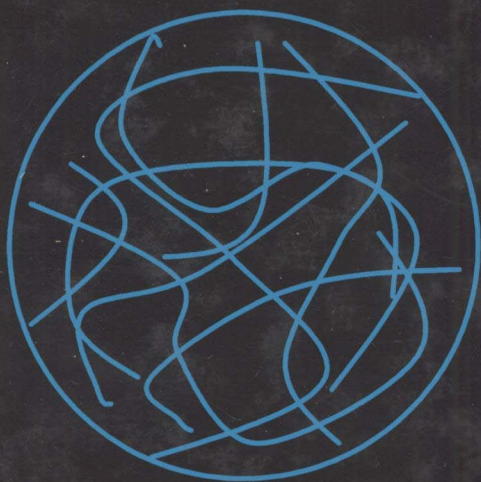


# **Ion Exchange and Solvent Extraction**

**A Series of Advances**



**Volume 18**



**CRC Press**  
Taylor & Francis Group

Edited by  
**ARUP K. SENGUPTA**

# **Ion Exchange and Solvent Extraction**

**A Series of Advances**

**Volume 18**

**Edited by  
ARUP K. SENGUPTA**



**CRC Press**

Taylor & Francis Group

Boca Raton London New York

---

CRC Press is an imprint of the  
Taylor & Francis Group, an **informa** business

CRC Press  
Taylor & Francis Group  
6000 Broken Sound Parkway NW, Suite 300  
Boca Raton, FL 33487-2742

© 2007 by Taylor & Francis Group, LLC  
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works  
Printed in Canada on acid-free paper  
10 9 8 7 6 5 4 3 2 1

International Standard Book Number-13: 978-0-8493-7397-8 (Hardcover)

This book contains information obtained from authentic and highly regarded sources. Reprinted material is quoted with permission, and sources are indicated. A wide variety of references are listed. Reasonable efforts have been made to publish reliable data and information, but the author and the publisher cannot assume responsibility for the validity of all materials or for the consequences of their use.

No part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access [www.copyright.com](http://www.copyright.com) (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC) 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

**Trademark Notice:** Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

**Visit the Taylor & Francis Web site at**  
**<http://www.taylorandfrancis.com>**

**and the CRC Press Web site at**  
**<http://www.crcpress.com>**

# **Ion Exchange and Solvent Extraction**

**A Series of Advances**

**Volume 18**

---

# Preface

No specialty thrives in isolation. The field of ion exchange grew over decades by permeating into myriad areas from deionization to drug delivery. As a result, new knowledge was created in many seemingly disjointed scientific disciplines. Scientists and researchers — while using, applying, and moving the boundaries of ion exchange — are often separated by their professional fields and literally unknown to each other. In order to bridge the gap and break the barrier in the field of ion exchange, the first international workshop on Frontiers and Interfaces of Ion Exchange was recently held during June 11–15, 2006, in Antalya, Turkey. Nearly 120 attendees from 24 countries attended the meeting. Invited speakers were selected to cover a broad range of specialty research areas, namely, catalysis, synthesis, molecular imprinting, green processes, drug delivery, nanotechnology, and obviously, water treatment and environmental pollution control. Several invited speakers had never attended an “ion exchange” meeting previously but their ongoing research and interaction during the workshop inevitably enriched the field.

In accordance with the spirit of the first international workshop on ion exchange and Volumes 14 and 16 of the series earlier edited by myself, the current volume contains seven chapters encompassing a wide gamut of topics; they truly reflect the diversity in the field of ion exchange. As the editor, I must also mention to potential readers that the publisher of the series has changed. Marcel Dekker, the publisher of the Ion Exchange and Solvent Extraction Series for the 17 volumes spanning a period over 40 years, has recently been taken over by Taylor & Francis. I have personally been assured by the administration of Taylor & Francis that the present series will continue and they recognize the importance of this expanding field. One more change is also on the way. Professor Yizhak Marcus has decided to step down as the editor of the “Solvent Extraction” part of the series and is being replaced by Dr. Bruce Moyer of Oak Ridge National Laboratory. I salute Professor Marcus for his invaluable contribution to this series for more than four decades and welcome Dr. Moyer as a worthy successor to make this series move forward with renewed energy.

