Assessment of thickness-dependent gas permeability of polymer membranes

M A Islam* & H Buschatz
GKSS Forschungszentrum Geesthacht GmbH, Institute of Chemistry, Kantstrasse 55, D-14513 Teltow, Germany

Received 28 February 2004; revised received 8 October 2004; accepted 10 November 2004

Morphological changes with thickness, and the subsequent effect on the membrane permeability have been discussed qualitatively. It is concluded that some morphological elements favor transport and some hinder. Flux models based on interface reaction have been successfully applied to describe quantitatively the thickness-dependence of the membrane-permeability and the model parameters (diffusion transport coefficient, surface reaction constants) evaluated.

Keywords: Membrane thickness, gas permeability, Fick’s law, diffusion equation, sorption-desorption rates.

IPC Code: B01D 71/00; G01N 15/00

Diffusional gas transport through polymer membranes is usually studied under different pressures and temperatures. Systematic studies on the thickness-dependence of the permeability are scarce and the conclusions are diverging. Some1,2 reported that the gas permeability is thickness-independent and some3-11 found it to be thickness-dependent. The thickness-dependence of the diffusion parameters was always attributed to the changes in the membrane morphology with the change of membrane thickness, and the experimental results were interpreted only qualitatively. Recently, two flux equations12,13 were proposed considering non-equilibrium reactions at the interface, which predicted the conditions for which the permeability would appear thickness-dependent. These two flux models give rise to the necessity of qualitative and quantitative re-evaluation of the available literature data on thickness-dependent membrane permeability. Thus, in the present paper: (i) the probable effect of the morphological changes (due to changes in thickness) on the membrane permeability has been discussed qualitatively, (ii) based on the two different flux equations derived in previous studies12,13, thickness-dependence of the membrane permeability has been discussed quantitatively, (iii) and finally the parameters of the models (diffusion transport coefficients and surface reaction constants) have been evaluated for two membranes reported by previous authors3,11. The analysis in the present paper would inspire the investigators to study thickness dependence of the membrane permeability and to determine surface reaction rate constants from sorption and permeability data.

Probable effect of morphological changes on permeability

Han et al.14 observed that with an increase in the thickness of the polyimide films, the degree of molecular in-plane orientation decreased and the concentration of microvoids increased. The authors assumed that the higher diffusion coefficient and water uptake in thicker film might have been resulted from both the microvoids (formed during film preparation) and the free volume (due to a decrease in chain order and in-plane orientation). However, Isoda et al.15 reported that the crystallinity of polyimide increased with an increase in the membrane thickness. The crystalline zones are impermeable to the penetrants16,17. Therefore, the crystallinity as a morphological factor would have negative impact on both diffusion and sorption properties. Thus, different elements of the membrane morphology affect the permeability differently, some favor transport and some hinder. Mensitieri et al.11 reported that the permeability of polyimide membranes increased with the increase in the membrane thickness. The authors assumed that the positive impact of the free volume was much higher than the negative impact of the crystallinity. Shishatskii et al.1 observed that the density of poly(vinyltrimethyl silane) and poly(trimethylsilyl...
norbornene) films varied inversely as the thickness, but the permeability was almost independent of the membrane thickness. In all the previous studies, only qualitative explanation was given for the thickness-dependent permeability.

**Thermodynamic justification of the diffusion equation**

Thermodynamic formulation of diffusion equation is as follows,

\[ J = -\kappa \frac{d\mu}{dx} \text{ with } \mu = \mu_0 + RT \ln C \]  \hspace{1cm} (1)

where \( J \) (mol.m\(^{-2}\).s\(^{-1}\)) is the flux through the membrane, \( \kappa \) (mol.m\(^{-4}\).s\(^{-1}\).Pa\(^{-1}\)) is the transport coefficient and \( \mu \) (J.mol\(^{-1}\)) is the chemical potential, \( \mu_0 \) (J.mol\(^{-1}\)) is the chemical potential at some reference state, \( R \) (J.mol\(^{-1}\).K\(^{-1}\)) is the universal gas constant, \( C \) (mol. m\(^{-3}\)) is the concentration and \( T \) is the absolute temperature (K) and \( x \) (m) is the position coordinate along the flow direction. In terms of the concentration \( C \) (mol.m\(^{-3}\)), Eq. (1) can be rewritten as

\[ J = -\kappa \frac{R T}{C} \frac{dC}{dx} \]  \hspace{1cm} (1a)

