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High Gas Permeability in Open-Structure Membranes

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Abstract−For most polymeric membranes, the gas permeability coefficient (P) is often interpreted as the product of diffusivity (D) and solubility (S) of a penetrant gas in the polymer (P=D S). The basic assumption is that molecular diffusion is primarily responsible for mass transport in the membrane permeation process. However, for some open structure membranes, such as poly(1-trimethylsilyl-1-propyne) [PTMSP] or poly(dimethylsiloxane) [PDMS], the high permeabilities of some gases yield much higher diffusivities when calculated from the above relationship (P=D S) than when calculated by using the direct kinetic measurement of diffusivity. It is hypothesized that this discrepancy is due to the convective transport of gas molecules through such open structured polymers. In most cases, the convective contribution to mass transport through membranes is negligible. However, for polymer membranes with high free volume, such as PTMSP, whose free volume fraction is 20 to 25%, the convective term may dominate the permeation flux. In this study, a non-equilibrium thermodynamic formalism is employed to properly treat the diffusion term and convective term that constitute the Nernst-Planck equation. The current analysis indicates that the total permeation flux, which consists of a diffusion term and a convective term, agrees well with the experimental data for several permeation systems: pure components propane and n-butane/PTMSP, pure gas hydrogen/PTMSP, and mixed gas hydrogen/PTMSP. Also, the permeation systems of a nonporous rubbery membrane, PDMS, and eight organophosphorus compounds were included in the study. It is recommended that the proposed model be validated by using other polymers with high free volumes and high permeabilities of gases and vapors, such as poly(1-trimethylgermyl-1-propyne) [PTMGeP] and poly(4-methyl-2-pentyne) [PMP].

Key words: Permeation Flux, Diffusion Flux, Convective (Bulk) Flux, Large Permeability, Poly(1-trimethylsilyl-1-propyne), Poly(dimethylsiloxane)

INTRODUCTION

1. Literature Survey

The permeation of small molecules through membranes was first observed over a century ago. During the last two decades, the rapid development of membrane technology has brought with it a wide variety of applications in the industrial and medical fields: the separation of gases, seawater, and azeotropic mixtures; the separation of ions, macromolecules, colloids, and cells; and the control of drug delivery. Due to its unique separation capabilities and low energy consumption, diffusion through membranes is of great technological importance, and there has been a growing interest in elucidating the permeation mechanisms. Thus, the evaluation of parameters such as the permeability coefficient P, the diffusion coefficient D, and the solubility coefficient S appears to be very important for assessing the feasibility of application of permeation systems to industrial and medical applications.

There are several methods used to experimentally measure solubility, permeability, and diffusivity as discussed by Felder and Huvard [1980] and Bae et al. [1993, 1994a, b, 1998]. In the general literature for example, Stern [1994], the most frequently used equation that correlates these three characteristic parameters for permeation systems is:

$$P=D\,S \tag{1}$$

Eq. (1) is an analytical statement of the solution-diffusion model of penetrant transport in polymers, which is the most widely accepted explanation of the mechanism of gas permeation in nonporous polymers. The permeation flux across the membrane is often assumed to be equal to the diffusional flux and therefore the influence of the bulk motion of the penetrants is ignored. Among the three transport parameters P, D, and S, the diffusion coefficient D is rarely measured directly. It is often calculated from experimental data as shown by Crank and Park [1968], Crank [1975], Koros et al. [1976], Zimmerman et al. [1998], Balik [1996], and Felder [1978], from steady-state permeability and solubility measurements; from a time-lag assessment from initial permeation data; the kinetic measurement and the differential permeation measurement, etc. For many dense and nonporous membranes, the diffusion coefficient of the penetrant, as determined from Eq. (1), using D=P/S, is consistent with other diffusivity measurements. However, for polymers with high free volume, Eq. (1) may not be fully representative of the permeation mechanism; in these cases using Eq. (1) may bring misleading results.

Recently, Anuraag [1997] studied the sorption, diffusion, and permeation of propane and n-butane in poly(1-trimethylsilyl-1-propyne) [PTMSP], a glassy polymer membrane with extremely high

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‡ This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

free volume (20 to 25%). The diffusion coefficients were determined from two different sets of data: 1) kinetic sorption data, and 2) steady-state permeability and solubility data. However, there was more than one order of magnitude difference between the diffusion coefficients calculated from the two sets of data, where the diffusivity determined from the steady-state permeability experiments was higher than that determined from the kinetic sorption data. Almquist [1995] determined the diffusion coefficients of eight organophosphorus chemicals in poly(dimethylsiloxane) [PDMS], a homogeneous nonporous membrane, using the kinetic sorption measurement and the time-lag measurement. Large discrepancies were also found between the diffusion coefficients calculated from the two sets of data, where the diffusivity determined from the time-lag measurement was higher than that determined from the kinetic sorption measurement by factors ranging from 1.5 to 8.1. The lack of agreement between different experimental measurements of diffusivity suggests either huge experimental errors or an inadequacy of the diffusion model on which the data analysis was based.

Because of such significant discrepancies in the apparent diffusivities, it is hypothesized that with high permeation flux through membranes, the bulk motion of the penetrants (convection) may contribute significantly to the overall mass flux. This paper proposes a model for penetrant transport through membranes utilizing terms for both the diffusional and convective transport. This model is then used to simulate the permeability coefficients for several permeation systems with PTMSP and PDMS membranes described by Anuraag [1997], Almquist [1995], Merkel et al. [2000], and Pinnau et al. [1996].

2. Background

Permeation is a phenomenological definition that refers to mass transfer through a medium, not only by diffusion but also by a variety of transport mechanisms under various driving forces. According to the definition, the molar flux of species i passing through a unit area per unit time, N_i, can be expressed using the same notation as Bird et al. [2002]:

$$N_i = c_i v_i = c_i(v_i - v^*) + c_i v^* \tag{2}$$

where c_i is the molar concentration of species i, v_i is the velocity of species i with respect to stationary coordinate axes, and v^* is the local molar average velocity. From Eq. (2), we can see that the molar flux N_i, relative to the stationary coordinate, is the sum of two terms: 1) the molar flux of i resulting from the convective motion of the fluid, $c_i v^*$ and 2) the molar flux of i resulting from the diffusion superimposed on the bulk flow, $c_i (v_i - v^*)$.

Diffusion is a universal phenomenon caused by random molecular motion under a concentration gradient that is responsible for material transfer from one point to another. The diffusion flux can also be seen as the relative motion of molecules with respect to the average velocity. Considering the permeation flux in the z direction, the "diffusional" flux for species i is defined as:

$$J_i^* = c_i(v_i - v^*) = -D_i \frac{dc_i}{dz} \tag{3}$$

where c_i is the concentration of species i inside the membrane.

