Chapter 2

Transport through polymer membranes

In this chapter I will give a short introduction in the process of transport through membranes, concentrating on the gas phase/rubbery polymer system. The transport from the gas phase through rubbery polymers can be described by the solution-diffusion model, which will be outlined in this chapter. Also a brief look at the experimental measurement of the permeability by means of the time-lag method and some interesting industrial applications are given.

2.1 The polymer matrix

Before looking at the mechanism of gas transport through membranes it is necessary to consider some features of the two principal microstructural conditions of polymeric material, the glassy and rubbery state.

It has been known for a long time that the mechanism of diffusion is very different in rubbery and glassy polymers. This is mainly due to the fact that glassy polymers are not in a true state of equilibrium. The difference in mechanism is reflected in the significant differences observed in the dependence of the diffusion coefficient, as well as the permeability and solubility coefficients, on the penetrant gas pressure or concentration in polymers and on the temperature [8]. For example, the diffusion coefficients for light gases in rubbery polymers are often independent of concentration. By contrast, in glassy polymers the diffusion coefficients are highly nonlinear functions of concentration and reach a constant value at sufficiently high concentration.

At temperatures below the glass transition temperature $T_g$ the polymer is in its glassy state and is hard and may be brittle, which is directly related to the restricted chain mobility. The intermolecular forces between the chains do not allow other movement
than vibrations. All structural properties as the distribution of cavities in the polymer have effectively become static quantities. Depending on the conditions during the formation of the glassy state (for example, the temperature gradient) the polymer is more or less trapped in a non-equilibrium state. In glassy polymers the penetrant diffusion is low but size selectivity is very good.

Above the glass transition temperature the polymer is in its rubbery state. In this state the polymers are generally tough and flexible, which is associated with freer chain motion. Rubbery polymers have very short relaxation times (compared to glassy polymers) and respond very rapidly to external stresses. Thus a change in temperature causes an “immediate” adjustment to the new equilibrium state. A similar immediate adjustment occurs when small penetrants are absorbed in a rubbery polymer. Larger segments of the polymer are thought to participate in the penetrant diffusion process due to internal chain motions such as chain rotations, translations and stronger vibrational motions. The penetrant diffusion is much faster than in a glassy polymer but size selectivity is lower.

In both the glassy and rubbery state the polymer properties can be further modified by the presence of crystalline phases, by stress induced orientations or as a function of cross-link density. They tend to place additional constraints on the mobility of the amorphous phase through which diffusion takes place. (It is partly because of these possible variations in polymer properties that there is such a wide range in experimental values of permeability coefficients)

Gas versus liquid permeation

Permeation through polymer membranes can occur from both the gas and the liquid phase. In gas permeation diffusion coefficients are independent of penetrant concentration in the membrane in contrast to vapor or liquid permeation. There the membrane may be highly swollen by a penetrating liquid. This opens up the structures with the result that the absolute flux rates through the membrane can be 2 or 3 orders of magnitude larger than for a (noncondensible) gas. Thus in vapor or liquid permeation the diffusion coefficients are strong (typically exponential) functions of concentration.

For vapor and liquid separation different theories have been used, for example: irreversible thermodynamics, preferential sorption-capillary flow theory or the solution-diffusion mechanism. But in permeation from the gas phase the picture is simpler and only the solution-diffusion mechanism is used.

As the process of permeation from vapor or liquid phases involves many extra difficulties I will limit myself to the permeation of small molecules from a gaseous phase. And even though polymers are used for various permeation processes in both their rubbery and glassy state, we shall concentrate on the permeation process in polymers in their rubbery state only. Thus in this thesis I shall express the transport properties in the cast
of the solution-diffusion picture.

## 2.2 Solution-diffusion mechanism

The first to use the term “solution-diffusion mechanism” was Graham [9] in 1866. He postulated that the penetrant leaves the external phase by dissolving in the membrane. It then undergoes molecular diffusion in the membrane, driven towards the downstream face by for example a concentration or pressure gradient, after which it evaporates again in the external phase. Thus the permeability coefficient $P$, defined by the ratio between the flux $J$ of the permeant species and its concentration gradient $\Delta c$ over the membrane of thickness $d$

$$J = P \frac{\Delta c}{d}$$

is given by the product of the diffusion coefficient $D$ and a solubility factor $S$

$$P = DS$$

A postulate of which the theoretical foundation will be shown next.