The breadth and synergy among many emerging areas in ion exchange serve as the primary theme of this current volume, which contains seven chapters written by professionals from academic institutions, research laboratories, and industries around the world. The volume indeed encompasses a wide range of topics.

It is recognized that the majority of the applications of ion exchange resins are geared toward the separation of ions from the aqueous phase. Polymer-based ion exchange resins can also serve as a medium (stationary phase) for carrying out chemical reactions and separating the reactants and products simultaneously. In such processes, sorption of solvent and mixture of solvents onto ion exchange

resins influence the overall effectiveness of the process application. Chapter 1 discusses how solvent sorption equilibria and kinetics vary with the elastic properties of ion exchange resins, which, in turn, are dependent on type of functional groups, ionic forms, polymer matrix composition, and the degree of cross-linking. The thermodynamic modeling approach can be applied to the mixtures of polar and weakly polar solvents, and it explicitly takes into account the elasticity of the polymer network.

In synthesis reactions limited by chemical equilibria, the process conversion can be enhanced by selectively separating the products as they are formed. Ion exchange resins can serve as the heart of many such processes by simultaneously acting as a catalyst (or a reactant) and a separating agent. Development and modeling such a chromatographic reactor-separator and, more specifically, the simulated moving bed reactor (SMBR) for the synthesis of acetaldehyde dimethylacetal or 1,1-dimethoxyethane (DME) and acetaldehyde diethylacetal or 1,1-diethoxyethane (DEE) using a cation exchange resin (Amberlyst 15) is the primary objective of Chapter 2. In addition to the development and validation of models, the chapter provides experimental data from a pilot SMBR unit in Novasep, France, for the synthesis of acetals (DME and DEE) from acetaldehyde and alcohol as reactants and Amberlyst 15 resin as the catalyst and a selective adsorbent as well.

Ion exchange resin-based drug formulations have been the subject of intense research for nearly two decades and the resulting products are gradually moving into the marketplace. Besides oral drug delivery, ion exchange resins are being explored for transdermal, nasal, ophthalmic, and site-specific routes. Obviously, the pertinent question is: What is the advantage of getting a drug released from ion exchange resins? Controlling the rate of dissolution and improving the chemical stability and taste are some of the critical areas where drug delivery through ion exchange offers well-observed advantages. Chapter 3 discusses various scenarios of drug delivery for a combination of drugs and ion exchange resins. In addition, the chapter attempts to elucidate how the process variables, namely, temperature, ionic strength, pH, molecular weight of the drug, and cross-linking in the resin influence the overall process of drug delivery.

The importance of designing and preparing support materials for catalysts, especially for metal catalysts, is now well recognized. Metal binding capacity, chemical-thermal stability, pore structure, physical morphology, and flexibility in imparting functional groups are some of the desirable attributes for the host materials. Also, there is now a new emphasis on biorenewable materials as hosts, wherever possible. Chitosan, a modified naturally available biopolymer with ion exchange properties for metals sorption, has of late come to the forefront as a support material for heterogeneous catalysis. Chapter 4 provides extensive coverage for preparation, usage, and performance evaluation of biopolymers as catalyst supports with particular emphasis on chitosan. The chapter includes many examples of reactions, namely, hydrogenation, oxidation, reduction, hydroxylation, and carbonylation catalyzed by biopolymer-supported catalysts.

Reverse osmosis (RO) and ion exchange are characteristically two different processes with no apparent similarity. RO is a nonselective pressure-driven

membrane process applied primarily to separate dissolved solids from water. It is, however, well documented that RO membranes reject different electrolytes or ions to different extents, that is, permeation of different ions through RO membranes varies, all other conditions remaining identical. Also, the rejection of a specific ion is influenced by the accompanying electrolytes in feed water. With an increased application of RO and nanofiltration (NF) processes in the area of water treatment and wastewater reuse, there is now a greater need in predicting the relative degree of rejection or permeation of various ions, including environmentally regulated species. Chapter 5 provides convincing experimental evidence and elucidates underlying scientific reasons to confirm that ion exchange selectivity data for various ions can be used as surrogate parameters to predict the relative permeability of different ions in RO and NF processes. A simple ion chromatograph can provide the requisite information leading to the development of a quantitative model describing individual salt permeability. For trace ions of environmental significance, namely, perchlorate, nitrate, cesium, arsenate, chromate, and selenate, the ion exchange selectivity approach offers an insight with respect to their relative permeability in pressure-driven membrane processes.

