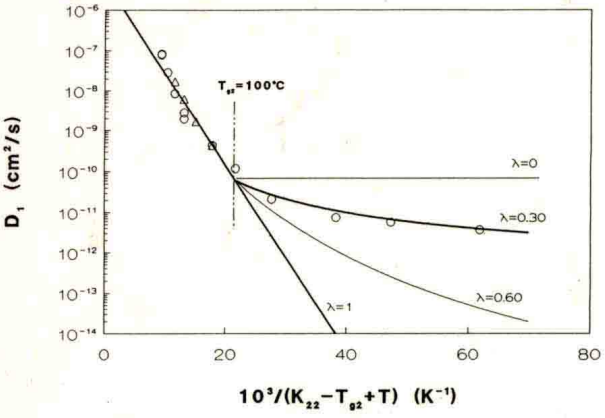
DIFFUSION IN POLYMERS



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Marcel Dekker, Inc. New York • Basel • Hong Kong

Library of Congress Cataloging-in-Publication Data

Diffusion in polymers / edited by P. Neogi.
p. cm. — (Plastics engineering ; 32)
Includes bibliographical references and index.
ISBN 0-8247-9530-X (alk. paper)
1. Polymers—Permeability. I. Neogi, P. (Partho).
II. Series: Plastics engineering (Marcel Dekker, Inc.) ; 32.
QD381.9.P45D53 1996
668.9—dc20 95-51156
CIP

The publisher offers discounts on this book when ordered in bulk quantities. For more information, write to Special Sales/Professional Marketing at the address below.

This book is printed on acid-free paper.

Marcel Dekker, Inc.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

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Preface

To most researchers in the area of diffusion in polymers, the 1968 book *Diffusion in Polymers* by J. Crank and G. S. Park is a very familiar and most appreciated one. An important reason for its success, and one that will never revisit this area again, is that the book appeared when research activity was about to explode with the advent of membrane separations, barrier membranes, new needs to study polymer devolatilization, and so on. It is now both out of print and out of date, as is one update of *Polymer Permeability* edited by J. Comyn. The two books, *Membrane Handbook* edited by W. S. Ho and K. K. Sirkar and *Polymer Gel Separation Membranes* edited by D. R. Paul and Y. P. Yampol'skii, stress diffusion only as a precursor to studying separations. Another, *Diffusion in and Through Polymers* by W. R. Vieth remains in the mainstream of diffusion in polymers.

This book began with the realization that fundamental changes have taken place in this area. Diffusivity is no longer a phenomenological coefficient and very firm validation from molecular theories now exists for Fick's law. High-speed computers have become available that, in principle, can be used to calculate these diffusivities. In practice the results are few, but present a very important view of the shape of things to come. The key results, however, are provided by real-world phenomenology, whether it concerns understanding the matrix of the solid polymers or predicting and correlating the diffusivities of small molecules. These are presented to complement the more abstract concepts. The molecular interpretations are not foregone, but at the same time numerical accuracy is the more important criterion.

Another development lies in the area of transport phenomena. It is no longer possible to be content with mechanisms-in-words, because mathematical restrictions now exist to quantify constraints rising out of thermodynamics, mass, momentum, and energy and species balances, and their methods of solutions have become more transparent. In particular, conventional transport phenomena used to address fluids had three important assumptions: homogeneity, isotropy, and local equilibrium. None of these applies to solid polymers uniformly. Some progress has been made in addressing these special effects.

A third development lies in advances in understanding the polymer matrix, covering the physical chemistry of solid state and architectures at the molecular level or at the scale of the membrane. Even in "structureless" melts, the study of molecular conformations has proved to be critical.

This book examines these aspects and will serve chemical engineers who are involved in separations, controlled release, development of barrier membranes, and transport phenomena in general; chemists, both physical chemists for some of the same reasons and those who synthesize and evaluate new materials; and finally physicists, to whom we owe the development of the molecular theories.

P. Neogi

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DIFFUSION IN POLYMERS

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Diffusion in Homogeneous Media

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I. INTRODUCTION

Recent advances in separation science and technology and in reaction engineering owe their origin, in part, to the development of specialized solid materials that interact kinetically as well as thermodynamically in a unique and controlled manner with multicomponent fluid mixtures. This ongoing technological growth has taken place in parallel with an improvement in our understanding of the fundamental properties of fluids in contact with solids. Noteworthy examples in the chemical and biochemical process industries include energy-efficient and nondestructive separation of molecular and macromolecular solutions by sorption onto solid substrates (Ruthven, 1984; Chase, 1984a,b; Norde, 1986; Yang, 1987), membrane separation of gases and liquids (Turbak, 1981; Drioli and Nakagaki, 1986; White and Pintauro, 1986; Sirkar and Lloyd, 1988), and chromatographic separation of multicomponent mixtures (Yau et al., 1979; Chase, 1984a,b; Belter et al., 1988; Brown and Hartwick, 1989). The fundamental mechanisms that govern the behavior of fluid/solid systems are also central to research and development in such diverse areas as enhanced oil recovery, toxic waste treatment, textile manufacturing, food technology, and biomedical engineering, and although significant progress has been achieved much still remains to be done.

