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NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

Characterization of polycarbonate nuclear track-etched membranes by means of the gas permeation method

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Abstract

The gas permeation technique has been applied to analyse flat polycarbonate nuclear track-etched membranes (TEMs), with pore size smaller than 100 nm. The samples analysed were the commercial membranes Nuclepore and the ones which are being developed at IPEN using the IEA-R1 research reactor (2 MW). A linear trend has been obtained for the flux versus transmembrane pressure for various gases, when measured at a constant temperature of 293 K, indicating a constant permeability for this kind of membranes. Furthermore, the permeability has shown a tendency of increasing when the molecular weight of the gases decreased following the Knudsen model predictions. An estimation of the pore radius for all TEMs were realized using the Knudsen equation and the results obtained were in good agreement with those determined by the SEM technique. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Despite the availability of several methods to estimate small pore size in membranes, these methods generally involve very small membrane areas, some analysis ambiguity and/or require sample modifications [1–4]. Even using a powerful technique such as atomic force microscope (AFM), it is very difficult to recognize pore sizes around 10 nm [5]. Therefore, the characterization of small pore size in the ultrafiltration range for porous membranes has been achieved only partially with the techniques presently available. The measurement of the gas permeability coefficient as a function of the mean pressure across the membrane has been used by some authors to characterize microporous and asymmetric membranes [6,7]. The main objective of the present work was to test the possibility of characterizing the polycarbonate nuclear track-etched membranes (TEMs) by means of this technique, in order to complement the classical methods of characterization.

The measurement of the flow rate of a gas through a porous medium has provided to be useful for determining the mean pore radius of porous material [8]. As the flow rate of the gas is a linear function of the mean pressure across the membrane, the permeability is obtained by the angular

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coefficient of the straight line fitted to the experimental data and the mean pore radius can be determined by using the appropriate theoretical diffusion equation [7].

Various transport mechanisms of gases through porous membranes can be distinguished depending on the structure of the membrane. These are: Surface, Knudsen and Poiseuille diffusion [9–11]. An illustration of these three gas transport mechanisms can be seen in Fig. 1.

The gas flux density through a membrane per unit area and per unit time is defined by [10,11]:

$$J = P\Delta p, \tag{1}$$

where J is the gas flux density (mole $\mathrm{s^{-1}\,m^{-2}}$), $P = P_s + P_k + P_p$, the total permeability (mole $\mathrm{s^{-1}\,m^{-2}\,Pa^{-1}}$) corresponding to the sum of those three gas transport processes and Δp is the pressure difference (Pa) across the membrane. Knudsen diffusion occurs when the size of the pore is smaller than the mean free path of the gas molecules [12]. In this case the gas molecule collide much more frequently with the pore wall than with another molecule and low molecular weight gases therefore are able to diffuse more rapidly than the heavier ones. For pore sizes smaller than 100 nm and at low pressures, Knudsen diffusion is the predominant transport mechanism and the total permeability is given by [13]

$$P = P_k = \frac{2\varepsilon\mu_k v r}{3RT\delta}, \tag{2}$$

where P_k is the permeability by Knudsen diffusion, ε is the porosity and equal to $n\pi r^2$, n is the number of pores per $\mathrm{m^2}$, r(m) is the mean pore radius of the membrane, μ_k is the shape factor which are equal to unity for uniform parallel straight pores normal to the surface of the membrane. For IPEN TEMs this factor was estimated to be 0.90 by considering angles effects according to our previous paper [14] and 0.80 for Nuclepore membranes [15], R is the gas constant (8.314 $\mathrm{J\,mol^{-1}\,K^{-1}}$), T is the absolute temperature (K), δ is the thickness of the membrane and v is the average velocity ($\mathrm{m\,s^{-1}}$) of the particular gas which is equal to $(8RT/\pi M)^{1/2}$. Substituting the average velocity and the porosity into Eq. (2), we obtain:

$$P = \frac{cr^3}{\delta\sqrt{M}}, \tag{3}$$

where the constant $c = (4n\mu_k/3)(2\pi/RT)^{1/2}$ and M is the molecular mass of the gas ($\mathrm{kg\,mol^{-1}}$). Therefore, if the gas transport mechanism follows the Knudsen diffusion equation, then the parameter P must present a linear dependence with $1/(M)^{1/2}$.

