Gas Permeation through Glassy Polymer Membranes with High Glass Transition Temperature

Hidehiro Kumazawa and Tatsumi Yamamoto
Department of Chemical Process Engineering, Toyama University, Toyama 930-8555, Japan
and
Seong-Youl Bae
Department of Chemical Engineering, Hanyang University, Ansan, Kyonggi-do 425-791, Korea

The sorption equilibria and permeation rates for carbon dioxide in such glassy polymer membranes with high glass-transition temperature as polyimide, polyetherimide, polysulfone and polyethersulfone membranes, were measured. The sorption isotherms for these systems can be described well in terms of the dual-mode sorption model, whereas the pressure dependences of the mean permeability coefficients are simulated better by a modified dual-mode mobility model than the conventional dual-mode mobility model in which the Henry’s law and Langmuir populations execute four kinds of diffusive movements.

Keywords: Gas permeability, Gas sorption equilibrium, Glassy polymer, Polyimide, Polysulfone, Polyethersulfone, Polyetherimide, Dual-mode sorption model, Dual-mode mobility model

1. Introduction

The sorption of gases and vapors in glassy polymers is generally more complex than in rubbery polymers. The sorption equilibria of gases in glassy polymers have been measured for many gas - glassy polymer systems, and have been described well in terms of a so-called dual-mode sorption model. In the dual-mode sorption model, sorbed molecules are retained in the polymer in two distinct ways, i.e., via Henry’s law dissolution and Langmuir-type adsorption. Currently, it is no exaggeration to say that this dual-mode concept at sorption equilibrium has been well established. Two sorbed populations, which are termed Henry’s law and Langmuir populations, respectively, can execute diffusive movements with different mobilities, while being at local equilibrium with each other. This parallel approach called dual-mode mobility model, has not been tested in many gas - glassy polymer systems, as opposed to the dual-mode sorption model, and the applicability of this model has not been confirmed yet. Besides, the two kinds of population should principally undergo movements with the two respective modes, but possibly execute jumps between the two modes. Basically, four kinds of diffusion step are possible. The transport model based on such a concept is called modified dual-mode mobility model. However, the applicability of this modified
model has never been examined satisfactorily. By considering such a present situation, existing data on sorption equilibria and permeation rates for carbon dioxide in such glassy polymer membranes with high glass-transition temperature as polyimide (PI) [1], polysulfone (PSF) [2], polyethersulfone (PES) [3] and polyetherimide (PEI) [4] membranes, were reexamined to discuss the mechanism of diffusion of a gas in glassy polymer membranes. In conjunction with the measured sorption equilibria, a gas diffusion mechanism was discussed by comparing it with the model; conventional and modified dual-mode mobility model.

2. Theoretical Background

The sorption of a gas in glassy polymers has been found to be described well by a so-called dual-mode sorption model [5]:

\[ C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + bp} \] (1)

This formula suggests that two different modes of sorbed molecules, i.e., Henry’s law dissolution mode (D) and Langmuir adsorption mode (H) should hypothetically exist.

By assuming that the two sorbed populations can execute diffusive movements with different mobilities while being at local equilibrium with each other, a dual-mode mobility model by gradients of concentration was proposed as follows [6]:

\[ J_x = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \] (2)

On the basis of this dual-mode model, the mean permeability coefficient, defined by

\[ \bar{P} = \frac{J_D}{\rho_D (p_2 - p_1)} \] (3)

is given as

\[ \bar{P} = k_D D_D + \frac{C'_H b D_H}{(1 + bp_2)(1 + bp_2)} \] (4)

The above dual-mode mobility model, however, does not incorporate possible diffusive movements from Henry’s law mode to Langmuir mode (D → H) and the reverse (H → D). Considering these two movements [7], the total diffusion flux should include four modes of diffusion, i.e., D → D, D → H, H → D and H → H, and the following modified dual-mode mobility model expression for the mean permeability coefficient, can be derived [8]:

\[ \bar{P} = k_D D_D + \frac{2k_p D_{DH}}{b(p_2 - p_1)} \ln \frac{1 + bp_2}{1 + bp_1} + \frac{C'_H b (D_{HH} + D_{DH}) - k_D D_{DH}}{(1 + bp_2)(1 + bp_2)} \] (5)

When the diffusive movement from Henry’s law mode to Langmuir mode is neglected, that is, \( D_{DH} \) is taken to be zero, Eq.(5) reduces to

\[ \bar{P} = k_D D_D + \frac{C'_H b (D_{HH} + D_{DH})}{(1 + bp_2)(1 + bp_2)} \] (6)

This agrees with Eq.(3), if \((D_{HH} + D_{DH})\) is set equal to \( D_H \).

