Differential permeation – Part I: A method for the study of solvent diffusion through membranes

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Abstract: We describe the differential permeation method for the study of the diffusion of solvents from a liquid (or liquid mixture) through flat or tubular membranes. This method consists of measuring the transient permeation rates through the membrane when one of its faces is suddenly put into contact with the liquid medium. The change in the transient rate with time is analyzed by numerical best fitting methods to determine the Fickian diffusion coefficient. A simplified equation is proposed for the fitting of the response of a tubular membrane. Deviations from the Fickian transport mechanism with concentration-independent diffusion coefficient can be evidenced and eventually analyzed by using other mechanistic models.

Key words: Differential permeation – solvent diffusion – flat and tubular membranes

Introduction

The measurement of diffusion, permeation and solubility coefficients is of considerable practical and theoretical interest. Three experimental methods can be used to determine the transport parameters of gases in polymers [1]:

1) Integral permeation method (also called time-lag method) in which the cumulative amount of a penetrant that has passed through a membrane is determined as a function of time.
2) Sorption method, in which the cumulative amount of a penetrant absorbed in a polymer is determined continuously.
3) Differential permeation method, in which the permeation rate through a membrane is measured directly as a function of time.

A more convenient variant, which uses a rectangular pulse at the upstream side of the membrane instead of a step concentration change, has been proposed by Palmai and Olaj [2].

Different techniques for the estimation of the diffusion coefficient of gases were well discussed in the literature [1, 2]. Although the diffusion of molecules issued from a liquid medium in polymers is very important for separation processes involving dense membranes, and more specifically the pervaporation process, little attention was paid to such a phenomenon [3].

In the study of the diffusion of solvents in polymer membranes, independently to technical problems which may be solved by an appropriate design of the apparatus (condensation of the permeate vapor, sensitivity of the detectors, . . .), other phenomena which are related to the interactions between a liquid solvent and the membrane may appear. This is due to the fact that the pervaporation process is based on the difference in the interactions between polymer and solvents, which in turn may cause changes in the polymer structure and, consequently, in the polymer properties.

The sorption method, which uses the microbalance output, is not suitable for liquids (due to strong buoyancy effect) neither is it suitable for

mixtures of penetrants. The advantages of the differential permeation method over the others in the case of gas permeation have been outlined in the literature [1].

Since the membrane in pervaporation is in contact with the feed liquid on one side while the other side is kept under low vapor pressures (by using vacuum or a sweeping gas), the differential permeation method appears to be the most attractive due to its very similar operating conditions: the membrane is put into contact with the liquid to be studied at time zero, and the permeation rate of solvents that is extracted from the other side into a gas stream is monitored as a function of time. Watson and Payne [4] used such a method to determine the influence of different parameters on the diffusion coefficients of organic compounds through a Silicone membrane. However, these authors used an approximation method which normally would not provide an indication of appropriateness of the concentration-independent Fick law.

In the first part, we would like to show that the differential permeation method when it is combined with the curve fitting method is not only interesting for the measurement of the diffusion coefficient, but also for the evidence of any deviation from the Fickian model for the study of some kinetic phenomena related to the behaviors of polymers in contact with solvents, such as swelling, chain re-organization, etc. In the second part, we report the use of this method to analyze a complex case, the diffusion of ethanol in water-ethanol mixtures through poly(vinyl alcohol) films of different crystallinity degrees, in which a two-pathway diffusion is evidenced.

Background

The permeation flux in the transient regime is obtained by solving the second Fick's law equations, which can be written in the following form for flat and tubular membranes:

Flat membrane

$$\frac{\partial C_i(t, x)}{\partial t} = \frac{\partial}{\partial x}\left(D_i \frac{\partial C_i(t, x)}{\partial x}\right) \tag{1}$$

Tubular membrane

$$\frac{\partial C_i(t, r)}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(D_i \frac{\partial C(t, r)}{\partial r}\right) \tag{2}$$

