

# Mass Transfer and Kinetics of Ion Exchange

edited by

**Lorenzo Liberti**

and

**Friedrich G. Helfferich**

# Mass Transfer and Kinetics of Ion Exchange

edited by

**Lorenzo Liberti**

Senior Researcher at the Water Research Institute  
of the National Research Council of Italy  
Associate Professor of Industrial Chemistry  
at the Faculty of Engineering  
University of Bari, Italy

and

**Friedrich G. Helfferich**

Professor of Chemical Engineering  
Pennsylvania State University  
University Park, PA 16802, USA

**1983 Martinus Nijhoff Publishers**

The Hague / Boston / Lancaster

Published in cooperation with NATO Scientific Affairs Division

**Proceedings of the NATO Advanced Study Institute on  
Mass Transfer and Kinetics of Ion Exchange,  
Maratea, Italy, May 31 - June 11, 1982**

**Library of Congress Cataloging in Publication Data**

NATO Advanced Study Institute on Mass Transfer and  
Kinetics of Ion Exchange (1982 : Maratea, Italy)  
Mass transfer and kinetics of ion exchange.

(NATO ASI series. Series E, Applied sciences ;  
no. 71)

"Published in cooperation with NATO Scientific Affairs  
Division."

"Proceedings of the NATO Advanced Study Institute  
on Mass Transfer and Kinetics of Ion Exchange, Maratea,  
Italy, May 31-June 11, 1982"—T.p. verso.

1. Mass transfer—Congresses. 2. Ion exchange—  
Congresses. I. Libert, Lorenzo. II. Haefliger, Friedrich G., 1908- . III. North Atlantic Treaty  
Organization. Scientific Affairs Division. IV. Title.  
V. Series: NATO advanced science institutes series.  
Series E, Applied sciences ; no. 71.  
TP156.KW37 1982 660.2'842 82-13391  
ISBN 90-247-2861-4

**ISBN 90-247-2861-4 (this volume)**

**Distributors for the United States and Canada: Kluwer Boston, Inc., 190 Old Derby  
Street, Hingham, MA 02043, USA**

**Distributors for all other countries: Kluwer Academic Publishers Group, Distribution  
Center, P.O. Box 322, 3300 AH Dordrecht, The Netherlands**

All rights reserved. No part of this publication may be reproduced, stored in a  
retrieval system, or transmitted, in any form or by any means, mechanical,  
photocopying, recording, or otherwise, without the prior written permission of the  
publishers,  
Martinus Nijhoff Publishers, P.O. Box 566, 2501 CN The Hague, The Netherlands

Copyright © 1983 by Martinus Nijhoff Publishers, The Hague

Printed in The Netherlands

## PREFACE

Ion exchange, its theory and its applications in laboratory and industry, can look back on a long and distinguished history and many view the 1950's as its high point. Indeed, it was at that time that most of the current uses of ion exchange were developed and reduced to practice, and the foundations laid for the theory as we know it today. However, in recent years there has been a resurgence of interest in ion exchange as one of the tools to overcome the many increasingly difficult problems posed by our growing need to recover valuable materials from waste and to prevent or correct damage to the environment. Therefore this is a good time to re-examine theory, established applications, and as yet unrealized potentials of ion exchange.

Like many others the technology of ion exchange relies heavily on three elements: synthesis, for suitable materials; thermodynamics, for equilibrium properties; kinetics, for dynamic performance. Of these three elements, synthesis, in a thoroughly matured field, builds largely on industrial know-how and proprietary information, leaving little room for input from the scientific community at large. Thermodynamics has been studied extensively for many years and brought to a high degree of perfection. The same cannot be said of kinetics, however, which still poses unsolved problems once we wish to probe beyond the simple "ideal" case of binary ion exchange of strong electrolytes with strong-acid or strong-base resins. It is from this background the idea of an international study meeting devoted to kinetics of ion exchange arose and the principal lectures given at that meeting have been collected in this volume.

No specialty thrives in isolation. The scope of the meeting was therefore broadened to include input from other fields of ion exchange -- from thermodynamic theory to industrial processes -- while kinetics and mass transfer remained the focal point. This gave the meeting the spice of contributions, formal and informal, from experts of many diverse backgrounds and nationalities, and helped to secure the broad-based support from NATO, the Italian Consiglio Nazionale delle Ricerche and Cassa per il Mezzogiorno, and industrial companies that made the conference possible in the first place.

