Pressure Dependence of Gas Permeability in a Rubbery Polymer

YASUTOSHI NAITO,* YOSHINORI KAMIYA, KATSUHIKO TERADA, KEISHIN MIZOGUCHI, and JIN-SHENG WANG

National Institute of Materials and Chemical Research, Tsukuba Ibaraki 305, Japan

SYNOPSIS

The effect of pressure on gas permeability of a rubbery polymer, 1,2-polybutadiene, is investigated for 15 gases with various molecular sizes and solubilities in the ranges of pressure up to 110 atm at 25°C. The permeability for slightly soluble gases (He, Ne, H_2, N_2, O_2, and Ar) decreases with increasing pressure, and that for soluble gases (CH_4, Kr, CO_2, N_2O, C_2H_4, Xe, C_2H_6, C_3H_6, and C_3H_8) increases with increasing pressure. Logarithms of permeability coefficient versus feed-gas pressure for the slightly soluble gases, CH_4 and Kr, is linear within each pressure range, whereas such plots become convex toward the pressure axis for more soluble gases, such as CO_2, N_2O, C_2H_4, Xe, C_2H_6, C_3H_6, and C_3H_8. By analyzing the pressure dependence of permeability using sorption data of the gases, contributions of concentration and hydrostatic pressure to the gas diffusivity are estimated.

INTRODUCTION

The effect of pressure on permeability for gases in rubbery polymers has been studied to better understand mechanisms of permeation and to develop membranes for gas separation.[1-8] In most of the studies, the pressure dependence of permeability coefficient is analyzed based on the relation

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

where $\bar{P}$ is the mean permeability coefficient, $\bar{D}$ is the mean diffusion coefficient which is defined by $\int_{C_1}^{C_2} DdC / \int_{C_1}^{C_2} dC$, and $\bar{S}$ is the mean solubility coefficient defined as the ratio of surface concentration difference of the membrane to the pressure difference across it. Using this relation and experimental results of gas permeation under high pressures, Stern and co-workers have concluded that the pressure dependence of permeability and hence diffusivity consist of two components: one related to the hydrostatic pressure and the other to the concentration of the penetrant.[4,5] Such analysis based on eq. (1), however, should be replaced with an exact method in which the concentration dependence of diffusion instead of the mean diffusion coefficient is taken into account, if solubilities of penetrant gases in the membrane are known as a function of pressure.

In this study we consider a fundamental equation of gas permeation with concentration-dependent diffusivity and investigate the permeation of some gases, in wide ranges of pressure, through a rubbery polymer whose gas solubilities have already been known. By the use of a new equation derived in our work, contributions of hydrostatic pressure and concentration to the pressure dependence of diffusivity are separately estimated from the effect of feed-gas pressure on the permeability. On the basis of the results, the mechanism of gas diffusion in the rubbery polymer is discussed.

THEORETICAL CONSIDERATIONS

Consider the permeation of gas penetrant through a planar membrane and under steady-state conditions. Such conditions can be achieved by maintaining the concentrations of the penetrant at the

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* To whom correspondence should be addressed.

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two surfaces of the membrane at different but constant values. The flux of permeation is constant and it can be written, for a solution–diffusion process, as

$$J = -D\left(\frac{\partial C}{\partial x}\right) = \text{constant} \qquad (2)$$

where D represents the diffusion coefficient and C is the concentration of the gas in the membrane at a position coordinate x. We assume that the concentration dependence of diffusion coefficient is given by[6]

$$D = D_0 \exp(\beta_h p + \alpha C) \qquad (3)$$

where D_0 is the diffusion coefficient at $C = 0$ and $p = 0$, and β_h and α are constants relating to hydrostatic pressure and concentration dependence, respectively.

The mean permeability coefficient is given as

$$\bar{P} \equiv \frac{JL}{\Delta p} \qquad (4)$$

where L is the thickness of membrane and Δp ($= p_2 - p_1$) is the pressure difference across the membrane. Substituting eq. (3) into eq. (2) and integrating over the membrane along the direction of thickness with constant flux, one can have[3,9]

$$\bar{P} = \frac{D_0 \exp(\beta_h p_2)}{\alpha \Delta p}\left[\exp(\alpha C_2) - \exp(\alpha C_1)\right] \qquad (5)$$

where C_2 and C_1 are the surface concentrations in equilibrium with the upstream pressure p_2 and the downstream pressure p_1. Hydrostatic pressure exerted on the membrane is equal to the upstream pressure p_2 in the permeation experiment, where the downstream side of the membrane is supported by an inflexible porous metal plate.