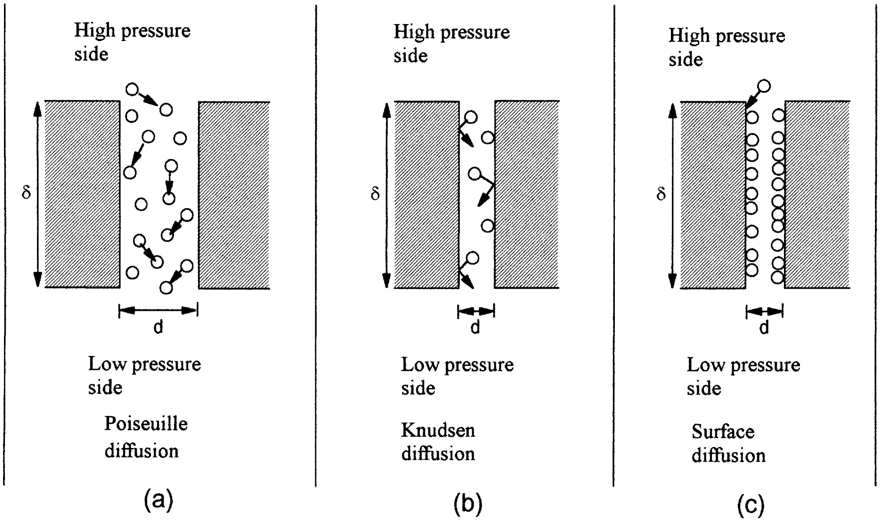

Fig. 1. Schematic drawings showing the main membrane gas transport mechanisms: (a) Poiseuille, (b) Knudsen and (c) surface diffusion.

2. Experimental

A gas permeation system (Fig. 2) was used for the determination of gas permeability through the TEMs. The equipment consisted of a pressurised gas cylinder, pressure regulator, membrane cell, pressure transducers and computer link for data logging. Membrane samples of 10 mm diameter were fixed in the gas permeation cell (Fig. 3) which was sealed by Nescofilm tape. This cell allows to apply a gas pressure on one side of the membrane (high pressure side) and to collect the gas passing through the membrane into a well known storage volume on the other side (low pressure). By monitoring the pressure on both sides of the permeation cell as a function of the time, the permeability of pure gases can be determined from the slope of the curve gas flow J (mol/(s m^2)) in the steady state, versus transmembrane pressure difference Δp (bar).

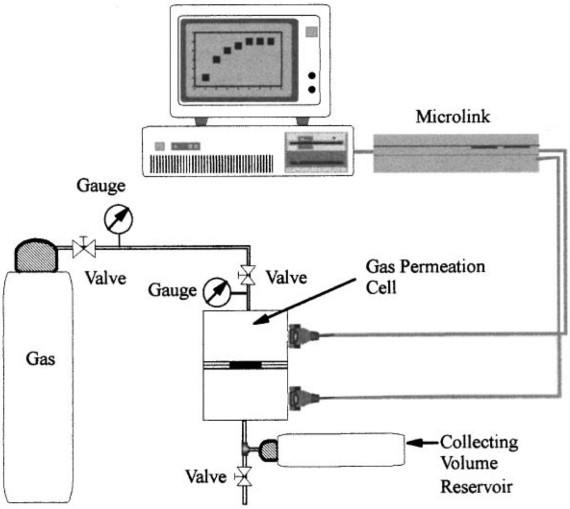

Fig. 2. Schematic diagram of gas permeation system.