The permeation flux N_i, unlike the diffusion flux, can be experimentally measured and is defined by:

$$N_i = P_i \frac{\Delta p_i}{\lambda} = P_i \left(\frac{p_{i2} - p_{i1}}{\lambda} \right) \tag{4}$$

where P_i is the permeability coefficient of species i, p_{i2} and p_{i1} are the upstream and downstream partial pressures of species i, respectively, and λ is the membrane thickness. The permeability coefficient P_i, calculated by using Eq. (4), is usually recognized as the observed permeability, which is calculated based on the total flux (diffusion and bulk flux) of the penetrant. Substituting Eqs. (3) and (4) into Eq. (2), we get:

$$N_i = P_i \left(\frac{p_{i2} - p_{i1}}{\lambda} \right) = J_i^* + c_i v^* = J_i^* + c_i \frac{N}{c} = J_i^* + c_i q = -D_i \frac{dc_i}{dz} + c_i q \tag{5}$$

where q represents the total volumetric flux. The last expression is known as the Nernst-Planck equation. It is obvious that the permeation flux N_i is different in principle from the diffusion flux J_i^*. However, they can be assumed to be approximately equal when v^* or q is very small:

$$N_i = P_i \left(\frac{p_{i2} - p_{i1}}{\lambda} \right) \approx J_i^* = -D_i \frac{dc_i}{dz} \tag{6}$$

Eq. (6) is commonly used to describe membrane permeation. The diffusion flux is often a very good approximation for the permeation flux. However, Eq. (6) is not valid for all membrane systems. The magnitude of error involved in using Eq. (6) depends on the relative contribution of the convective term in Eq. (5), $c_i v^*$, to the permeation flux. When the permeation flux is very large, as in the examples discussed in the present paper, the convective term may be significant. Permeation flux that takes into consideration of both the diffusion flux and the bulk flux of penetrants has been discussed in detail by Hwang and Kammermeyer [1975], Frisch [1956], and Kamaruddin and Koros [1997].

The permeability coefficient P_i, calculated by using Eq. (6), is usually recognized as the diffusion-based permeability that is a function of diffusivity and solubility of the penetrant in the membrane material. If the observed permeability, rather than the diffusion-based permeability, is used to calculate the average diffusion coefficient, the result will overestimate the actual value. The extent of the error depends on the relative contribution of the convective flux.

EXPERIMENTAL DATA

1. PTMSP Membrane

Polyacetylene-based polymers were extensively studied for gas separation applications during the 1990s. In particular, poly(1-trimethylsilyl-1-propyne) [PTMSP], a silica-containing di-substituted acetylene polymer with a glass transition temperature greater than 250 °C, has attracted the most attention within the group of polyacetylenes due to its unique properties: the lowest density of any known polymer (~0.75 g/cm^3); a very high excess free volume of 20 to 25% (For comparison, the excess free volume of conventional glassy polymers ranges between 2-6%); the highest gas permeability of all known synthetic polymers; high permeability to large, condensable gases than to small, permanent gases, etc. as reported by Pinnau and Toy [1996]. In view of PTMSP's unique properties, conventional theories governing gas and vapor transport in dense polymer films may not adequately describe their transport in PTMSP. There-

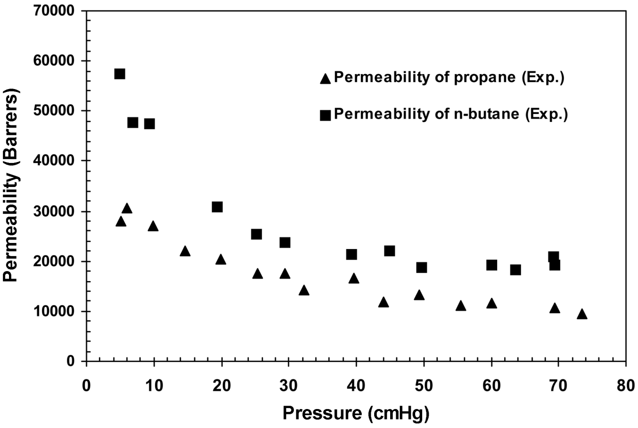

Fig. 1. Permeability of pure components propane and n-butane in PTMSP @ 35 °C (Anuraag and Freeman's data).

fore, the PTMSP membrane system was used to test the effect of the convective term in a transport model that consisted of both diffusive and convective transport terms.

1-1. Pure Components Propane and n-Butane/PTMSP Systems

The experimental details for pure propane and n-butane/PTMSP systems are given in Anuraag's thesis [1997]. Briefly, a constant volume/variable pressure method was used by Felder and Huvard [1980] to determine the steady-state propane and n-butane permeabilities at 35 °C and pressures up to 700 torr. As shown in Fig. 1, the permeability coefficients for propane and n-butane in PTMSP decrease with increasing upstream pressure up to 30 cm Hg, above which the permeability coefficients are relatively independent of pressure. This phenomenon may be caused by the penetrant molecules that "fill up" the free volume in the membrane with increasing pressure and thus retard the diffusion process. As the free volume is filled, the permeation becomes less dependent on the upstream pressure of the penetrant gas.

The interval kinetic sorption methods were used to monitor the absorption of propane and n-butane vapor by the PTMSP membrane at 35 °C. The sorption data, presented in Fig. 2, are described by the dual-mode sorption model as reported by Felder and Huvard [1980]. These data were subsequently used to calculate the solubility coefficients for propane and n-butane in PTMSP.

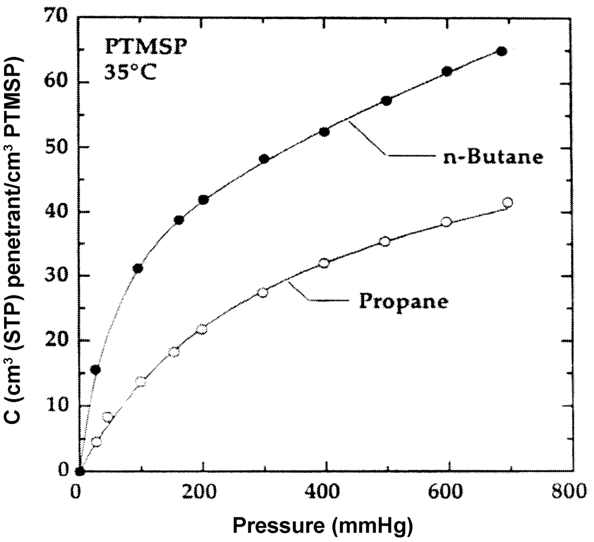

Fig. 2. Propane and n-butane sorption isotherms in PTMSP @ 35 °C (Anuraag and Freeman's data).

The diffusion coefficients were determined in two ways: 1) from the kinetic sorption data, and 2) from the steady-state permeability and solubility data. The experimental data acquired in the kinetic sorption experiments were fit to a Fickian sorption model as shown by Crank [1975]:

$$\frac{M_t}{M_\infty}=1-\sum_{n=0}^{\infty}\frac{2\alpha^2}{\beta_n^2(\beta_n^2+\alpha^2+\alpha)}\exp\left(\frac{-\beta_n^2 Dt}{\lambda^2}\right)$$

where β_n and β are defined by the expression below:

$$\alpha\equiv\beta_n\tan\beta_n\equiv\frac{k_c\lambda}{KD}$$

In the above equations, M_t is the mass uptake at time t, M_∞ is the uptake at equilibrium, D is the diffusion coefficient (cm^2/s), λ is the membrane thickness (cm), k_c is a convective mass transfer coefficient (cm/s), and K is the solubility constant. Here, equilibrium between the penetrant gas at the surface of the membrane and the penetrant gas in the gas phase was assumed to occur instantaneously; thus β was set equal to infinity, and the corresponding values of β_n, tabulated by Crank [1975], were used accordingly. The value of diffusivity was determined to be the value that resulted in the best fit of the model to the experimental data, as determined by a least-squares method. The model was found to provide a good representation of the experimental data, except near the end of the kinetic sorption process (i.e., $0.9<M_t/M_\infty<0.98$). The deviations of the model from the experimental data toward the end of the sorption process are attributed to the polymer relaxation-controlled absorption of the penetrant and can be described by a non-Fickian sorption model demonstrated by Berens and Hopfenberg [1978]:

$$\frac{M_t}{M_\infty}=1-(1-\alpha_R)\frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left(\frac{-D(2n+1)^2\pi^2 t}{\lambda^2}\right)-\alpha_R\exp\left(\frac{-t}{\tau}\right) \quad (7)$$

where α_R is the fraction of the total mass uptake due to protracted non-Fickian drift (i.e., relaxation), and τ is the first-order relaxation constant which characterizes the time scale of the protracted drift. When appropriate, the values of diffusivity and the parameters α_R and τ were determined to be those values that resulted in the best fit of the model in Eq. (7) to the experimental sorption data, as determined by a least-squares method. The results of this analysis are shown in Table 1. For those cases with no reported values of τ and α_R, the Fickian model could adequately describe the experimental data.