3. Discussion

3.1 Sorption equilibria

Homogeneous dense membranes of polyimide (PI, Upilex R, \( T_g = 285 \) °C, Ube Industries, Japan), polysulfone (PSF, Trayslon-PS, \( T_g = 190 \) °C, Toray, Japan), polyethersulfone (PES, TALPA 1000, \( T_g = 225 \) °C, Mitsui Chemicals, Japan) and polyetherimide (PEI, FS-1400, \( T_g = 216 \) °C, Sumitomo Bakelite, Japan) were examined as the glassy polymer membrane with high
Typical examples of measured sorption isotherms are shown in Figure 1, which represents the sorption isotherms for CO$_2$ and C$_2$H$_4$ in PSF membranes [2]. Each isotherm exhibits a similar downward concave pattern, characteristic of glassy polymers. The sorption behavior can be simulated by the dual-mode sorption model, via Eq. (1). The values of the dual-mode sorption parameters in Eq. (1) were estimated by using the Marquardt method [9], and for CO$_2$ they are listed in Table 1. The solid curves in Figure 1 represent the sorption isotherms calculated using Eq. (1) with these estimates. Sorption isotherms for CO$_2$, O$_2$ and N$_2$ in PES and PEI membranes [3, 4] and for CO$_2$ in PI membrane [1] at various temperatures also exhibit similar non-linear patterns simulated well by the dual-mode sorption model. In Table 1, the values of the dual-mode sorption parameters for CO$_2$ in PI, PES and PEI membranes [1, 3, 4] are also listed.

### 3.2 Permeabilities

The experimental results of mean permeability coefficients for CO$_2$, O$_2$ and N$_2$ in PEI membranes [4] and for CO$_2$ in PI membranes [1] are shown as a function of upstream gas pressure in Figures 2 and 3, respectively. The mean permeability coefficients to CO$_2$ at glass-transition temperature (Tg) to discuss the mechanism of diffusion of a gas in glassy polymer membranes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp. ['C]</th>
<th>$k_0$ [m/(STP$/\text{m}^2$/MPa)]</th>
<th>$b$ [MPa$^{-1}$]</th>
<th>$c_2$ [m/(STP$/\text{h}$)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSF</td>
<td>30</td>
<td>6.38</td>
<td>1.92</td>
<td>20.5</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>5.87</td>
<td>1.75</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>5.40</td>
<td>1.66</td>
<td>18.4</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>5.01</td>
<td>1.53</td>
<td>17.1</td>
</tr>
<tr>
<td>PEI</td>
<td>25</td>
<td>6.89</td>
<td>4.16</td>
<td>18.3</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5.92</td>
<td>3.42</td>
<td>17.9</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>4.73</td>
<td>2.58</td>
<td>15.0</td>
</tr>
<tr>
<td>PES</td>
<td>30</td>
<td>7.91</td>
<td>5.13</td>
<td>17.2</td>
</tr>
<tr>
<td>PI</td>
<td>30</td>
<td>12.2</td>
<td>16.8</td>
<td>7.39</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10.3</td>
<td>12.1</td>
<td>5.67</td>
</tr>
<tr>
<td></td>
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</tr>
<tr>
<td></td>
<td>60</td>
<td>6.83</td>
<td>6.27</td>
<td>3.34</td>
</tr>
</tbody>
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Fig. 1 Sorption isotherms for CO$_2$ and CH$_4$ in PSF membrane at different temperatures.

Fig. 2 Mean permeability coefficients for CO$_2$, O$_2$ and N$_2$ in PEI membrane at 25°C (filled symbols), 30°C(open symbols) and 40°C(half-filled symbols) as functions of upstream pressure.
each temperature exhibited pressure dependence, characteristic of glassy polymer membranes, whereas those to O₂ and N₂ were almost independent of gas pressure. The permeability coefficients for CO₂ and CH₄ in PSF [2] and for CO₂ in PES [3] exhibited also similar pressure dependence. Then, it was checked whether the dual-mode mobility model is applicable or not to the observed pressure dependences of the mean permeability coefficients to CO₂.