It is not for the organizers and lecturers to say that the meeting was a success. This must be judged from future perspectives by those who derived benefit from attending the meeting or from reading the contributions presented there. We are glad, however, to express our deep appreciation for the untiring work of the other members of the Scientific Board of this meeting: Prof. G. Dickel, Prof. J.A. Marinsky, Dr. J.R. Millar, Prof. R. Passino, and Prof. V. Soldatov, and for the support of all who helped us provide a stimulating climate, both technical and social for a true meeting of minds.

Lorenzo Liberti

Friedrich G. Helfferich

## TABLE OF CONTENTS

Preface	V
1. John R. Millar	
On the Synthesis of Ion-Exchange Resins	1
On the Structure of Ion-Exchange Resins	23
2. Robert Kunin	
The Nature and Properties of Acrylic Anion Exchange Resins	45
3. Jacob A. Marinsky	
Selectivity and Ion Speciation in Cation-Exchange Resins	75
4. George Eisenman	
The Molecular Basis of Ionic Selectivity in Macroscopic Systems	121
5. Friedrich G. Helfferich	
Ion Exchange Kinetics — Evolution of a Theory	157
6. Lorenzo Liberti	
Planning and Interpreting Kinetic Investigations	181
7. Reinhard W. Schlögl	
Non-Equilibrium Thermodynamics - a General Framework to Describe Transport and Kinetics in Ion Exchange	207

## VIII

- |     |  |     |
|-----|--|-----|
| 8.  | Gerhard Klein<br>Column Design for Sorption Processes  | 213 |
| 9.  | Alirio E. Rodrigues<br>Dynamics of Ion Exchange Processes  | 259 |
| 10. | Roberto Passino<br>Simplified Approach to Design of<br>Fixed Bed Adsorbers                                       | 313 |
| 11. | Patrick Meares<br>Ion-Exchange Membranes   | 329 |
| 12. | G. Dickel<br>The Nernst-Planck Equation in<br>Thermodynamic Transport Theories                                   | 367 |
| 13. | A. Berg, T.S. Brun, A. Schmitt and K.S. Spiegler<br>Water and Salt Transport in<br>Two Cation-Exchange Membranes | 395 |

## ON THE SYNTHESIS OF ION-EXCHANGE RESINS

John R. Millar

(formerly Senior Research Scientist  
Duolite International, Inc.)

### Introduction:

Ion exchange is a phenomenon which has been around on Earth from very early times, perhaps something of the order of  $10^9$  years, and in the Galaxy probably for a trifle longer. Recognition of the phenomenon (in soil) is conventionally attributed to Way, and Thompson, about 130 years ago (1); though it may well have been used by Moses on the bitter waters of Marah several millenia before (2), this was on Divine recommendation (3) and inadequately documented.

All practical ion-exchange materials, inorganic and organic, are essentially insoluble matrix structures containing mobile ions capable of reversible exchange with ions of similar charge in a surrounding solution. The processes of such exchange, and their rates, form the subject of later sections of the present symposium.

The early materials, naturally occurring greensands or zeolites, were used for base exchange, i.e. the replacement of one cation in solution for the cation present in the ion-exchanger. Apart from water-softening (4), (replacement by sodium of the magnesium or calcium ions which formed precipitates with, and thus interfered with the detergent properties of, soap) zeolites were also used in sugar treatment to reduce molasses formation (5).

Synthetic aluminosilicates were later made, and naturally occurring polymers like coal (6) or cellulose (7) were chemically modified, but it was not until the mid-thirties of the present century that a completely synthetic organic material capable of base exchange was reported. The pioneering work was that of Adams and Holmes of the Chemical Research Laboratory at Teddington, near

London. They prepared crosslinked polymeric materials by the condensation of various polyhydric phenols with formaldehyde and demonstrated their capability for cation exchange on the (very weakly ionized) phenolic groups. The extension was soon made to the condensation of aromatic polyamines with formaldehyde to give materials on which strong mineral acids could be taken up, and in January 1935 their paper was published in the Transactions of the Society of Chemical Industry (8). From their presentation it is clear that they had foreseen almost every major application of ion-exchange; all that was missing were the practical materials to achieve them.

Adams and Holmes' first materials had partially-ionized functional groups, and thus both their ion-exchange capacity and their exchange rates were pH-dependent. Within ten years strongly-acidic (9) and -basic (10) functional groups had been incorporated in step-wise condensation polymers, and by 1950 these materials were being overtaken in the market by chain-growth (addition) polymer materials based on poly(styrene) (11, 12).

