Mass spectrometric estimation of gas permeation coefficients for thin polymer membranes

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Abstract

We have developed a new method to estimate the permeation coefficient of gases through polymer membranes. A fixed volume of gas is put in a gas cell and introduced into ultra-high vacuum (UHV). After positioning the gas cell face to face to a quadrupole mass spectrometer the partial pressure of the gases are measured as function of time. In a simple model the partial pressure as function of time obeys an exponential law. A formula is derived to calculate the permeation coefficient with the time constant of the partial pressure decay and geometric parameters of the gas cell as input.

Using these parameters the method gives absolute permeation values without calibration. If the time constant is difficult to establish (this may happen for membranes with a low permeation coefficient) the permeation coefficient can be estimated by extrapolating the partial pressure to \( t = 0 \). The method can be used to study the permeation behaviour of individual components of gas mixtures. The sample size can be about two orders of magnitude smaller than usually used in conventional permeation measurements. The method is illustrated with oriented polypropylene (OPP) and polyethylene terephthalate (PET) membranes of different thickness. The estimated permeation coefficients are in reasonable agreement with values obtained from a control experiment using a gas chromatograph and with values from the literature.

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1 Introduction

A detailed understanding of gas permeation through thin polymer membranes is important for applications in medicine, food packaging and for chemical separation processes. Permeation coefficients for various polymer membranes have been measured by different methods [1][2]. Electrochemical principles of measurement can be used for oxygen and water permeation [3][4][5][6][7]. For these and other gases (including noble gases) there are a number of methods which involve vacuum on the permeation side of the membrane [8]. Usually the gas is at a certain pressure on one side of the membrane while the other side is evacuated to at least \( 10^{-4} \) Pa. The total pressure increase on the vacuum side of the membrane as function of time can be used to determine the permeation coefficient [5][8]. Another way is to collect a sufficient amount of permeated gas in a vacuum vessel and subsequently let it through a gas chromatograph [9]. Several detection principles have been applied for the gas chromatograph [9], among them mass spectrometry [10]. Mass spectrometers on their own have been used in a variety of configurations to study permeation phenomena in a basically qualitative way [11].

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These methods use rather large sample sizes (usually 44 mm diameter) to estimate permeation coefficients; most of them need to be calibrated against a standard sample. Most investigations have been concerned with studying the permeation of pure gases because of experimental limitations.

The principal importance of investigating the permeation of gases and gas mixtures through polymer membranes comes from the fact that not all components in gas mixtures permeate independently due to plasticization and compression effects [12][13].

The aim of this paper is to present a new method for determination of permeation coefficients by using a mass spectrometer as detector. In principle it is calibration free and uses much smaller samples. The method can be used to study the permeation of individual components in gas mixtures.

We want to demonstrate the principle of measurement, derive a formula to calculate the permeation coefficient and discuss possible ways to improve the accuracy of the method. We will illustrate the new method by estimating permeation coefficients for polyethylene terephthalate (PET) and oriented polypropylene (OPP). Because oxygen permeation is important for most applications we will cover this gas first. Because the data base for permeation coefficients of noble gases through PET and OPP is rather small in the literature we have included some noble gases in our investigations as well.

2 Experiment

The experiments were carried out in an UHV system at base pressure in the $10^{-8}$ Pa range pumped with a turbomolecular pump. Figures 1a and 1b show the basic idea of the permeability apparatus. After filling the gas cell (Figure 1b) with the gas or gas mixture to be studied, the cell is covered with a polymer membrane and sealed. The seal consists of two pieces of polytetrafluoroethylene with the polymer membrane between them. The gas cell is made of stainless steel and has an exposed sample diameter of 4 mm diameter, i.e. the sample area is two orders of magnitude smaller than usually used in permeation experiments [5][14][15]. A further reduction of the sample area by another order of magnitude seems possible without much technical difficulty. Four hours after introducing the gas cell with the polymer membrane into the load lock chamber (Figure 1a) it was transferred into the main chamber. The polymer membrane on top of the gas cell is then positioned to face a quadrupole mass spectrometer. The mass spectrometer monitors the partial pressures for various mass/charge ratios ($\frac{m}{q}$) of gases coming from the gas cell simultaneously as function of time. Because the gas volume is fixed the gas cell is depleted of gas due to permeation and a pressure drop of partial pressure can be measured by the mass spectrometer (Figure 1a) and visualized as function of time on the computer screen. We have used a standard quadrupole mass spectrometer (Micromass PC, Vacuum Generators) with an electron multiplier (SEM) detector in analogue mode. The mass spectrometer had been previously used for a couple of years.

