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Characterization of Hydrophobic Microporous Membranes from Water Permeation

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ABSTRACT

This paper deals with the characterization of four hydrophobic microfiltration membranes from water permeation measurements. A method proposed by McGuire et al. is used. The method uses a mathematical technique of smoothing spline fit in order to obtain a smooth pore distribution function without the need of a priori assumptions about the nature or shape of the distribution. Good agreement between the discrete distribution determined by a classical method and the continuous distribution determined from the McGuire method was obtained.

Key Words. Characterization; Porous membranes; Pore size; Water permeability; Hydrophobic membranes

INTRODUCTION

The measurement of pore size and pore size distribution is very important in the evaluation and characterization of microfiltration membranes. Pore size and pore size distributions can be estimated by indirect methods (retention measurements of well-characterized macromolecules) or they can also be measured directly by various methods (2).

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Synthetic microfiltration membranes do not generally possess a uniform pore size but have a pore size distribution. Of the direct methods, characterization via liquid permeation has the advantage of determining the pore size distribution (not just the average pore size). Besides, with this method only transmembrane pores that are available for flow (not pores that are blocked) are evaluated. Finally, in this method the membrane is tested in its wet state, and as a consequence the characterization obtained will be useful when the membrane is used in that condition. For these reasons we have chosen this technique for the characterization of microfiltration membranes.

In this technique the flux of a nonwetting fluid (contact angle $\vartheta > 90°$ with the membrane material) is measured as a function of the pressure drop across the membrane. Because the studied membranes are hydrophobic, we used water as the nonwetting fluid. All pores of the membrane were completely dry at the start of the experiment. Application of a low pressure drop caused no flux through the membrane. At Δp_{min} the largest pores become permeable, and smaller and smaller pores become permeable as the pressure increases. When the pressure is increased further, the flux increases linearly with pressure (see Fig. 1). It is possible to determine the pore size distribution from analysis of this curve, which is usually referred to as the flow–pressure curve.

Our analysis of the flow–pressure curve was performed by using two different methods. In the first method a discrete pore size distribution was assumed and the corresponding histogram could be obtained. The second method was proposed recently by McGuire et al. (1), and the result is a smooth continuous pore size distribution curve without the need to assume a priori a common statistical distribution (3).

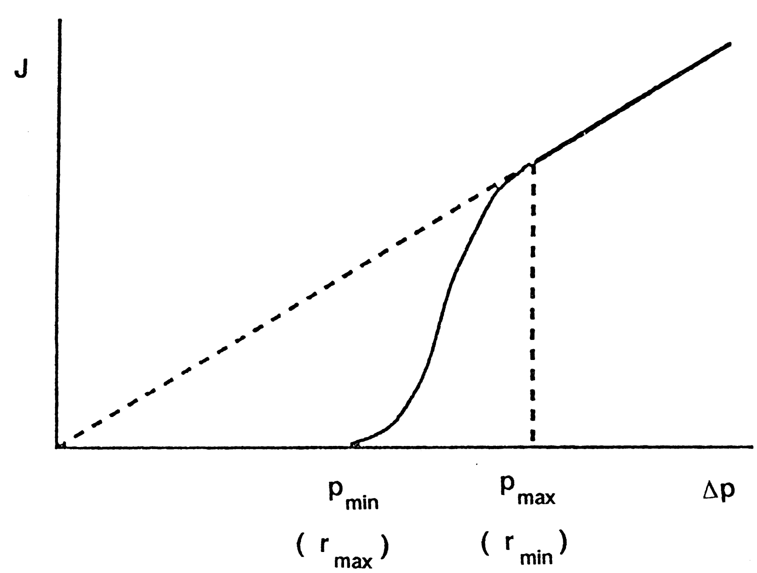

FIG. 1 A theoretical flow–pressure curve. The dotted line shows the Hagen–Poiseuille line.

We used the water permeation technique for the determination of the pore size distribution of four hydrophobic membranes. Analysis of the flux pressure results obtained has been performed by following the two above-mentioned methods.

THEORY

The present technique is a characterization method for hydrophobic porous membranes in the wet state. We assume that the membrane does not possess a uniform pore size but presents a pore size distribution. At the start of the experiment all pores of the membrane are filled with air. Application of a low pressure drop causes no flux through the membrane. As the pressure drop across the membrane is increased beyond some minimum pressure $\Delta p_{\min}$, the largest pores in the membrane are flooded with water, and the water flows through these penetrated pores. As the pressure drop is increased further, smaller pores become flooded successively. The radius of the smallest flooded pore, assuming circular pores, is related to its flooding pressure (the pressure at which a nonwetting fluid penetrates the pore) through the Cantor equation:

$$r = -\frac{2\gamma \cos\vartheta}{\Delta p} \qquad (1)$$

where γ is the water surface tension, ϑ is the contact angle, and Δp is the pressure drop across the membrane.