The decade of the fifties was one of tremendous activity in the ion-exchange field, particularly in the area of synthesis, and a staggering variety of materials became available for experiment. Initially, the emphasis was on the functional group, with crosslinked poly(styrene) being the first choice for modification. Later other addition polymers, such as the acrylics, received attention. Towards the end of the decade, as the result of the pioneering research by Pepper and his co-workers in Britain, and Gregor, Boyd, Bonner and others in the U.S., the modification of ion-exchange properties as a function of structure began to be understood (13). This paved the way for the introduction of macroporous matrices, in which structural modification was introduced at a supra-molecular level (14).

The sixties commenced with the feeling that ion-exchange was at the height of its powers, and nothing was impossible. The chelating resins dreamed of by Griessbach, Skogseid, and Mellor, and hopefully synthesized by so many workers in the fifties (15, 16), became a symbol of the sixties. Their exchange rates, slow because of their relatively low dissociation, were enhanced somewhat by the use of macroporosity, but as a result of the careful investigative work by a number of workers it became clear that the ion-specific resin, the "philosophers stone of the 50's", was indeed a myth. Many of the other cheerful predictions of the enthusiasts were weighed in the economic balance and found wanting, and, as a colleague of mine succinctly put it, the sixties could be regarded as ion-exchange's Decade of Disillusion (17). A great deal of very high quality work, both on synthesis and application, was published; nevertheless the overall tone was less optimistic than during the Golden Age.

The seventies were, perforce, more pragmatic. The limitations of ion-exchange were now recognized, and the economic requirements

of any process were better understood, as a result of the global economic situation. In particular energy and the environment became important consideration, which led to the exploitation of the ion exchange process to the full with the tools already available. As clean water, and the penalties for throwing water away in a contaminated state, became more expensive, so did the efficient use of a low energy cost means of recycling it become more attractive. When the contaminant itself was at a low-level, yet intrinsically of some value, removal and concentration by ion exchange could go some way towards subsidizing environmental protection.

Today, ion-exchange is a mature technology, but it is as true today as it was twenty years ago that the development of ion exchange resins and their applications progresses more rapidly than the theory.

Despite a present (1982) slowdown in several of the industries which historically have used large amounts of ion-exchange resins, it is predicted that present usage will have increased by a factor of some  $3\frac{1}{2}$  times before the end of this century (see Table I). For this reason alone, the necessity for state-of-the-art reviews such as those of the Society of Chemical Industry (18), and the present meeting, is obvious.

#### Characteristics of a Practical Ion-Exchanger

The requirements for such a material have been categorized by Wheaton and Hatch as "quantitative performance, quality, and economics" (19). Naturally the ideal exchanger will combine high ion-exchange capacity, appropriate selectivity, rapid kinetics, and low price. It will probably surprise few readers to be told that this ideal does not exist, and that all practical materials are compromises.

Certain characteristics, however, can be expected. The resin (to use a conventional abbreviation) should be insoluble in, and unattacked by the medium in which the exchanging ions are dissolved. Its working life should be long enough to make the process cost-effective, and it should not give rise to foreign materials (other than the counter-ion) in the process stream. The resin should show the appropriate polarity, and selectivity. For the exchange of cations, for example, it should possess on its matrix negatively charged groups, and show under the exchange conditions a distribution coefficient sufficiently in favor of the ingoing ion that the process is feasible. As to its performance, it should show a sufficiently high ion-exchange capacity on a volume basis, and an adequate rate of exchange under the process conditions, such that equilibrium is established without the ion-exchange installation being grossly oversized, nor the leakage of the ingoing ion unacceptably high.

**Table I**  
**Estimated World Ion-Exchange Production**  
**(1967-2000)**

(Figures are given in thousands of cubic meters)

AREA	YEAR						
	1967	1970	1974	1977	1981	1984	2000
N. AMERICA	35	40	78	50	61	90	250
W. EUROPE	16	19	35	30	32	45	100
E. EUROPE & U.S.S.R.	4	5	9	16	20	30	60
JAPAN & REST OF ASIA	3	4	10	7	17	35	50
OTHER	2	2	6	3	10	15	20
TOTAL	60	70	138	125	140	205	500

NOTE: THESE FIGURES ARE TAKEN FROM A NUMBER OF SOURCES AND OFFER ONLY GUESSTIMATES OF THE QUANTITIES INVOLVED, AND THEIR GEOGRAPHICAL DISTRIBUTION. SEE, E.G.,

REPORTS ON PROGRESS OF APPLIED CHEMISTRY,  
 55, 66-76, (1970)

REPORTS OF PROGRESS OF APPLIED CHEMISTRY,  
 59, 235-41, (1974)

CHEMICALS, 8-11, 12-18, (1981)