Sorption of highly soluble gases in rubbery polymers usually follows the Flory–Huggins dissolution. According to a simplification of the Flory–Huggins equation,[10] the concentration is expressed as

$$C = [k_D \exp(\sigma C)]p \cong \frac{k_D p}{1 - \sigma k_D p} \qquad (6)$$

where k_D is the Henry's law coefficient and σ [$= 2(1 + \chi)\bar{V}_R/22410$] is a constant relating to interaction parameter χ, the partial molar volume of dissolved gas is $\bar{V}_R$, and 22,410 is a conversion factor. Units used here are $\text{cm}^3(\text{STP})/\text{cm}^3(\text{polymer})$ for C and cm^3/mol for $\bar{V}_R$.

Under the conditions of $p_2 \gg p_1 \cong 0$ (i.e., $C_2 \gg C_1 \cong 0$), where gas permeation experiments are usually performed, we obtain from eqs. (5) and (6) the mean permeability coefficient as a function of the upstream pressure[9,11]:

$$\bar{P} = \frac{D_0 \exp(\beta_h p_2)}{\alpha p_2}\left[\exp\left(\frac{\alpha k_D p_2}{1 - \sigma k_D p_2}\right) - 1\right] \qquad (7)$$

This equation instead of eq. (1) should be used for analyzing the pressure dependence of gas permeability, when values of the dissolution parameters k_D and σ are known.

When the feed-gas pressure is restricted to the range satisfying

$$p_2 \ll \left|\frac{2}{4\sigma k_D - \alpha k_D}\right| \qquad (8)$$

which is a condition necessary for $d \ln \bar{P}/dp_2 =$ constant, we have the following equation:

$$\bar{P} = D_0 k_D \exp\left[\beta_h p_2 + \left(\sigma + \frac{\alpha}{2}\right)k_D p_2\right] \qquad (9)$$

This is the same equation as derived for slightly soluble gases previously.[6,7] By analyzing permeation data within the low-pressure range in terms of eq. (9), we will estimate the contributions of hydrostatic pressure and penetrant-induced plasticization to the pressure dependence of permeability for all the gases investigated.

EXPERIMENTAL

The syndiotactic 1,2-polybutadiene used is the same as that investigated previously.[11-13] A 300-μm film provided kindly by Japan Synthetic Rubber Co. was employed in gas permeation experiments.

Fifteen gases (He, Ne, H_2, N_2, O_2, Ar, CH_4, Kr, CO_2, N_2O, C_2H_4, Xe, C_2H_6, C_3H_6, and C_3H_8) were tested. Molecular diameters of the gases[14] are listed together with their partial molar volumes occupied in polybutadiene and dissolution parameters[12,13] in Table I. All the gases of research grade (99.0% pure at least), obtained from Takachiho Chemical Industry and Japan Oxygen Co., were used without further purification.

Permeabilities of gases were determined at 25°C by a method based on manometric determination of

Table I Molecular Diameter, Partial Molar Volume, and Dissolution Parameters

Gases	Molecular Diameter, d	Partial Molar Volume, $\bar{V}_R$	$k_D \times 10^2$	$\sigma \times 10^3$
He	2.576	23	1.14	—
Ne	2.858	32	1.66	—
H_2	2.915	40	2.70	—
Ar	3.465	40	9.90	—
O_2	3.541	47	7.73	—
Kr	3.61	44.0	33.4	—
N_2	3.749	45	4.00	—
CH_4	3.796	44	22.6	1.4[a]
N_2O	3.816	44.6	132	4.4
CO_2	3.897	43.8	81	4.1
Xe	4.055	53.0	143	5.3[b]
C_2H_4	4.232	52.0	118	3.1
C_2H_6	4.418	57.0	182	3.6
C_3H_6	4.670	71.8	509	8.0
C_3H_8	5.061	79.8	497	9.8

Units: d, A; $\bar{V}_r$, cm^3/mol; k_D, cm^3 (STP)/cm^3 (polymer) atm; σ, cm^3 (polymer)/cm^3 (STP).

[a] Value estimated from a linear relationship between σ and $\bar{V}_R$ for hydrocarbons (carbon number n = 2–5), whose data are reported in ref. 13.

[b] Value calculated using Eq. (9) from data of $(d \ln \bar{P}/dp_2)_{p_2 \approx 0}$ and values of α and β_h given in Table IV.