Synthetic polymer-based materials constitute the majority of the ion exchange market and this trend is unlikely to change in the near future. Nevertheless, many naturally occurring biorenewable materials exhibit ion exchange properties resulting from the presence of a variety of chemical functional groups. In this regard, chitosan is probably a leading candidate due to the presence of both carboxylate and amino functional groups. Also, chitosan is amenable to chemical modification for improved chemical stability and mechanical strength. Chapter 6 provides a detailed account of how chitosan and its modified forms can find applications in separation and purification of metal ions.

The packed- or fixed-bed process where the mobile liquid passes through stationary ion exchange beads in a column is by far the most popular unit operation due to its simplicity of construction and operation. This method is routinely used for water softening, water demineralization, and removal of target-contaminating ions. Poor kinetics is one of the major limitations of the ion exchange process and intraparticle diffusion is often the rate-limiting step in the majority of the applications. During the exhaustion cycle, there are three specific zones for a solute in a fixed bed, viz., saturated, unused, and mass-transfer zone (MTZ). For intraparticle diffusion-controlled processes, the length of MTZ is proportional to the square of the diameter of the spherical ion exchange resin beads. Reducing the bead size reduces the length of the mass-transfer zone; however, the pressure drop across the bed increases with smaller particle sizes. "Short-Bed Ion Exchange" is a gainful compromise between the two: It offers faster kinetics with an acceptable pressure drop using skid-mounted ion exchange units. Chapter 7 provides specific advantages of short-bed units and presents many novel applications of ion exchange.

**Arup K. SenGupta**  
*Lehigh University, Pennsylvania*

---

# Editor

**Arup K. SenGupta, Ph.D.**, is the P.C. Rossin Professor in the Department of Civil and Environmental Engineering, Lehigh University, Bethlehem, Pennsylvania. Dr. SenGupta is the author or coauthor of more than 100 scientific publications in peer-reviewed journals and conference proceedings, as well as the recipient of the 2004 International Ion Exchange Award from Cambridge University, Great Britain. He was the North American Editor of *Reactive and Functional Polymers* from 1996 to 2006. He is a member of the American Chemical Society (ACS), American Institute of Chemical Engineers (AIChE), Association of Environmental Engineering and Science Professors (AEESP), and American Water Works Association (AWWA). Dr. SenGupta received his B.S. degree (1972) in chemical engineering from Jadavpur University, Kolkata, India, and his Ph.D. degree (1984) in environmental engineering from the University of Houston, Texas.



---

# Contributors

**Yoshinari Baba**

Department of Applied Chemistry  
Miyazaki University Japan  
Miyazaki, Japan

**Manjula Bajpai**

Polymer Research Laboratory  
Government Model Science College  
(Autonomous)  
Jabalpur, India

**Sunil K. Bajpai**

Polymer Research Laboratory  
Government Model Science College  
(Autonomous)  
Jabalpur, India

**Hans-Jörg Bart**

Lehrstuhl für Thermische  
Verfahrenstechnik  
Technische Universität Kaiserslautern  
Kaiserslautern, Germany

**Francisco Peirano Blondet**

Laboratoire Génie de l'Environnement  
Industriel  
Ecole des Mines  
Alès, France

**Craig J. Brown**

Chemionex, Inc  
Pickering, Ontario, Canada

**R. Chiarizia**

Chemistry Division  
Argonne National Laboratory  
Argonne, Illinois

**Ganesh K. Gandhi**

Laboratory of Separation and Reaction  
Engineering (LSRE)  
University of Porto  
Porto, Portugal

**Bohumír Grüner**

Institute of Inorganic Chemistry  
Czech Academy of Sciences  
Řež, Czech Republic

**Eric Guibal**

Laboratoire Génie de l'Environnement  
Industriel  
Ecole des Mines  
Alès, France

**A.W. Herlinger**

Department of Chemistry  
Loyola University — Chicago  
Chicago, Illinois

**Katsutoshi Inoue**

Department of Applied Chemistry  
Saga University  
Saga, Japan

**Zdenek Kolarik**

Karlsruhe, Germany

**Markku Laatikainen**

Laboratory of Industrial Chemistry  
Lappeenranta University of  
Technology  
Lappeenranta, Finland