The diffusion coefficients were also calculated from the steady-state permeability and solubility data as determined by Koros et al. [1976]. The results from these calculations are compared to those from the kinetic sorption data in Fig. 3, which exhibits significant discrepancies between them. The diffusion coefficients calculated from the steady-state permeability and solubility are consistently higher one order of magnitude than those calculated from the kinetic sorption data.

1-2. Pure Gas Hydrogen/PTMSP System

Table 1. Diffusion coefficients and parameters τ and α_R for propane and n-butane at 35 °C (Anuraag and Freeman's data)

	Pressure range (mmHg)	$D\times10^7$ (cm^2/sec)	τ (sec)	α_R
Propane	0-54	2.4±0.2	240±130	0.07±0.04
	54-103	2.2±0.06	1,200±700	0.056±0.01
	103-204	1.76±0.04	6,600±1200	0.067±0.004
	204-302	1.5±0.03	3,800±500	0.128±0.005
	302-400	1.47±0.02		
	400-503	1.42±0.02		
	503-602	1.26±0.02		
	602-700	0.94±0.01		
n-Butane	0-51	1.46±0.04	2,200±1900	0.020±0.006
	51-100	1.19±0.03	7,100±1200	0.074±0.005
	100-200	1.32±0.04	5,900±700	0.114±0.005
	200-301	1.13±0.03	5,300±500	0.178±0.005
	301-400	1.27±0.03	6,200±400	0.180±0.005
	400-506	0.90±0.03	3,000±200	0.251±0.008
	506-602	0.98±0.04	8,500±300	0.384±0.005
	602-700	0.78±0.04	5,700±140	0.473±0.007

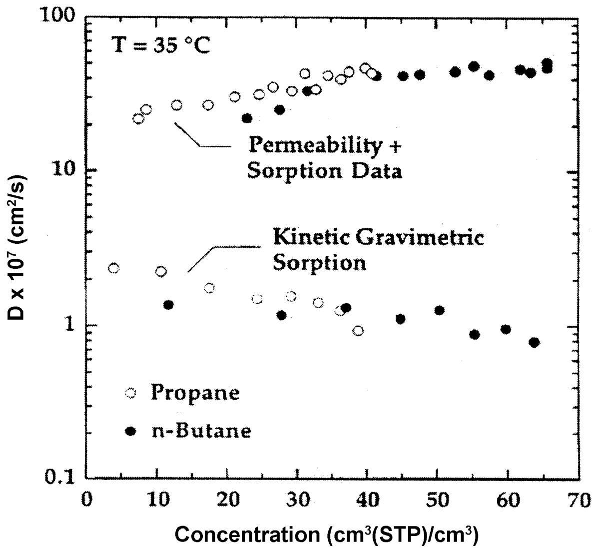

Fig. 3. Diffusion coefficients of pure propane and n-butane in PTMSP @ 35 °C estimated from steady-state and transient experiments (Anuraag and Freeman's data).

The permeability coefficient of pure gas hydrogen through PTMSP membrane was determined at 35 °C by using the constant pressure/variable volume method. The permeability coefficient data for hydrogen is presented in Fig. 4. The sorption was measured with the kinetic sorption method as described by Merkel et al. [2000]. The dual-mode sorption model accurately describes the sorption of pure gas hydrogen into PTMSP membrane. The isothermal sorption data are summarized in Fig. 5.

1-3. Hydrogen and Propane Mixture/PTMSP System

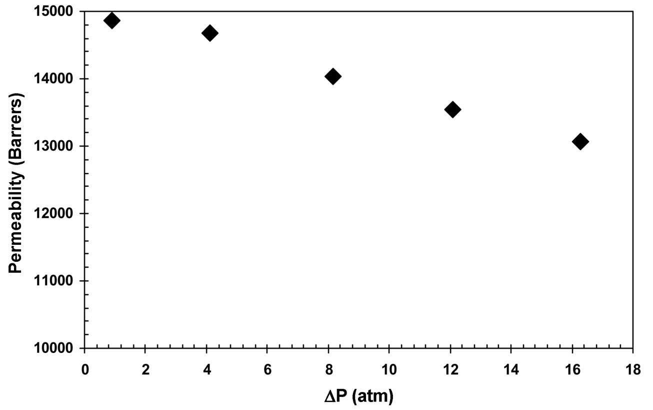

Fig. 4. Pure gas hydrogen permeability in PTMSP @ 35 °C (Merkel, Bondar, Nagai, and Freeman's data).

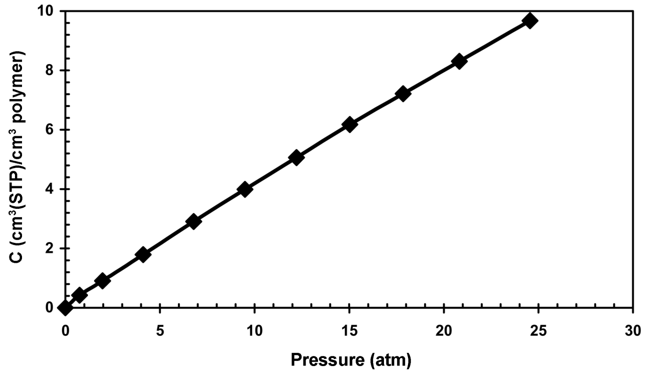

Fig. 5. Pure gas hydrogen sorption in PTMSP @ 35 °C (Merkel, Bondar, Nagai, and Freeman's data).

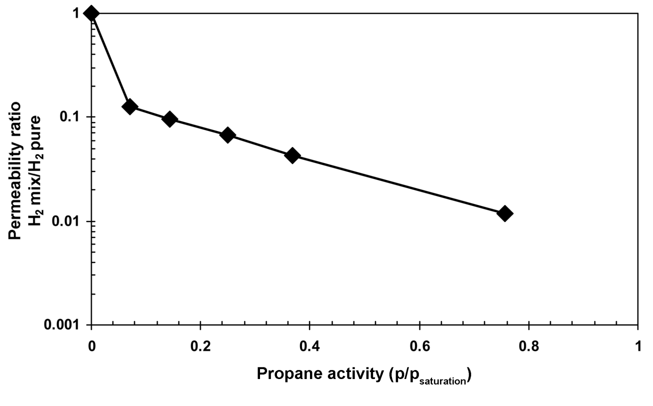

Fig. 6. Hydrogen-blocking ratio in the mixture with propane in PTMSP @ 24 °C (Pinnau, Casillas, Morisato, and Freeman's data).