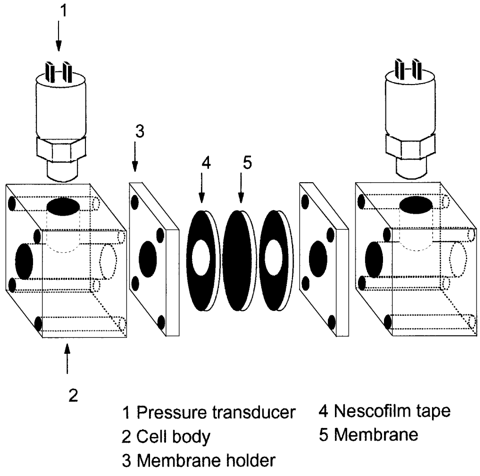

Fig. 3. Schematic diagram of gas permeation cell.

3. Results and conclusions

In this study, Nuclepore commercial membranes with nominal pore diameter of 15, 30 and 50 nm as well as TEMs developed at IPEN with mean pore diameter of 60, 65 and 72 nm, have been tested. The IPEN TEMs were produced by the fission track registration technique in Makrofol KG (8 μm thickness) using the IEA-RI research reactor (2 MW) [14]. A typical SEM microphotography of IPEN TEMs is presented in Fig. 4, for a membrane sample with mean pore diameter of 72 nm and pore density of 4.5E8 pores/cm^2.

Fig. 5 shows the linear dependence of the flux density with the transmembrane pressure across Nuclepore membrane of nominal pore diameter of 15 nm in accordance with Eq. (1) for several gases. Nuclepore membranes with nominal pore diameters of 30 and 50 nm gave equally good linearities. In Fig. 6 are presented the results of P versus $(1/M)^{1/2}$ obtained for the membrane with 15 nm pore diameter. For all membrane tested the permeabilities were inversely proportional to the square root of the molecular mass, in good agreement with Knudsen predictions (Eq. (3)).

A considerable variation of permeability in different Nuclepore samples having the same nominal pore size was observed and as example, Fig. 7 and Table 1 show the results obtained for 30 nm pore diameter membranes. The reason for such variation may be explained by the presence of multiple pores (clusters) in these commercial membranes. For IPEN TEMs is possible to observe such pore cluster formations (see Fig. 4) even they had been made with high level of pore uniformity due to

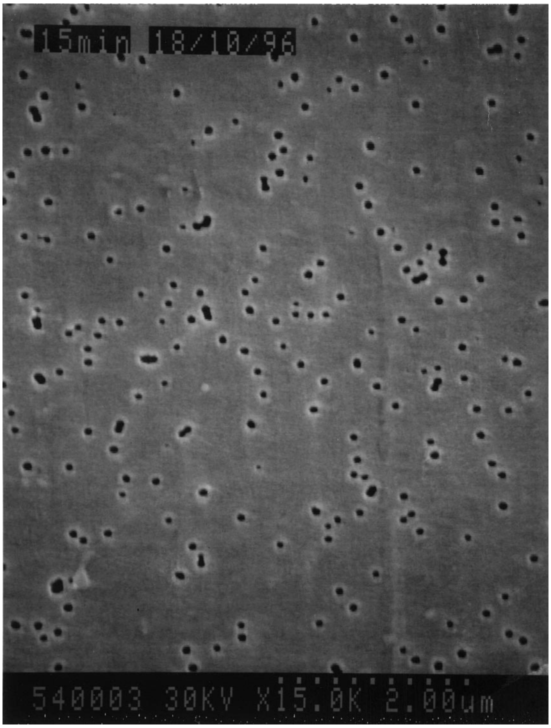

Fig. 4. Sample of TEMs developed at IPEN. Mean pore density: 4.5×10^8 pores/cm^2. Mean pore size: 72 nm.

the particular irradiation geometry used in their preparation [14].

To estimate the pore radius for these membranes we have considered only the lowest value of the measured permeability, where the number of pore clusters is expected to be minimum. As can be seen in Table 1, the permeability coefficient for sample No. 1 was the smallest and according to Table 2 the corresponding value of 2*r* calculated using the Knudsen equation was in better agreement with the one obtained by SEM.