According to Fick’s law, however, the flux is proportional to the concentration gradient,

\[ J = -D \frac{dC}{dx} \]  \hspace{1cm} (2)

where \( D \) (m\(^2\).s\(^{-1}\)) is the diffusion coefficient. To validate the Fick’s law, the diffusion coefficient \( D \) should be related to the transport coefficient \( \kappa \) as follows [By Eq. (1a) and Eq. (2)],

\[ D = \frac{\kappa R T}{C} \]  \hspace{1cm} (2a)

In theoretical treatment of diffusion processes, usually it is assumed that that \( D \) is a constant. Barrie\(^{18}\) reviewed a number of cases, in which \( D \) increased or decreased with the change in concentrations. In the event that \( D \) is inversely proportional to concentration, Eq. (1) with \( \kappa \) =constant is the most appropriate equation to describe the flux. It should be mentioned here that neither Eq. (1) with \( \kappa \) = constant nor Eq. (2) with \( D \) = constant could be considered ideal. Islam\(^{19}\) reported that the form of the diffusion equation completely depends on how the resistance force is defined (practically the resistances are described empirically). In this work, the permeability versus thickness relation will be discussed based on Eq. (1) with \( \kappa \) =constant and Eq.(2) with \( D \) = constant.

**Permeability versus thickness relation predicted by Fick’s law (Eq. (2) with \( D \) = constant)**

The steady state flux is given by

\[ J = \frac{D(C_0 - C_L)}{L} \]  \hspace{1cm} (3)

where \( C_0 \) and \( C_L \) (mol.m\(^{-3}\)) are the gas concentration respectively on the feed and permeate side interfaces, and \( L \) (m) is the membrane thickness. In analyzing the diffusion transport, it is usually assumed that the interface concentrations and the pressure are in equilibrium\(^{20-22}\), and the flux is given by the following relation,

\[ J = \frac{D \gamma (P_0 - P_L)}{L} \]  \hspace{1cm} (4)

where \( \gamma \) is the Henry’s solubility constant, and \( P_0 \) and \( P_L \) (Pa) are the gas pressure respectively on the feed and permeate side. Accordingly, the permeability \( \xi \) is given by

\[ \xi = \frac{L J}{P_0 - P_L} = D \gamma = \text{constant} \]  \hspace{1cm} (5)

Eq. (5) shows that the permeability is constant, and is independent of thickness. For this reason, the experimentally observed thickness-dependence of the permeability is always attributed to the membrane morphology.

Recently, Islam et al.\(^{12,13}\) analyzed in details the role of adsorption and desorption rate in steady state flow and showed that the steady state flux at the interfaces is given as follows,

at \( x = 0 \):

\[ J = -k_1 P_0 - k_2 C_0 \]  \hspace{1cm} (6a)

at \( x = L \):

\[ J = -k_1 P_L + k_2 C_L \]  \hspace{1cm} (6b)

where \( k_1 \) (mol.m\(^{-2}\).s\(^{-1}\).Pa\(^{-1}\)) and \( k_2 \) (m.s\(^{-1}\)) are the sorption and desorption rate constants, respectively. The interface concentrations \( C_0 \) and \( C_L \) can be expressed from Eqs (6a-b) as follows,

\[ C_0 = \gamma P_0 - J / k_2 \quad \text{and} \quad C_L = \gamma P_L + J / k_2 \]

with \( \gamma = k_1 / k_2 \)  \hspace{1cm} (6c)
Combining Eqs (3 & 6c), for the permeability $\xi$,

$$\xi = \frac{J}{(P_0 - P_L)/L} = \frac{D_P}{1 + 2D/(k_L L)} = \frac{(k_1/2)L}{1 + (k_2/2D)L}$$

... (7)

Unlike Eq. (5), Eq. (7) shows that the permeability $\xi$ depends on the thickness $L$.