Comparative gas permeation measurements for a wide range of gases were carried with a commercial permeation measurement system (GTR 30-XR from Yanaco Inc. [15]). In this device the permeation coefficient is estimated by collecting the permeated gas in a vessel over a period of time and subsequent injection into a gas chromatograph.

The temperature was measured with a thermocouple prior to positioning the gas cell face to face to the mass-spectrometer. Although the mass spectrometer tube gets quite warm (60°C) the gas cell is at a much lower temperature (around 30°C) because it is not in direct contact with the mass spectrometer. By and large, the stability of the mass spectrometer during the experiments over several days was satisfactory. Only at partial pressures in the low $10^{-11}$ Pa range (detection limit of an analogue mass spectrometer) did partial pressure vs. time curves become noisy.

Because we are concerned with quantitative measurements we have to investigate the linearity of the partial pressure response of the quadrupole mass spectrometer. It is documented that not all such devices have an analogue output which is linearly related to the partial pressure [16]. We have introduced gas into the UHV chamber and measured the partial pressure response with the mass spectrometer and the total pressure with a Bayard-Alpert ion gauge. The measured
data points for He, Ne, N and Ar could be fitted to a straight line. The ratio of partial pressure readings of different isotopes of the same gas were in good agreement with the ratio of their natural abundance. We have corrected the absolute values of the measured partial pressures using the sensitivity factors according to the manual of the mass spectrometer.

We have investigated OPP [17] and PET polymer membranes as examples for a low and a higher permeation polymer. Both are used in a wide range of applications, as for instance in food packaging.

3 Calculation of permeation coefficient

Both OPP and PET are glassy polymers at room temperature. This fact makes a comprehensive treatment of diffusion and solution processes even for noble gases impossible or inaccurate [18][19]. Fortunately, in steady state permeation the mass spectrometer detects permeated species. In this paper we are not concerned to separate diffusion and solution as can be done with the time-lag method [8].

To derive a formula which relates the time-dependent drop of partial pressure to the permeation coefficient we assume that the gas cell is initially filled with a certain amount of gas and separated from any further supply. Permeation of gas through the polymer membrane leads to a depletion of gas inside the gas cell. The permeation of gas molecules through the membrane is driven by the pressure difference between inside (filled with gas) and outside (UHV) of the gas cell. In a simple model we assume that the number of permeating molecules is proportional to the number of remaining gas molecules in the gas cell.

\[ \frac{dN}{dt} = \text{const.} \cdot N(t) \] (1)
giving an exponential law,

\[ N(t) = N_0 \exp(-t \cdot \tau) \] (2)

with \( N(t) \) as number of gas molecules in the gas cell at the time \( t \), the number of gas molecules filled into the cell \( N_0 = N(0) \) and \( \tau \) a time constant. The time \( t_0 = t(0) \) is the time when the pump of the introduction chamber is switched on. Within seconds a significant pressure difference is established. The time constant actually takes both diffusion and solution into account which have been previously described by an exponential law [14].

