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A. Hernandez[a]; F. Martinez-villa[a]; J. A. Ibañez[b]; J. I. Arribas[a]; A. F. Tejerina[a]
[a] DEPARTAMENTO DE TERMOLOGIA FACULTAD DE CIENCIAS, UNIVERSIDAD DE VALLADOLID, VALLADOLID, SPAIN [b] DEPARTAMENTO DE FISICA FACULTAD DE CIENCIAS, UNIVERSIDAD DE MURCIA, MURCIA, SPAIN

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An Experimentally Fitted and Simple Model for the Pores in Nuclepore Membranes

A. HERNANDEZ and F. MARTINEZ-VILLA

DEPARTAMENTO DE TERMOLOGIA
FACULTAD DE CIENCIAS
UNIVERSIDAD DE VALLADOLID
47071 VALLADOLID, SPAIN

J. A. IBAÑEZ

DEPARTAMENTO DE FISICA
FACULTAD DE CIENCIAS
UNIVERSIDAD DE MURCIA
30001 MURCIA, SPAIN

J. I. ARRIBAS and A. F. TEJERINA

DEPARTAMENTO DE TERMOLOGIA
FACULTAD DE CIENCIAS
UNIVERSIDAD DE VALLADOLID
47071 VALLADOLID, SPAIN

Abstract

The porosities (percentage of empty volume over the total volume) of several Nuclepore membranes are measured by means of a pycnometric method which is shown. If cylindrical pores are assumed, the porosities can be calculated from the surface pore densities and mean pore radii, both measured by microscopy. The disagreement between these two methods implies that the pores are not cylindrical in shape. A model is proposed that assumes an internal pore radius, r_i, different from the external one, r_e (mean pore radius). When it is assumed that there is a mean angle, Φ, between the pores and the membrane surface, this angle can be calculated if we assume that the experimental surface pore density is the maximum one compatible with the model. From a comparison of calculated and experimental Φ, the maximization of the surface pore density can be tested.

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INTRODUCTION

The membranes used in microfiltration are generally prepared by casting a polymer solution (a mixture of cellulose nitrate and cellulose acetate in some mixture of solvents) on a suitable surface and then gelling the liquid film slowly by exposing it to humid air, (*1*). The final membrane consists of two continuous phases. One of them is the solid matrix and the other is a series of continuous pores filled with water and some residual solvent which are removed by drying (*2*).

In recent years, methods other than solvent casting have been developed for producing microporous membranes. The first of the new membranes was the Nuclepore membrane (*3*). This membrane is made by irradiating a thin polymeric film in a field of nuclear particles and then chemically etching the film to produce essentially straight-through circular pores. The process is based on a patent of Price and Walker (*4*). The patent describes the production of microporous mica by the radiation-track-etch method, but the Nuclepore membrane is actually made from a thin polycarbonate film which is more readily handled than mica. These membranes are available in pore sizes ranging from 0.01 to 12.0 μm. The principal advantages of Nuclepore membranes over solvent-cast membranes are that the pores are of rather precisely defined radii and go straight through the membrane. The Nuclepore membrane is also more uniform in thickness and weight. Because of these advantages, the Nuclepore membrane has found application in gravimetric aerosol filtration, particle size classification, microscopic analysis, certain areas of citology, chemotaxis, blood rheology studies, and plasmapheresis (*5*). Although the porosity (20–30%) of Nuclepore membranes is much lower than that of solvent-cast membranes (70–80%), the water permeabilities of the two types of membrane are actually comparable because the Nuclepore membrane is less than 10% as thick and the tortuosity of the pores is essentially unity.