Solutions for constant D:
(boundary conditions)

$$C_i(0, x) = 0 \qquad C_i(0, r) = 0 \tag{3a}$$

$$C_i(t, 0) = C_{i0} \qquad C_i(t, b) = C_{i0} \tag{3b}$$

$$C_i(t, l) = 0 \qquad C_i(t, a) = 0 \tag{3c}$$

$$J_{\text{flat}} =$$

$$\frac{DAC}{l}\left(1 + 2\sum_{n=1}^{\infty}\left((-1)^n \exp\left(\frac{-n^2\pi^2 Dt}{l^2}\right)\right)\right) \tag{4}$$

$$J_{\text{tubular}} =$$

$$\frac{2\pi DLC}{\ln(b/a)}\left(1 + 2\ln(b/a)\right.$$

$$\left. \times \sum_{n=1}^{\infty}\left(\frac{J_0(\alpha_n a)J_0(\alpha_n b)}{J_0^2(\alpha_n a) - J_0^2(\alpha_n b)}\exp(-\alpha_n^2 Dt)\right)\right), \tag{5}$$

where α_n is the positive root of equation $U_0(a\alpha_n) = 0$ with

$$U_0(r\alpha_n) = J_0(r\alpha_n)Y_0(b\alpha_n) - J_0(b\alpha_n)Y_0(r\alpha_n) \tag{6}$$

and J_0 and Y_0 being the zero order Bessel functions of the first and second kind, respectively [1].

These expressions of flux are valid for any component in the mixture. In our experimental conditions, i.e., constant concentration C of the penetrant at one face of the membrane (or at the outer face of the tubular membrane) and quasi-nil concentration at the other face (or the inner face of the tubular membrane) at time $t \geq 0$ and nil concentration everywhere at time $t = 0$, the expressions of permeation flux versus time for both cases can be obtained analytically for concentration-independent Fickian diffusion (4) and (5): where D is the diffusion coefficient, A is the membrane area, l is the membrane thickness, L is the length of the membrane tubing, b and a are respectively the outer and inner radii of the tubing [5, 6].

Analytical solutions can also be obtained in some other boundary conditions [6]. In other cases, e.g., concentration-dependent Fickian models, variable boundary conditions, the Fick equations may be solved numerically.

The diffusion coefficient can be rapidly but roughly estimated by using the $t_{1/2}$ value, i.e., the time at which the permeation flux reaches the half

of the asymptotic permeation rate J_0. For greater accuracy, Rogers et al. [7] used a small-time curve-fitting method, and Pasternak et al. [8] presented alternate small-time formulas applicable over wider ranges of time. Felder et al. suggest the use of a moment method which includes data points of the transient response instead of part of them [5].

All these methods, except one, require a knowledge of J_0. Moreover, they do not provide an indication of the validity of the concentration-independent Fickian model used for the data analysis.

In this work, we propose the use of a numerical curve fitting method (instead of a linearization [7]) starting from the small-time part, but not limited to it. The fitting is extended to a maximum of data points of the response, and as the extension progresses, the quality of the fit is checked. With the development of fast personal computer and fitting software, this can be done much more easily nowadays. Such method provides an indication of the appropriateness of the Fickian model, and makes possible a detection of any departure from the ideal Fickian model, in any range of time. Eventually, other diffusion models might be established and checked in a similar procedure.

The determination of the permeability coefficient in steady state regime (and the sorption coefficient if the Fickian model is valid for the whole response) is also possible with this method when the detector is correctly calibrated. If only the diffusion phenomenon is studied, no calibration will be needed.

In this case, dimensionless permeation rate and time are used:

$$J_r = \frac{J}{J_0} \tag{7}$$

$$t_r = \frac{Dt}{l^2}, \tag{8}$$

where J_0 is the steady-state permeation rate. Equations (4) and (5) can be rewritten as:

$$J_r = 1 + 2B \sum_{n=1}^{\infty} K_n \exp(-\beta_n t_r) \tag{9}$$

for a flat membrane:

$$K_n = (-1)^n \tag{10}$$

$$\beta_n = n^2 \pi^2 \tag{11}$$

$$B = 1 \tag{12}$$

and for a tubular membrane:

$$K_n = \frac{J_0(\alpha_n a) * J_0(\alpha_n b)}{J_0^2(\alpha_n a) - J_0^2(\alpha_n b)} \tag{13}$$

$$\beta_n = \alpha_n^2 l^2 \tag{14}$$

$$B = \ln\left(\frac{b}{a}\right) \tag{15}$$

α_n are the roots of the zero-order Bessel function of the first kind

J_r varies in the range of 0 to 1, while t_r can exceed 1.