Once the gas cell is positioned face to face to the mass spectrometer (at \( t = 4 \) hours) the gas molecules permeating through the polymer are detected by the mass spectrometer. Even state of the art quadrupole mass spectrometers have an efficiency of less than \( 10^{-4} \) and therefore the detected number of gas molecules is only proportional to the number of gas molecules permeating through the polymer membrane. The analogue signal of the mass spectrometer giving the partial pressure is proportional to the change of the number of gas molecules inside the gas cell. Hence the pressure inside the mass spectrometer \( p(t) \) obeys the same law as given in eq. (2).

\[ p(t) = p_0 \exp(-t \cdot \tau) \] (3)

We define \( \Phi(t) \) as gas flux through the membrane a part of which is detected in the mass spectrometer.

\[ p(t) = \frac{p_0}{\Phi_0} \cdot \Phi(t) \] (4)

Conservation of gas molecules number requires:

\[ N_0 = \int_0^\infty \Phi(t) dt \] (5)

Eq. (4) and (5) yield:

\[ N_0 = \frac{\Phi_0}{p_0} \int_0^\infty p(t) dt \] (6)

With eq. (3) this yields:

\[ N_0 = \frac{\Phi_0}{p_0} \int_0^\infty p_0 \exp(-t \cdot \tau) dt \] (7)

\[ N_0 = \frac{\Phi_0}{\tau} \text{ or } \Phi_0 = N_0 \cdot \tau \] (8)

Permeation is flux per area, normalized to a certain pressure difference and film thickness:

\[ k = \frac{\Phi_0}{A \cdot d \cdot \Delta p} = \frac{N_0 \text{STP}}{A \cdot d \cdot \Delta p} \cdot \frac{\tau}{(9)} \]

with \( A \) the membrane area and \( d \) the membrane thickness. \( N_0, A \) and \( d \) are technical parameters of the gas cell, the time constant is measured during the experiment. For a gas mixture the evaluation is carried out for each mass channel separately. We have measured the partial pressure response as function of total pressure (estimated with a Bayard-Alpert type gauge). Because a linear relationship was observed in the partial pressure range between \( 10^{-7} \) and \( 10^{-10} \) Pa we assume that the relative sensitivity factors of the mass-spectrometer are constant.

A permeation unit which is widely used is the \( \text{cm}^3 \text{STP} / \text{m}^2 / \text{day} / \text{atm} \). In this unit eq. (9) becomes:

\[ k = \frac{V \cdot \tau}{A} = l \cdot \tau \] (10)

with \( V \) as volume, \( l \) as length of the gas cell, \( A \) as effective permeation area of the polymer membrane and \( \tau \) as the time constant in the partial pressure vs. time curve. This simplification
assumes the gas cell to be of cylindrical or prismatic shape. The permeation coefficient is simply the product of one quantity estimated from the partial pressure vs. time curve (the time constant) and one geometric parameter (the volume/area ratio).

There are two main results of the mathematical treatment given above.

First, by estimating the time constant of the decay of partial pressure vs. time it is possible to estimate the permeation coefficient directly without any calibration or reference sample. This mode is suitable for membranes with sufficiently large permeability and hence sufficiently high time constants (provided the time constant is not so small as to empty the gas cell during pumping in the load lock chamber).

Second, if the gas permeation is too low and there is only little slope in the partial pressure vs. time curves (and hence the error of the permeation coefficient would be rather big) the permeation coefficient can be estimated by extrapolating the partial pressures to t=0. However, to relate the extrapolated value to the gas permeation coefficient a calibration against a gas with a higher permeation coefficient of the same sample or a different sample with known permeation coefficient and gas sensitivity factors is necessary in this case.

4 Data treatment

Before we enter a quantitative discussion of the permeation coefficients we have to access the validity of our assumptions given in the derivation in the preceding paragraph. So far, experiments have focussed on gases with low mass numbers (i.e. up to argon at mass 40). We will demonstrate that in these cases an exponential law for the experimental partial pressure vs. time curve (as predicted in (3)) is followed and that reasonably accurate permeation coefficients can be obtained.