For a pressure difference below $\Delta p_{\min}$ ($= 2\gamma \cos\vartheta / r_{\max}$), the membrane is impermeable. When the pressure difference reaches the value $\Delta p_{\min}$, the fluid begins to flow through the biggest pores. By increasing Δp, smaller and smaller pores become permeable. For $\Delta p_{\max}$ ($= 2\gamma \cos\vartheta / r_{\min}$), all pores are permeable and the flux becomes proportional to the pressure difference according to the Hagen–Poiseuille relation (Fig. 1).

In this work we used two methods in order to obtain a pore size distribution from analysis of the flow-pressure curve: the first method results in a discrete pore size distribution, and the second method results in a continuous pore size distribution curve.

Discrete Pore Size Distribution

We carried out m experimental measurements (Δp_i, J_i), $i = 1, \ldots, m$. Taking into account Eq. (1), we know that for each experimental J_i the radius of the smallest wet pore, r_i, is

$$r_i = -\frac{2\gamma \cos\vartheta}{\Delta p_i} \qquad (2)$$

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We continued to approximate the pore size distribution function with a discrete distribution with $m - 1$ classes, each with a width $\Delta r_j = r_j - r_{j+1}$, $j = 1, \ldots, m - 1$. The values R_j ($= r_j - \Delta r_j/2$) represent the center point of the class j. If we assume cylindrical pores, we can write

$$J_i = \frac{\pi}{8\eta\tau L}\left(\sum_{j=1}^{i} n_j R_j^4\right)\Delta p_i \tag{3}$$

where n_j is the number of pores of class R_j (that is, the number of pores with radii between r_j and r_{j+1}), η is the water viscosity, L is the membrane thickness, and τ is the membrane tortuosity. Taking into account Eq. (3), the n_j values can be determined from experimental data (Δp_i, J_i) as

$$n_j = \left[\left(\frac{J_{j+1}}{\Delta p_{j+1}}\right) - \left(\frac{J_j}{\Delta p_j}\right)\right]\frac{8\eta\tau L}{\pi R_j^4} \tag{4}$$

and the pore size distribution as

$$\frac{n_j}{\Delta r_j} = \left[\left(\frac{J_{j+1}}{\Delta p_{j+1}}\right) - \left(\frac{J_j}{\Delta p_j}\right)\right]\frac{8\eta\tau L}{\pi R_j^4 \Delta r_j} \tag{5}$$

In this work the combination of constants $\eta\tau L$ is used as the normalization constant. Using this normalization procedure, the relative number of pores with radii between r_j and r_{j+1} can be determined, but the absolute number of pores cannot.

Continuous Pore Size Distribution

Following the method of McGuire et al. (1), we consider that the membrane has a pore size distribution represented by $f(r)$. We consider that the membrane area is large enough so that the pore size distribution can be considered continuous. Then the number of pores with radii between r and $r + dr$ is given by $f(r)\,dr$. The total flux through the membrane at $\Delta p > \Delta p_{\min}$ is given by

$$J = \int_{r(\Delta p)}^{r_{\max}} \frac{\pi\Delta p}{8\eta\tau L} x^4 f(x)\,dx = C\,\Delta p \int_{r(\Delta p)}^{r_{\max}} x^4 f(x)\,dx \tag{6}$$

where

$$C = \pi/8\eta\tau L$$

Taking a derivative of Eq. (6) with respect to Δp gives

$$\begin{aligned}\frac{dJ}{d(\Delta p)} &= C\int_{r(\Delta p)}^{r_{\max}} x^4 f(x)\,dx + \frac{C2\gamma\cos\vartheta}{\Delta p} f(r)r^4 \\ &= \frac{J}{\Delta p} + \frac{C2\gamma\cos\vartheta}{\Delta p} f(r)r^4\end{aligned} \tag{7}$$

Rearrangement and substitution of Eq. (1) gives the final expression for the pore size distribution function:

$$f(r) = \left(\frac{dJ}{d(\Delta p)} - \frac{J}{\Delta p} \right) \frac{\Delta p^5}{C(2\gamma \cos \vartheta)^5} \tag{8}$$

Therefore, if we know the flow–pressure curve, we can calculate the distribution function using Eq. (8). The constant $C(2\gamma \cos \vartheta)^5$ will be used as a normalization constant, and as a consequence the relative number of pores of a specific radius inside a determined interval can be calculated, but the absolute number of pores cannot.