In the numerical fitting, we introduced two more adjustable parameters, the J_0 and a time delay which accounts for the uncertainty on the starting time. Generally, the number of experimental points is very high and allows a precise fitting if the diffusion model is appropriate.

In case of membrane thickness heterogenity, the resulting flux is calculated by using the model of "patchwork membrane": The membrane is considered to be a combination of patches of membranes of constant thickness whose surface areas, S_i, are proportional to the probability for finding such a thickness in a discrete Gaussian distribution centered at the mean value of thickness l_0.

Standard Gaussian distribution:

$$y(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(\frac{-(x-1)^2}{2\sigma^2}\right)$$

$$\text{with} \quad 0 < x < 2 \tag{16a}$$

Mean thickness value of a patch i:

$$l_{m,i} = l_0 * \frac{\int_{l-\delta}^{l+\delta} y(x) x \, dx}{\int_{l-\delta}^{l+\delta} y(x) \, dx} \tag{16b}$$

Surface area of patch i:

$$S_i = \int_{l-\delta}^{l+\delta} y(x) \, dx \tag{16c}$$

Total flux through the membrane:

$$J_{total} = \sum_{i=1}^{n} (J_i(l_{m,i}) * S_i) . \qquad (16d)$$

Experimental procedure

Membranes: Silicone TS 605 membrane (thickness: 1.25×10^{-4} m) was provided by Rhône-Poulenc. Silicone tubing (Silastic tubing) was purchased from Dow Corning Corp. Its internal and external radii are 1.5×10^{-4} m and 3.165×10^{-4} m, respectively. Poly(vinyl alcohol) film (thickness: 3.3×10^{-5} m) was provided by "Papeteries de Mauduit".

Apparatus

The cells (glass cell for flat membranes or potted membrane tubings) and the experiment set-up are shown in Fig. 1. The membrane and cell are first dried on-line under dry sweeping gas, and then dipped into the liquid tank. In the case of dilute solutions of organics which are extracted by the membrane, the volume of the liquid should be high enough to ensure constant concentration of organics during the experiment. The permeation rate can be monitored by means of appropriate instrumental detectors. We used the mass spectrometer (Nermag 10-10-R) for chloroform, and Flame ionization detector (FID) (Intersmat IGC 16) for other organics. However, other sensors, such as electron capture detector, thermal conductivity detector, or humidity detector, can also be used. Mass spectrometer would be the most universal sensor provided that an automatic safety valve is inserted on the effluent line to protect the instrument from accidental leak. Otherwise a prior separation on chromatographic column would be needed and affect the time interval between data points.

A source of errors derives from spurious time delays due to holdup times, residence and mixing times in chambers adjacent to the membrane. In order to minimize these times, the volume of different parts of the effluent line was minimized and attention was focused on parts which can promote mixing. A pure time delay can be easily taken into account by introducing it as a parameter in the equation for curve fitting.
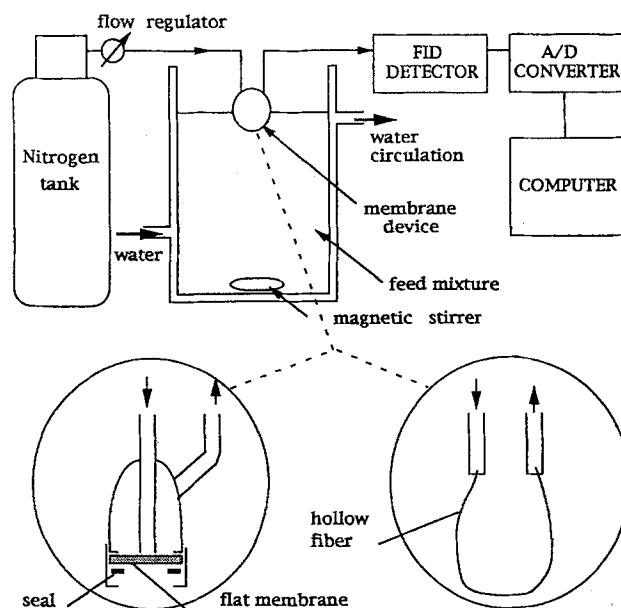

Fig. 1. Differential permeation apparatus and membrane devices for flat membranes and hollow fibers

Special care has also to be taken to avoid any leak by diffusion through sealing materials, connectors, tubings. The sweeping gas flow rate must be adjusted according to the permeability and the membrane area to ensure low vapor pressure in the effluent gas.

