

Diffusive and Bulk Flow Transport in Polymers

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Synopsis

The transport properties of polymer membranes in various forms which have a wide variety of practical applications, such as ultrafiltration, dialysis and blood oxygenation, depend upon the structure (homogeneous or heterogeneous) and the transport characteristics of the membrane material. Among many possible driving forces of transport, the pressure gradient and the concentration gradient are considered to be the most general forces encountered in practical use of polymer membranes. The transport of various permeants (gas, dissolved gas, liquid solvent, and solute) through porous and homogeneous (nonporous) polymer membranes under these driving forces is discussed. In the absence of a pressure gradient, the transport of permeants can be described as diffusion, regardless of the permeant phase and the membrane structure. In the presence of a pressure gradient, the transport of permeants may occur by diffusion and/or bulk flow of the permeants, depending upon the membrane structure and the nature of the permeant. In homogeneous membranes, many noninteracting permeants such as gases and nonsolvent vapors permeate by diffusion under applied pressure gradient; however, solvent in homogeneously swollen membranes moves by bulk flow and the diffusion depending on the degree of swelling of the membrane. In heterogeneous membranes under applied pressure, most permeants move by bulk flow.

INTRODUCTION

The transport through a polymer membrane has been utilized in a variety of practical uses in recent years. For instance, desalination by reverse osmosis and by electrodialysis, hemodialysis, and blood oxygenation all utilize the semipermeability of polymer membranes. Polymer membranes can be subjected to varieties of driving force gradient such as concentration, pressure, electric potential, heat, etc., and the corresponding flux of permeants can be utilized to facilitate the separation or concentration of component(s) in mixture. In this paper, the transport of permeants by flow and diffusion which occurs under concentration gradient and/or pressure gradient is exclusively studied. No other driving forces or chemical reactions which may occur in or across the membrane are considered.

The successful use of polymer membranes in those membrane processes entirely depends on the semipermeability or transport properties of the membranes. Therefore, an effort to elucidate transport properties of a polymer membrane based on the known chemical and morphologic prop-

erties of the membrane, beyond the observation of phenomenologic coefficients, is important for the true understanding of the phenomena.

In this paper, the two types of transport, namely, diffusive and flow transport, which are very closely related and seem to occur frequently and concurrently to other types of transport, are selected and examined under conditions where no other types of transport play significant roles as a function of membrane structure.

The selection of these two types of transport in polymers is based on the following considerations. First, there has been considerable debate and confusion whether the transport of liquid permeant occurs by molecular diffusion or by bulk flow, even in a simple case such as water through a polymer membrane under hydraulic conditions where no other possible driving force is encountered.

Secondly, the recent development of hollow fiber technology provided one of the most practical forms of polymer membranes. Perhaps the majority of practical applications of polymer membranes in the future would be in the form of hollow fibers. Because of geometric limitations of hollow fibers, the many possible driving forces other than pressure and concentration, e.g., electric potential, are impractical to apply in this particular form of polymer membrane.

Thirdly, the better understanding of these two types of transport as a function of polymer chemistry and morphology of the membrane will provide information needed for better understanding of more complicated membrane phenomena, since these two transport mechanisms are generally associated with volume flux observed in processes with additional driving forces such as electrodialysis and electrophoresis.

The discussion presented in this paper, therefore, is not aimed at an oversimplification of the general membrane processes, but is aimed at the comprehension of basic mechanisms of diffusion and flow, which undoubtedly play an important role in more complicated phenomena, as a function of membrane structure by selecting relatively simple conditions.

The discussion of diffusion and flow in a polymer membrane cannot be carried out without considering another much debated and controversial subject of membrane models, i.e., porous versus nonporous membranes.

As long as small permeant molecules are transported through polymer membranes, there must be spaces within the polymer membrane matrix which allow the passage of the permeants. Whether or not these spaces can be visualized and characterized by a similar manner used to characterize a pore of macroscopic capillary is a debatable question. The modes of transport of permeants that occur in these spaces are also influenced by the selection of the model. Regardless of the types of membrane models, however, the distinction of porous and nonporous membranes is somewhat arbitrary. There is a gradual transition of typically nonporous to typically porous structure as characterized by the transport properties.