In the solution-diffusion model we consider an isothermal homogeneous stationary membrane in which particles at a position $r$ are dissolved with a local concentration $c(r)$. The particle flux $J$ is assumed to behave in the regime of a linear irreversible process with the gradient of the chemical potential as the driving force. The flux is given by

$$J(r) = c(r)v(r)$$

where $v(r)$ is the average velocity of the dissolved particles. In the linear regime $v(r)$ can be written as

$$v(r) = \frac{1}{c} F_{th}$$

$$= -\frac{1}{c} \nabla \mu(r)$$

where $F_{th}$ is the thermodynamic force, $\zeta$ a friction coefficient and $\mu$ the chemical potential of the dissolved particles. The latter can be written as

$$\mu(r) = \mu^0 + RT \ln c(r) + \mu_{ex}(r)$$
in which $\mu^0$ is the standard chemical potential of the ideal gas phase based on unit molar concentration, $c$ is the local concentration and $\mu_{\text{ex}}(\mathbf{r})$ is the excess chemical potential of the dissolved species with respect to the ideal gas state. Equations 2.3, 2.4 and 2.5 give

$$\mathbf{J}(\mathbf{r}) = \frac{-RT}{\zeta} \nabla c(\mathbf{r}) - \frac{c(\mathbf{r})}{\zeta} \nabla \mu_{\text{ex}}(\mathbf{r}).$$  \hspace{1cm} (2.6)$$

Equating $RT/\zeta$ with the diffusion coefficient $D$, eq. 2.6 can be written as

$$\mathbf{J}(\mathbf{r}) = -D \exp(-\mu_{\text{ex}}(\mathbf{r})/RT) \cdot \nabla \{c(\mathbf{r}) \exp(\mu_{\text{ex}}(\mathbf{r})/RT)\}. \hspace{1cm} (2.7)$$

Equation 2.7 is still general. We now consider a membrane with thickness $d$ in the $x$-direction and infinite dimensions in the $yz$-plane. The interfaces at $x = 0$ and $x = d$ are in contact with concentrations $c_1$ and $c_2$ ($\Delta c = c_2 - c_1$) and we assume that an ideal gas phase is in equilibrium across both interfaces. Hence $\mu$ is continuous at the interfaces. Furthermore $\mu_{\text{ex}}$ is assumed to be constant throughout the homogeneous membrane. This implies that any concentration dependence of $\mu_{\text{ex}}$ is negligible. Thus
2.3 Experimental measurement of permeabilities.

\[ \mu^0 + RT \ln c_1 = \mu^0 + RT \ln c(0) + \mu_{ex} \]  

(2.8)

or

\[ c(0) = c_1 \exp(-\mu_{ex}/RT) \]  

(2.9)

similarly

\[ c(d) = c_2 \exp(-\mu_{ex}/RT). \]  

(2.10)

If \( \mu_{ex} \) is constant then \( \nabla \mu_{ex} \) is zero. Then, for a stationary flux \( J(r) \) we find that according to equation 2.6, \( c(x) \) is a linear function of \( x \) and the gradient in equation 2.7 is equal to \( (c(d) - c(0))/d \). Equation 2.7 now reduces to

\[ J = -DS \frac{\Delta c}{d}, \]  

(2.11)

with

\[ S = \exp(-\mu_{ex}/RT). \]  

(2.12)

Equation 2.11 expresses the solution-diffusion mechanism.  

Note that it is not necessary to explicitly simulate a membrane with actual interfaces. This would place high constraints on the MD simulations. All the information needed from the simulations is the diffusion constant \( D \) in the bulk polymer and the excess chemical potential \( \mu_{ex} \) of the particles in the bulk polymer compared to the ideal gas phase.

2.3 Experimental measurement of permeabilities.

The simplest method to experimentally measure both the permeability coefficient \( P \) and the diffusion coefficient \( D \) is the **time-lag method**. This method was first proposed by Daynes [10] and refined by Barrer[11]. In this technique the membrane is initially evacuated from any residual gas by applying vacuum to both sides of the membrane for several hours. A schematic set-up of the experiment is show in fig. 2.2. Then at time \( t = 0 \) the upstream side of the membrane is exposed to the desired gas at the desired pressure \( P_{feed} \). From that moment on the pressure on the downstream side is measured and plotted. A typical plot of the pressure vs. time is also shown in fig. 2.2. From the
Figure 2.2: Left: Schematic representation of the set-up of a time-lag measurement. Before the experiment the valve (a) is closed and vacuum is applied to valves (b) and (c). Then (b) is closed and at time $t = 0$ valve (a) is opened and $P_d$ is recorded. Right: A typical time-lag plot. From the time-lag $\theta$ the diffusion constant can be calculated directly and from the slope $dP_d/dt$ the permeability coefficient can be calculated.