Results and discussion

Figure 2 shows the responses of a flat silicone membrane to ethanol and a tubular silicone membranes to chloroform, both solvents are dissolved in water. In the case of chloroform, the solution was very dilute (0.3 ppm), but the determination is still possible with the mass spectrometer detector. One can observe the similar patterns (sigmoidal), in spite of the difference in the solutions derived for flat and tubular membranes. In both cases, good fittings were obtained by using the concentration-independent Fickian models in the whole concentration range. No drift of the response at longer times was observed in these cases, i.e., there is no observable relaxation in the polymer network.

Table 1 lists the values of different parameters and those of the diffusion coefficient obtained, by fitting with Eqs. (9)–(12), for different organic solutes in dilute aqueous solutions and the Silicone TS605 membrane. It can be observed from these

Table 1. Diffusion coefficient and permeability coefficients of some organic solutes in aqueous solutions as determined from differential permeation data through Silicone TS 605 flat membrane at 30 °C

Solute	Solute concentration (g/l)	Diffusion coefficient ($cm^2 s^{-1} \times 10^7$)	Permeability ($cm^2 s^{-1} \times 10^8$)
Ethanol	1.0	6.6	5.37
n-Propanol	1.0	6.1	15.3
n-Butanol	1.0	5.2	28
n-Pentanol	1.0	4.1	50.8
Phenol	0.5	1.5	9.9
Pyridine	0.1	0.8	59.3
Benzene	0.01	9.8	5210
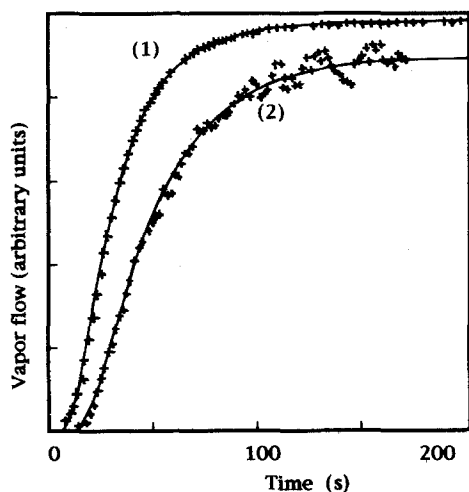
Fig. 2. Permeation fluxes in the transient regime for: 1) silicone flat membrane and a 1% aqueous solution of ethanol with a flame ionization detector and 2) silicone hollow fiber (silastic) and 0.3 ppm chloroform in water with a mass spectrophotometer detector. Experimental points and curves obtained by fitting Eq. (9) and Eqs. (10)–(12) for 1) and Eq. (9) and Eqs. (13)–(15) for 2)
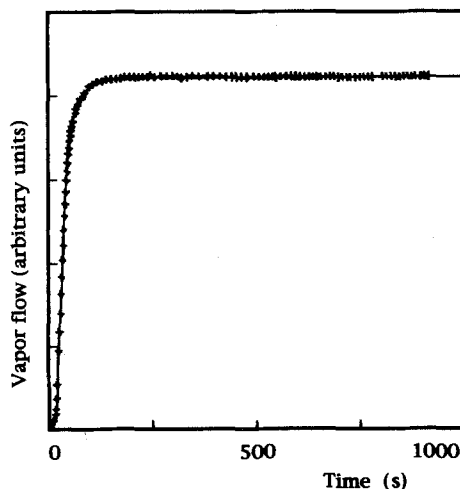
Fig. 3. Fitting of the experimental permeation fluxes obtained with a cylindrical tubing (Silastic) and a 0.5 wt.% aqueous solution of ethanol at 30 °C by using Eq. (9) with both Eqs. (10)–(12) and Eqs. (13)–(15). The same values were obtained for the permeability and the diffusion coefficient ($13 \cdot 10^{-6}$ cm^2 s^{-1}) and the calculated transient permeation curves are identical

values that for the series of short chain aliphatic n-alcohols, the permeability coefficient increases greatly as the number of Carbon atoms increases, but the diffusion coefficient is not altered to a great extent. This means that the longer the alcohol chain, the higher its sorption by the silicone polymer. Some aromatic solutes (pyridine, benzene) give rise to very high permeability with rather low diffusivity, indicating their strong sorption by the membrane.