First, we want to discuss the influence of the background gases in the chamber on the partial pressure.

Figure 2 shows a mass spectrum of the UHV background at a total pressure of $2 \times 10^{-8}$ Pa. Regions where the $\frac{m}{q}$ ratios regions show low background partial pressure are particularly suitable for permeation measurements, because the partial pressure vs. time curves can be used without background correction. As can be seen from Figure 2 the favorable regions cover all noble gases in this range which makes them good candidates for estimation of permeation coefficients. Usually there is no problem with oxygen ($\frac{m}{q}=32$). Care must be taken to avoid using oxygen containing organic substances in the vacuum chamber which might be cracked in the mass spectrum to yield $\frac{m}{q}=32$. The main peak in the mass spectrum for nitrogen ($\frac{m}{q}=28$) coincides with the carbon monoxide peak. This has to be taken into account if nitrogen permeation is studied and will be discussed below.

Second, we have to consider the effect of outgassing of the gas cell and the polymer itself and also the time needed for the gas cell to reach a constant temperature in front of the mass spectrometer. We have investigated the partial pressure vs. time curves for empty gas cells, i.e. a gas cell without gas permeation and found that for several hours after starting the experiment a small, but significant part of the partial pressure signal is caused by outgassing. Although corrections are possible for these effects we have decided that for most cases it is easiest to discard the first 10 hours of the experiment. This period is not essential for measurements lasting around 80 hours.

In summary, the background pressure at the $\frac{m}{q}$ ratio of interest it is subtracted from the measured partial pressure and the initial period of the experiment will be discarded.

5 Results and discussion

In this section we want to discuss experimental results and evaluate whether they are in agreement with the model developed in the preceding paragraphs. In order to discuss this question from different aspects we have changed a number of experimental parameters. For many applications (for instance food packaging) permeation of gases from the ambient are most important. Therefore
we have started with experiments about permeation of nitrogen and oxygen through different polymers. To demonstrate some more general aspects of the method we have used noble gases as well. Water vapor permeation through polymer membranes will be investigated in a separate study.

5.1 Oxygen and nitrogen permeation

Figure 3 shows partial pressure vs. time curves for the permeation of nitrogen, oxygen and argon through 20 $\mu$m thick OPP. These curves were obtained on pure gases. To illustrate the capability of the method we have recorded the partial pressure for different m/q values of each gas (Figure 3).

Table I compares permeation coefficients obtained by mass spectrometer, GTR control experiments and the literature. For oxygen there is good agreement between permeation coefficients measured with the mass spectrometer and those from the control experiment. The permeation coefficients for nitrogen estimated by mass spectrometer are more than twice the values from the control experiment and the literature (table I). As shown in Figure 2 we have a strong background signal at $\frac{m}{q}=28$. At $\frac{m}{q}=28$ we have the CO signal as well and at $\frac{m}{q}=14$ there is contribution from CH$_x$ cracking products. Therefore it is extremely difficult to obtain the permeation coefficient for nitrogen by this method. Carbon monoxide might influence the nitrogen readings in a similar way as illustrated in Figure 4 for the hydrogen readings in the presence of argon. The upper curve in Figure 4 shows the hydrogen monitor curve. As there is no extra amount of hydrogen when the sample is introduced the jump by almost 30% at $t=4$ h is likely to be caused by the presence of argon. The pressure readings for nitrogen might be influenced in a similar way by the presence of carbon monoxide at the same $\frac{m}{q}=28$ value.
Figure 3: Permeation curves for different $\frac{m}{q}$ of $N_2$, $O_2$ and $Ar$ through OPP 20 µm thick, at 35°C.
5.2 Permeation of noble gases

Neon has three isotopes $^{20}$Ne, $^{21}$Ne and $^{22}$Ne. The isotopes $^{20}$Ne and $^{22}$Ne occur naturally at a ratio of 1:10, $^{21}$Ne contributes less than 1%. Figure 5 shows the partial pressure vs. time curve for $^{20}$Ne and $^{22}$Ne. Both curves run parallel (except at very low pressures for $^{22}$Ne where the detection limit of the mass spectrometer is reached). The estimated permeation coefficient (table I) for both isotopes is higher than measured in the control experiment; literature values were not available.

