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Research article

Photoacoustic detection based permeation measurements: Case study for separation of the instrument response from the measured physical process

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ABSTRACT

In a carrier flow based permeation system the measured permeation curve is the convolution of two processes: the intrinsic permeation process and the transfer of the permeated molecules through the measuring system. The latter one is quantified by the instrument response function (IRF). The possibility of calculating the IRF from permeation curves measured at various volumetric flow rates of the carrier gas is examined. The results are in partial agreement with preliminary expectations: the dependency of the calculated IRF on the volumetric flow rate of the carrier gas indeed follows roughly the expected tendency; however it is not completely independent from the physical properties of the measured membrane sample. This discrepancy can most probably be attributed to the imperfect design of the applied permeation cell. Overall it is expected that the proposed method for determining the instrument transfer function is a valuable tool for improving the design of permeation measuring systems.

1. Introduction

1.1. Carrier flow based permeation measurements

A carrier flow based gas permeation system (Fig. 1) [1] consists of a diffusion cell (marked with the abbreviation DC in Fig. 1), which is divided into two chambers, the feed and receiving chamber, which are hermetically separated by the measured membrane sample. The operation of the system has two phases. During the purging phase the entire inner volume of the gas handling of the system is purged by the carrier gas (i.e. high purity nitrogen in the present case). During the measurement phase, which is initialised by electronically controlled switching of the magnetic valve (marked as MV in Fig. 1) the feed chamber is purged with the feed gas (either pure carbon-dioxide or methane in the present case) while the receiving chamber is purged with the carrier gas. Molecules permeated through the membrane from the feed chamber into the receiving chamber are swept into a detection unit, i.e. in our case a photoacoustic cell (marked as PAC in Fig. 1) by the carrier gas flow controlled by a mass flow controller (marked as MFC in Fig. 1).

In order to differentiate the permeated molecules from the molecules of the carrier gas the applied detection method has to be selective. Among the possible methods Beer-Lambert law based optical absorption measurement techniques are fairly popular [2], as well as photoacoustic (PA) detection, which is a special type of optical absorption method that already has been applied successfully in permeation measurements [3–5]. Previous research has shown that a properly optimised PA system outperforms conventional optical absorption detection techniques as far as the minimum detectable concentration and the response time is concerned [6].

A permeation curve (marked in the following as $c_M(t)$) describes the dependence of concentration of the permeating molecules measured within the detection unit as a function of time elapsed since the start of the feed gas purging. By applying a numerical fitting method on the experimentally determined $c_M(t)$, the permeation parameters of the measured membrane (D, S and P i.e. the diffusivity, the solubility and the permeability, respectively) can be calculated [7]. For this, one could fit either the entire permeation curve or only its late, steady state part. The latter, referred to as time-lag method, is mathematically a much simpler procedure and therefore it is widely applied [8]. On the other hand, the full curve fitting was already shown to be less influenced by measurement errors and artefacts [5], therefore it is preferable.

1.2. Distortion of the permeation curve due to the measuring system

It is important to emphasise that from the theory of diffusion (see e.g. [7]) one cannot deduce an exact mathematical expression for $c_M(t)$ but rather for the theoretical curve $j_T(t)$, which is the temporal variation

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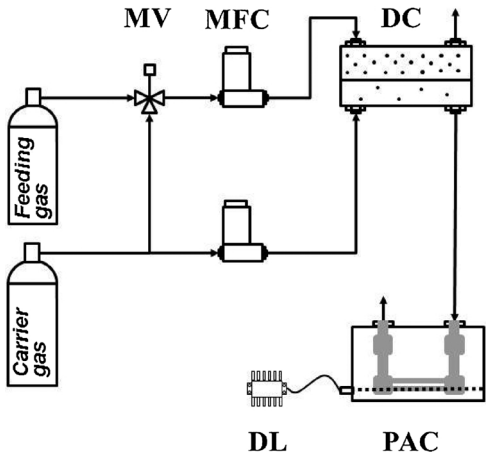

Fig. 1. Schematic of the carrier gas and photoacoustic detection unit based membrane permeation measurement system. The following abbreviations are used: MV: magnetic valve, MFC: mass flow controller, DC: diffusion cell, DL: diode laser light source, PAC: photoacoustic detection cell.