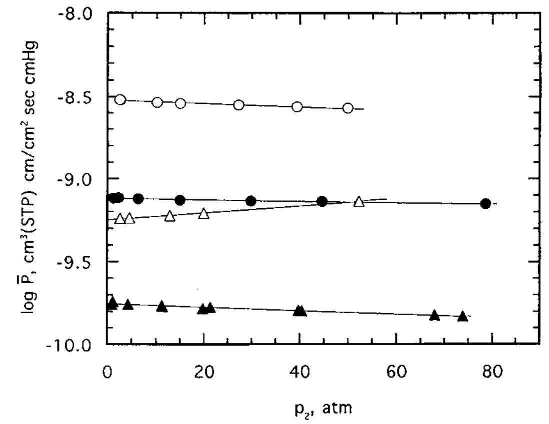

Figure 1 Pressure dependence of permeability for H_2 (○), CH_4 (△), O_2 (●), and N_2 (▲).

the pressure of permeated gas.[6,7] Feed-gas pressures up to 110 atm were employed, and the pressure of permeated gas on the low-pressure side of the apparatus was always kept within 1% at least of the feed-gas pressure during experiments.

RESULTS AND DISCUSSION

The permeation rates of gases through the polybutadiene film at steady state were measured as a function of the feed-gas pressure, and permeability coefficients at various pressures were calculated according to eq. (4). All data are shown as a plot of logarithm of $\bar{P}$ versus p_2 in Figures 1–3. As can be seen in the figures, the plots for slightly soluble gases are linear, whereas those for highly soluble gases are convex toward the pressure axis.

Within the low-pressure range limited by eq. (8), the plots of log $\bar{P}$ versus p_2 for all the gases exhibit good linearity. The linear portions should follow eq. (9) according to the aforementioned theoretical considerations. Slopes of the linear portion $\beta_h + (\sigma + \alpha/2)k_D$ and the pre-exponential factor P_0 $(=D_0k_D/76)$ of eq. (9) are obtained for each gas, as presented in Table II. The table shows that the slopes for all gases except He increase with increasing gas solubility (i.e., the Henry's law coefficient k_D). This tendency has been known and interpreted as a result of competition between contributions of hydrostatic pressure and concentration to the pressure dependence of permeability.[2,4-7] However, it seems necessary to estimate more quantitatively the two contributions in order to correlate them to molecular properties of gases.

To divide the pressure dependence of permeability into the two effects, relatively low-solubility gases are classified into four groups—(He), (Ne, H_2), (Ar, O_2, Kr), and (N_2, CH_4, N_2O, CO_2)—with similar molecular diameters but different solubilities. According to the method proposed in the previous articles,[6,7] the hydrostatic pressure parameter β_h and the concentration parameter $(\sigma + \alpha/2)$ for each group except (He) were determined from the linear relation between $(d \ln \bar{P}/dp_2)_{p_2 \approx 0}$ and k_D, which are shown in Figures 4 and 5. Results are presented in Table III.

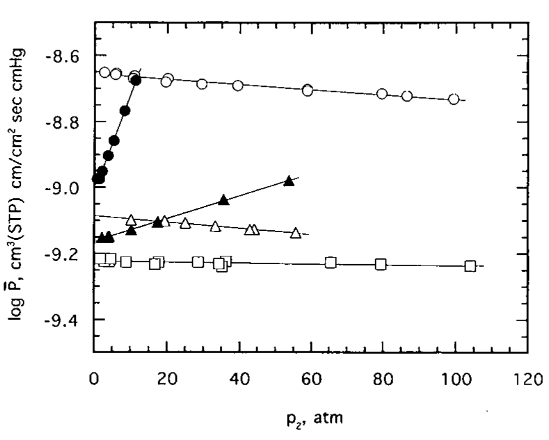

Figure 2 Pressure dependence of permeability for He (○), Ne (△), Ar (□), Kr (▲), and Xe (●).

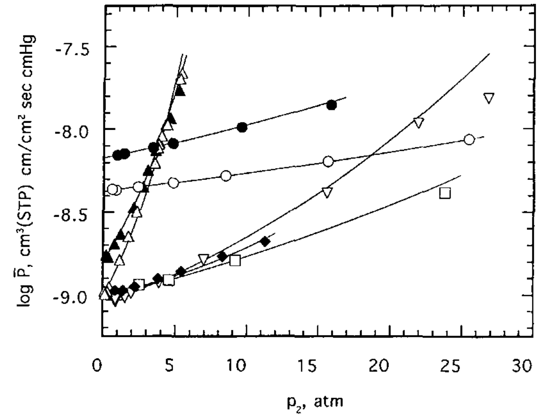

Figure 3 Pressure dependence of permeability for CO_2 (○), N_2O (●), Xe (◆), C_2H_4 (□), C_2H_6 (▽), C_3H_6 (▲), and C_3H_8 (△).