Curve-fitting for cylindrical membranes, which involves Bessel functions, is tedious due to complex arithmetic calculations. Therefore, we tried to

use Eqs. (9)–(12) for flat membrane and Eqs. (9), (13)–(15) for tubular membranes to fit the response of the tubular membrane. The system of Silastic membrane-aqueous solution of ethanol and Flame Ionization Detector was chosen because of the low level of noise in the signals obtained. Surprisingly, very good fitting was obtained with the equations for flat membranes (as good as in the case of equations for tubular membranes), with the membrane thickness as the only known parameter (Fig. 3). The calculated curve is identical to the one obtained with equations for the flat membrane. The values obtained for the

diffusion coefficient and for the permeability are also identical (a differences less than 1% from the best fits).

In order to check the validity of this equation in the case of a cylindrical membrane, simulations were performed by using both equations, and the difference between the two permeation rates are calculated as a function of time. As numerical solutions of the equation for tubular membrane depends largely on the absolute values of the outer and inner radii of the tubing, the values of the relative deviation from the reduced permeation flux for the true response of the tubular membrane are plotted as a function of the reduced time (Fig. 4). The use of these reduced parameters make possible the comparison of the two equations, which is otherwise impossible. It can be observed that the magnitude of the deviation depends on the values of b and a, more precisely, on the b/a ratio. For $b/a < 2$, the deviation is less than 1% for $t_r > 0.05$ (Fig. 4), i.e., for the range of time of true interest (for shorter time, the permeation rate is practically nil). The absolute deviation is maximum at t_r about 0.10 and it increases as the b/a ratio increases. For instance, in the case of $b/a = 1.2$, the maximum deviation is less than 0.1%. In the case of $b/a = 2$ (e.g., the Silastic tubing), such a deviation is about 1%. The values of the diffusion coefficients obtained by independent fittings with Eqs. (10)–(12) and (13)–(15) for different cases are practically identical. The fact that a same and unique value is obtained by the numerical best-fitting with both equations shows the good reliability of the use of the simpler Eq. (4) for the determination of the diffusion coefficient of penetrants through tubular membranes. Although there is no clear explanation for the same transient permeation rates obtained in both membrane geometries, this result can be favorably used in the determination of the diffusion coefficient of solvents through tubular membranes.

Influence of the inhomogeneity of the membrane thickness

The thickness of a film is more or less uniform depending on the preparation technique and the natures of the polymer and the solvent. In order to evaluate the effect of thickness fluctuation on the transient permeation rate, we performed numerical simulations of the response of a sample whose
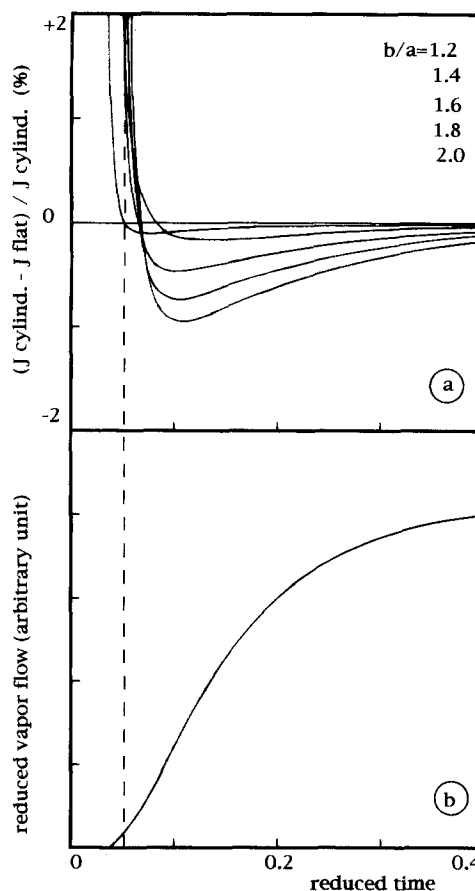

Fig. 4. Relative differences in the calculated transient permeation fluxes obtained with Eq. (9) associated with Eqs. (10)–(12) (flat membrane) and with Eqs. (13)–(15) (tubular membrane) as a function of reduced time, for tubular membranes of a same value of thickness (0.5 mm) and of different values of b/a (1.2; 1.4; 1.6; 1.8; 2). The sigmoidal curve in the lower part is the reduced permeation flux versus reduced time

characteristics correspond to Silastic ones, by using the following procedure:

The membrane is regarded as a patchwork. The thickness of the patches varies according to a discrete Gaussian distribution centered at the mean value of the membrane thickness (Eq. (16)).

