TEA	triethylamine
TEOA	triethanolamine
THF	tetrahydrofuran
THM	trihalomethane
TFC	thin film composite
TMC	trimesoylchloride
TOC	total organic carbon
TPC	terephthaloyl chloride
UF	ultrafiltration

## References

- 1 Hermans, S., Mariën, H., Van Goethem, C., and Vankelecom, I.F.J. (2015). Recent developments in thin film (nano)composite membranes for solvent resistant nanofiltration. *Curr. Opin. Chem. Eng.* 8: 45–54.
- 2 Morgan, P.W. (1965). *Condensation Polymers: By Interfacial and Solution Methods*. New York: Interscience Publishers.