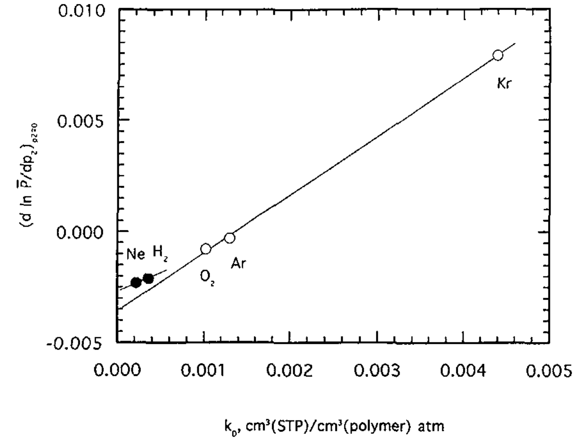

Figure 4 Pressure-dependence parameter near $p_2 = 0$ plotted as a function of Henry's law coefficient for two groups of gases, (H_2, Ne) and (O_2, Ar, Kr).

As can be seen in the table, there are no clear differences in values of the parameters between the two groups (Ar, O_2, Kr) and (N_2, CH_4, N_2O, CO_2). This is different from the cases of low-density polyethylene (LDPE) and polypropylene (PP),[6] though the parameters determined for the polybutadiene are in the same order of magnitude as those for the two polymers.

This method, however, cannot be applied for highly soluble gases, such as Xe, C_2H_4, C_2H_6, C_3H_6, and C_3H_8, because their molecular sizes are too different to be classified into groups having similar diameters. Therefore, assuming the β_h value of these highly soluble gases to be about -4×10^{-3} atm^{-1} from the results of the slightly soluble gases, we estimated values of $(\sigma + \alpha/2)$ for these gases and then calculated values of α using σ values previously obtained from the sorption isotherms.[12,13] The results are presented in Table IV, in which α values of N_2O, CO_2, and CH_4 are also shown. In the calculation of α for CH_4, a value of σ estimated from a linear relation between σ and partial molar volume $\bar{V}_R$ for a series of hydrocarbons (carbon number n = 2–5)[13] was used (Table I). It is thought that though the β_h value used for the highly soluble gases may contain a large error, the estimated values of α are fairly confident, because the hydrostatic pressure effect is very small compared to the concentration effect.

Table II Pressure Dependence of Permeability in the Vicinity of p_2 = 0, and Permeability and Diffusivity Coefficients Extrapolated to p_2 = 0

Gases	$(d \ln \bar{P}/dp_2)_{p_2\approx 0} \times 10^3$	P_0 (= $D_0k_D/76$) $\times 10^9$	$D_0 \times 10^7$
He	−1.7	2.2	145
Ne	−2.3	0.83	38
H_2	−2.1	3.0	85
Ar	−0.29	0.62	4.8
O_2	−0.77	0.76	7.5
Kr	7.9	0.69	1.6
N_2	−2.1	0.19	3.7
CH_4	5.1	0.56	1.9
N_2O	41	6.7	3.9
CO_2	24	4.3	4.0
Xe	68	0.97	0.52
C_2H_4	50	0.97	0.62
C_2H_6	74	0.87	0.36
C_3H_6	280	1.6	0.24
C_3H_8	326	0.98	0.15

Units: P_0(= $D_0k_D/76$), cm^3 (STP) cm/cm^2 s cmHg; D_0, cm^2/s.

Using values of equilibrium and kinetic parameters presented in Tables I–IV, we predicted the

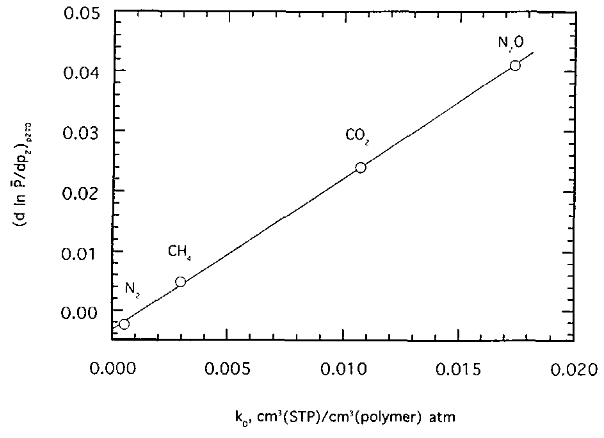

Figure 5 Pressure-dependence parameter near $p_2 = 0$ plotted as a function of Henry's law coefficient for a group of gases (N_2, CH_4, CO_2, N_2O).