of the permeation flux of the molecules through unit area of the membrane. For simple permeation processes the latter one can be written as [7]:

$$j_T(t) = \frac{P \bullet p}{l}\left(1 + 2 \bullet \sum_{n=0}^{\infty} (-1)^n \bullet e^{-\frac{n^2 \bullet \pi^2 \bullet D \bullet t}{l^2}}\right) \quad (1)$$

where $P = D{\cdot}S$, p is the partial pressure of the feed gas maintained within the feed chamber and l is the thickness of the membrane sample. Therefore, a phenomenological relationship should be introduced, which relates the theoretically calculated $j_T(t)$ to the experimentally measured $c_M(t)$:

$$c_M(t) = \frac{A}{Q_c} \bullet (j_T(t) * h(Q_c, \tau)) \quad (2)$$

where A is the surface area of the membrane and Q_c is the volumetric flow rate of the carrier gas. Q_c appears in the denominator in Eq. (2) because the carrier gas flow not only transfers the permeated molecules from the receiving chamber to the detection cell but it actually also dilutes their concentration and the degree of dilution at first approximation is inversely proportional to Q_c. The function $h(Q_c,\tau)$, which can be seen as an instrument response function [9], represents the influence of the measuring system on the measured permeation curve. In Eq. (2) the mathematical operator of convolution (convolution and deconvolution are marked with the sign of * and $\frac{1}{*}$, respectively) expresses the fact that the two processes (i.e. the permeation through the membrane and the transport of the permeated molecules to the point of detection) are separable, which also means that under ideal conditions $j_T(t)$ is independent of Q_c and $h(Q_c,\tau)$ is independent of the material parameters (i.e. D, S, P and l) of the measured membrane. The outstanding importance of Eq. (2) is that once $h(Q_c,\tau)$ is determined and if it is proven to be independent from the measured membrane sample and the feed gas, then there is the possibility of calculating back from the measured permeation curve ($c_M(t)$) the permeation flux though the membrane ($j_T(t)$) as:

$$j_T(t) = \frac{Q_c}{A} \bullet \left(c_M(t) \frac{1}{*} h(Q_c, \tau)\right) \quad (3)$$

and thus the distorting effect of the measuring system can be eliminated and from the deduced $j_T(t)$ curve the permeation parameters of the measured membrane can be determined accurately.

The measuring system can influence the measured permeation curve in several ways, i.e. $h(Q_c,\tau)$ is dependent on several factors:

- First of all, there is a delay time (marked in the following as τ) during which the permeated molecules from the receiving chamber are transported into the detection cell by the carrier gas. This delay time can be approximated as [10]:

$$\tau \approx \frac{V_D}{Q_c} \quad (4)$$

where V_D is the total volume of the detection part of the permeation measuring system i.e. the sum of the volumes of the receiving chamber, the detection unit and the gas handling in-between them.

- Adsorption/desorption effects, resulting from the interaction of the permeated molecules with the inner surfaces of the measuring system influences both τ and $h(Q_c,\tau)$ [11]. Careful selection of materials of the system's components (e.g. in many cases stainless steel) and the application of special coating on the inner surfaces can help to reduce the effect of adsorption/desorption. Nevertheless in practice adsorption/desorption effects can never be completely eliminated.
- Additionally the permeation measuring system might leak to the ambient, and the permeated molecules might diffuse into the o-rings used for sealing. These are possible construction deficiencies, which can also influence $h(Q_c,\tau)$ but they can be eliminated by careful optimisation of the permeation system (as implemented for the case of the measuring system reported here).

In principle these effects can be incorporated into a $h(Q_c,\tau)$ function. However, for an improperly designed permeation system, the processes of permeation and measurement might not be separable at all, i.e. Eqs. (2) and (3) are not applicable, and therefore permeation measurements with such systems are burdened with inaccuracy. Indeed recently Verwolf et al. performed permeation measurements with various commercially available permeation instruments and found large variations in the deduced permeation parameters [12]. Based on their work it can be assumed that the operation of these instruments lacks a method with which first the instrument response function can be determined and then the measured permeation curve can be corrected with $h(Q_c,\tau)$ in accordance with Eq. (3). Furthermore based on their results Verwolf et al. pointed out the importance of the performance based optimisation of the design of the permeation cell, which should primary target the homogenisation of the temperature and the carrier gas flow distribution within the receiving chamber [12]. However they did not suggest a method for verifying the appropriateness of a permeation cell design, which is the subject of the presented work.

