



permselective membranes

edited by
C. E. ROGERS

PERMSELECTIVE MEMBRANES

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DIVISION OF MACROMOLECULAR SCIENCE
CASE WESTERN RESERVE UNIVERSITY
CLEVELAND, OHIO

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Preface

Over the last decade it has become increasingly evident that the unique gas, vapor, or liquid permeability behavior of synthetic polymer membranes is of great fundamental and practical importance. The utilization of well-characterized permselective membranes for many novel separation or selective barrier processes is of interest for diverse fields of physical science, industrial technology, and biological consideration.

The accelerating research and development efforts concerned with film and membrane materials, processes, and applications have many goals. An ultimate aim of research in this field is to establish mechanisms and laws relating solubility and transport in multi-component systems with the molecular properties and characteristics of the components. Conversely, the nature of the movement of a penetrant in a solid can afford information about concurrent molecular processes related to such characteristics of the solid as the flexibility and conformation of the molecular chains, the nature of the interaction between adjoining molecular segments, and the overall morphology. In this sense, transport measurements can be considered as extremely sensitive molecular probe techniques suitable for detailed characterizations of polymer microstructure.

From the practical and technical viewpoint, knowledge of solution, diffusion, and permeation behavior is essential for the successful design and use of many products such as packaging films and other protective coatings. This knowledge is especially necessary for the efficient development of permselective membranes to satisfy the exacting specifications required for use as media for reverse osmosis desalination, artificial kidney and lung components, and for other precise separations of multicomponent penetrant mixtures. The emerging field of ion exchange membranes is a very important area of study in this respect.

Many recent advances in membrane science and technology have been made possible by continuing progress in other fields of polymer science and engineering. The interdependence of polymer structure and transport behavior—a major factor affecting the ultimate properties of films and membranes—is of increasing importance as our ability to control polymer synthesis and to characterize polymer

structure have become more precise and predictable. It is to be expected that even more dramatic progress in membrane technology will result from the ever quickening pace of research in related areas of science spurred on by the increased awareness of the present and potential importance of membrane phenomena.

Some of the most recent work pertaining to several areas of membrane science and technology was presented at the Symposium on Permselective Membranes of the 158th American Chemical Society meeting held in New York City, in September 1969. This symposium was sponsored jointly by the Division of Polymer Chemistry and the Division of Colloid and Surface Chemistry. The large attendance and active discussions which characterized both the formal symposium presentations and the informal discussion period that followed are indicative of the intense interest in these topics. This issue of the *Journal of Macromolecular Science—Physics* constitutes a permanent record of the formal proceedings for future reference, in anticipation that it may serve, in some part, to stimulate further studies of membrane phenomena.

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Transport of Dissolved Oxygen through Silicone Rubber Membrane*

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Summary

The transport of dissolved oxygen in water through a silicone rubber membrane was studied theoretically and experimentally. The apparent oxygen permeability coefficients of silicone rubber were measured at various membrane thicknesses, temperatures, and concentration levels. The permeation flux was measured under both steady- and unsteady-state conditions. For the first time, the thickness effect of dissolved gas permeation has been studied. It was found that the apparent permeability increases with increasing membrane thickness and approaches asymptotically to the gas phase permeability. A general equation was developed to explain this phenomenon based on the concept of immobile boundary layers. It was also observed that the apparent oxygen permeability increased exponentially with increasing concentration levels in water. The temperature dependency of permeability was of the Arrhenius type.

*This work was supported by the National Institutes of Health.

INTRODUCTION

Even though there are numerous publications dealing with studies of gas permeation through membranes, very few are concerned with dissolved gases. A recent study by Yasuda [1,2] on permeation of oxygen dissolved in water presents an interesting comparison of gas-to-gas permeabilities of oxygen with those of oxygen in water-to-oxygen in water. Among many polymer membranes employed, silicone rubber showed a marked difference in its magnitude of permeability from other membranes. Another related study by Robb [3] demonstrates that the oxygen diffusion from water into a submerged cage covered by a thin silicone membrane is adequate to sustain life of test animals for several days. The transport of dissolved gases through membranes is an indispensable phenomenon in the physiology of respiration and in the development of the artificial lung and artificial gills.