**Permeability versus thickness relation predicted by Eq.(1) with $\kappa=$constant**

Assuming that the pressure has negligible contribution to the diffusion flux, the steady state flux predicted by Eq.(1) is as follows,

$$J = \frac{\kappa RT}{L} \ln \frac{C_0}{C_L}$$

... (8)

Combining Eqs (6c,8), for $P_L \to 0$,

$$J = \frac{\kappa RT}{L} \ln \left[ \frac{k_1 P_0}{J} - 1 \right]$$

... (8a)

Considering that $C_0$ is much higher than $C_L$ (i.e. $k_1 P_0/J$ is much higher than 1, Eq.(8a) is simplified to Eq. (8b)

$$J \approx \frac{\kappa RT}{L} \ln \left[ \frac{k_1 P_0}{J} - 1 \right]$$

... (8b)

Then the permeability $\xi$ is described by Eq. (9)

$$\xi = \frac{LJ}{P_0} = \frac{\kappa RT}{P_0} \ln \left[ \frac{k_1 P_0}{J} \right]$$

... (9)

After a simple mathematical treatment, Eq. (9) is reduced to Eq. (10).

$$\xi \exp(\xi/a) = k_1 L \quad \text{with} \quad a = \frac{\kappa RT}{P_0} \quad \text{... (10)}$$

Eq. (10) also predicts that the permeability is thickness-dependent.

**Model validation**

Taylor et al.$^3$ studied the dependence of the permeability on membrane thickness for the transport of water vapour through vulcanized rubber. The investigators observed that when the feed side pressure was maintained at about 1.0×10³ Pa (with permeate side pressure $P_L \to 0$), the concentration distribution was almost linear and the permeability was independent of membrane thickness as predicted by Eq. (4) or (5). Such low pressure on the feed side seemed not satisfactory to draw a general conclusion. The authors$^3$ further reported that for a bit higher feed side pressure (ca. 3×10³ Pa), the steady state concentration profile was almost exponentially decreasing through the membrane, and the permeability increased with an increase in the membrane thickness. They concluded that the water vapour permeation through vulcanized rubber did not obey Fick’s diffusion law. The authors reached to such drastic conclusion, for in describing the diffusion transport, they applied Eq. (4), which was derived with the assumption that the interface concentration was always in equilibrium with the gaseous phase. The permeability versus thickness data have been reproduced from Taylor et al.$^3$ (Fig. 10 of the reference) and presented in Fig. 1 in the present work. The data are fitted to Eqs (7) and (10), which are derived with the assumption that the steady state interface concentration are not in equilibrium with the vapour pressure in the gaseous phase. The fitted values of the parameters are described in Table 1.

Table 1—Fitted values of the gas transport parameters (Eqs (7) & (10)) through some polymer membranes

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Parameters of Eq. (7)</th>
<th>Parameters of Eq. (10)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ mol.m².s⁻¹.Pa⁻¹</td>
<td>$k_2/(2D)$ m⁻¹</td>
</tr>
<tr>
<td>Rubber$^3$</td>
<td>2.67×10⁻⁸</td>
<td>1.29×10⁴</td>
</tr>
<tr>
<td>Dry Kapton®$^{11}$</td>
<td>5.38×10⁻¹²</td>
<td>7.08×10⁴</td>
</tr>
<tr>
<td>Wet Kapton®$^{11}$</td>
<td>2.73×10⁻¹²</td>
<td>4.55×10⁴</td>
</tr>
</tbody>
</table>