Another type of membrane is made by exposing a polypropylene film to consecutive steps of cold stretching, hot stretching, and heat setting (*6*). The pore radii range from 0.02 to 0.04 μm. These membranes are water repellent, but surfactant-treated, water-wettable membranes are also available. As a filtration medium, the "molecular weight cut-off" of these membranes is approximately 100, putting it in the ultrafiltration rather than the microfiltration range. Another type of membrane is made from polyolefin dissolved in a suitable hot solvent which is then thermally quenched. On cooling, the solution separates into two continuous phases, and then the residual solvent is extracted. Other membranes are those from expanded polytetrafluoroethylene (PTFE) and the asymmetric membranes (*7, 8*).

We have studied both the Nuclepore membranes as porous media and some of the consequences of their porous structure. Thermoporometric analysis of Nuclepore membranes (*9*) has shown a distribution for the pore radii between 50 and 150% of the mean pore radius, including a high peak for it which is a little larger than that obtained from microscopy or from Teorell's half time method (*10*).

Porosity can be directly measured by the pycnometric method, as shown later in this paper, and also by assuming cylindrical pores. Disagreements between these methods have led us to establish a pore model which assumes an internal radius r_i and an external radius r_e. The internal radius can be altered to make the two porosities agree.

When the mean angle between pores and the membrane's surface, Φ, is assumed to be less than $\pi/2$, then the internal radius differs from r_i and the Φ angle can be calculated if the experimental surface pore density is assumed to be at a maximum compared to the pore model. Comparison of calculated and experimental Φ allows determination of whether the surface pore density is maximized or not.

POROSITY MEASUREMENTS

The porosity, defined as the percentage of empty volume over the total volume, is given by

$$\theta = \left(\frac{V_e}{V_t}\right)100 = \left(\frac{V_t - V_{\text{mat}}}{V_t}\right)100 = \left(1 - \frac{V_{\text{mat}}}{V_t}\right)100 \qquad (1)$$

where V_e is the empty volume of the membrane and V_t is its total volume:

$$V_t = d\pi R_0^2 \qquad (2)$$

where d is the membrane thickness, R_0 is the radius of the membrane (circular in shape), and V_{mat} is the volume of the solid matrix of the membrane. In order to obtain the porosity θ, V_{mat} is obtained from the following masses:

(1) m_1 of a dried membrane
(2) m_2 of a pycnometer leveled with pure water at 298.0 ± 0.1 K

(3) m_3 of a pycnometer containing the membrane and leveled with pure water at 298.0 ± 0.1 K

These masses are related by

$$m_3 = m_2 + m_1 - V_{mat}\rho_{H_2O} \tag{3}$$

where ρ_{H_2O} is the water density at 298.0 ± 0.1 K (0.9970 g/cm^3 (*11*)).

By solving Eq. (3) for V_{mat} and substituting into Eq. (1),

$$\theta = \left(1 - \frac{m_1 + m_2 - m_3}{d\pi R_0^2\rho_{H_2O}}\right)100 \tag{4}$$

where R_0 (measured with a cathetometer) and the thickness d (measured by microscopy in a transversal section) are known. Equation (4) allows us to obtain the porosity θ. It has been assumed that, according to manufacturer's data, there is no water absorption into the polycarbonate matrix.

On the other hand, the porosity can be obtained from

$$\theta' = A_t/A_g = \pi r_e^2 N \tag{5}$$

assuming the pores are cylindrical in shape, and A_t is the membrane area available for transport, A_g is the geometric area of the membrane, N is the surface pore density, i.e., the number of pores per surface unit, and r_e is the mean pore radius (both N and r_e are measured by microscopy).

In Table 1 the values of N, r_e, θ, and θ' are shown for several Nuclepore membranes. It is evident that θ is always larger than θ'. This inequality implies that there is an internal radius r_i.