The usual technical solution in permeation measurements for the suppression of the effect of $h(Q_c,\tau)$ on $c_M(t)$ is to increase Q_c until $c_M(t)$ becomes practically independent of Q_c. This tendency of $c_M(t)$ is interpreted in a way that for permeation measurements executed at high Q_c values the effect of the measurement system on c_M is suppressed. The underlying assumption can be expressed mathematically as:

$$h(Q_c \to \infty, \tau) = 1 \quad (5)$$

On one hand, the validity of Eq. (5) is a plausible assumption, which is supported by the fact that in a series of permeation measurements it was indeed observed that by increasing Q_c the deduced permeation parameters converge to limiting values, which are actually independent of Q_c [4]. On the other hand, performing permeation measurements with high Q_c values is not always feasible because, as it follows from Eq. (2), there is an overall inverse proportionality between Q_c and the concentration of the permeated molecules in the detection cell. Therefore by increasing Q_c the signal to noise ratio (S/N) of the concentration measurement decreases and parameters can be calculated only from noise permeation curves with large uncertainty, especially in case of low permeability samples. Indeed in our recent publication [5] it was shown that the S/N of the concentration measurement has to be kept above 50 at least during the late, quasi steady-state part of the permeation process otherwise there will be a considerable uncertainty

(more than 10% relative error) in the deduced permeation parameters especially when the full curve fitting method is applied. Consequently, in order to maintain the required S/N low permeability membranes can only be measured with low Q_c values for which the limit given by Eq. (5) is not approached and thus the distortion effect of $h(Q_c,\tau)$ cannot be disregarded.

2. The proposed method for the determination of $h(Q_c,\tau)$

The basic idea of the reported work is to determine $h(Q_c,\tau)$ from permeation measurements performed on membrane samples, which have permeability high enough so they can be measured both in the low and high Q_c ranges. These two ranges are defined in a way that in the former range $c_M(t)$ has Q_c dependence while in the latter range $c_M(t)$ becomes Q_c independent [4] (except that the measured permeation curve becomes noisier with increasing Q_c values). In the following superscripts, *low* and *high* indicates whether the measurement is performed in the former or latter range, respectively. Eq. (3) can be written for either case and by taking into account the fact that $j_T(t)$ is independent from the actual value of Q_c one gets:

$$h(Q_c^{low},\tau)\frac{1}{*}h(Q_c^{high},\tau)=\frac{Q_c^{low}}{Q_c^{high}}\bullet\left(c_M(t)(@Q_c^{low})\frac{1}{*}c_M(t)(@Q_c^{high})\right) \quad (6)$$

Furthermore if Q_c^{high} is high enough that the limit set by Eq. (5) is approached then Eq. (6) simplifies to:

$$h(Q_c^{low},\tau)=\frac{Q_c^{low}}{Q_c^{high}}\bullet\left(c_M(t)(@Q_c^{low})\frac{1}{*}c_M(t)(@Q_c^{high})\right)=RTD(Q_c^{low}) \quad (7)$$

Based on Eq. (7) one can characterise a permeation measurement system by calculating its $h(Q_c,\tau)$ function from permeation measurements performed with test samples both in the low and high ranges of Q_c values. Clearly this procedure is applicable only if the deduced $h(Q_c,\tau)$ function is found to be independent from the actual test membrane and feed gas. On the other hand, once a sample independent $h(Q_c,\tau)$ function is generated it facilitates accurate determination of the permeation parameters (by Eq. (3)) even for samples with low permeability, which are measurable only with low Q_c values. Furthermore Eq. (7) can also be used to determine the Residence Time Distribution (RTD) of the permeation measuring system too, which is the probability distribution of the amount of time that a molecule spends within the measuring system after permeating through the membrane [10]. Various order central moments of the RTD function can be calculated helping the better understanding of the transport processes within the measuring system.

In the following, the applicability of the proposed method for the determination of the instrument response function is investigated by reanalysing previously measured permeation curves of a photoacoustic detection based permeation measuring instrument.

3. Experimental data for reanalysis

The present work is based on measurement results from our previous publication [4]. In the following the measurement set-up of a carrier flow based permeation system using a PA detection unit is briefly described while further details are given in the original publication [4]. The feed gas was either methane (99.995% purity) or carbon-dioxide (99.9995% purity). The carrier gas was nitrogen (99.9995% purity). The minimum detectable concentration (MDC) by the PA detection unit is 0.5 ppm and 50 ppm for methane and carbon-dioxide, respectively. Various polymer samples were measured with various Q_c values, which however never exceeded 500 sccm (standard cm^3 per minute) as above this limit gas flow through the PA cell generates excessive acoustic noise, which increases considerably the MDC of the system. There is a set of samples (namely the polyethylene and the silicone rubber sample with thickness of 0.06 mm and 2.5 mm, respectively) for which the measured permeation curves and deduced permeation parameters become Q_c independent already when Q_c is well below 500 sccm, while for the other set this is not the case (see Fig. 3 in Reference [4]). These latter set is excluded from the forthcoming analysis as the prevailing Q_c dependency indicates the inapplicability of Eq. (5) for these samples in case of $Q_c \leq$ 500 sccm. Therefore in the following only the former set of measured samples is considered. The deduced permeation parameters of the analysed samples are shown in Table 1 together with Q_c^{max}, which is the largest volumetric flow rate of the carrier gas at which the permeation measurements are performed and at which the listed permeation parameters are determined. Q_c^{max} is also used as Q_c^{high} whenever Eq. (7) is applied for $h(Q_c,\tau)$ determination.