**Parna Mukherjee**

California Polytechnic State University  
San Luis Obispo, California

**Erkki Paatero**

Lappeenranta University of  
Technology  
Laboratory of Industrial Chemistry  
Lappeenranta, Finland

**Michel Perrut**

Separex  
Champigneulles, France

**Jiří Rais**

Nuclear Research Institute Řež plc  
Řež, Czech Republic

**Alírio E. Rodrigues**

Laboratory of Separation and Reaction  
Engineering (LSRE)  
University of Porto  
Porto, Portugal

**Tuomo Sainio**

Laboratory of Industrial Chemistry  
Lappeenranta University of  
Technology  
Lappeenranta, Finland

**Sutanjay Saxena**

Polymer Research Laboratory  
Government Model Science College  
(Autonomous)  
Jabalpur, India

**Viviana M.T.M. Silva**

Laboratory of Separation and Reaction  
Engineering (LSRE)  
University of Porto  
Porto, Portugal

**Geoffrey W. Stevens**

Department of Chemical and  
Biomolecular Engineering  
The University of Melbourne  
Victoria, Australia

**Thierry Vincent**

Laboratoire Génie de l'Environnement  
Industriel  
Ecole des Mines  
Alès, France

# Table of Contents

<i>Preface</i> .....	vii
<i>Editor</i> .....	xi
<i>Contributors</i> .....	xiii
<b>Chapter 1</b> Sorption of Solvent Mixtures in Ion Exchange Resins: Influence of Elastic Properties on Swelling Equilibrium and Kinetics .....	1
<i>Tuomo Sainio, Markku Laatikainen, and Erkki Paatero</i>	
<b>Chapter 2</b> Development of Simulated Moving Bed Reactor Using a Cation Exchange Resin as a Catalyst and Adsorbent for the Synthesis of Acetals .....	45
<i>Viviana M.T.M. Silva, Ganesh K. Gandhi, and Alirio E. Rodrigues</i>	
<b>Chapter 3</b> Ion Exchange Resins in Drug Delivery .....	103
<i>Sunil K. Bajpai, Manjula Bajpai, and Sutanjay Saxena</i>	
<b>Chapter 4</b> Biopolymers as Supports for Heterogeneous Catalysis: Focus on Chitosan, a Promising Aminopolysaccharide .....	151
<i>Eric Guibal, Thierry Vincent, and Francisco Peirano Blondet</i>	
<b>Chapter 5</b> Ion Exchange Selectivity as a Surrogate Indicator of Relative Permeability of Homovalent Ions in Reverse Osmosis Processes.....	293
<i>Parna Mukherjee and Arup K. SenGupta</i>	
<b>Chapter 6</b> Chitosan: A Versatile Biopolymer for Separation, Purification, and Concentration of Metal Ions .....	339
<i>Katsutoshi Inoue and Yoshinari Baba</i>	
<b>Chapter 7</b> Short-Bed Ion Exchange .....	375
<i>Craig J. Brown</i>	
<i>Index</i> .....	405

---

# 1 Sorption of Solvent Mixtures in Ion Exchange Resins: Influence of Elastic Properties on Swelling Equilibrium and Kinetics

*Tuomo Sainio, Markku Laatikainen, and  
Erkki Paatero*

## CONTENTS

1.1	Introduction .....	2
1.2	Sorption and Swelling Equilibria.....	3
1.2.1	Model Development.....	3
1.2.1.1	General Condition for Phase Equilibrium.....	4
1.2.1.2	Gibbs Energy of Mixing: Liquid Lattice Model and Counterion Condensation Theory.....	6
1.2.1.3	Shear Modulus and Swelling Pressure.....	9
1.2.2	Experimental.....	11
1.2.2.1	Resin Properties .....	11
1.2.2.2	Mechanical Measurements.....	12
1.2.2.3	Measurement of the Swelling Ratio and Solvent Uptake.....	13
1.2.3	Results and Discussion.....	14
1.2.3.1	Elastic Properties .....	14
1.2.3.2	Equilibrium Swelling.....	22