The characterization of fluid/solid systems is particularly difficult when the dispersion of the components of the fluid within the solid medium is determined

solely by intimate details of the molecular structure of both the fluid and the solid. For example, the very high sorptive specificity of some rigid microporous materials is directly related to the geometrical and topological constraints imposed by the pore structure on the components of the adsorbing fluid. Solids that fall into this class include the zeolites (Weisz, 1973; Satterfield, 1980; Ruthven, 1984), which are cyrstalline media possessing pore apertures in the range of 0.3–1.0 nm, with the actual aperture size depending on the origin and/or method of manufacture of a given zeolite. Another example of a rigid medium that exhibits a high degree of selectivity is molecular sieving carbon, which contains local pore bottlenecks smaller than 0.5 nm (Juntgen et al., 1981). The specificity of this material is most clearly demonstrated by its ability to separate nitrogen from air. The mechanism for the separation process is kinetic in origin in that the diffusion rates of oxygen and nitrogen within the pores of molecular sieving carbon usually differ by a factor of 10 or more even though the sizes of the molecules of these two species differ by only a few percent.

When the "solid" material is also nonrigid, the analysis of diffusion is much more complicated. At a given temperature one is confronted with the need for detailed information on the time evolution of the size, shape, and number of the microvoids or cavities locally within the medium as well as the required characterization of the fluid–solid intermolecular interactions. The temperature dependence of the translational, rotational, and intramolecular motion of the membrane atoms and particles and the concomitant existence of phase transitions (glassy amorphous states to rubbery or liquid crystalline states and vice versa) further complicates the description. In view of the rapidly growing technological importance of materials of this type, particularly polymers, much effort has been expended in elucidating the numerous subtle effects associated with these intramembrane characteristics (Crank and Park, 1968; Stern and Frisch, 1981; Vieth, 1991; Roe, 1991).

The material presented and discussed in this chapter is primarily of an introductory nature, and later chapters in the book should be consulted for details of more specific methods of analysis and applications. The general framework of the presentation provided here takes the following form. In Section II the flux equations for homogeneous fluids are initially considered with reference to formulations based on both nonequilibrium thermodynamics (phenomenological description) and nonequilibrium statistical mechanics (molecular description). These equations generally form the basis for the development of the flux relations for porous media and membranes, and in closing Section II the diffusion equations for such systems are presented and their limitations discussed. In Section III the novel methodology of molecular simulation, particularly molecular dynamics, and its application to diffusion in fluid/solid systems are of primary concern. Examples and applications are described for three different methods of modeling the internal structure of permeable media: (1) idealized pore shapes in

rigid media, (2) random bicontinuous media with a stationary solid phase, and (3) random media with a mobile solid phase (polymers). Finally, in Section IV concluding comments are provided.

II. DIFFUSION FUNDAMENTALS

A. Flux Equations for Homogeneous Fluids

The conservation equation for component i within an infinitesimally small volume element of a nonuniform, homogeneous system centered at $\mathbf{r}$ at time t in the absence of chemical reactions is given by

$$\frac{\partial \rho_i}{\partial t} = - \nabla \cdot \rho_i \mathbf{u}_i \tag{1}$$

where ρ_i and $\mathbf{u}_i$ are the local mass density and velocity of component i at $\mathbf{r}$ and at time t. The group of terms $\rho_i \mathbf{u}_i$ is the flux of i relative to a stationary laboratory frame of reference, i.e.,

$$\mathbf{J}_i' = \rho_i \mathbf{u}_i \tag{2}$$

and is generally considered to be composed of two terms: (1) a convective contribution arising from the local bulk motion of the fluid and (2) the residual microscopic thermal motion of the molecules of component i relative to this convective flow. The definition one employs for the velocity of the bulk convective motion is largely a matter of convenience, and one of the most common frames of reference is based on the center-of-mass velocity of the fluid at $\mathbf{r}$ and at time t which, for a ν-component fluid, is given by

$$\mathbf{u} = \frac{\sum_{i=1}^{\nu} \rho_i \mathbf{u}_i}{\sum_{i=1}^{\nu} \rho_i} \tag{3}$$

Thus, defining the mass diffusion flux of component i relative to the center of mass of the fluid as

$$\mathbf{J}_i'^{\mathrm{b}} = \rho_i(\mathbf{u}_i - \mathbf{u}) \tag{4}$$

where the superscript b refers to the barycentric frame of reference, Eq. (1) may be written as

$$\rho \frac{Dx_i}{Dt} = - \nabla \cdot \mathbf{J}_i'^{\mathrm{b}} \tag{5}$$