Table 1
Summary of the results of permeation measurements.

Sample	Feed gas	D Diffusivity [m^2/s]	S Solubility [1/Pa]	Q_c^{max} Carrier gas flow rate at which these parameters were determined [sccm]
Polyethylene	CH_4	1.78×10^{-11}	1.07×10^{-6}	400
Polyethylene	CO_2	3.06×10^{-11}	2.32×10^{-6}	300
Silicone rubber	CH_4	1.68×10^{-9}	5.11×10^{-6}	400
Silicone rubber	CO_2	1.85×10^{-9}	1.75×10^{-5}	200

On the permeation curves measured for these samples and feed gases deconvolution was performed in accordance with Eq. (7) and the Q_c dependent transfer functions and residence time distributions were determined.

4. Results and discussion

In Fig. 2 the calculated residence time distributions for the permeation measurements in case of CO_2 feed gas and polyethylene membrane sample can be seen for various Q_c values. Fig. 3 shows the dependence of the various RTD moments i.e. the mean (3a) and the variance (3b.) calculated for various membranes (PE – polyethylene, Si – silicone rubber) and permeating analytes (CH_4 – methane, CO_2 – carbon dioxide). Fig. 3 also indicates the calculated delay time (τ) as defined by Eq. (4) by taking account that $V_D \approx 60\,cm^3$ for the present system.

Fig. 2 shows that the calculated RTD functions become narrower and shift toward the y-axis i.e. they converge toward a Dirac-delta function as Q_c is increasing. Indeed mathematically the deconvolution of two identical functions is a Dirac-delta function. Accordingly the

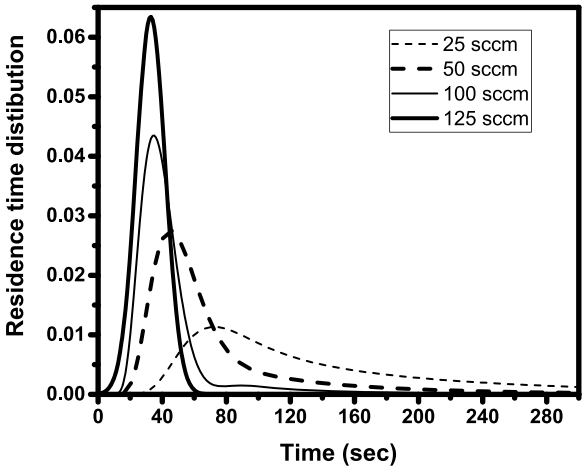

Fig. 2. Calculated residence time distributions for CO_2 permeation measurements on the polyethylene membrane sample.

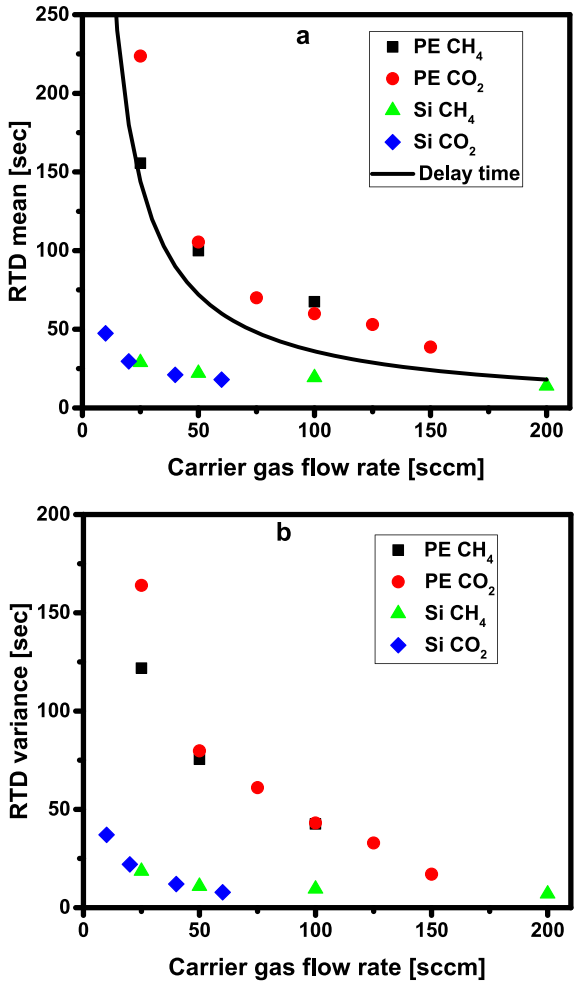

Fig. 3. Mean (3a.) and variance (3b.) of the residence time distributions for various samples and feed gases. The calculated delay time (see Eq. (4)) is also shown on 3a.