1.3	Solvent Diffusion and Swelling Kinetics.....	29
1.3.1	Model Development.....	30
1.3.1.1	Maxwell–Stefan Approach.....	31
1.3.1.2	Fick’s Law.....	32
1.3.2	Experimental.....	32
1.3.3	Results and Discussion.....	33
1.3.3.1	Fickian Diffusion Coefficients at Constant Swelling Ratio.....	34
1.3.3.2	Swelling and Shrinking Kinetics.....	35
1.4	Summary and Conclusions.....	39
	Acknowledgments.....	41
	References.....	41

## 1.1 INTRODUCTION

The behavior of strong acid cation exchangers in nonaqueous solvents and in aqueous-organic solvent mixtures has been extensively investigated during the past decades.<sup>1–9</sup> Modeling of multicomponent sorption equilibria and of diffusion of liquids in a swollen cross-linked polymer network plays a key role in understanding ion exchange resin catalysis and membrane separation processes. It is well known that the solvent sorption equilibria and resin swelling kinetics are influenced by the nature of the functional group, the counterion, and the polymer matrix, as well as the cross-link density of the resin. The purpose of the present work is to investigate the role of the elastic properties of the resin on these two phenomena in solvent mixtures. We also demonstrate the use of a thermodynamic modeling approach in describing sorption and swelling equilibria as well as swelling kinetics of ion exchange resins. The essence of this approach is that the elastic properties of the resin are explicitly taken into account.

The work is divided into two parts as follows. We begin by deriving a general condition for phase equilibrium in rubbery cross-linked polymers by using thermodynamics of polymer solutions and rubbery materials. An expression for the solvent activities in the liquid and resin phases is given. In this context we also present a number of models commonly used for describing the elasticity of gels and calculating the swelling pressure in the gel phase. To quantify the elastic properties of strong and weak acid cation exchange resins, we present shear modulus data obtained from direct mechanical measurement of single particles and swelling pressure data obtained from vapor sorption isotherms. The applicability of various elasticity models is discussed in the light of such data. Further, the thermodynamic phase equilibrium model is used as a semipredictive tool to describe sorption and swelling equilibria in some example systems.

For rubbery polymers, swelling and shrinking kinetics in solvent mixtures is controlled by diffusion of liquids inside the particle. This is the topic of the second part. We demonstrate how the elastic properties of the resin can be taken into account in a relatively simple manner by including them in the chemical potential

driving force for diffusion. Literature data of solvent diffusion coefficients in strong cation exchange resins are scarce. To give an idea of the influence of the extent of resin swelling on the solvent diffusion coefficients of common solvents, we present some experimental data for strong cation exchange resins.

## 1.2 SORPTION AND SWELLING EQUILIBRIA

Conventional heterogeneous models based on analogies to surface adsorption are adequate in describing the distribution of compounds between a fluid and a rigid material, and are often used for ion exchange resins as well. However, the concept of fixed adsorption sites does not reflect the sorption phenomenon in swollen resins, which have a more or less flexible polymer structure. When the polymer network is expanded, only a fraction of the sorbed molecules are in the vicinity of the functional groups that are usually considered as the adsorption sites, and solvent-solvent interactions also have to be included. Therefore, statistical models derived from the thermodynamics of polymer solutions and gels<sup>10,11</sup> have recently been used to describe the observed phase equilibria in systems consisting of a solvent mixture and an ion exchange resin.<sup>12-17</sup> Similar models have also been tested in systems containing a binary solvent mixture, solutes, and a resin.<sup>18,19</sup> This approach has also been applied to the dynamic modeling of chemical reactors.<sup>12,13,20,21</sup>

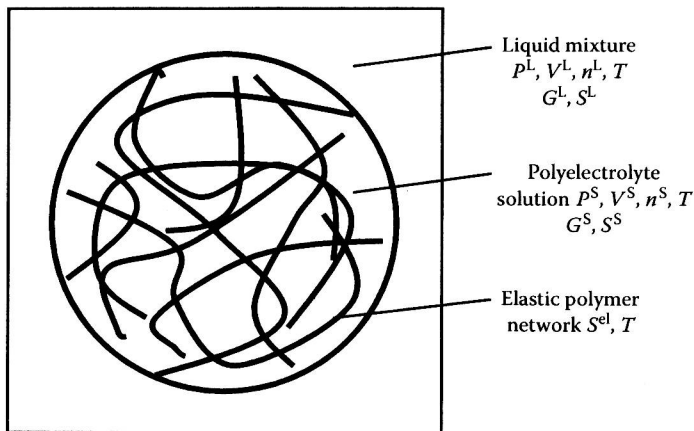
Here we illustrate the use of a thermodynamic treatment in calculating the equilibrium states of systems containing solvent mixtures (or other neutral components) and moderately or densely cross-linked ion exchange resins. Only nonreactive systems are considered, but extension to reactive systems is straightforward.<sup>22</sup>