PERPENDICULAR PORES

From the fact that $\theta > \theta'$, it is evident that the pores are not cylinders but that there is a widening inside the pores. Therefore, the mean pore may be assumed to have an internal radius r_i larger than the external one r_e. We know that pores have nearly circular cross sections on the membrane surfaces as well as inside the membrane, and that widening increases continuously up to the center of the membrane and then decreases symmetrically, so we can assume the mean pore is a revolutionary parabola whose parameters must be fitted in order to adjust the

TABLE 1

Values of N, r_e (measured by scanning microscopy), θ, and θ′ (obtained from Eqs. 4 and 5). The Thickness, d, of the Membranes, Which Is Needed in Order to Use Eq. (4), Has Been Measured by Transmission Microscopy and Coincides with That Given by the Manufacturer, $d = 10 \pm 1$ μm

Membrane	$N \times 10^{-9}$ (pores/m^2)	r_e (μm)	θ (dimensionless)	θ′ (dimensionless)
M02	3000 ± 100	0.060 ± 0.001	23.8 ± 1.6	3.4 ± 1.0
M04	940 ± 50	0.190 ± 0.003	30.5 ± 1.5	10.4 ± 3.0
M06	270 ± 41	0.217 ± 0.004	21.7 ± 2.0	4.0 ± 1.2
M08	306 ± 45	0.340 ± 0.006	36.1 ± 1.0	11.4 ± 3.2
M10	50.7 ± 2.5	0.411 ± 0.008	21.2 ± 2.0	2.7 ± 0.9
M20	25.2 ± 2.0	0.780 ± 0.009	15.7 ± 1.7	4.8 ± 1.3
M50	5.3 ± 1.5	1.820 ± 0.010	9.8 ± 1.0	5.4 ± 1.5

experimental results for porosity. The mean pore, assumed to be perpendicular to the membrane surface, is shown in Fig. 1(a).

The generating parabola (see Fig. 1a) is

$$y(x) = -4\,\frac{r_i - r_e}{d^2}\,x^2 + 4\,\frac{r_i - r_e}{d}\,x + r_e \qquad (6)$$

Therefore, the mean volume of a parabolic pore is

$$V_{\text{par}} = \pi \int_0^d y^2(x)dx = \pi\left(\frac{8}{15}\,r_i^2 + \frac{4}{15}\,r_i r_e + \frac{3}{15}\,r_e^2\right)d \qquad (7)$$

while the mean volume of a cylindrical pore is

$$V_{\text{cyl}} = \pi r_e^2 d \qquad (8)$$

In order to obtain r_i from r_e, we can use

$$\frac{\theta}{\theta'} = \frac{V_{\text{par}}}{V_{\text{cyl}}} = \frac{8}{15}\left(\frac{r_i}{r_e}\right)^2 + \frac{4}{15}\left(\frac{r_i}{r_e}\right) + \frac{3}{15} \qquad (9)$$

where r_i is an adjustable parameter. This equation permits us to obtain r_i from θ, θ′, and r_e (see Table 1). In Table 2 the values of r_i are shown for the Nuclepore membranes we have studied. In Fig. 2 the internal radius r_i is