RTD moments converge to zero as well (Fig. 3a and b). However, as Q_c^{low} approaches Q_c^{max}, artificial oscillations in the $h(Q_c^{low},\tau)$ function calculated with the help of Eq. (7) occur. This is a well-known artefact of deconvolution [13], which is caused by the increasing similarity of the two functions on which deconvolution is applied. Due to this effect only those Q_c^{low} values are shown in Figs. 2 and 3 for which oscillation does not occur. Due to these artificial oscillations no further insight can be gained about the way $h(Q_c^{low},\tau)$ approaches to a Dirac-delta function whenever $Q_c^{low} \rightarrow Q_c^{max}$.

Fig. 3a illustrates that RTD mean values loosely follow the delay time curve. However, while RTD mean (and also RTD variance) values show only very slight dependence on the feed gas, they are clearly influenced by the measured membrane sample. From this it can be concluded that for the studied permeation system it is not possible to separate the permeation process and the response of the actual permeation measuring system, i.e. the design of the system has to be improved.

Fig. 3a shows that for samples with high permeability (i.e. silicone rubber membrane) the measured RTD points are well below the delay time curve, while for lower permeability sample (i.e. polyethylene membrane) these points are fairly close to the curve. One can give a speculative explanation for this observation, which is in agreement with the conclusions of Verwolf et al. [12]. Most probably due to the improper design of the receiving chamber of the permeation cell there are dead volumes in it, which are not purged effectively by the carrier gas. Therefore those permeating molecules arriving into these dead volumes are trapped there for a time much longer than the characteristic delay time of the system calculated by Eq. (4). For membranes with low permeability the permeation process is slow therefore there is sufficient time for those trapped molecules to diffuse out from the dead volumes into the flow channels of the carrier gas through the receiving chamber, which is however not the case for high permeability membranes. This effect can be interpreted as an apparent reduction of the volume of the receiving chamber. Actually from the measured data it can be interpreted that about half of the volume of the receiving chamber acts as a dead volume in case of a highly permeable sample. Obviously those parts of the membrane, which are right above these dead volumes, give a reduced contribution to the permeation process, which means that in accordance with Eq. (2) the deduced permeation parameters are inaccurate too. These findings clearly indicate the importance of the proper permeation cell design as suggested by Verwolf et al. [12].

5. Conclusion and outlook

The instrument response function is a critical parameter of a permeation measuring system. It influences the measured permeation curves (see Eq. (2)) and can be used to correct the results of permeation measurements whenever the measurement can be performed only with insufficiently high carrier gas volumetric flow rates (see Eqs. (3) and (7)). Therefore there is a clear need for a method with which $h(Q_c,\tau)$ can be determined. This work proposes a method for this purpose, which is based on the permeation measurement in a wide range of Q_c values using Eq. (7). Furthermore based on Eq. (7) residence time distribution functions can be calculated and the various order central moments of this function gives a better insight into the transfer properties of the measuring system. However, it turns out that the proposed method for the separation of the instrument response is applicable only if the determined $h(Q_c,\tau)$ is independent from the measured membrane sample and the feed gas, while the opposite case most probably indicates the improper design of the permeation system. Consequently the proposed method can be used to improve and verify permeation cell design too. Indeed the results of the presented analysis indicate that our currently used permeation cell has to be re-designed in order to eliminate or at least minimise dead volumes in its receiving chamber and to homogenise the flow pattern of the carrier gas in it as much as possible. After re-designing the permeation cell the presented analysis is planned to be executed once again by using a larger number of membrane samples. It is expected that with the re-designed permeation cell the instrument response function will become independent from the measured membrane samples (or at least the dependency will be largely suppressed), i.e. the accuracy of the deduced permeation parameters will be considerably improved. Furthermore the design of the PA detection unit is under modification too in order to surpass the 500 sccm limit on the applicable volumetric flow rate of the carrier gas, which currently excludes many types of membrane samples from the analysis.

Finally once there is a permeation measuring system for which $h(Q_c,\tau)$ is known accurately, this opens up the possibility to study unconventional (non-Fickian) permeation processes too.

Conflict of interest

The authors declare that there are no conflicts of interest.

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