The permeability coefficient for hydrogen in PTMSP membrane upon exposure to a mixture of hydrogen and propane was determined at 24 °C by using the constant pressure/variable volume method from Pinnau et al. [1996]. The hydrogen-blocking ratio, which is defined as the ratio of mixed gas hydrogen permeability to the pure gas hydrogen permeability, is illustrated in Fig. 6 as a function of propane activity. For the pure gas hydrogen, the permeability coefficients were measured at 35 °C. However, in this study it was assumed that the hydrogen permeation properties are not sensitive to temperature in the range of 24 °C to 35 °C. Therefore, the pure gas data for hydrogen at 35 °C were assumed to be good estimates

Table 2. Solubility, diffusivity, and permeability coefficients of organophosphorus chemicals in PDMS at 25 °C (Almquist and Hwang's data)*

Chemical name	Solubility (cm^3 (STP)/cm^3 polymer)			Diffusivity (10^9 cm^2/sec)			Permeability (10^9 cm^3 (STP) cm/cm^3 polymer cmHg)		
	S_1	S_2	S_2/S_1	D_1	D_2	D_2/D_1	P_1	P_1	P_2/P_1
Dimethyl methylphosphonate (DMMP)	81.5	106	1.3	441	675	1.5	35,900	71,400	2.0
Diethyl methylphosphonate (DEMP)	358	303	0.85	120	713	5.9	43,000	216,000	5.0
Dimethyl hydrogenphosphonate (DMHP)	40.3	41	1.0	780	1,528	2.0	31,400	62,700	2.0
Diethyl hydrogenphosphonate (DEHP)	182	199	1.1	265	1,014	3.8	48,200	202,000	4.2
Trimethylphosphate (TMP)	159	117	0.74	271	704	2.6	43,100	82,400	2.1
Triethylphosphate (TEP)	965	787	0.82	59	476	8.1	56,900	375,000	6.6
Trimethylphosphite (TMPhite)	27	45.5	1.7	346	2,754	8.0	9,340	125,000	13
Triethylphosphite (TEPhite)	152	794	5.2	194	1,270	6.5	29,500	579,000	20

*subscript 1: adsorption experiments; subscript 2: permeation experiments

Adsorption Data:

☐ Solubility is calculated from weight gain of membrane sample at equilibrium.

☐ Diffusivity is calculated by modeling the experimental data, varying diffusivity value.

☐ The value of D giving the best "least-squares" fit of the model to the experimental data is reported.

☐ Permeability is calculated by multiplying solubility and diffusivity.

Permeation Data:

☐ Solubility is calculated from steady-state permeability and time-lag diffusivity.

☐ Diffusivity is calculated by time-lag. Experimental data is extrapolated down to the time axis to obtain the time-lag value and the diffusivity is calculated by using that value of the time lag.

☐ Permeability is calculated from the steady-state permeation measurement.

of those at 24 °C.

The sorption of mixed gas hydrogen into PTMSP membrane was calculated by using an extension of the dual-mode model, which permits the description of sorption of binary, non-interacting penetrant mixtures as described by Koros [1980]:

$$c_A = k_{dA} p_A + C'_{HA} \frac{b_A p_A}{1 + b_A p_A + b_B p_B} \tag{8}$$

where p_A and p_B are the partial pressures of the two components, respectively, and the pure component affinity constants and Henry's law parameters are assumed to be unaffected by the presence of a second component. In actuality, however, the behavior of the hydrogen and propane mixture may not be correlated so simply with those of pure components due to the interactions between them.

2. Permeation Systems with PDMS Membrane: Organophosphorus Chemicals/PDMS

Poly(dimethylsiloxane) [PDMS], a nonporous silicon rubber, is the most permeable rubbery polymer. Due to its very flexible polymer backbone with long-range segmental motion that is active even at very low temperatures, PDMS has the lowest diffusivity-selectivity of all rubbery polymers. Unlike conventional glassy polymers used for permanent gas separations, PDMS is more permeable to many organic vapors than to simple gases due to their high solubilities, a property of silicon rubber that can be utilized in many applications.

The permeability, solubility, and diffusivity for each of eight organophosphorus chemicals in PDMS membrane were measured at their saturation concentration by two different experimental methods: 1) permeation experiments, and 2) absorption experiments, as reported by Almquist [1995] and Almquist and Hwang [1999]. The resulting data are presented in Table 2. All tests were carried out at 25 °C (±3 °C).

Absorption experiments were conducted using a quartz spring balance to measure the solubility of test chemicals in PDMS membrane. In the organophosphorus chemicals/PDMS system, the absorption isotherms for all the test chemicals, except TMPhite and TEPhite, were either linear or slightly convex to the partial pressure axis, with the Flory-Huggins parameters (χ values) being greater than ~1.6. The absorption isotherms for TMPhite and TEPhite were highly convex to the partial pressure axis with χ values of approximately 0.9 as reported by Almquist [1995].

The diffusion coefficients of eight organophosphorus chemicals in silicon rubber were calculated in two ways: 1) time-lag measurements, and 2) the kinetic sorption measurements. For the kinetic sorption measurements, the value of the diffusion coefficient was determined by a nonlinear least-squares fit of a Fickian model to the experimental data. In all cases, the diffusion coefficient obtained from the kinetic sorption data was significantly less than the diffusion coefficient calculated from the time lag.

THEORY

1. Background

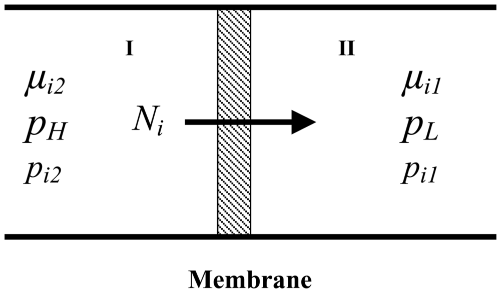

Fig. 7. Steady state membrane transport.

Membrane transport models have been derived from two independent general approaches: 1) theory based upon irreversible thermodynamics, and 2) theory based upon assumptions of transport mechanisms. Since the phenomena of mass transport across membranes are irreversible processes, the phenomenological theories of nonequilibrium thermodynamics were used to describe the membrane permeation process. We know from the theory of irreversible thermodynamics that the transport phenomena can be described by means of linear equations relating cause (driving force) with effect (flux) as described by De Groot [1952] and Katchalsky and Curran [1967]. In an irreversible process (and thus in membrane transport), free energy is dissipated continuously (if a constant driving force is maintained) due to the entropy production. Near the equilibrium, the flux of each flow bears a linear relationship not only to the conjugated driving force, but also to all the other forces to which the system is subjected.

2. Proposed Model

2-1. Entropy Production in the Discontinuous System

Consider an irreversible process that occurs in an experimental test system consisting of two large fluid reservoirs connected by a membrane as shown in Fig. 7. Each reservoir consists of a homogeneous mixture of n substances (non-electrolytes) that do not chemically react. The total system is closed so that no mass can be exchanged with the surroundings. The sub-systems I and II, or reservoirs, however, are open systems, and mass can be transferred from one sub-system (I) to the other (II), through the membrane only. Each reservoir is homogeneous. However, the thermodynamic properties between the two reservoirs change discontinuously across the membrane as shown by De Groot [1952], while they vary continuously within the membrane.

When conservation of mass and energy and the Gibbs equation are applied to reservoirs I and II, the expression for the internal production of entropy for the overall isothermal system is obtained as shown below:

$$T\left(\frac{d_iS}{dt}\right)=T\sigma=-\frac{d(\Delta G)}{dt}=-\sum_{i=1}^{n}N_i\Delta\mu_i \tag{9}$$

where T is the temperature of the system, d_iS/dt is the internal entropy production rate due to irreversibility that is expressed by σ, N_i is the permeation flux of species i, ΔG is total Gibbs free energy change, and $\Delta\mu_i$ is the chemical potential change of i between two reservoirs.