The occurrence of the diffusive transport and bulk flow are dependent not only on the type of driving force but also on the structural and conforma-

tional factors of polymers and on the nature (phase) of permeants. Although it is easy to associate the diffusive transport with nonporous membranes and the bulk flow transport with porous membranes, these associations represent only a part of the occurrence of the diffusive and bulk flow transport in polymers. In order to clarify the combinations of these factors considered in this paper, the conclusion of the discussion is presented first in Table I.

TABLE I
Occurrence of Diffusion D and Bulk Flow F in Polymer Membranes

Permeant	Membrane	Driving force	
		ΔP	ΔC
Gas	homogeneous	D	D
	heterogeneous	$F + (D)$	D
Liquid	homogeneous	$D + F^a$	D
	heterogeneous	$F + (D)$	D
Dissolved gas ^b	homogeneous	D	D
	heterogeneous	$F + D^c$	D
Solute	homogeneous	$D + F^b$	D
	heterogeneous	$F + (D)$	D

^a The magnitude of F depends on the degree of swelling; at low degree of swelling $F = 0$.

^b At least one side of a membrane faces liquid in which gas is dissolved.

^c Values depend on the phase which occupies the pore.

DIFFUSION AND BULK FLOW

Diffusion occurs under chemical potential gradient of the permeant which is a consequence of concentration and/or pressure difference. Bulk flow occurs only with across-membrane pressure difference. In this sense, the osmotic flow of a solvent across a perfect semipermeable membrane is the diffusive transport of a liquid. Since the chemical potential gradient is created by pressure gradient, not all of the flux that takes place under applied pressure difference can be considered as bulk flow. The distinction between bulk flow and diffusion is dependent on the flow characteristics of a membrane. It can be illustrated by the example of water transport, as follows. The flux of radioactive water J_d' in the absence of applied pressure is related to the external concentration gradient $\Delta c/\Delta x$ across a membrane and to the diffusive permeability P by

$$J_d' = -P (\Delta c/\Delta x).$$

When the same membrane is exposed to pressure difference, the flux J_p is related to the pressure gradient $\Delta p/\Delta x$ and to the piezometric permeability K by

$$J_p = -K (\Delta p/\Delta x).$$

If no bulk flow occurs, P (in cm^2/sec) and K (in $\text{cm}^3 \text{ sec}/\text{g}$) are related¹ as follows:

$$K = PV_1/RT$$

where V_1 is the molar volume of water.

In the general case, J_p can be considered as the sum of a diffusive flux J_d and a flux due to bulk flow J_f ; i.e.,

$$J_p = J_d + J_f.$$

Hence, the flux due to bulk flow

$$J_f = J_p - J_d$$

or

$$J_f = (K - PV_1/RT) (\Delta p/\Delta x)$$

is defined as the flux in excess of diffusive flux at applied pressure gradient. The diffusive and bulk flow transport in a polymer membrane can be distinguished by comparison of flux coefficient under piezometric and isobaric conditions. Examples are given in the following sections.

GAS TRANSPORT

The measurement of the transport of gas through a polymer membrane is generally carried out by applying a pressure gradient across the membrane, i.e., by using vacuum or superatmospheric pressure. In this case, it is rather difficult to distinguish between bulk flow and diffusive flow from flux data of a single experiment with one gas. But the determination of diffusive and bulk flow transport can be made by observation of (a) pressure dependence of permeability coefficient, and (b) selectivity among different gases.² The gas flux can be created without applying total pressure difference across a membrane by having two different gases at the same pressure, i.e., N_2 separated by a membrane from He. Under these conditions, the diffusive flux of gas can be observed.³ Gases and vapors permeate most of flawless homogeneous polymer membrane by diffusive mechanism, and the permeability constants measured by isobaric condition (P') are identical to those obtained under applied pressure (K), as shown in Table II. With porous membranes, however, these two permeability coefficients (i.e., K and P') are often different by orders of magnitude. Some characteristic data are collected in Table II. Therefore it should be realized that the permeability coefficient K of porous membranes measured under applied pressure cannot be used to compute the flux in the absence of total pressure difference. A good example is the water vapor transmission under isobaric condition with the membrane separating two compartments with different relative humidity. Under this condition, water vapor permeates by diffusion through a porous membrane, and its extent can be accurately estimated only by the value of P' , if a membrane is heterogeneous.