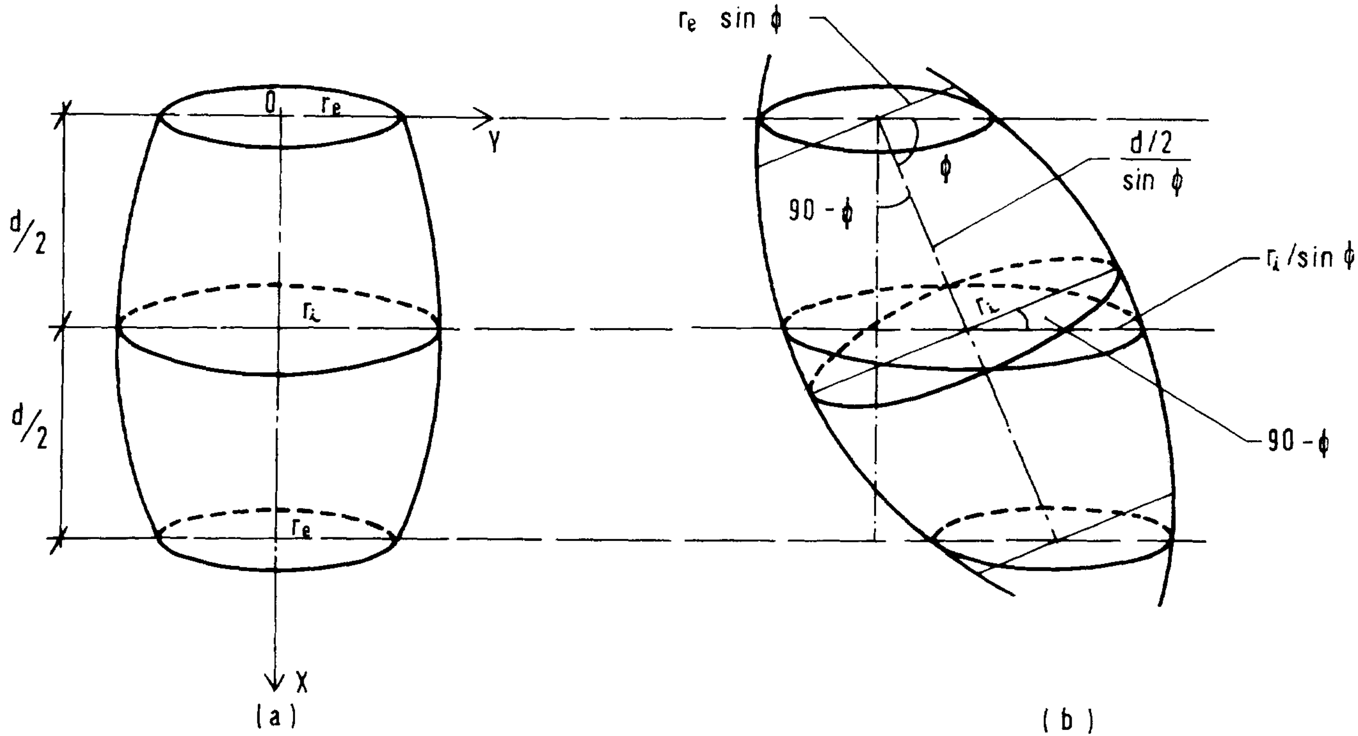

FIG. 1. A mean pore perpendicular to the membrane surface (a), and, taking into account that the pores are actually sloped, with respect to the membrane surface with a mean angle Φ (b). The pore radii are very much smaller and the thickness of the membrane, *d,* is very much greater than have been drawn. Therefore, the generating parabola is much flatter that in the drawing.

TABLE 2
Values of the Internal Radii of mean pores, r_i. These Radii Have Been Obtained from Eq. (9), i.e., Assuming Pores Perpendicular to the Membrane Surface

Membrane	r_i (μm)
M02	0.20 ± 0.02
M04	0.38 ± 0.02
M06	0.63 ± 0.02
M08	0.72 ± 0.02
M10	1.46 ± 0.02
M20	1.68 ± 0.02
M50	2.77 ± 0.02

plotted versus the external one r_e. Note that both the radii (r_i and r_e) represent mean values.

NONPERPENDICULAR PORES

Actually, the pores are not perpendicular to the membrane surface but are sloped with a mean angle Φ. A sloped mean pore is shown in Fig. 1(b). With nonperpendicular pores, the Eq. (7) no longer holds and has to be replaced (see Fig. 1b) by

$$V_{\text{par}} = \pi\left(\frac{8}{15} r_i^2 + \frac{4}{15} r_i r_e \sin\Phi + \frac{3}{15} r_e^2 \sin^2\Phi\right) \frac{d}{\sin\Phi} \tag{10}$$

From Eqs. (8) and (10) we obtain

$$\frac{\theta}{\theta'} = \frac{V_{\text{par}}}{V_{\text{cyl}}} = \frac{8}{15}\frac{(r_i/r_e)^2}{\sin\Phi} + \frac{4}{15}\left(\frac{r_i}{r_e}\right) + \frac{3}{15}\sin\Phi \tag{11}$$

which has two unknowns, r_i and Φ, assuming θ and r_e are measured. Therefore, we need another equation. In order to obtain this additional equation, note that the maximum pore surface density is, according to Fig. 3,