Table II

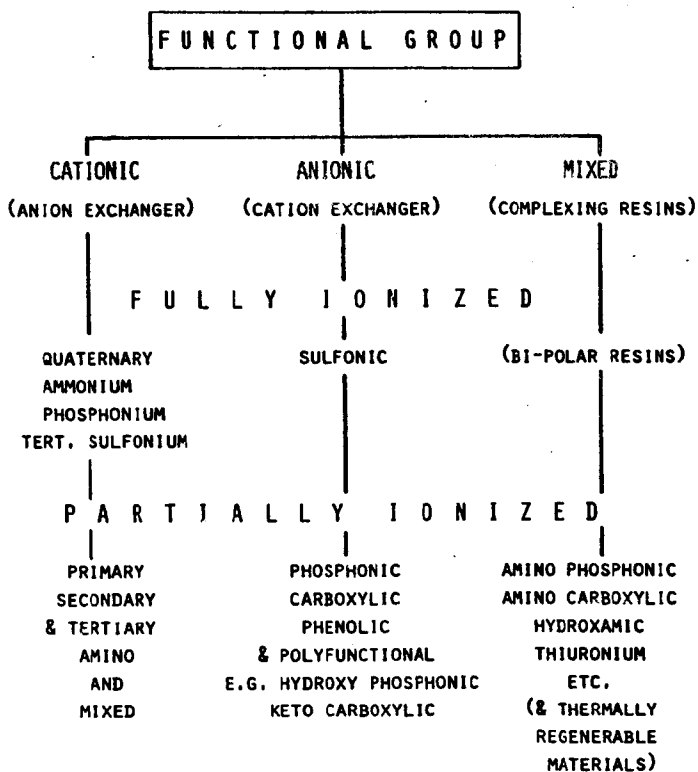


Table III

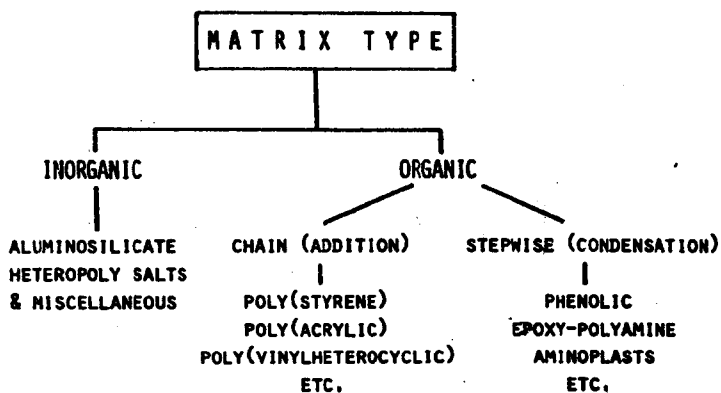
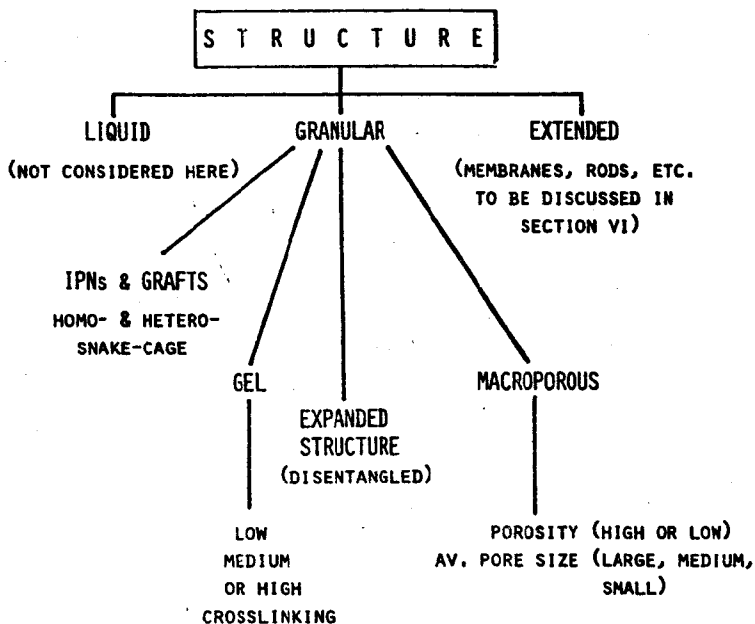


Table IV



Economically, it is necessary that the original installation cost of the resin be relatively modest, its running costs moderate, and its replacement (when eventually required) a sufficiently small fraction of the total cost of the project, making any alternative more expensive.