TABLE II
P and *K* of Gases in Polymers*

Membrane	Gas	<i>K</i>	<i>P'</i>
Homogeneous Polymer			
Poly(dimethylsiloxane)	N ₂	281	288
	O ₂	605	595
	CO ₂	3240	3210
Poly(4-methylpentene-1)	N ₂	7.83	619
	O ₂	32.3	26.8
	CO ₂	92.6	87.8
Polyethylene, density = 0.920	N ₂	0.973	0.932
	O ₂	3.15	2.88
	CO ₂	13.2	12.6
Porous Membrane			
Porous polypropylene	N ₂	6,500.	3300.
Porous polysulfone	N ₂	27,000.	4800.
Porous cellulosic membrane	CO ₂	200,000.	7600.
Porous cellulosic membrane	CO ₂	900,000.	11,000.

* *K* and *P'* values $\times 10^{10}$, in units of (cm³(S.T.P.) cm)/(cm² sec cm Hg).

The values of *K* for porous membranes obtained by a vacuum-type apparatus generally provide misleadingly high water permeabilities.

LIQUID TRANSPORT

The most significant factor to be considered in transport of liquid permeants through polymer membrane is the interaction of liquid with the polymer. If a liquid permeant has a relatively low degree of interaction with the polymer, the permeation rate of the liquid is essentially identical with the saturated vapor permeability of the liquid.^{4,5} The "conditioning effect" or relaxation phenomenon and minor morphologic changes cause the differences between liquid and saturated vapor permeabilities.⁶ As the interaction between liquid permeant and the polymer increases, the permeability characteristics of dry and wet (saturated with the liquid) membranes differ significantly and the equilibrium uptake of the liquid becomes the predominantly important factor which determines the permeability properties of the membrane. In this case, the diffusive permeability is given by

$$\ln (P/D_0) = -\beta[X(1 - \alpha)/(1 + \alpha X)] - \ln [1 + X] \quad (1)$$

where *D*₀ is the self-diffusion constant of the liquid at the same temperature, α and β are ratios of free volume parameters (of which details can be seen in reference 1), and *X* is a parameter which is related to the volume fraction *H* of the liquid in the membrane by $X = (1 - H)/H$.

The bulk flow permeability $K_f = K - (PV_1/RT)$ can be expressed by an equation of the following form:

$$K_f = \Phi[(1/X) - (1/X_0)]$$

derived from the frictional resistance of macromolecule, where Φ is a proportionality constant, and X_c is the limiting value of X above which no bulk flow occurs in the membrane.⁷

Examples of water permeabilities K and PV_1/RT of water-swollen polymer membranes are shown in Table III as functions of the parameter X . It is important to recognize that bulk flow occurs in homogeneous polymer membranes as soon as the equilibrium liquid content H exceeds a certain critical value which is dependent on the nature of the liquid. Bulk flow becomes the predominant mechanism of liquid transport at a high degree of swelling. Whether bulk flow occurs or not has very important implication on the proper understanding of solute transport, since the transport of solvent has decisive influence on it.

TABLE III
 PV_1/RT and K of Water in Water-Swollen Polymers^a

$X = (1 - H)/H$	K	PV_1/RT
0.16	1.27×10^{-6}	70.8×10^{-10}
0.28	1.17×10^{-6}	61.9×10^{-10}
0.67	2.56×10^{-7}	39.8×10^{-10}
1.63	2.92×10^{-8}	13.1×10^{-10}
1.13	6.26×10^{-8}	16.2×10^{-10}
3.76	1.45×10^{-10}	1.47×10^{-10}
5.66	1.70×10^{-10}	1.10×10^{-10}
7.33	1.48×10^{-10}	0.705×10^{-10}

^a PV_1/RT and K in units of $\text{cm}^2/\text{sec atm}$.