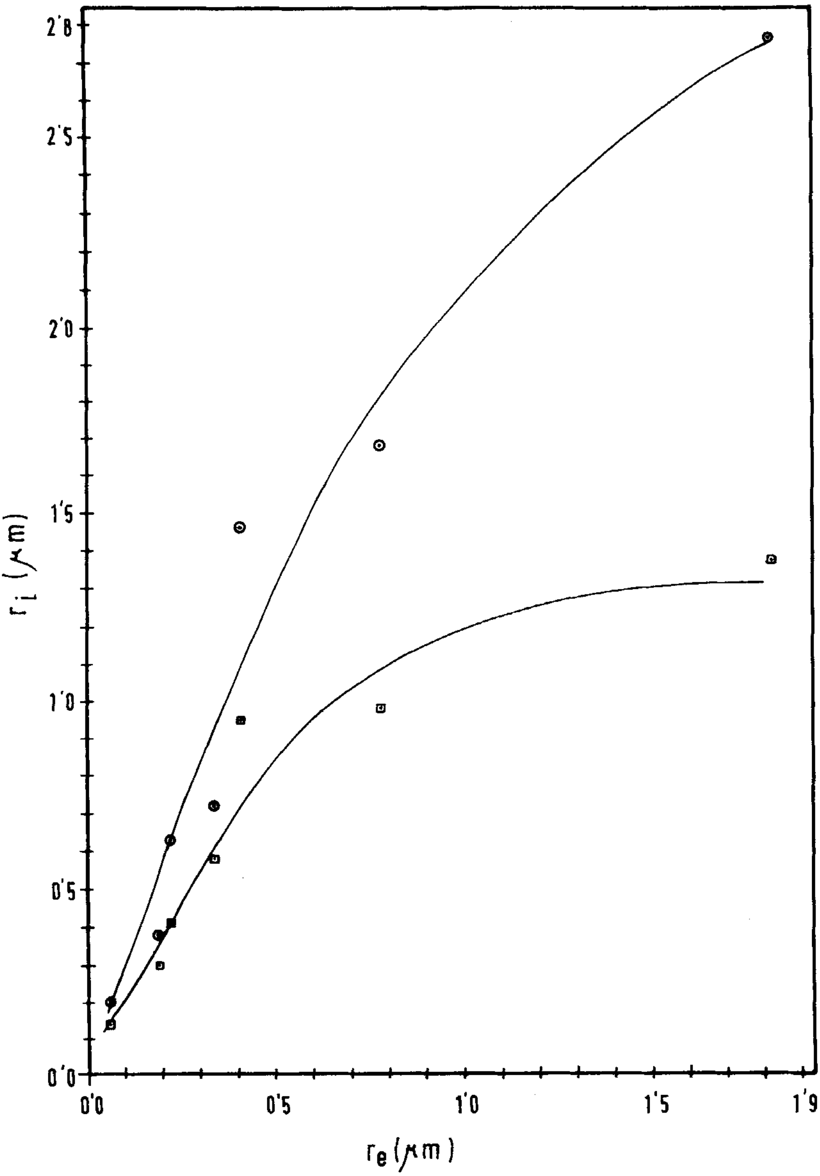

FIG. 2. Internal radii r_i as a function of external radii r_e. (○): For a mean pore assumed to be perpendicular to the membrane surface. The equation of a fitted parabola is $(0.10 \pm 0.08) + (2.93 \pm 0.30)r_e - (0.55 \pm 0.15)r_e^2 = r_i$. (□): Assuming a mean angle Φ between pores and the membrane surface. The fitted parabola is $(0.06 \pm 0.13) + (1.82 \pm 0.45)r_e - (0.62 \pm 0.23)r_e^2 = r_i$.