2-2. Conjugated Fluxes and Forces within the Membrane Phase

Taking the discontinuity of the system into consideration, we treat the changes in both entropy and chemical potential as changes of those variables outside the membrane. On the other hand, the changes within the membrane take place continuously perpendicular to the membrane surface (z direction). Instead of Eq. (9), therefore, the following differential equation can be used for a differential segment dz:

$$T\frac{d\sigma}{dz}=-\sum_{i=1}^{n}N_i\frac{d\mu_i}{dz} \tag{10}$$

In the above equation, the chemical potential change occurs within the membrane phase. For an isothermal system, the Gibbs-Duhem equation is expressed as:

$$\sum_{i=1}^{n}x_i d\mu_i=V_m dp \tag{11}$$

where V_m is the total molar volume of the mixture. The substitution of Eqs. (5) and (11) into Eq. (10), yields the following equation:

$$T\frac{d\sigma}{dz}=-\sum_{i=1}^{n}J_i^*\frac{d\mu_i}{dz}-NV_m\frac{dp}{dz}=-\sum_{i=1}^{n}J_i^*\frac{d\mu_i}{dz}-q\frac{dp}{dz} \tag{12}$$

where q is the total volumetric flow rate within the membrane phase. It is reasonable to assume that q stays constant within the membrane phase from one end to the other at steady state. The chemical potential change of component i can be replaced with the fugacity change that can be replaced by activity or mole fraction as shown below:

$$d\mu_i=RTd\ln f_i=RTd\ln(f_i^o\gamma_i x_i) \tag{13}$$

With the substitution of Eq. (13) into Eq. (12), the rate of lost work can be written as:

$$T\frac{d\sigma}{dz}=-q\frac{dp}{dz}-\sum_{i=1}^{n}J_i^*RT\frac{d\ln(\gamma_i x_i)}{dz} \tag{14}$$

From the above equation, it is clear that the entropy production term is written as the sum of the products of the fluxes q and J_i^*, and forces dp/dz and $RTd\ln(\gamma_i x_i)/dz$.

According to the theory of irreversible thermodynamics, there exists a linear relationship between fluxes and forces, and each flux is proportional to all the driving forces in the system. Within the membrane phase these linear relations can be written as:

$$\left\{\begin{array}{l} q=L_{00}\frac{dp}{dz}+\sum_{i=1}^{n}L_{0i}RT\frac{d\ln(\gamma_i x_i)}{dz} \\ J_1^*=L_{10}\frac{dp}{dz}+\sum_{i=1}^{n}L_{1i}RT\frac{d\ln(\gamma_i x_i)}{dz} \\ \vdots \\ J_j^*=L_{j0}\frac{dp}{dz}+\sum_{i=1}^{n}L_{ii}RT\frac{d\ln(\gamma_i x_i)}{dz} \end{array}\right. \tag{15}$$

where L_{ii} is a generalized phenomenological coefficient. The above equations can be combined with Eq. (5) to obtain the expression for species mass flux with respect to a stationary observer, which is measurable in the laboratory.

2-3. Conjugated Fluxes and Force for a Single Component Permeation System (Binary System)

When a single component permeates through a membrane, the system can be viewed as a binary system, where the membrane is considered as the second species. This is a very peculiar case, since the membrane does not move with respect to the observer, which yields $N_2=0$. Furthermore, $J_1^*+J_2^*=0$ for a binary system when Eq. (5) is summed up for all species, and thus the diffusion flux for the second component (membrane) is not needed. The second term in Eq. (14) becomes:

$$J_1^*RT\frac{d\ln(\gamma_1 x_1)}{dz}+J_2^*RT\frac{d\ln(\gamma_2 x_2)}{dz}=J_1^*RT\frac{d\ln(\gamma_1 x_1/\gamma_2 x_2)}{dz} \tag{16}$$

Substitution of Eq. (16) into Eq. (14) yields:

$$T\frac{d\sigma}{dz}=-q\frac{dp}{dz}-J_1^*RT\frac{d\ln(\gamma_1 x_1/\gamma_2 x_2)}{dz} \tag{17}$$

Therefore the linear expressions for fluxes may be written as:

$$\begin{aligned} q&=-L_{00}\frac{dp}{dz}-L_{01}RT\frac{d\ln(\gamma_1 x_1/\gamma_2 x_2)}{dz} \\ J_1^*&=-L_{10}\frac{dp}{dz}-L_{11}RT\frac{d\ln(\gamma_1 x_1/\gamma_2 x_2)}{dz} \end{aligned} \tag{18}$$

When Eqs. (18) and (5) are combined, the flux expression for the permeating species is obtained. However, a simplified equation may be more practical after several assumptions are introduced as shown below. The first assumption is that the coupling terms are negligibly small compared with the principal conjugated terms. The second assumption involves the second term in the diffusion equation. Among the four variables inside the parentheses, only the mole fraction of the diffusing species will significantly change as a function of position within the membrane phase. Therefore Eq. (18) can be reduced to:

$$\begin{cases} q\approx-L_{00}\dfrac{dp}{dz} \\ J_1^*\approx-L_{11}RT\dfrac{d\ln x_1}{dz}=-D_1\dfrac{dc_1}{dz} \end{cases} \tag{19}$$

Thus, for the penetrant component 1, the last expression in Eq. (5) may be used for the total flux through the membrane. It is clear that the total permeation flux is the sum of the diffusional flux, $-D_i(dc_i/dz)$, and the convective (bulk) flux, c_1q, which is proportional to the pressure gradient in the membrane.

For the permeation of a binary mixture through membrane (ternary systems including membrane phase), similar expressions of the permeation flux for each of the components can be obtained.

2-4. General Model for the Simulation of the Permeability Coefficient

For most glassy polymer membranes such as PTMSP, the sorption is well described by the dual mode sorption model. With the assumption that sorption equilibrium exists between the membrane surface and the adjacent fluid both in the upstream and downstream, the Nernst-Planck equation, Eq. (5), is integrated by using the following boundary conditions:

$$\begin{cases} z=0; & c_{z=0}=k_d p_H+C'_H\dfrac{bp_H}{1+bp_H} \\ z=1; & c_{z=l}=k_d p_L+C'_H\dfrac{bp_L}{1+bp_L} \end{cases} \tag{20}$$

where membrane thickness is λ and p_H and p_L are upstream and downstream pressure, respectively. Since the downstream pressure is always controlled near 0 atm for the permeation measurement, that is, $p_L\approx0$, the following equation is obtained:

$$N=\frac{q\left(k_d p_H+C'_H\dfrac{bp_H}{1+bp_H}\right)}{1-\exp\left(-\dfrac{q\lambda}{D}\right)} \tag{21}$$

For most rubbery membranes such as PDMS, the sorption is well described by Henry's law for low concentrations of gases and vapors. With the assumption that sorption equilibrium exists between the membrane surface and the adjacent fluid both in the upstream and downstream, the Nernst-Planck equation is integrated by using the following boundary conditions:

$$\begin{cases} z=0 & c_{z=0}=S\times p_H \\ z=\lambda & c_{z=l}=S\times p_L \end{cases} \tag{22}$$

When the downstream pressure is negligible, the following equation is obtained:

$$N=\frac{q\cdot S\cdot p_H}{1-\exp\left(-\dfrac{q\lambda}{D}\right)} \tag{23}$$

When the permeation flux of penetrants reaches a steady state, the following equations are derived by using Eq. (19), $q=-L_{00}(dp/dz)$:

$$\int_0^l q\,dz=-\int_{p_H}^{p_L}L_{00}\,dp \tag{24a}$$

$$q=\overline{L}_{00}\frac{\Delta p}{\Delta z}=\overline{L}_{00}\frac{p_H-p_L}{\lambda} \tag{24b}$$

where $\overline{L}_{00}$ is averaged through the membrane and can be defined as:

$$\overline{L}_{00}=\frac{\int_{p_H}^{p_L}L_{00}\,dp}{q_H-p_L} \tag{24c}$$

$\overline{L}_{00}$ can be viewed as the reciprocal of the resistance of the membrane to the convective transport of the penetrants.