By extrapolation of the steady-state part of the curve, the time-lag $\theta$ can be obtained and the diffusivity can be calculated with:

$$D = \frac{d^2}{6\theta}, \quad (2.13)$$

where $d$ is the membrane thickness. The permeation coefficient $P$ can be calculated from the slope of the straight steady-state part directly, using:

$$P = \frac{1}{P_{feed}} \cdot \frac{V_d}{\rho RT A} \cdot \frac{dP_d}{dt}, \quad (2.14)$$

in which $P_{feed}$ is the applied upstream pressure, $V_d$ the downstream compartment volume, $M_{gas}$ the molecular weight of the penetrant gas at density $\rho$ and $A$ the membrane area.

The solubility coefficient $S$ is usually calculated from the diffusion and the permeability coefficients, using the relation $P = DS$. But if the permeation rate is too fast it is not possible to determine the diffusion coefficient with the desired accuracy. Then $S$ has to be measured separately.
2.4 Industrial applications

The type and structure of polymer film used depends on the application on hand. One major application is the packaging industry. In this industry there usually is a demand for high barrier properties. For example, for the packaging of carbonated soft drinks the package should not allow the permeation of carbon dioxide, oxygen or water. For this purpose one normally uses poly(ethylene terephthalate) (PET)[12]. In the packaging of products containing fats and oils like fried snacks and meat, protection against the effects of oxygen and light is required.

An interesting exception to the simple barrier demands is the storage of blood platelets [13]. Blood platelets are living cells that both consume oxygen to live and generate carbon dioxide as a metabolic byproduct. This generation of carbon dioxide presents a large problem, since it tends to cause undesirable changes in the pH unless the carbon dioxide can escape. An added requirement enters because the aqueous solution containing the platelets should not lose significant amounts of water by permeation. This case, therefore, illustrates the need for an advanced controlled atmosphere package that is able to allow relatively free exchange of oxygen and carbon dioxide while essentially preventing outward permeation losses of water.

But not only the type of polymer can be adjusted to the needs, also the macroscopic structure of the membrane can be altered. As shown in figure 2.3 one can use a variety of barrier structures besides that of a simple film to control the exchange between the

Figure 2.3: Primary types of barrier structures. a) Monolithic, single polymer. b) Laminate of two or more polymers. Middle high barrier layer e.g. EvOH, covered with surface layers. These interact with the environment which could damage the middle layer. c) Reactively formed, or coated laminate. d) Polymer filled with inorganic platelet’s or higher barrier polymer lamellae to enhance the turtuosity of the path of the penetrants.
internal and external environment.

For example, in an application where there is a need for a barrier to oxygen an often used polymer is ethylene-vinyl alcohol (EvOH). EvOH has a very low permeability to oxygen in the dry state. The problem however is that it loses its barrier properties at high relative humidities, so in those cases an interface layer is placed on the EvOH membrane such that it is shielded from the humid environment.

Another application which has large industrial interest is the selective separation of gases by use of membranes. In these cases there is a need for both high selectivity and high permeability. Silicone polymers have been used as selective membranes mainly because of the latter requirement. Even though for example the selectivity of the membranes of $\alpha(O_2/CO_2)$ is only 2.0 thus allowing only an oxygen enrichment of 30% [14], the rate of permeation is so large that it is still useful in certain applications. The enhancement of the selectivity usually has a negative influence on the rate of permeation, so for every application a new tradeoff has to be made. An interesting example of the enhancement of the selectivity is the use of polymer films containing metal complexes. The incorporation of cobalt-porphine complexes in a copolymer of poly(alkyl methacrylate) produced an increase of the selectivity $\alpha(O_2/CO_2)$ from 3.4 to 12.8. The complex selectively absorbs (according to a Langmuir isotherm) and transports oxygen in the membrane [15, 16].

Another class of applications are the bio(medical) applications, for example the usage of polymers as contact lenses. Contact lenses are classified based on their mechanical strength and physical behavior as “hard”, to denote glassy polymers, or “soft” for amorphous or semicrystalline polymers [17]. Important properties for polymers used as contact lenses are surface wettability and flexure and high oxygen permeability. Silicone films have been used as a material for the past three decades [18]. Presently the polymer used in hard lenses is usually PMMA (polymethylmethacrylaat). Most of the present soft contact lenses are prepared from poly(2-hydroxyethyl methacrylate) (PHEMA), but also polypeptide films are used as contact lenses (as well as in other biomedical applications) [19].

Controlled drug release is another biomedical application. The therapeutic efficacy of drugs can be greatly enhanced and their toxicities reduced by delivering the drugs at a controlled rate. Controlled release drug administration not only means prolongation in the duration of drug delivery, but also implies predictability and reproducibility. A number of therapeutic transdermal (through-skin) products employing silicone rubbers (including PDMS) are commercially available. For example for the controlled release of anesthetic vapors [20] or steroids [21].

In all these and other applications computer modeling of the permeation transport could be of crucial importance to either a better understanding of the process or even the design of new polymers.