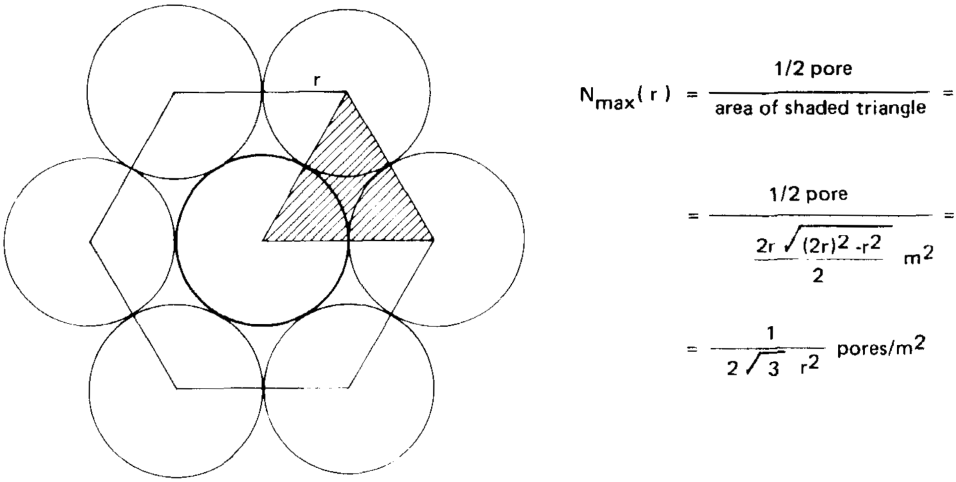

FIG. 3. If no overlapping is allowed, the maximal surface pore density is reached when sections perpendicular to the x-axis with maximal radius r are like those shown. Then the maximal surface pore density is $N_{max}(r) = 1/2\sqrt{3}r^2$ pores/m^2.

$$N_{max}(x = 0) = \frac{1}{2\sqrt{3}r_e^2} \tag{12}$$

on the surface of the membrane, and

$$N_{max}\left(x = \frac{d}{2}\right) = \frac{1}{2\sqrt{3}(r_i/\sin\Phi)^2} \tag{13}$$

in the middle of the membrane. These two equations have been obtained by assuming that there is no overlap between the pores on the surface or in the middle of the membrane. The measured pore surface density, N, must coincide with $N_{max}(x = d/2)$ if the pore surface density is maximized. Then, from Eqs. (12) and (13), we have

$$\frac{N}{N_{max}(x = 0)} = \frac{\sin^2\Phi}{(r_i/r_e)^2} \tag{14}$$

which is the additional equation we were looking for, assuming N and r_e are measured.

For finding the unknowns $\sin\Phi$ and r_i/r_e:

$$\sin \Phi = \frac{15(\theta/\theta')(N/N_{max}(x = 0))}{8 + 4\sqrt{N/N_{max}(x = 0)} + 3(N/N_{max}(x = 0))} \quad (15)$$

$$\frac{r_i}{r_e} = \frac{15(\theta/\theta')\sqrt{N/N_{max}(x = 0)}}{8 + 4\sqrt{N/N_{max}(x = 0)} + 3(N/N_{max}(x = 0))} \quad (16)$$

from which Φ and r_i can be calculated,given the measured values of r_e, N, and θ, and using Eqs. (5) and (12).

In Table 3 the calculated values of Φ, r_i, and other significant dimensions ($r_e \sin \Phi$, $r_i/\sin \Phi$, and $d/\sin \Phi$) of the mean pore are shown.

In Fig. 2 the values of r_i obtained for sloped pores are plotted as well as the corresponding values of r_i calculated by assuming pores perpendicular to the membrane surface, both versus the external radii r_e.