### 1.2.1 MODEL DEVELOPMENT

The system under consideration consists of three parts: a homogeneous liquid phase, a homogenous polyelectrolyte solution, and an elastic cross-linked polymer network (Figure 1.1). A cross-linked polymer network may swell to a variable extent depending on the external liquid-phase composition, the affinity of the polymer for the solvents, and the number of cross-links. The configurational entropy of a cross-linked polymer network decreases as the extent of swelling increases. This brings about a tensile force that opposes the expansion of the network, which is observed as an increase in the pressure of the polymer phase. Consequently, there exists a pressure difference (swelling pressure) between the polymer phase and the external liquid phase.

In the present context, only the distribution of neutral liquid compounds between the liquid phase and ion exchange resin particles is relevant: the dissociated counterions cannot leave the resin phase due to the condition of electroneutrality. However, the counterions contribute to the free energy of the polymer phase and the effect is taken into account by the mixing entropy of the free counterions.

It should be noted that although electrolyte solutions are not considered here, the modeling approach can be extended to systems with ionic species by including



**FIGURE 1.1** The system consists of three parts: multicomponent liquid mixture (L); a homogeneous polyelectrolyte solution (S); and an elastic polymer network (el). The thermodynamic quantities are explained in the text.

the condition of electroneutrality in each phase as an additional constraint.<sup>11</sup> This enables calculation of the equilibrium state of the system without employing the Donnan potential concept.

### 1.2.1.1 General Condition for Phase Equilibrium

The first and second laws of thermodynamics yield Equation (1.1) for an isothermal reversible transition under constant external pressure. In Equation (1.1),  $U^{sys}$  and  $S^{sys}$  are the total internal energy and the entropy of the system, and  $W$  is the work done by the system. Exact and inexact differentials are denoted with  $d$  and  $\delta$ , respectively.

$$-dU^{sys} - \delta W + TdS^{sys} = 0 \quad (1.1)$$

According to the classical theory of rubber elasticity, deformation of the polymer network does not involve changes in the internal energy or volume of the polymer network, but only changes in its configurational entropy.<sup>10</sup> If only the expansion work is taken into account and if the liquid-phase pressure equals that of the surroundings, Equation (1.1) may be written as shown in Equation (1.2), where  $S^{el}$  denotes the configurational entropy of the polymer network, and  $T$  and  $p$  are temperature and pressure. The liquid and polymer phases are denoted by superscripts L and P.

$$-dU^L - p^L dV^L + TdS^L - dU^P - p^L dV^P + TdS^P + TdS^{el} = 0 \quad (1.2)$$

Temperature and external pressure are assumed constant, and Equation (1.2) can be rearranged into the form shown in Equation (1.3), where  $G$  is the Gibbs energy, and  $n^L$  and  $n^P$  denote the number of moles in liquid and polymer phases, respectively. It should be noticed that the Gibbs energy of the polymer phase is evaluated at liquid-phase pressure because of cancellation of terms.

$$d\left(G^L(T, p^L, n^L) + G^P(T, p^L, n^P) - TS^{\text{el}}\right) = 0 \quad (1.3)$$

Since reversible transitions pass through equilibrium stages, Equation (1.3) gives a condition for equilibrium in the system: *the expression in the parentheses has its minimum value at equilibrium*. However, it is worthwhile to elaborate the equilibrium condition somewhat further. As a first step, the effect of the elastic response of the polymer network can be expressed in terms of more easily measured quantities than  $-TdS^{\text{el}}$ . As a second step, the Gibbs energies in Equation (1.3) can be replaced with the Gibbs energy of mixing by using the material balance.