For glassy polymer membranes, the following expression is obtained by substituting Eqs. (4) and (24b) into Eq. (21):

$$P=\frac{\overline{L}_{00}\left(k_d p_H+C'_H\dfrac{bp_H}{1+bp_H}\right)}{1-\exp\left(-\dfrac{\overline{L}_{00}p_H}{D}\right)} \tag{25}$$

The corresponding expression for rubbery membranes is obtained by substituting Eqs. (4) and (22) into Eq. (23):

$$P=\frac{\overline{L}_{00}\cdot S\cdot p_H}{1-\exp\left(-\dfrac{\overline{L}_{00}p_H}{D}\right)} \tag{26}$$

2-5. Assumptions and Interpretations of $\overline{L}_{00}$

The physical meaning of the parameter $1/\overline{L}_{00}$ is the mass transfer resistance to convective flow as seen in Eq. (19). For the permeation systems with PTMSP membrane, the parameter, $1/\overline{L}_{00}$, is assumed to have an exponential relationship with the upstream sorption of the penetrants, c_H:

$$\frac{1}{\overline{L}_{00}} = a\cdot\exp(b\cdot c_H) \qquad (a>0,\ b>0) \qquad (27)$$

where a and b are constants with positive values that are characteristic of the resistance of the membrane to the convective (bulk) motion of the penetrants. Constant represents the intrinsic resistance of the convective flow when there is no sorption. Thus, for the same membrane material, the value of a should not change with different penetrants. However, constant b represents an intrinsic property of the penetrants. Therefore, the value of b will change with different penetrants in the membrane.

The kinetic diffusion coefficients of propane and n-butane in PTMSP decrease with increasing penetrant concentration in the polymer as shown by Anuraag [1997]. Similar results are obtained by Merkel et al. [2000] for both the average diffusion coefficient and the effective diffusion coefficient of pure gas hydrogen in PTMSP. Usually, diffusion coefficients can be viewed as the product of a mobility term and a thermodynamic term. The mobility term, which is directly related to the resistance to the motion that a penetrant encounters while diffusing through a polymer matrix, monotonically decreases with increasing concentration for the permeation systems with PTMSP membrane as demonstrated by Anuraag [1997] and Merkel et al. [2000]. This suggests that the net free volume of the polymer-penetrant mixture decreases as additional penetrant is added to PTMSP, resulting in antiplasticization or penetrant clustering in polymer as accounted by Dixon-Garrett et al. [2000].

For the permeation systems with PTMSP membrane, the possibility of swelling effects due to the sorption of the penetrants inside the membrane was considered. An attempt was made to correlate the membrane resistance with the following equation:

$$\frac{1}{\overline{L}_{00}} = \frac{a\cdot\exp(b\cdot c_H)}{a'+b'p_H} \qquad (a>0,\ b>0,\ a'>0,\ b'>0) \qquad (28)$$

The parameters on the right-hand side of Eq. (28) are all positive values that characterize the resistance of the membrane to the convective (bulk) motion of the penetrants, and the denominator accounts for the possible swelling effects. Fitting the model in Eq. (28) to the experimental data by using a least-squares method, we found the value of b' to be negligibly small compared with the other parameters. Thus, ignoring the swelling effects from the penetrants sorption should not introduce significant error in the systems that were considered in this study. Since the solubility coefficients and the permeability coefficients of the organophosphorus chemicals in PDMS were measured at only one concentration, a relationship between the membrane resistance $1/\overline{L}_{00}$ and the upstream sorption c_H for the eight organophosphorus chemicals could not be derived.

RESULTS AND DISCUSSION

1. Simulation of the Permeability Coefficients for the Pure Components Propane and n-Butane/PTMSP System

For the pure components propane and n-butane/PTMSP system, the parameter $\overline{L}_{00}$ was calculated by using Eq. (25). When $1/\overline{L}_{00}$ is plotted as a function of the amount of upstream sorption c_H for both propane and n-butane, and the data are correlated with Eq. (27), two sets of parameters with the same a value and different b values were obtained, which are presented in Table 3. When Eq. (27) was substituted into Eq. (25), the permeability coefficients of propane and n-butane, respectively, were theoretically calculated as a func-

Table 3. a and b coefficients for the membrane resistance of different permeation systems with PTMSP membrane

Permeation systems	a cmHg*sec/cm^2	b cm^3(polymer)/cm^3(STP)
Propane/PTMSP	1,662,340	0.0791
n-Butane/PTMSP	1,662,340	0.0476
Hydrogen/PTMSP	1,662,340	0.328266
Mixed gas hydrogen/PTMSP	399,386	0.0588425

Table 4. Simulation results for propane in PTMSP at 35 °C (Anuraag and Freeman's data)

Δp (cmHg)	P (Exp.) (Barrers)	c_H (cm^3 (STP)/cm^3 polymer)	$D\times10^7$ (cm^2/sec)	$\overline{L}_{00}\times10^7$ (cm^2/cmHg sec)	P (Cal.) (Barrers)	P (Cal.)/P (Exp.)	$c_H\cdot q\times10^3$ (Cal.) (cm^3/cm^2 sec)
5.05	27,900	7.48	2.40	3.66	24,929	0.89	1.23
5.95	30,580	8.61	2.36	3.60	26,224	0.86	1.53
9.85	26,976	12.94	2.18	2.01	27,971	1.04	2.70
14.70	22,067	17.35	2.00	1.24	26,458	1.20	3.81
19.85	20,497	21.18	1.84	0.93	23,858	1.16	4.64
25.45	17,618	24.62	1.70	0.74	21,125	1.20	5.27
29.35	17,603	26.68	1.62	0.69	19,448	1.10	5.60
35.25	14,206	29.40	1.51	0.43	17,281	1.22	5.97
39.65	16,614	31.18	1.44	0.52	15,921	0.96	6.19
44.05	11,889	32.79	1.37	0.35	14,742	1.24	6.37
49.35	13,191	34.54	1.30	0.38	13,521	1.02	6.54
55.55	11,161	36.38	1.22	0.31	12,314	1.10	6.71
60.05	11,615	37.60	1.17	0.33	11,559	1.00	6.81
69.45	10,712	39.88	1.08	0.26	10,234	0.96	6.97
73.55	9,483	40.79	1.04	0.24	9,742	1.03	7.02

Table 5. Simulation results for n-butane in PTMSP at 35 °C (Anuraag and Freeman's data)