Obviously, to take advantage of the calibration free method there must be sufficient slope in...
the partial pressure vs. time curve. However, even if there is not enough slope in these curves, permeation coefficients can be estimated. This can be done by extrapolating the partial pressure to $t=0$. For instance, OPP has a much higher permeation coefficient than PET towards nitrogen, oxygen and noble gases [5][8][14]. This means that the slope in the partial pressure vs. time curve is lower and the error margin bigger. Only if the permeating gas has small molecules (such as helium, neon) or very thin membranes are used (difficult to prepare) a sufficiently big slope can be obtained.

Figure 4 compares argon permeation through 20 $\mu$m thick OPP and 12 $\mu$m PET. Because PET has good barrier properties for gas permeation there is only very little slope in the partial pressure vs. time curves. Consequently, an accurate estimation of permeation constants from the slope is very difficult. Instead, the partial pressure at $t=0$ can be used. A straightforward way is to use the same gas on another polymer which has a sufficiently high permeability. Then:

$$\frac{p_{\text{OPP}}(t=0)}{p_{\text{PET}}(t=0)} = \frac{\tau_{\text{OPP}}}{\tau_{\text{PET}}}$$

From Figure 4 we obtain a $\frac{p_{\text{OPP}}(t=0)}{p_{\text{PET}}(t=0)}$ value of 18 which is in reasonable agreement with the value of 23 estimated in the GTR control experiments. Table II shows some permeation values obtained on PET.

Table II: comparison of permeation coefficients PET (different thickness)

<table>
<thead>
<tr>
<th>m/q</th>
<th>mass spectrometer</th>
<th>GTR (control exp.)</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>@35$^\circ$C</td>
<td>@35$^\circ$C</td>
<td>@25$^\circ$C</td>
</tr>
<tr>
<td>He 100 $\mu$m</td>
<td>4</td>
<td>1300</td>
<td>1100</td>
</tr>
<tr>
<td>Ar 12 $\mu$m</td>
<td>20</td>
<td>140</td>
<td>100</td>
</tr>
</tbody>
</table>

units: cm$^2$/day/atm
Figure 6: Permeation curves for nitrogen, oxygen and argon (in air) through OPP 20 µm thick, at 30°C.

5.3 Gas mixtures

The mass spectrometric estimation of permeation coefficients is inherently suitable to estimate individual permeation coefficients of components of gas mixtures. However, great care must be exercised in interpreting these values because the sensitivity of the mass spectrometer for one component can be influenced by the presence of another component. Figure 6 shows results for the permeation of air (nitrogen, oxygen and argon) through OPP.

It is quite remarkable that a trace gas such as argon which has a fraction of less than a percent in air is clearly visible in the spectrum. This is due to the high sensitivity of the mass spectrometer to argon and the absence of much background contribution at mass 40. In this case, the partial pressure readings for nitrogen and oxygen appear not to be significantly influenced by the presence of the low amount of argon.

We have then investigated a gas mixture with higher amount of argon and oxygen by using a custom made gas mixture containing 34% N₂, 33% O₂ and 33% Ar. Figure 7 shows the partial pressure vs. time curves and as expected the argon and oxygen signals are considerably higher compared to air (Figure 6). However, within the experimental error there is no difference between the permeation coefficient for the pure gases (table I) and the permeation coefficients estimated from the experiments in Figures 6 and 7. Different permeation coefficients in dependence on the gas composition have been reported for gases which show more chemical interaction with the polymer such as CO₂ permeating through polycarbonate [12].