The results obtained by N2 gas permeation for the six TEMs samples having different pore sizes are shown in Fig. 8 and Table 2 presents the permeabilities as well as the values of the mean pore diameters (2*r*) estimated by the Knudsen equation. It was not possible to measure the experimental values of 2*r* and *n* for the Nuclepore membrane with nominal pore diameter of 15 nm, due to difficulty in obtaining clear SEM microphotography.

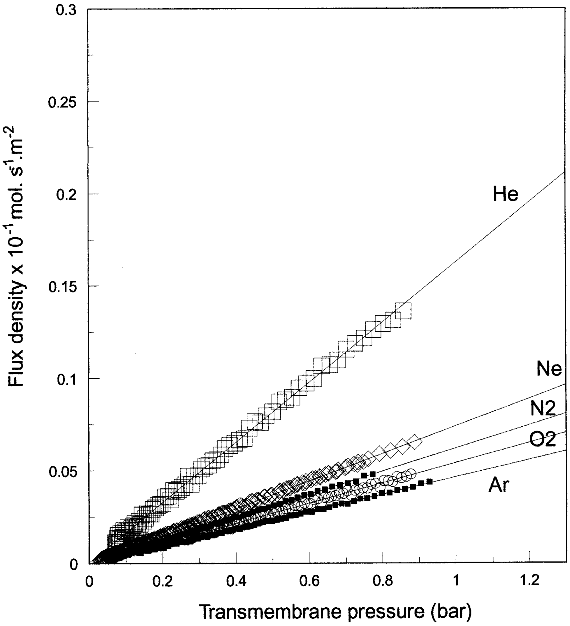

Fig. 5. Flux densities of several gases plotted as a function of transmembrane pressure for a Nuclepore membrane with nominal pore diameter of 15 nm. Other samples yielded similar results.

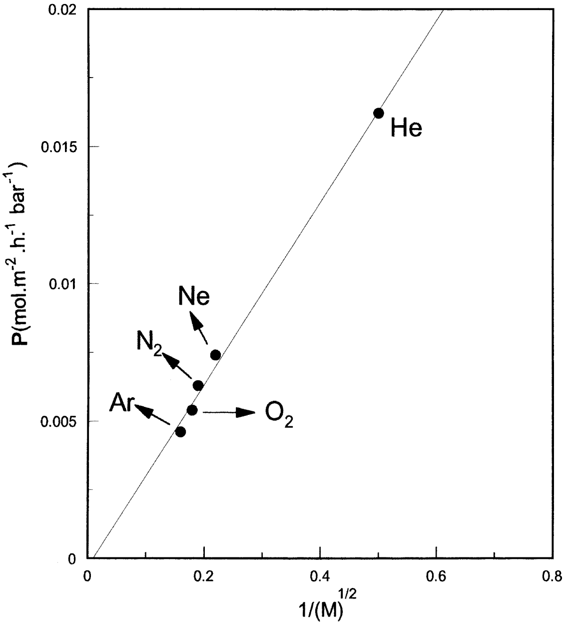

Fig. 6. Variation of the permeability (*P*) as a function of the gas molecular mass (*M*) for Nuclepore TEM, nominal pore diameter of 15 nm.

According to the Nuclepore catalogue [16] the mean pore size and the mean pore density are held to a tolerance range of + 0%, − 20% and + 15%, − 15% of the rated values respectively. Thus, the results obtained in this work by SEM for the commercial membranes are in good agreement with the values reported by Nuclepore, at least within the tolerance ranges.