The total permeation rate at a given time is obtained by summing the individual permeation rates through different patches, each of them is weighed by a surface area coefficient which is previously calculated by an integral of the Gaussian probability in the corresponding range of thickness.

The simulated responses for different values of the standard deviation (and for the same first

order moments for the thickness) are shown in Fig. 5. The larger the deviation, the higher the permeation rate. It can be noted that the shape of the curve changes with the value of the standard deviation. It is therefore possible to calculate the standard deviation of the thickness distribution of a membrane by numerical fitting of the experimental data by using Eq. (16) when the diffusion coefficient is constant. We found a value of 5% for the standard deviation for the thickness of the Silastic tubing. As a consequence of the influence of the distribution of the membrane thickness around a mean value, a small standard deviation in the membrane thickness is the pre-requisite condition to avoid mis-interpretation of the behavior of a polymer in permeations of liquids.

Fig. 5. Calculated permeation fluxes versus time for membranes of the same mean thickness (167 μm) but with different standard deviation of their thickness (0.02, 0.1, 0.2). The thickness distributions are given at the center of the figure

Evidence of different types of deviation from the Fickian diffusion with constant diffusion coefficient

One can conclude that there is a deviation from this diffusion law when a good fitting cannot be obtained. Some cases of deviation are given below.

Deviations due to a change in the chain organization in the polymer film

Polymer chains in a solid material may change their configuration under the effect of the penetrating solvent. Such changes may be very complex. The incorporation of solvent molecules in a polymer network leads to an increase in the free volume, a decrease in the glass transition temperature, and therefore an increase in the chain mobility. The swelling stress tend to expand the polymer network, which opposes by its elasticity. This results in a change in a chain organization which affects, more or less, the permeation rate. The monitoring of the permeation rate provides an opportunity to evidence a change in the polymer structure. A study of the influence of operating conditions, the original structure of the material, and its change with time, with the operating conditions, and with the nature of the solvent (or the composition of a solvent mixture) would allow a better understanding of the behavior of a polymer-solvent system. We do not have the ambition to describe all possible behaviors in this paper. Instead, we will show some examples
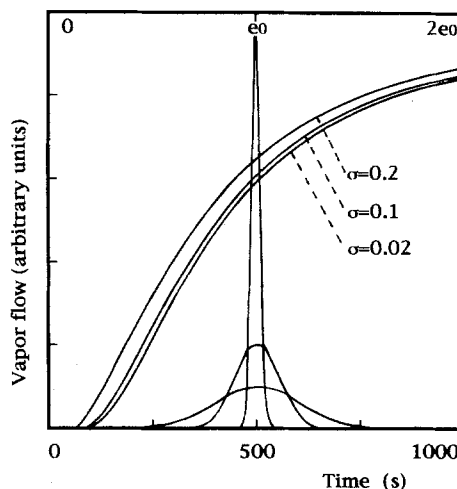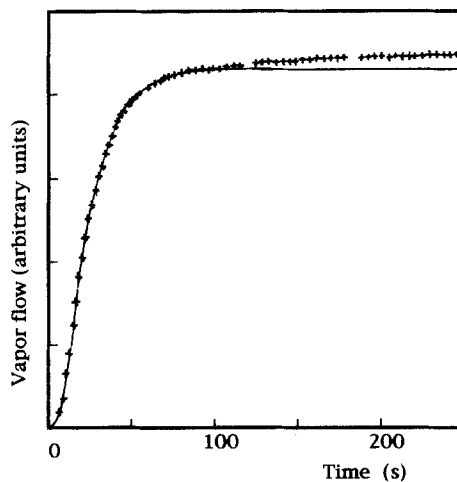

Fig. 6. Experimental points and calculated curves for the Silastic tubing and a 1% aqueous solution of 2-pentanone at 30 °C

to illustrate the potential of the differential permeation method.