The stress in a cross-linked polymer network due to a deformation by an external force is obtained from the classical theory of rubber elasticity. The stress that opposes further swelling of a swollen spherical cross-linked polymer network (i.e., tensile force per unit area of swollen sample) is calculated as shown in Equation (1.4), where  $V^0$  is the volume of the unswollen undeformed sample, and  $\alpha$  is the deformation factor. The stress, denoted with  $\pi_{\text{sw}}$  in Equation (1.4), should be interpreted as an additional pressure exerted on the polymer phase, and is termed *swelling pressure*.<sup>10</sup> Consequently, the resin phase pressure is  $p^P = p^L + \pi_{\text{sw}}$ . The factor  $3\alpha^2$  in the denominator of Equation (1.4) originates from the spherical geometry and the assumption of isotropic swelling. Since  $3\alpha^2 d\alpha V^0 = dV^P$ , the change in the configurational entropy of the polymer network can be expressed in terms of the swelling pressure and the volume of the polymer phase, as shown in Equation (1.5).

$$\pi_{\text{sw}} = -\frac{T}{3\alpha^2 V^0} \frac{dS^{\text{el}}}{d\alpha} \quad (1.4)$$

$$-TdS^{\text{el}} = \pi_{\text{sw}} dV^P \quad (1.5)$$

In order to introduce the reaction and mixing quantities, the Gibbs energies of the liquid and polymer phases at the liquid-phase pressure can be expressed as in Equation (1.6) and Equation (1.7), provided that system temperature and liquid-phase pressure are chosen as the reference state. The numbers of components in the liquid and solid phases are denoted by  $NL$  and  $NP$ , respectively.  $G_i^0$  is the standard Gibbs energy of a pure component  $i$ , and  $\Delta_{\text{mix}}G$  is the Gibbs energy change due to mixing of the components.



$$G^L(T, p^L, n^L) = \sum_{NL} n_i^L G_i^0(T, p^L) + \Delta_{\text{mix}} G^L(T, p^L, n^L) \quad (1.6)$$

$$G^P(T, p^L, n^P) = \sum_{NP} n_i^P G_i^0(T, p^L) + \Delta_{\text{mix}} G^P(T, p^L, n^P) \quad (1.7)$$

By substituting Equation (1.5) through Equation (1.7) into Equation (1.3), and using the material balance  $n_i^P + n_i^L = n_i^0$ , the equilibrium condition can be expressed in terms of quantities that can be evaluated from experimentally measured data. The equilibrium compositions of both phases are then obtained by minimization of the objective function  $Y$  given in Equation (1.8).

$$Y = \Delta_{\text{mix}} G^L(p^L) + \Delta_{\text{mix}} G^P(p^L) + V^P \pi_{\text{sw}} \quad (1.8)$$

Although phase equilibrium calculation by numerical minimization of Equation (1.8) is straightforward, an alternative phase equilibrium condition can be derived from it. Firstly, an infinitesimally small amount  $dn_i^L$  of component  $i$  is transferred across the phase boundary from the liquid phase to the resin phase. If the system is initially at equilibrium, the objective function changes, as shown in Equation (1.9). Because of the equilibrium assumptions, the derivative  $(\partial Y / \partial n_i^L)_{TPnj}$  is equal to zero, and substituting Equation (1.6) and Equation (1.7) into Equation (1.9) results in a well-known relationship, shown in Equation (1.10), which states that the chemical potentials of each component are equal across the phase boundary. Here  $R_g$  is the gas constant,  $a$  is activity, and  $V_m$  is the partial molar volume.

$$dY = \frac{\partial G^L}{\partial n_i^L} (-dn_i^L) + \frac{\partial G^P}{\partial n_i^S} dn_i^L + \pi_{\text{sw}} \frac{\partial V^P}{\partial n_i^S} dn_i^L \quad (1.9)$$

$$R_g T \ln a_i^L(T, p^L) = R_g T \ln a_i^P(T, p^L) + V_{m,i} \pi_{\text{sw}} \quad (1.10)$$

### 1.2.1.2 Gibbs Energy of Mixing: Liquid Lattice Model and Counterion Condensation Theory

In order to calculate the equilibrium phase compositions by minimizing the objective function  $Y$  in Equation (1.8), an expression is required for the Gibbs energy change when mixing the solvents, the polymer, and the dissociated counterions. In the present work, the lattice theory by Flory and Huggins<sup>10</sup> is used (for other models, see, for example, Reference 14). The mixing Gibbs energy is given in Equation (1.11) for the polymer phase, but the same equation may also