Note that, in writing V_{par} as in Eq. (11) and $N_{max}(x = d/2)$ as in Eq. (13), some acceptable approximations have been made:

(1) The sloped pores have been assumed to have sections parallel to the membrane, approximately circular in shape, which has been experimentally confirmed.
(2) The values $r_e \sin \Phi$ and $r_i/\sin \Phi$ are approximately valid for the corresponding dimensions in Fig. 1(b) if the generating parabola is soft. But, for example, for the M02 membrane and perpendicular pores, when x goes from 0 to $d/2 = 5$ μm, y goes from 0.06 to 0.20 μm, i.e., $|\Delta y|/|\Delta x| = 0.05$, which is a very soft parabola.

DISCUSSION

Our model is the simplest one compatible with experimental results. In fact, it is essentially phenomenological because it contains a hypothesis

FIG. 4. An electron transversal microphotograph of a longitudinal section of a pore of the membrane M20. This pore is typical for Nuclepore membranes and is very close in shape to the mean pore assumed in our model. The microscopy magnification factor is 2000, but a 250% amplification is shown, i.e., the picture shown corresponds to a magnification factor of 5000.

TABLE 3
Values of the Mean Angle between Pores and the Membrane Surface, Φ, and of The Internal Radii, r_i. These Values Have Been Obtained from Eqs. (5), (12), (15), and (16), i.e., Taking into Account That the Pores Are Sloped. Values of Other Significant Dimensions (see Fig. 1b) of Pores Are Also Shown

Membranes	Φ (deg)	$r_e \sin \Phi$ (μm)	r_i (μm)	$r_i/\sin \Phi$ (μm)	$d/\sin \Phi$ (μm)
M02	25 ± 1	0.030 ± 0.003	0.14 ± 0.01	0.31 ± 0.02	23 ± 2
M04	32 ± 1	0.101 ± 0.003	0.30 ± 0.02	0.55 ± 0.03	19 ± 2
M06	24 ± 1	0.087 ± 0.003	0.41 ± 0.02	1.03 ± 0.04	25 ± 2
M08	37 ± 1	0.204 ± 0.003	0.58 ± 0.03	0.97 ± 0.03	17 ± 2
M10	24 ± 1	0.163 ± 0.003	0.95 ± 0.04	2.39 ± 0.05	25 ± 2
M20	17 ± 1	0.223 ± 0.003	0.97 ± 0.04	1.65 ± 0.04	35 ± 3
M50	11 ± 1	0.330 ± 0.003	1.33 ± 0.05	7.32 ± 0.10	55 ± 5

about mean pore geometry, but the internal radius is kept free and adjustable to the experimental results for N and θ. This model explains the observed discrepancies between pore radii measured by microscopy, r_e, and those measured by half time and thermoporometric methods, which give some values between r_e and r_i.

We have determined that the internal radii r_i (for perpendicular as well as for sloped pores) follow a parabolic function of the external radii r_e (see Fig. 2). This result was foreseeable due to the fact that chemical etching is stopped by washing the membranes. Etching is more easily stopped when the external radii are large. For small external radii, water takes more time to get to the center of the membrane and the etchant has more time to act.

The mean angle between pores and the membrane surface is hard to measure because experimental errors can easily be 50%. Nevertheless, from microphotographs of longitudinal sections of membranes, it can be seen that the mean angles are near the maximal value given by the manufacturer ($\Phi_{max} \simeq 30°$) and very close to the calculated values shown in Table 3, except for the M50 membrane.

The discrepancy between calculated and experimental values of Φ for M50 implies that $N \neq N_{max}(x = d/2)$, i.e., the pore surface density is not maximized.

The pore surface densities should be maximized in order to reach maximal water permeabilities, which are desirable in microfiltration processes. On the other hand, large pore surface densities increase the fraction of multiple pores, i.e., the molecular weight cut-off, and this effect is more important for membranes with large external pore radii, such as M50. Therefore, in manufacturing membranes with large external pore radii, a compromise between large water permeabilities and a precise molecular weight cut-off has to be attained.

Figure 4 shows a microphotograph of a typical pore of membrane M20, which has a shape very close to that assumed by us for the mean pore.

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