## Synthesis

Ion-exchangers can conveniently be categorized in several ways; by functional group, by matrix, and by structure (see accompanying Tables). In order to maintain a perspective on what appears to be an impossibly broad picture it is as well to recall that of the 140,000 or so cubic meters of synthetic organic ion-exchangers which were sold last year, well over 120,000 were poly(styrene)-based strong-acid or strong-base gel resins in bead form, substantially the same as those developed in the early fifties.

Chemically, the synthesis of organic polymer-based ion exchangers can follow two main routes (see Figure 1). Of these, the direct polymerization of functional monomers is the least common, for a number of reasons. The requirement of insolubility, with its usual involvement of a crosslinking monomer, makes the appropriate choice of the latter difficult, especially if suspension polymerization methods are to be used. The monomers themselves are specialty chemicals and correspondingly expensive. They also tend to be reactive in ways other than those to be employed in the synthesis, for example by hydrolysis or oxidation.

More often, a cheap commodity monomer is prepared in crosslinked form, and appropriate chemical reactions are performed to introduce the required functional group. This brings up a fundamental limitation on such syntheses, that incompleteness of reaction, or the occurrence of side reactions, cannot be avoided by the conventional purification techniques of organic chemistry. Thus, only clean-cut, essentially quantitative reactions are suitable for this route, and the most operationally economical synthetic scheme is also usually the cheapest in practice.

As can be seen from Table V, the selection of an organic matrix for anything other than a very exotic or high-priced material is essentially limited to addition polymers based on styrene, or acrylic monomers, and condensation products of phenols or amines with formaldehyde or epichlorhydrin. Some of the reactions which may be carried out on these matrices are illustrated in Figures 2, 3, and 4. None of these is new, and all the products have been described in earlier reviews (19, 20).

The phenol-formaldehyde matrices which are still in use are macroporous in nature, and are mainly used in specialized sorption processes (21), for which they are well suited. The styrene and

Figure 1

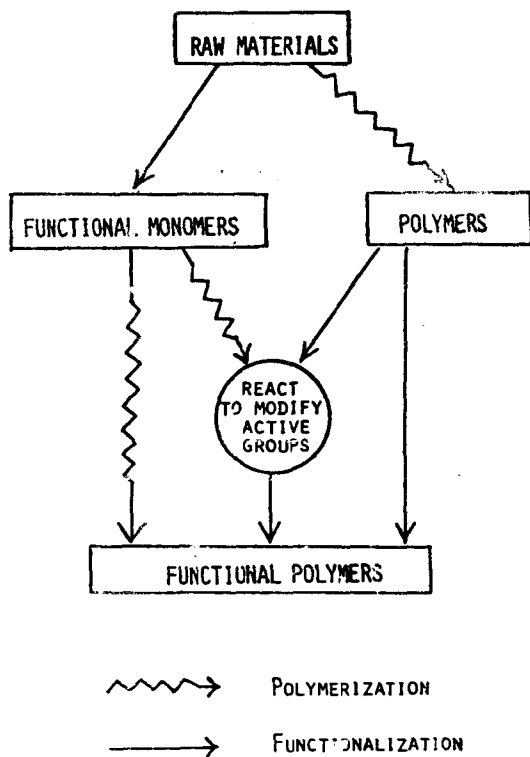


Table V  
Comparative<sup>a</sup> Bulk Monomer Prices  
(U.S.A., April 1982)

<u>ADDITION</u>		<u>CONDENSATION</u>	
VINYL CHLORIDE	1.0	FORMALDEHYDE <sup>b</sup>	1.1
STYRENE	1.5	PHENOL	1.4
ACRYLONITRILE	1.8	EPICHLORHYDRIN	1.5
ETHYL ACRYLATE	2.3	MELAMINE	2.0
VINYL TOLUENE	2.6	TRIETHYLENETETRAMINE	2.5
METHACRYLIC ACID	3.1	BISPHENOL A	2.6
BUTYL METHACRYLATE	3.5	TETRAETHYLENE PENTAMINE	3.0
TMPTMA <sup>c</sup>	6.4		
EGDMA <sup>d</sup>	6.8	m-PHENYLENE DIAMINE	7.6
DIVINYLBENZENE <sup>b</sup>	9.0		
2-VINYL PYRIDINE	13.2	RESORCINOL	17.3

a) ETHYLENE = 1.0 (AT 55¢ PER KILO)

b) AS 100% ACTIVE PRODUCT (44% HCHO; 55% DVB)

c) TRIMETHYLOLPROPANE TRIMETHACRYLATE (CROSSLINKER)

d) ETHYLENE GLYCOL DIMETHACRYLATE (CROSSLINKER)

Figure 2  
Polystyrene Resin  
(Post Treatment)