Δp (cmHg)	P (Exp.) (Barrers)	c_H (cm^3 (STP)/cm^3 polymer)	D×10^7 (cm^2/sec)	$\overline{L}_{00}\times10^7$ (cm^2/cmHg sec)	P (Cal.) (Barrers)	P (Cal.)/ P (Exp.)	$c_H\cdot q\times10^3$ (Cal.) (cm^3/cm^2 sec)
4.85	57,525	22.85	1.46	2.51	46,379	0.81	2.20
6.95	47,790	27.51	1.40	1.68	44,692	0.94	3.04
9.42	47,464	31.54	1.35	1.43	42,281	0.89	3.90
19.35	30,897	41.39	1.22	0.79	34,715	1.12	6.59
25.15	25,422	45.26	1.17	0.58	31,580	1.24	7.79
29.35	23,764	47.68	1.13	0.48	29,641	1.25	8.53
39.25	21,324	52.74	1.07	0.39	25,774	1.21	9.92
44.85	22,031	55.34	1.03	0.38	23,894	1.08	10.51
49.75	18,693	57.53	1.00	0.34	22,385	1.20	10.92
60.15	19,326	61.96	0.95	0.31	19,522	1.01	11.51
63.55	18,292	63.37	0.93	0.29	18,671	1.02	11.63
69.25	20,890	65.69	0.90	0.32	17,328	0.83	11.76
69.35	19,157	65.73	0.90	0.32	17,306	0.90	11.77

tion of upstream pressure. The results are shown in Tables 4 and 5. There are good agreements between the experimental data and the simulated results. The convective (bulk) fluxes for propane and n-butane were calculated by using $c_H\cdot q$. The results show that the convective flux increases with increasing upstream pressure and levels off while under high upstream pressure. This is consistent with the assumptions made about $1/\overline{L}_{00}$, the resistance of the membrane to the penetrants with convective motion. Since the sorption of the penetrants inside the membrane increases as the upstream pressure increases, this leads to an exponential increase in membrane resistance with upstream pressure. The driving force for the convective flux also increases with increasing upstream pressure. However, it is the combined effect of the driving force and the membrane resistance that determines the magnitude of the convective flux, and at high upstream pressure, the increase of the membrane resistance dominates over the increase of the driving force. These results also demonstrate that the convective (bulk) flux plays a very important role at high upstream pressure and cannot be ignored in open-structured materials such as PTMSP.

2. Simulation of the Permeability Coefficients for the Pure Gas Hydrogen/PTMSP System

For the pure gas hydrogen/PTMSP system, the parameter $\overline{L}_{00}$ was calculated by using Eq. (25). Since the sorption of pure gas hydrogen in PTMSP is very small compared to the sorption of hydrocarbons, the effects of the downstream pressure, which was kept at 1 atm, were ignored. In the range of pressure gradients between upstream and downstream with the hydrogen/PTMSP system, the calculated diffusion coefficients were relatively constant as described by Merkel et al. [2000]. In the present work, the average diffusion coefficient was used such that the calculated $1/\overline{L}_{00}$ had the same exponential relationship with the upstream sorption, c_H, as shown in Eq. (27). Since in Eq. (27) the parameter a is an intrinsic property of the membrane material, the value of a should be the same as that of the pure components propane and n-butane/PTMSP system. For different diffusion coefficients, we attempted to get different a values by plotting $1/\overline{L}_{00}$ versus c_H and least-square fitting. We finally got the average diffusion coefficient for the hydrogen/PTMSP system by interpolating the a values; we then used this average diffusion coefficient to calculate $\overline{L}_{00}$. A value of b was obtained by plotting $1/\overline{L}_{00}$ as a function of c_H and forcing into Eq. (27). The results are presented in Table 3. When Eq. (27) was substituted into Eq. (25), the permeability coefficients of pure gas hydrogen were theoretically calculated as a function of pressure difference across the membrane. The results are shown in Table 6. There is good agreement between the experimental and simulated data. The convective (bulk) flux for pure gas hydrogen was also calculated by using $c_H\cdot q$. The results show a tendency similar to that for pure components propane and n-butane/PTMSP system.

3. Simulation of the Permeability Coefficients for the Hydrogen in the Mixture with Propane/PTMSP System

For hydrogen in a mixture with propane/PTMSP system, the blocking ratio of hydrogen, which is defined as the ratio of the mixed gas hydrogen permeability to the pure gas hydrogen permeability, was calculated with the following equation:

Table 6. Simulation results for pure gas hydrogen in PTMSP at 35 °C (Merkel, Bondar, Nagai and Freeman's data)

Δp (cmHg)	P (Exp.) (Barrers)	c_H (cm^3 (STP)/cm^3 polymer)	$\overline{L}_{00}\times10^7$ (cm^2/cmHg sec)	P (Cal.) (Barrers)	P (Cal.)/ P (Exp.)	$c_H\cdot q\times10^3$ (Cal.) (cm^3/cm^2 sec)
69.30	14,872	0.92	4.78	14,706	0.99	8.32
312.36	14,675	2.18	2.93	14,686	1.00	58.90
620.06	14,039	3.78	1.57	14,429	1.03	119.90
919.52	13,547	5.34	0.99	13,697	1.01	150.58
1238.57	13,064	7.00	0.66	12,852	0.98	154.22

$$\frac{P_{1(mix)}\frac{\Delta p_{1(mix)}}{\lambda}}{P_1\frac{\Delta p_1}{\lambda}}=\frac{-D_{1(mix)}\frac{dc_{1(mix)}}{dz}+L_{00(mix)}c_{1(mix)}\frac{dp_{total}}{dz}}{-D_1\frac{dc_1}{dz}+L_{00}c_1\frac{dp_1}{dz}} \tag{29}$$

Eq. (19) was used to express the observed permeation flux of hydrogen through PTMSP for both binary and ternary systems. When calculating the parameter $L_{00(mix)}$, we made several assumptions: 1) Since propane condenses more readily than hydrogen, and due to the blocking effect of propane, the diffusional term of mixed gas hydrogen was assumed to be negligible; 2) for the pure gas hydrogen, the diffusion coefficient was assumed to be insensitive to temperature in the range of 24 °C to 35 °C, and therefore the average diffusion coefficient for pure hydrogen in PTMSP calculated at 35 °C was used for the analysis of the hydrogen and propane mixture data conducted at 24 °C; and 3) the effect of the downstream pressure on the experimental measurement is negligible, and so the variables c_1 and $c_{1(mix)}$ could be substituted with the upstream sorption, and the pressure difference across the membrane was approximated as the upstream pressure.

The following equation was obtained when Eq. (29) was integrated across the membrane and simplified:

$$\frac{P_{1(mix)}}{P_1}=\frac{\bar{L}_{00(mix)}c_{1H(mix)}p_{Htotal}}{D_1c_{1H}+\bar{L}_{00}c_{1H}p_{1H}} \tag{30}$$

$\bar{L}_{00(mix)}$ was solved using Eq. (30), and the results are presented in Table 7. When $1/\bar{L}_{00(mix)}$ was plotted as a function of the total upstream sorption of the mixture, $c_{H(total)}$, and a least-squares analysis was used to fit the data into Eq. (27), the values of a and b were obtained, which are presented in Table 3. The results show that the a value is different from that for the pure penetrant/PTMSP systems. Since the ternary system is more complicated than the binary system, thereby necessitating many assumptions to calculate $1/\bar{L}_{00(mix)}$, it is not an unexpected result that the consistency of the a value is lost between the binary and ternary systems for the same membrane material. However, the results show the same exponential relationship between the membrane resistance and the total upstream sorption, and there is good agreement between the experimental data of the blocking ratio of hydrogen and the simulated results. The convective (bulk) flux for mixed gas hydrogen was also calculated by using $c_H \cdot q$. The results show that the convective flux initially increases with increasing propane activity and then decreases at very high propane activity. This is consistent with the fact that the membrane resistance to the convective motion of mixed gas hydrogen tends to increase with the total upstream sorption of the mixture, and the blocking effect of propane becomes more significant as its activity increases.