The mean permeability coefficient data for CO₂ in PEI membrane at 25, 30 and 40°C [4] were plotted on the basis of Eq. (4) in Figure 4. The plots do not conform to Eq. (4), i.e., conventional dual-mode mobility model depicted by broken lines. The solid curves represent the calculated relations using Eq.(5) with the estimates of $D_{oa}$, $D_{oh}$ and $(D_{oa} + D_{oh})$ listed in Table 2. Figure 5 shows the pressure dependence of the mean permeability coefficients of the same system at 35°C, which was calculated from the permeability data measured by Barbari [10]. The solid curve also represents the corresponding relation-

### Table 2: Diffusion parameters for CO₂ in different membranes via a modified dual-mode mobility model

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temp.</th>
<th>$D_{oa} \times 10^{13}$</th>
<th>$D_{oh} \times 10^{13}$</th>
<th>$(D_{oa} + D_{oh}) \times 10^{13}$</th>
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<tr>
<td>PEI</td>
<td>25</td>
<td>4.4</td>
<td>4.1</td>
<td>0.78</td>
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<td>5.0</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>10.2</td>
<td>7.6</td>
<td>0.83</td>
</tr>
<tr>
<td>PEI [10]</td>
<td>35</td>
<td>10.5</td>
<td>2.2</td>
<td>0.56</td>
</tr>
<tr>
<td>PI</td>
<td>30</td>
<td>0.518</td>
<td>0.645</td>
<td>0.275</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.896</td>
<td>0.672</td>
<td>0.355</td>
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</tr>
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<td></td>
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<td>2.69</td>
<td>0.740</td>
<td>1.60</td>
</tr>
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<td>4.53</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>51.2</td>
<td>29.1</td>
<td>5.55</td>
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<td></td>
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<td>62.8</td>
<td>30.4</td>
<td>7.25</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>75.1</td>
<td>33.9</td>
<td>8.85</td>
</tr>
<tr>
<td>PES</td>
<td>30</td>
<td>11.5</td>
<td>9.94</td>
<td>4.96</td>
</tr>
</tbody>
</table>

![Fig. 3](image1)

**Fig. 3** Mean permeability coefficients for CO₂ in PEI membrane as a function of upstream pressure at different temperatures.

![Fig. 4](image2)

**Fig. 4** Test of dual-mode mobility model and comparison with a modified dual-mode mobility model for permeabilities of PEI to CO₂.

![Fig. 5](image3)

**Fig. 5** Test of dual-mode mobility model and comparison with a modified dual-mode mobility model for permeabilities of PEI to CO₂ at 35°C, measured by Barbari [10].
ship calculated by Eq.(5) with the estimates listed in Table 2.

Similarly, the mean permeability data for CO\textsubscript{2} in PI [1] and PES [3] and for CO\textsubscript{2} and C\textsubscript{H}\textsubscript{4} in PSF [2] at different temperatures were plotted on the basis of Eq.(4). The plots are not also on the straight lines at all. The deviation from the straight line becomes especially large at higher applied gas pressure. Figure 6 demonstrates a typical example of these plots. Figure 7 illustrates the mean permeability coefficients for CO\textsubscript{2} in PSF membranes at 35°C plotted against the term $1/(1+b_{p1})$, which were taken from Erb and Paul [11]. The solid curves in Figures 6 and 7 represent the corresponding relations calculated by Eq.(5) with the estimates listed in Table 2.

From the comparison of the present permeability data with Eq.(5), the plausible values of diffusivities $D_{00}$, $D_{01}$ and $(D_{11}+D_{10})$ were evaluated, because $D_{11}$ cannot be distinguished from $D_{10}$ using Eq.(5). As depicted as the solid curves in Figure 4 through 7, at every temperature, they are found to be in reasonable agreement with experimental points over the whole range of applied gas pressures for the five systems. Of course, it should be kept in mind that the good data-theory fits based on Eq.(5) are at least partially due to the fact that Eq.(5) has one more parameter than the conventional dual-mode mobility model.

3.3 Deviation from the conventional dual-mode mobility model

When the temperature for permeation runs is much lower than the glass-transition temperature ($T_g$) of the polymer, that is, $T_e$ of the polymer is very high as compared to the experimental temperature, the pressure dependence of the mean permeability coefficient to CO\textsubscript{2} is apt to deviate from the prediction by the conventional dual-mode mobility model, and to be predicted by the modified dual-mode mobility model. This has been confirmed in the systems of CO\textsubscript{2} - PI ($T_e$=285°C), CO\textsubscript{2}, CH\textsubscript{4}-PSF ($T_e$=190°C), CO\textsubscript{2}-PES ($T_e$=225°C) and CO\textsubscript{2}-PEI ($T_e$=216°C) [1-4].

On the other hand, when the experimental temperature is not so much lower than $T_e$ of the polymer, also, the pressure dependence of the mean permeability coefficient tends to deviate from the prediction by the conventional dual-mode mobility model, and to obey a dual-mode mobility model with concentration-dependent diffusivities proposed by Zhou and Stern [12]. The pressure dependence of
diffusivities of Henry’s law and Langmuir populations can be regarded as the result of the plasticization action of sorbed CO₂ to the polymer.