Mensitieri et al.$^{11}$ studied the transport of oxygen in dry and water saturated Kapton® polyimide films with different thicknesses. The authors observed a sharp increase of permeability as the thickness
increased in the range of 13-50 μm. For higher membrane thickness, the permeability increased at a slower rate. The change in the permeability was attributed to the different polymer morphologies such as crystallinity level, crystallinity orientation and excess free volume content, characterizing samples of different thicknesses. The permeability versus thickness data have been reproduced from Mensitieri et al. (Fig. 3 of the reference) and presented in Fig. 2 of the present work. The data are fitted to the Eqs (7) and (10). The curves are differentiated by a letter (D or W denoting dry or wet membrane) followed by a number (7 or 10 denoting the equations to which the data are fitted). The fitted values of the parameters are again described in Table 1. In this case, the permeability versus thickness relationship predicted by Eq. (7) describes the data better. Thus, both Figs 1 & 2 show that, the permeability versus thickness relationship could be described satisfactorily by Eq. (7) or (10). It appears that the permeability versus thickness data could be described quantitatively without taking into account the morphological effect, on condition that the appropriate flux equation has been chosen. However, it should not be forgotten that in developing the model, the hydrodynamic boundary layers in the fluid phases were neglected, and the diffusion flux equations (including Fick’s law) are always approximations. Therefore, satisfactory curve-fittings in the Figs 1 and 2 should not undermine the effect of morphological changes on the permeability.

The two-parameter model discussed in this paper would provide opportunity to evaluate the sorption and desorption rate constants from the permeability versus thickness data. The procedure is as follows: The Henry constant γ is determined from sorption experiments. The model parameters k_1 and k_2/2D are determined by fitting the permeability versus thickness data to Eq. (7). Then the surface constant k_3 could be evaluated from the relation k_3 = k_1/γ (Eq. 6c). Consequently, the value of the diffusion coefficient D could also be estimated. The consistency of the fitted value of the model parameters could not be verified, however, as the data on sorption-desorption rate constants k_1 and k_2 (determined by independent experiments) are not available in the literature. The present analysis would stimulate the investigators to consider sorption-desorption always a reversible process (as it is in reality) in studying the kinetics of ‘sorption’ processes.

**Conclusions**

Probable effect of morphological changes (due to changes in the film thickness) on the membrane permeability has been discussed qualitatively and it is concluded that different elements of the membrane morphology affect the permeability differently—some favour transport and some hinder. It is very difficult to predict what net effect the morphological changes could have on the permeability. Flux models based on interface reaction could be applied to describe quantitatively the thickness-dependence of the permeability. Based on the equilibrium sorption and the permeability data, the surface reaction rate constant could be evaluated. The present analysis would enable the
researchers to interpret the permeability versus thickness data quantitatively, rather than being satisfied with qualitative interpretation with morphological changes. The models would be more precise, if some correction for morphological effect is incorporated.

Acknowledgement
The authors express their deep gratitude to the Alexander von Humboldt Foundation for awarding Dr. Islam a Georg–Forster Fellowship for conducting research at the GKSS Research Center Geesthacht GmbH. M. A. Islam is highly indebted to Prof. D. Paul for ensuring pleasant research and scientific atmosphere at the Institute.

Nomenclature

\[ C = \text{gas concentration in polymer phase, mol gas/m}^3 \text{polymer} \]
\[ C_0 = \text{gas concentration at the feed side interface, mol.m}^{-3} \]
\[ C_L = \text{gas concentration at the permeate side interface, mol.m}^{-3} \]
\[ D = \text{diffusion coefficient, m}^2.s^{-1} \]
\[ J = \text{flux through the membrane, mol.m}^{-2}.s^{-1} \]
\[ k_1 = \text{gas sorption rate at the surface, mol.m}^{-2}.s^{-1}.Pa^{-1} \]
\[ k_2 = \text{gas desorption rate at the surface, m.s}^{-1} \]
\[ L = \text{membrane thickness, m} \]
\[ P_0 = \text{gas pressures at the feed side, Pa} \]
\[ P_L = \text{gas pressures at the permeate side, Pa} \]
\[ R = \text{universal gas constant, J. mol}^{-1}.K^{-1} \]
\[ T = \text{temperature, K} \]
\[ x = \text{position coordinate along the flow direction, m} \]

Greek Symbols

\[ \gamma = \text{Solubility of the gas in the membrane described by Henry's law, mol.m}^{-3}.Pa^{-1} \]
\[ \kappa = \text{Transport coefficient, mol}^2.m^{-4}.s^{-1}.Pa^{-1} \]
\[ \mu = \text{Chemical potential, J.mol}^{-1} \]
\[ \xi = \text{Gas permeability, mol.m}^{-1}.s^{-1}.Pa^{-1} \]

References