DISSOLVED GAS TRANSPORT

Although dissolved gas can be dealt as a case of solute transport, it provides a special situation which does not occur with general solutes. Since a gas can exist and permeate the membrane in the absence of solvent (liquid), the general situation can be expressed by the combination of gas-membrane-liquid, liquid-membrane-gas, and liquid 1-membrane-liquid 2, where the first component represents the phase which contacts the in-flux side of a membrane and the last component, the out-flux side.

If the liquid (solvent of dissolved gas) does not alter the permeability characteristics of the polymer, such as water with hydrophobic polymers, the permeability coefficient of homogeneous polymers to dissolved gas is essentially the same as that of dry polymer in gas-membrane-gas situation (gas permeability).^{8,9} The dissolved-gas transfer rate through the membrane is dependent upon the (external) partial pressure gradient but not on the (external) concentration gradient of a gas. Therefore, the solubility of the gas in the liquid does not affect the dissolved gas permeability of a polymer membrane, providing that the liquid (or liquids) does not alter the membrane. Although, in principle, the true (ideal) dissolved gas permeability of a homogeneous polymer membrane can be derived from the gas-phase experiment, the actual dissolved-gas (oxygen) transfer rate

through a polymer membrane can be considerably smaller than that. This discrepancy is caused by the boundary layer resistance. The contribution of boundary layer resistance is small if the transport resistance of a polymer is large and becomes more and more significant as the transport resistance of the membrane becomes smaller. The dissolved oxygen permeability of silicone rubber, which has the highest gas permeability among existing polymers, has been found to be considerably smaller than the corresponding gas permeability.^{8,9,10}

The imbibition of the solvent should, in principle, increase the characteristic permeability of dissolved gas due to the plasticizing effect of the solvent; however, the actual transport rate of dissolved gas may or may not be increased by the swelling, depending on the solubility of the gas in the solvent. The solubilities of gases in many liquids are smaller than those in polymers.

The dissolved gas permeability of a porous polymer membrane is dependent on whether the pores are filled with gas or liquid.¹¹ Depending on the wettability of the polymer by the liquid, the pores may be filled with the liquid or may remain filled with air. If the liquid penetrates into the pores, the dissolved gas permeability of porous membrane becomes close (in order of magnitude) to that of the liquid. In any situation, gas permeability of porous membranes (ordinarily measured by gas-membrane-gas situation) has no direct correlation to their dissolved gas permeabilities. Examples of gas and dissolved gas permeabilities are shown in Table IV.

TABLE IV
Transmission Rate of Gas and Dissolved Oxygen through Porous
and Nonporous Membranes

Membrane	Transmission rate of oxygen, cm ³ (S.T.P.)/cm ² sec cm Hg	
	Gas-Mem.-Gas	Gas-Mem.-Water
Homogeneous Polymer		
Poly(dimethylsiloxane)	3.90×10^{-6}	1.81×10^{-6}
Porous Membranes		
Silicone-coated Millipore filter	2.51×10^{-2}	1.35×10^{-7}
Olefin paper	7.60×10^{-2}	1.97×10^{-7}
Porous polysulfone membrane	9.16×10^{-3}	2.97×10^{-6}

SOLUTE TRANSPORT

The general situation for transport of a single solute in solvent through a membrane can be best described by the irreversible thermodynamic description of membrane transport developed by Kedem and Katchalsky,¹²

$$J_v = L_p(\Delta p - \sigma \Delta \pi_s)$$

$$J_s = \bar{C}_s(1 - \sigma)J_v + \omega \Delta \pi_s$$

where J_v and J_s are the net volume and solute flux; L_p , σ , and ω are the hydraulic conductivity, Staverman reflection coefficient, and solute permeability coefficient, respectively; \bar{C}_s is the mean solute concentration in the membrane; and Δp and $\Delta\pi_s$ are the hydraulic and osmotic pressure difference between the solutions on either side of the membrane, respectively.