To further illustrate the method we have measured the permeation coefficient as function of film thickness. Figure 8 shows the partial pressure of nitrogen, oxygen and argon as function of time for the three thicknesses. As expected the slope decreases with increasing membrane thickness. Within the error margin of the experiment this decrease follows an $\frac{1}{3}$ relationship.
Figure 7: Permeation curves for $N_{0.34}O_{0.33}Ar_{0.33}$ gas mixture through OPP 20 µm thick, at 30°C.

Figure 8: Permeation coefficients in dependence of film thickness for nitrogen, oxygen and argon (in air) through OPP at 30°C.
5.4 Accuracy issues

The permeation coefficient depends exponentially on temperature. Typical activation energies of $35 \text{ kJ mol}^{-1}$ (argon through PET) mean that the permeation coefficient doubles at a temperature increase of around $15^\circ \text{C}$. To obtain accurate slopes in the partial pressure vs. time curve it is therefore essential to keep the temperature constant during the experiment. In our experiment the temperature was measured with a thermocouple at the gas cell position while the gas cell was removed. Therefore the maximum temperature error is assumed to be $\pm 2^\circ \text{C}$. The geometric parameters in (10) can be obtained with an error of less than $\pm 5\%$. The error margin of the permeation coefficients caused by the experimental conditions is believed to be $\pm 25\%$. This is a reasonable error margin. When using different devices (GTR and OXTRAN) to measure oxygen permeation through PET we found differences in the same region between these two methods. From tables I and II it appears that the permeation coefficients estimated by mass spectrometer are systematically too high. This might be caused by the gas cell heating up to a slightly higher temperature than measured with the thermocouple.

This cause can be excluded and the error margin substantially reduced by fitting the thermocouple directly to the holder of the gas cell. The accuracy of the method can be further increased by filling the gas cell in vacuum (such avoiding outgassing) and using pulse counting electronics for the mass spectrometer (such increasing the accessible partial pressure range into the $10^{-13} \text{ Pa}$ range). At present small differences of the permeation coefficient between pure gases and gas mixtures are difficult to detect due to the large error margin. By implementing the changes listed above an experimental accuracy of better than $\pm 10\%$ appears possible which makes it more suited for study of gas mixtures. It is worthwhile to mention that within practical limitations the film thickness is an important parameter which can be used to get more or less slope in the partial pressure vs. time curve for the same polymer without need to change the gas species.

If $p(t=0)$ extrapolation is used to determine the permeation coefficient an accurate sample positioning system is required. In the experiments presented here we were mainly concerned measuring the time constant $\tau$ which does not require highest accurate to position the sample.

We want to stress the point that at this stage a very simple mathematical model has been used. A more refined model which may take into account the different nature of interaction between different gases (for instance oxygen, nitrogen and noble gases) and the polymer will certainly lead to an improved estimation of permeation constants.

Because of the completely different nature of the mass spectrometric method and all other permeation methods we consider the values given in Tables I and II as in reasonable agreement with control experiments and literature.

The method presented here should be able to handle samples smaller than 2 mm diameter if precise sample positioning is possible.

6 Conclusions

We have set up a quadrupole mass-spectrometric method to study permeation of pure gases and gas mixtures through small sized polymer membranes. The advantage of the method is that it permits calibration free estimation of permeation coefficients. Different gases can be monitored simultaneously in real time.

For the investigated polymers and permeating gases the partial pressure vs. time curves can be explained by a simple model assuming an exponential law for the partial pressure as function of time. A number of experimental examples which show this exponential relationship have been presented. The permeation coefficients have been directly estimated from the time constant of the partial pressure decay and geometric parameters of the gas cell. If the partial pressure decay is too low to obtain the slope with sufficient accuracy the permeation coefficients can be estimated by extrapolation of the partial pressure to $t=0$.

Permeation coefficients obtained by the mass spectrometric method are in reasonable agreement with values obtained by independent control experiments and values from the literature.
Suggestions have been made to improve the accuracy of the method.

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References