4. Simulation of the Permeability Coefficients for the Organophosphorus Chemicals/PDMS System

For the organophosphorus chemicals/PDMS system, the parameter $\bar{L}_{00}$ was calculated by using Eq. (26). For these eight organophosphorus chemicals, the solubility coefficients and the permeability coefficients were measured at only one concentration. Therefore, the permeability coefficients and calculated diffusion coefficients were reported as effective, or average, values over the concentration range of chemical in the polymer. A relationship between the membrane resistance, $1/\bar{L}_{00}$, and the upstream sorption, c_H, could not be derived for the eight organophosphorus chemicals. A plot of $1/\bar{L}_{00}$ as a function of the boiling points of the eight organophosphorus chemicals shows with only one exception (TMPhite), that the change in membrane resistance with boiling point is relatively small. Therefore, the average value of the membrane resistance was

Table 7. Simulation results for hydrogen in the mixture with propane in PTMSP at 24 °C (Pinnau, Casillas, Morisato and Freeman's data)

$p_{C_3H_8}$ (cmHg)	$R^*_{H_2}$	c_{total} (cm^3 (STP)/cm^3 polymer)	$\bar{L}_{00(mix)}\times10^7$ (cm^2/cmHg sec)	R_{H_2} (Cal.)	R_{H_2} (Cal.)/R_{H_2}	$c_H\cdot q\times10^3$ (Cal.) (cm^3/cm^2 sec)
46.208	0.127480	27.42	4.29	0.148316	1.16	3.23
92.72	0.095150	41.05	2.25	0.094550	0.99	4.56
161.12	0.067436	53.50	1.27	0.057054	0.85	5.26
237.88	0.042587	63.43	0.68	0.037369	0.88	5.42
489.44	0.011732	87.31	0.13	0.013669	1.17	4.26

*Hydrogen blocking ratio.

Table 8. Simulation results for organophosphorus chemicals in PDMS at 25 °C (Almquist and Hwang's data)

Chemical name	Boiling point (°C)	λ (cm)	p_H (cmHg)	P (Exp.) (Barrers)	S (cm^3/cm^3)	D×10^9 (cm^2/sec)	$\bar{L}_{00}\times10^9$ (cm^2/cmHg sec)	P (Cal.) (Barrers)	P (Cal.)/ P (Exp.)	$c_H\cdot q\times10^3$ (Cal.) (cm^3/cm^2 sec)
DMMP	182	0.033	0.100	714,000	81.5	441	6,948.22	1,076,808	1.51	3.07
DEMP	194	0.038	0.039	2,160,000	358.0	120	15,365.66	1,765,564	0.82	1.78
DMHP	171	0.025	0.140	627,000	40.3	780	8,838.74	785,346	1.25	3.92
DEHP	189	0.031	0.065	2,020,000	182.0	265	16,797.94	1,542,853	0.76	3.08
TMP	197	0.023	0.033	824,000	159.0	271	12,110.25	835,983	1.01	0.94
TEP	215	0.036	0.012	3,750,000	965.0	59	32,338.29	1,563,481	0.42	0.48
TMPhite	111	0.056	2.100	1,250,000	27.0	346	2,204.58	7,043,478	5.63	264.13
TEPhite	156	0.057	0.260	5,790,000	152.0	194	14,650.88	4,909,317	0.85	22.39

numerically calculated from seven of the eight organophosphorus compounds. This average value was substituted into Eq. (26) to theoretically calculate the permeability coefficient for each of the eight organophosphorus chemicals. The results are shown in Table 8. There is good agreement between the experimental data and the simulated data. Two exceptions, however, are TEPhite and TMPhite, which have the highest and lowest boiling points, respectively, in this study. The convective (bulk) flux for each of the eight organophosphorus chemicals was calculated by using $c_H q$.

CONCLUSION

The contribution of convective (bulk) flux to the overall permeation flux in membrane permeation systems cannot always be ignored, especially when open-structured polymeric membranes are used. Based upon the theory of irreversible thermodynamics, a transport model is proposed that considers both the diffusion and convective (bulk) fluxes. This model was used to simulate the permeability coefficients for several permeation systems with PTMSP membrane, which is an extremely open-structured material with a high excess free volume (20 to 25%). Good correlation with the experimental data reveals that the permeability coefficient can be predicted by knowing the equilibrium sorption of the penetrants in the feed and permeate sides of membrane and the kinetic diffusion coefficient. From the Nernst-Planck equation, the convective flux was also calculated by using the proposed model. It is noted that for binary systems with PTMSP membrane, the convective flux increases with increasing upstream pressure or pressure difference across the membrane, but levels off at very high pressures. For the mixed gas hydrogen/PTMSP system, the convective flux first increases and then decreases at a very high upstream pressure. This is consistent with the assumptions made regarding the exponential relationship between the membrane resistance and the upstream equilibrium sorption, and the obvious blocking effect of the more condensable hydrocarbon at very high activity. For the organophosphorus chemicals/PDMS system, good correlations show that the proposed model also can be applied to permeation systems with nonporous rubbery membranes.

It is recommended that the current proposed model be applied to other open-structured membrane materials, such as poly(1-trimethylgermyl-1-propyne) [PTMGeP] as detailed by Langsam and Savoca [1988] and poly(4-methyl-2-pentyne) [PMP] as discussed by Morisato and Pinnau [1996], since they exhibit high permeability coefficients toward gases and vapors. They also possess large fractional free volume. However, further experimental work is needed to measure the kinetic diffusion coefficients of penetrants in these materials in order to predict permeability coefficients.

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NOMENCLATURE

a, b : parameters defined in Eq. (27)
b_A, b_B : Langmuir affinities of components A and B [1/cmHg]
c : equilibrium concentration [cm^3 (STP)/cm^3 polymer]
C'_{HA} : Langmuir capacity parameter of component A [cm^3 (STP)/cm^3]
D : diffusion coefficient [cm^2/sec]
G : Gibbs free energy [kJ]
J^* : diffusional flux [mol/cm^2sec]
k_{dA} : Henry's law parameter of component A [cm^3 (STP)/cm^3 cmHg]
L_{ij} : generalized phenomenological coefficient
$\bar{L}_{00}$: average coefficient defined in Eq. (24c) [cmHg sec/cm^2]
λ : membrane thickness [cm]
N : molar flux [mol/cm^2 sec]
P : permeability coefficient [Barrer]
p : pressure [cmHg]
q : total volume flux [cm^3/cm^2sec]
S : solubility coefficient [cm^3 (STP)/cm^3 polymer cmHg]
T : temperature [K]
t : time [sec]
V_m : molar volume [cm^3/mol]
v : velocity with respect to stationary coordinate axis [cm/sec]
v^* : local molar average velocity [cm/sec]
x : mole fraction
z : direction perpendicular to the membrane surface [cm]
α_R : fraction of the total mass uptake due to protracted non-Fickian drift
γ : activity coefficient
μ : chemical potential [kJ/mol]
σ : rate of entropy production due to irreversibility [J/sec K]
τ : first order relaxation constant [sec]

Superscript

— : over-bar refers to the average value

Subscripts

H : feed side of membrane
i : species i
L : permeate side of membrane
mix : mixture
t : time
∞ : equilibrium attained at infinite time

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