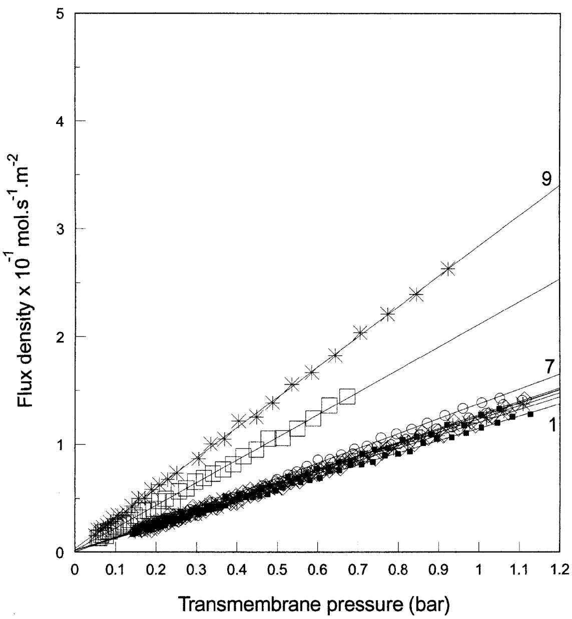

Fig. 7. Variation of the nitrogen flux density with the transmembrane pressure obtained for some 30 nm pore diameter Nuclepore TEMs.

As shown in Table 2, the average $2r$ results calculated by the Knudsen equation present good agreement with the values determined through direct measurements by SEM for all TEMs used in this work. Therefore, if we know the pore density in advance, through adjustment of the irradiation time during the manufacturing of these membranes, it is possible to estimate with good accuracy small pore size with diameter lower than 100 nm by the permeation method. This technique seems to apply

Table 1

Nitrogen permeabilities obtained (see Fig. 7) for some Nuclepore membranes with 30 nm nominal pore diameter

Sample no.	Permeability (10^{-1} mol/(s m^2 bar))	$2r$ (nm) by Knudsen theory
1	1.13	30.2
2	1.19	30.7
3	1.22	31.0
4	1.24	31.1
5	1.25	31.2
6	1.26	31.3
7	1.37	32.2
8	2.10	37.1
9	2.82	41.0

Table 2

Results obtained for the TEMs studied in this work by nitrogen permeation technique

Membrane samples	N_2 Permeability (10^{-1} mol/(s m^2 bar))	$2r$(nm) values calculated by Knudsen equation	Average $2r$(nm) obtained by SEM technique	Average pore density n determined by SEM technique (pore/m^2)
IPEN 1 (IP1)	5.61	57.5	(60.0 ± 2.5)	(5.2 ± 0.2) E12
IPEN 2 (IP2)	7.06	62.8	(65.0 ± 2.5)	(5.0 ± 0.2) E12
IPEN 3 (IP3)	8.55	69.4	(72.0 ± 2.5)	(4.5 ± 0.2) E12
Nuclepore 1 (N1)	0.075	12.3	— (15)[a]	— (6E12)[a]
Nuclepore 2 (N2)	1.13	30.2	(28.0 ± 3.0) (30)[a]	(6.1 ± 0.2) E12 (6E12)[a]
Nuclepore 3 (N3)	3.14	42.4	(42.0 ± 3.0) (50)[a]	(6.1 ± 0.2) E12 (6E12)[a]

[a] values reported in the Nuclepore catalogue.

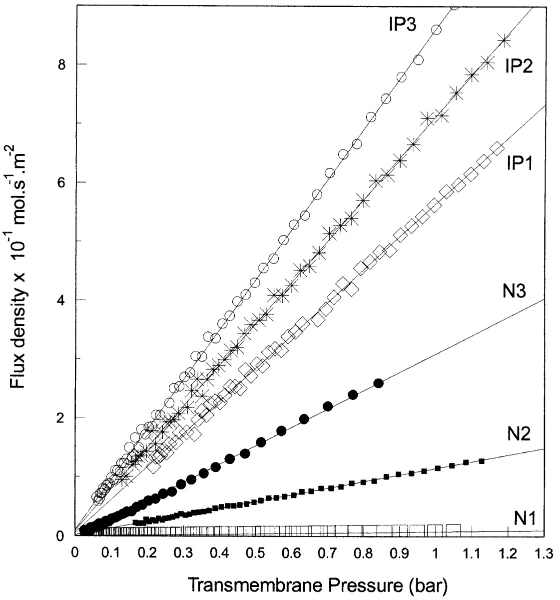

Fig. 8. Variation of the nitrogen flux density as a function of the transmembrane pressure for all TEMs tested in this work.

also well to analyse pore sizes around and even lower than 10 nm, where other methods present some limitations.

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