Figure 6 shows a case in which the permeate rate slowly increases with time at the end of the transient regime of the Fickian diffusion. It may correspond to a case of slow relaxation of the polymer network which was already mentioned in some cases of vapor sorption [9]. The amplitude, and the time-dependence of this increase would depend on the polymer-solvent system. Chain reorganization is a distinct phenomenon and the

change in the permeation rate will not obey the Fickian kinetic, i.e., a good fitting could not be obtained with the Fickian kinetic equation. However, much effort would be required to describe such a phenomenon. In this case the properties of the material changes with time and lead to a changing concentration profile in the film thickness.

Figure 7 shows the cases of permeation of organic solvents through a poly(vinyl alcohol) film in which a maximum was observed. The permeation rate decreases steadily after the maximum, or passes by a plateau. Other independent experiments showed that the crystallinity degrees of the film increases consecutively to the permeation [10]. These results were interpreted on the basis of a solvent-induced crystallization. The differential permeation method allowed to evidence a drastic decrease in the diffusive transport with time, which was showed, by means of complementary studies, to be due to the chain re-organization into (impermeable) crystalline regions.

Deviations due to competitive diffusive transports in a two-pathway diffusion

Figure 8 shows a case of two-pathway diffusion which will be analyzed in details in part II of the paper [11]. We observed two sigmoidal permeation waves; both of which can be fitted with the Fickian model with concentration-independent diffusion coefficients.

Deviations due to a dependence of the diffusion coefficient on the local concentration

During the transient regime, the penetrant concentation profile in the membrane changes with time: the local-concentration will increase with time at any point in the membrane. If the diffusion coefficient varies with the penetrant concentration, the transient permeation pattern will deviate from the Fickian sigmoidal pattern. Although we did not observe any case of this type, the qualitative change in the transient pattern could be predicted from the concentration-dependent diffusion law. For instance, if the diffusion coefficient increases with the penetrant concentration, the small time permeation rate will be lower, and
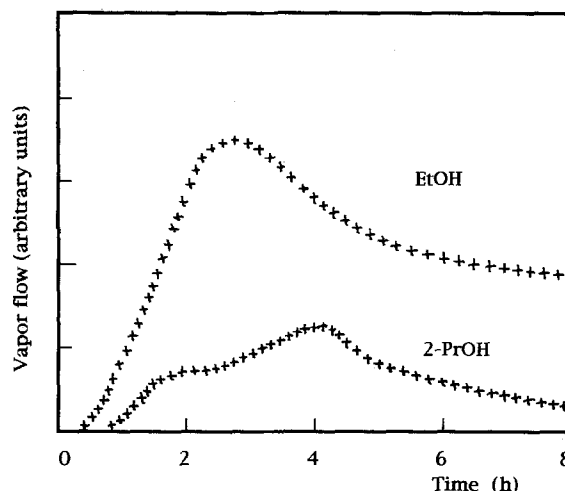

Fig. 7. Permeation rates of ethanol and 2-propanol through the PVA membrane versus time (30 °C). The experimental points at large time, showing the slow drift of the permeation rates
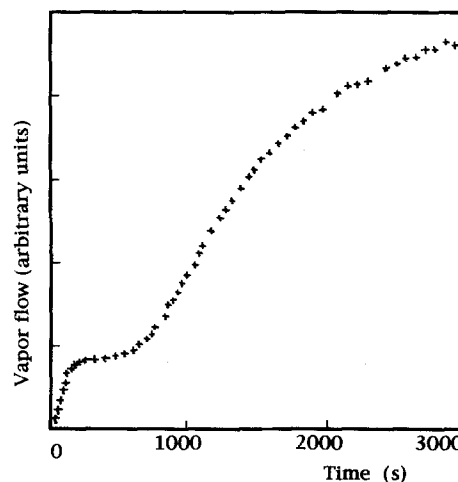

Fig. 8. Experimental points obtained with a semi-crystalline PVA membrane (40% crystallinity) and the water-ethanol mixture containing 35 wt.% water at 40 °C

the large time permeation rate will be higher than those of the concentration-independent diffusion law. Numerical fittings could also be performed with different models to find the most suitable one.

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