EXPERIMENTAL MATERIALS AND METHOD

Four flat-sheet hydrophobic microporous membranes were used in this study. The PVDF membranes are marketed by Millipore as Durapore 450 and 200, and Inmobilon. The PTFE membrane is marketed by Gelman Instrument Co. as TF450 and is a composite membrane formed by an actual porous PTFE layer on a polypropylene screen support. The properties of the membranes, as reported by the manufacturers, are listed in Table 1. Membranes were tested as received with no pretreatment.

Distilled water was used as the nonwetting fluid for the permeation measurements. A schematic diagram of the liquid displacement apparatus is shown in Fig. 2. The membrane cell was supplied by Millipore (catalogue reference XX4404700). At this point it is necessary to point out that the effective surface of filtration of a disk filter depends on the configuration of the filter holder. The one used in this work includes a 42-mm diameter photoengraved grille of stainless steel with 23% of its surface drilled. Compressed nitrogen was used to generate the applied pressure.

To construct the flow–pressure curve the pressure drop was increased slowly until flux was detected. This pressure was taken to be equal to Δp_{min}. As successively higher pressures were applied, the corresponding flux was calculated from the measurement of the time necessary for a specific volume

TABLE 1
Properties of Membranes Used as Indicated by the Manufacturer

Membrane	Thickness (μm)	Pore diameter (μm)
Durapore 450	125	0.45
Inmobilon	125	0.45
Durapore 200	125	0.22
TF 450	175	0.45

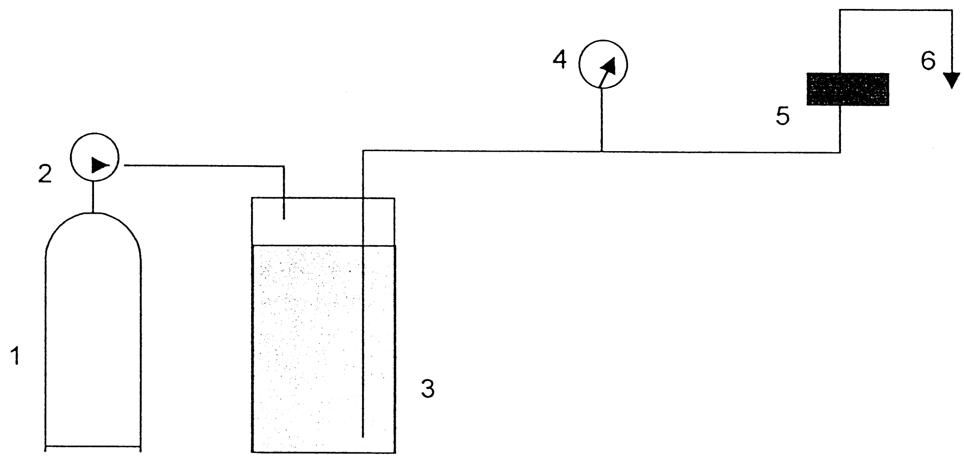

FIG. 2 Schematic representation of the experimental apparatus used to generate the flow–pressure curve. (1) Nitrogen tank, (2) pressure regulator, (3) water tank, (4) pressure indicator, (5) membrane cell, (6) water out.

of water to flow. The flux values shown here are average results for different measurements (with oscillations lower than 5%) when steady conditions were achieved. Times of about 15 minutes were necessary. All experiments were carried out at 293 K.

RESULTS AND DISCUSSION

Proceeding as indicated above, we obtained the flow–pressure data that appear in Figs. 3–6. In order to relate permeating pressures to pore sizes through Eq. (1), the surface tension of water and the contact angle of water with the membrane must be specified. A value of 72×10^{-3} N/m is taken for γ (4). For water on PVDF a contact angle of 115°, as measured by Lee et al. (5) for the PVDF Millipore membranes, has been used. Contact angles varying from 108 to 115° for the water–Teflon pair have been reported in the literature (6). A value of $\vartheta = 114°$ has been used in the present work because it is the value most frequently employed. From Eq. (1) can be seen that differences in the calculated pore radius will vary by approximately 24% if a value of 108° is considered instead of the value used.

The histograms shown in Figs. 7–10 were obtained by using the mentioned data for γ and ϑ, and Eq. (5).