Compared to the dual-mode sorption model wherein all of the sorption parameters are assumed to be constant irrespective of the amount of sorbed species, an extended dual-mode sorption model has independently been proposed by Kamiya et al. [13] that both Henry’s law and Langmuir capacity constants are affected by the concentration of sorbed species of the plasticization ability to the polymer. Afterwards, Mi et al. [14] derived a new relation to express the sorption isotherm of plasticizing penetrants, which has only one adjustable parameter:

$$C = S \times p \times 
\exp\left( A \left\{ \frac{T_e(C) - T_e(0)}{T_e(0)} \right\} \right)$$

(7)

where $T_e(0)$ and $T_e(C)$ refer to the glass transition temperatures of the polymer containing a dissolved penetrant at concentration 0 and C, respectively. Their sorption isotherm can simulate an inflection point at a high penetrant pressure as the extended dual-mode sorption model [13] does.

Thus far, the deviations from the conventional dual-mode sorption and mobility models have separately been studied theoretically and experimentally. However, simultaneous deviation from both models was observed in cases of CO₂ in poly-4-methyl-1-pentene membrane at 20°C [15] and in polystyrene membrane at 60°C and 70°C [16] and in cellulose triacetate membrane at 50°C and 60°C [17]. The plasticization effect of sorbed CO₂ on both the sorption and diffusion processes tends to be brought about in glassy polymer membranes near the glass transition temperature. Recently, this behavior was simulated based on the concept that only one population of sorbed gas molecules is present [18]. Actually, a sorption theory of Mi et al. [14] which tacitly has a premise that only one population of sorbed gas molecules exists, was combined with a gas-polymer-matrix model proposed by Raucher and Sefcik [19] based on the same premise:

$$D = D_0 \exp(\beta C)$$

(8)

According to such a combined model, the mean permeability coefficient can be derived as follows:

$$\bar{P} = \frac{D_0}{\beta(p_2-p_1)} \left( \exp(\beta C_2) - \exp(\beta C_1) \right)$$

(9)

It should be noted that only two parameters ($A$ and $\beta$) to be adjusted are contained, if Eq.(9) is combined with Eq.(7).

4. Conclusion

The sorption isotherm of gases in glassy polymers with high glass-transition temperature can be described well by the dual-mode sorption model. The pressure dependences of the mean permeability coefficients to CO₂ in glassy polymer membranes with high $T_e$ are simulated better by the modified dual-mode mobility model than the conventional dual-mode mobility model in which the Henry’s law and Langmuir populations execute four kinds of diffusive movements.

Nomenclature

A = parameter involved in Eq.(7), K⁻¹
b = Langmuir affinity constant, Pa⁻¹
C = total sorbed concentration, m³ (STP)/m²
C₀ = concentration of Henry’s law population, m³(STP)/m²
Cₜ = concentration of Langmuir population,
\[ \frac{m'}{m} = \text{Langmuir capacity constant,} \frac{\text{m'}(\text{STP})}{m} \]
\[ D = \text{diffusion coefficient in polymer membrane,} \frac{m'}{s} \]
\[ J = \text{permeation flux,} \frac{m'(\text{STP})}{(m's)} \]
\[ k_0 = \text{Henry's law constant,} \frac{m'(\text{STP})}{(m' Pa)} \]
\[ L = \text{thickness of membrane,} m \text{ or } \mu m \]
\[ \bar{P} = \text{mean permeability coefficient,} \frac{m'(\text{STP})m}{(m'sPa)} \]
\[ \rho = \text{pressure,} Pa \text{ or MPa} \]
\[ S_0 = \text{solubility coefficient at the limit of} p=0, \frac{m'(\text{STP})}{(m'Pa)} \]
\[ T_g = \text{glass transition temperature,} K \text{ or } ^\circ C \]
\[ x = \text{position coordinate in the net flux direction,} m \]
\[ \beta = \text{dissolved gas - polymer interaction parameter appearing in Eq. (8),} \frac{m'}{m'}(\text{STP}) \]

**Subscripts**
- \( D \) = Henry's law mode
- \( DD \) = within Henry's law mode
- \( DH \) = from Henry's law mode to Langmuir mode
- \( h \) = Langmuir mode
- \( HD \) = from Langmuir mode to Henry's law mode
- \( HH \) = within Langmuir mode
- \( s \) = steady-state
- \( 1 \) = downstream surface
- \( 2 \) = upstream surface

**Literature cited**