The explicit determination of coefficients as characteristic membrane parameter is possible only for solute-solvent-membrane systems which are unperturbed by change of external factors such as Δp , $\Delta\pi_s$, and \bar{C}_s . Many polymer membranes, particularly solvent-swollen membranes which allow high enough transport of solutes and solvents, are rather highly perturbed by these external factors. Parameters obtained without considering this aspect may not provide meaningful numbers insofar as the interpretation of membrane characteristics based on the physical and chemical nature of polymers is concerned.

In the diffusive process such as dialysis (where $\Delta p = 0$), the membrane characteristics can be best determined by employing very dilute solutions of a solute, i.e., small \bar{C}_s and π_s . Even under such conditions, the membrane parameter such as the equilibrium solvent uptake is often dependent on the nature of the solute and cannot be treated as a fixed value parameter. The diffusive permeability P_2 can be best described by an expression similar to eq. (1) for the solvent permeability,

$$\ln (P_2/D_{20}) = \ln \gamma - \ln (1 + X) - \beta_2 [X(1 - \alpha)/(1 + \alpha X)]$$

where D_{20} is the diffusion constant of the solute in the solvent; γ is the molal partition coefficient (g solute per g solvent in membrane/g solute per g solvent in solution); β_2 is the corresponding parameter to the solute; and X , in this case, is based on the volume fraction of solvent in a membrane at equilibrium with the solution.¹³

The semilog dependence of P_2 on parameter X and on parameter β_2 (which is related to the molecular size of the solute) is expected. It has been shown¹⁴ that P_2 of relatively small-sized solute in highly swollen membranes indeed follows the dependence on X . The most logical approach in interpretation of the parameter β_2 is that the cross-sectional area of the solute is proportional to β_2 . However a meaningful value of the cross-sectional area of each solute is difficult to obtain. It can be only estimated from the corresponding radius r of hydrodynamic volume. Data available for this kind of analysis¹⁵ is limited to cellulose membranes which may not be ideal models of homogeneous polymers due to relatively high degree of molecular aggregates. Regardless of detailed argument on whether β_2 is proportional to r or r^2 , it seems to be quite evident that the diffusive permeability P_2 can be generally expressed by the equation, which differs substantially from equations based on simple two-phase model (capillary model) of membranes.

Although distinction of porous and homogeneous membranes is quite arbitrary, most porous membranes have much greater pore size than the

size of most solutes considered. Consequently, the diffusive permeability is proportional to the porosity, i.e., to the parameter H , and lacks the semi-logarithmic dependence on the corresponding parameter $(1/H) - 1$.

SIGNIFICANCE OF MEMBRANE FACTORS IN BULK FLOW AND DIFFUSIVE TRANSPORT

The actual transport rate of permeant is dependent not only on the permeability coefficient (which has been so far discussed) but also on other additional membrane factors such as membrane thickness and asymmetry. The effect of membrane thickness and asymmetry has a different degree of significance on the total flux of a permeant depending upon diffusive or bulk flow processes. As can be visualized by comparing equations for K and P as functions of parameter X , there is no theoretical upper limit to K , whereas P has the upper limit of the self-diffusion constant or diffusion constant of a solute in the pure solvent. Therefore, the total thickness of a membrane (regardless of uniformity or asymmetry) plays a very important role in determining the total flux of a permeant in diffusive processes. In bulk flow transport, the thickness becomes negligible if K becomes overwhelmingly large. In such a case, therefore, the asymmetry of membrane provides a great advantage of reducing the effective thickness or of increasing mechanical strength without losing the total flux.

With uniform membranes (which have no gradient of characteristic transport properties in the direction of membrane thickness, regardless of porosity or nonporosity), the increase in P always leads to increase in K . Due to the above-mentioned reasons, the correlation between P and K becomes less evident with asymmetric membranes such as coagulated cellulose acetate membranes.¹⁶ In processes in which diffusive and bulk flow transport plays comparable roles such as hemodialysis, this aspect of asymmetric membrane may be advantageous in practical operation.

The permeability of a membrane, in general, is not a membrane constant, except for the ideal case of gases in flawless homogeneous polymers, and depends on the external conditions. The diffusive permeability P and the piezometric permeability K should be distinguished and be properly interpreted in corresponding processes. The occurrence of diffusive and bulk flow transport in polymer membranes is summarized in Table I.

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