In order to obtain a continuous pore size distribution Eq. (8) has been used. As indicated by McGuire et al. (1), different numerical problems have been encountered when using this equation which explains why it has not been used in the past. In order to eliminate these problems, they proposed passing some type of smoothing spline through the experimental data (Δp_i, J_i) and using this

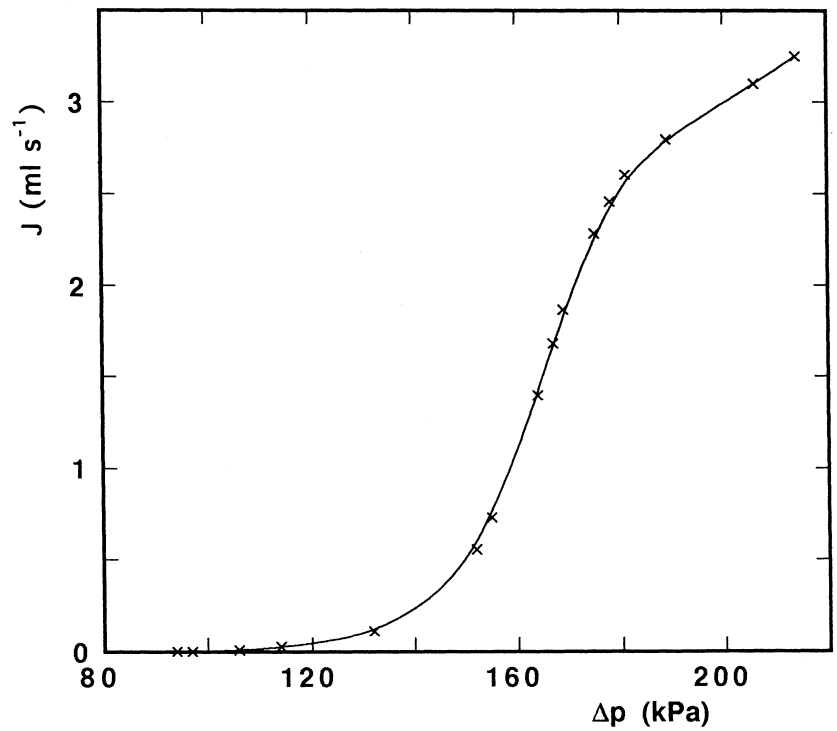

FIG. 3 Flux vs pressure plot for Durapore 450 membrane. The line corresponds to the smoothing spline obtained as indicated in the text.

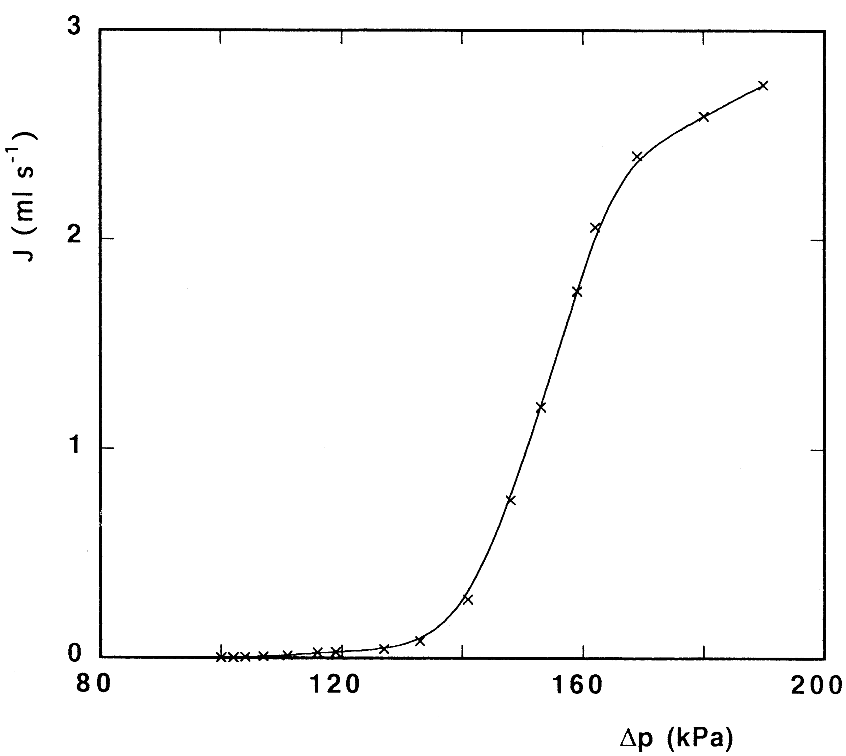

FIG. 4 Flux vs pressure plot for Inmobilon membrane. The line corresponds to the smoothing spline obtained as indicated in the text.