The purpose of the present study was to investigate fundamental factors involved in the transport of dissolved gases through membranes. Variables studied are temperature, thickness of membrane, and concentration of dissolved oxygen in water.

THEORY

A model adopted in the following analysis is a rather general one. A schematic view of cross section of the membrane is shown in Fig. 1. It is assumed that both sides of the membrane are covered by thin layers of immobile fluid, which would give an extra resistance to permeation. The transport of dissolved gas through such a system consists of the following stepwise processes:

1. Diffusion through the boundary layer
2. Sorption into the membrane
3. Diffusion through the membrane
4. Desorption out of the membrane
5. Diffusion through the boundary layer

Each step presents a resistance of different magnitude to the gas transport. For practical purposes, however, the resistances of some steps are negligible in comparison with those of others. In the case of gas-phase permeation, processes 1 and 5 are not involved, and the resistances due to the steps 2 and 4 may even be negligible. However, for dissolved-gas permeation, a large boundary resistance may result due to steps 1, 2, 4, and 5. The presence of these boundary resistances will reduce the available driving force for diffusion inside the membrane.

The conventional definition of permeability Q is given by a steady-state flow equation:

$$F = Q (\Gamma_1 - \Gamma_2) / L \quad (1)$$

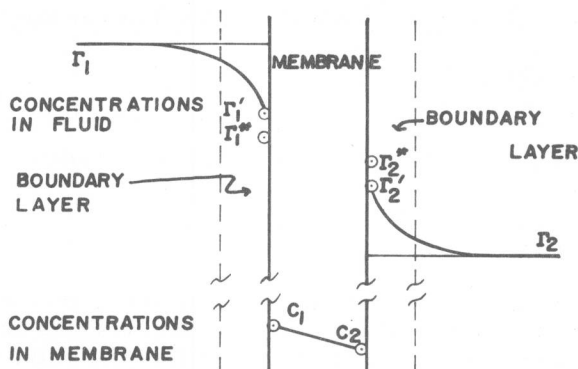


FIG. 1. Concentration profile across the membrane.

If diffusivity is independent of concentration, the same steady-state flux can also be written for the inside of the membrane as

$$F = D(C_1 - C_2)/L \quad (2)$$

Should diffusivity be concentration dependent, an average diffusivity can be used. Since the inside concentrations C_1 and C_2 are very difficult to measure, the permeability is frequently used to report the flow data. However, permeability is generally not a constant nor is it a property of a membrane. Rather, it is a phenomenological coefficient, which does not indicate the actual mechanism of the transport process.

Because it is very difficult to separate steps 2 and 4 from steps 1 and 5 experimentally, it is convenient to lump the resistances of steps 1 and 2 in a group, and steps 4 and 5 in another. Then the flow equation for one side of the membrane can be written

$$F = (\Gamma_1 - \Gamma_1^*)/r_1 \quad (3)$$

and for the other side,

$$F = (\Gamma_2^* - \Gamma_2)/r_2 \quad (4)$$

where r_1 and r_2 are film resistances including resistances of sorption and desorption if there are any. The fictitious quantities, Γ_1^* and Γ_2^* , are the concentrations which would have produced the inside concentrations C_1 and C_2 , respectively under equilibrium conditions. If a linear isotherm (Henry's law) is applicable,

$$C_1 = S\Gamma_1^* \quad (5)$$

$$C_2 = S\Gamma_2^* \quad (6)$$

If Eqs. (3) to (6) are combined with Eq. (2), then one can solve for F :

$$F = \frac{DS(\Gamma_1 - \Gamma_2)}{DS(r_1 + r_2) + L} \quad (7)$$

Comparing Eq. (7) with Eq. (1), the following is obvious:

$$Q = \frac{DSL}{DS(r_1 + r_2) + L} \quad (8)$$

This equation tells exactly how the observed permeability changes as the thickness of a membrane varies. Also, it shows that the film resistance could be significant when the diffusivity of the membrane is large, or when the thickness of a membrane is small. If there is no such film present, then the film resistance simply becomes zero, and the observed permeability reduces to the familiar form:

$$Q = DS \quad (9)$$

EXPERIMENTS

Both steady- and unsteady-state permeabilities were measured for oxygen dissolved in water through silicone rubber membranes (Dow Corning Medical Grade Silastic) with nominal thicknesses of 5, 10, 20, 40, and 62 mils. In addition, two more membranes were made of Dow Corning's Silastic RTV-501 having thicknesses of 180 and 277 mils. The oxygen concentration in water was measured with a Beckman Model 777 laboratory oxygen analyzer. Distilled water was degassed before preparing a dissolved oxygen solution by boiling the water and purging it by nitrogen gas. The oxygen-containing water was prepared by bubbling air into the degassed water until a desired oxygen concentration was obtained.

The steady-state measurements of oxygen flux were easily achieved by having two flowing streams of different oxygen concentrations on each side of the membrane. Two magnetic stirrers gave good agitation on both sides. At steady-state, the oxygen partial pressures of inlet and outlet streams were measured. From the material balance for dissolved oxygen,

$$\frac{QA(\Gamma_1 - \Gamma_2)}{L} + qS_W(\Gamma_0 - \Gamma_2) = 0 \quad (10)$$

the permeability was calculated by the following equation:

$$Q = qS_W \left(\frac{L}{A} \right) \left(\frac{\Gamma_2 - \Gamma_0}{\Gamma_1 - \Gamma_2} \right) \quad (11)$$

The first term in Eq. (10) represents the oxygen transport through the film; the second term represents the oxygen depletion from the water flowing over the upstream face of the membrane.

The unsteady-state measurements were also necessary because of experimental difficulties encountered in the steady-state measurements for thicker membranes. One side of the membrane was sealed and the other side was in contact with a large reservoir of dissolved oxygen solution. Of course, good agitation was maintained during the experiments by the same magnetic stirrers. The buildup of oxygen partial pressure was recorded as a function of time. From the material balance,

$$VS_w \frac{d\Gamma_2}{dt} = \frac{QA(\Gamma_1 - \Gamma_2)}{L} \quad (12)$$

Since Γ_1 remains virtually constant, Eq. (12) can be rewritten

$$Q = - \frac{VLS_w}{A} \frac{d \ln (\Gamma_1 - \Gamma_2)}{dt} \quad (13)$$

Thus, the unsteady-state permeability can be easily calculated from the slope of the oxygen pressure buildup plot (Fig. 2). Various oxy-

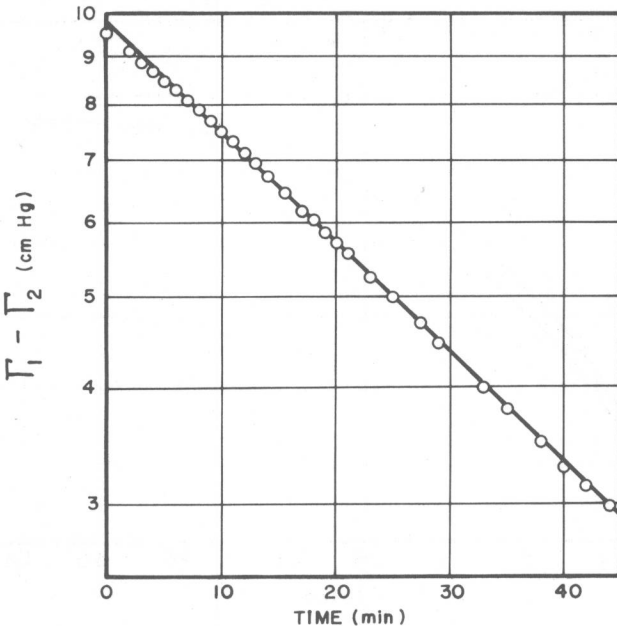


FIG. 2. Typical unsteady-state data.