Table III **Mean Molecular Diameter, Mean Partial Molar Volume, Hydrostatic Pressure Parameter, and Concentration Parameters Relating to Dissolution and Diffusion**

Groups of Gases	Mean Value of d	Mean Value of $\bar{V}_R$	$-\beta_h \times 10^3$	$(\sigma + \alpha/2) \times 10^2$
Ne, H_2	2.89 ± 0.04	36	2.6	1.9
Ar, O_2, Kr	3.54 ± 0.07	44	3.5	3.4
N_2, CH_4, N_2O, CO_2	3.82 ± 0.06	44	3.3	3.4

Units: β_h, 1/atm; $\sigma + \alpha/2$, cm^3 (polymer)/cm^3 (STP).

pressure-dependent permeability for each gas in terms of eq. (7) or eq. (9). The results are shown as solid lines in Figures 1, 2, and 3. As can be seen in the figures, there is good agreement between calculated values and experimental data.

Now we look quantitatively at the hydrostatic pressure parameters and the concentration parameters estimated here. As mentioned earlier, the hydrostatic pressure and the concentration parameters given in Table III are not clearly dependent on mean molecular size, in contrast to those previously obtained for the same groups of gases in LDPE and PP, though their orders of magnitude are the same. As can be seen in Table IV, however, values of the concentration parameter for hydrocarbons, N_2O, and CO_2, are apparently dependent on their molecular size. Plotting α against partial molar volume gives a straight line, as shown in Figure 6, in which data for C_4 hydrocarbons are ones obtained from kinetic study of the sorption.[11] By interpolating this linear relation, we estimated the α value of Xe as 7.9×10^{-2} cm^3 (polymer)/cm^3(STP) (Table IV), and then its σ value given in Table I was obtained from data of $d \ln \bar{P}/dp_2$ using the α value and $\beta_h = -4 \times 10^{-3}$ atm^{-1}.

Table IV **Concentration and Hydrostatic Pressure Parameters**

Gases	$\alpha \times 10^2$	$-\beta_h \times 10^3$
CH_4	7.2	3.3
C_2H_4	8.6	4^a
C_2H_6	8.1	4^a
C_3H_6	10.9	4^a
C_3H_8	12.9	4^a
N_2O	5.8	3.3
CO_2	5.7	3.3
Xe	7.9^b	4^a

Unit: α, cm^3 (polymer)/cm^3 (STP).

[a] Assumed value used for estimating α values of highly soluble gases.

[b] Value estimated from a linear relationship between α and $\bar{V}_R$ for organic and inorganic gases (Fig. 6).

The linear increase of α with partial molar volume indicates that the plasticization effect of penetrant gas on the diffusivity depends on volume change (sorptive dilation) of polymer (i.e., the product of partial molar volume and concentration). This view is consistent with the result of an isothermal glass transition study that the plasticizing ability of penetrant, which is given as the proportionality constant between temperature and concentration at glass transition point, is in proportion to its partial molar volume.[15]

CONCLUSION

Permeabilities of fifteen gases in 1,2-polybutadiene were measured as a function of feed-gas pressure at 25°C. The data were analyzed using sorption isotherms of the gases, and contributions of hydrostatic pressure and concentration to the pressure dependence of diffusivity for each gas were separately estimated. It is not clear whether the hydrostatic pressure parameter is dependent on molecular size of the gases, but apparently the concentration parameter increases linearly with the molecular size, such as molar volume of the dissolved molecule. This

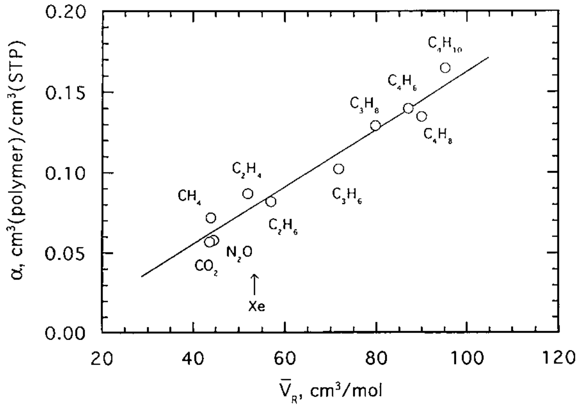

Figure 6 Concentration parameter of diffusion plotted as a function of partial molar volume.

means that the plasticizing effect of penetrant gas on its diffusivity can be described by the volume change of polymer due to dissolution of the penetrant.

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