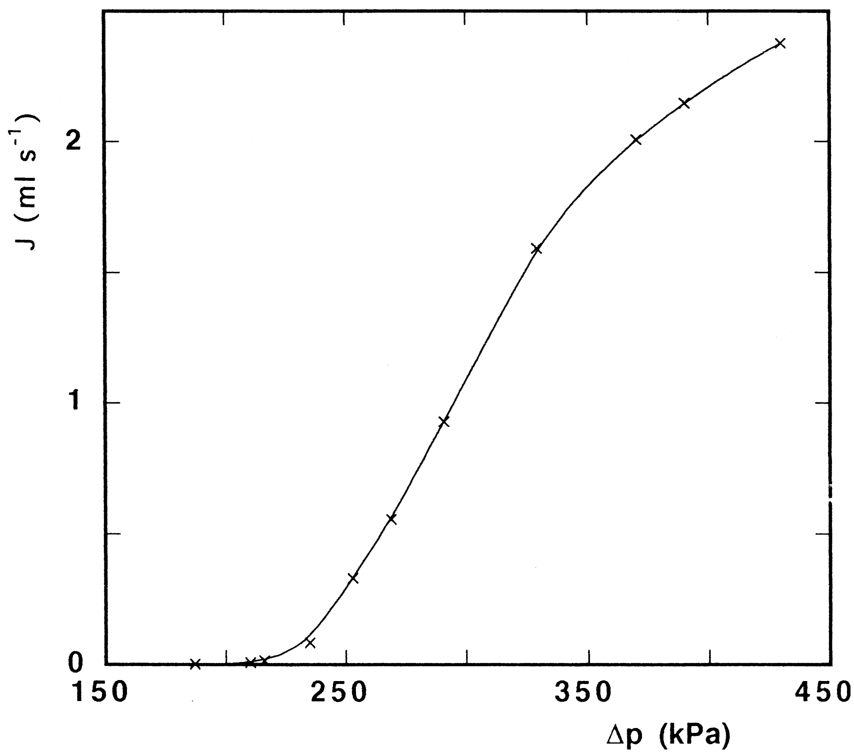

FIG. 5 Flux vs pressure plot for Durapore 200 membrane. The line corresponds to the smoothing spline obtained as indicated in the text.

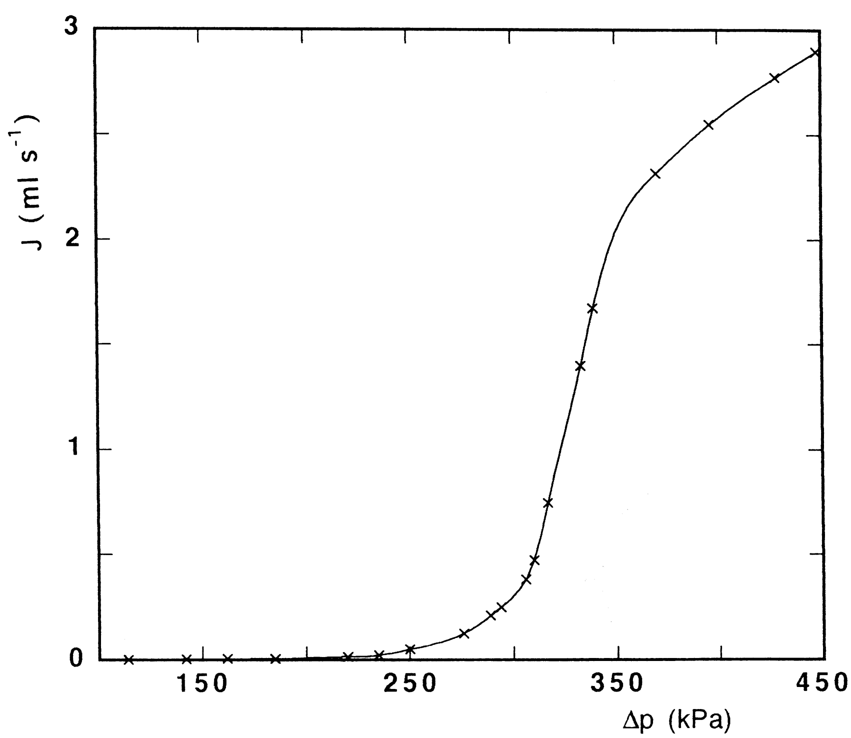

FIG. 6 Flux vs pressure plot for TF 450 membrane. The line corresponds to the smoothing spline obtained as indicated in the text.

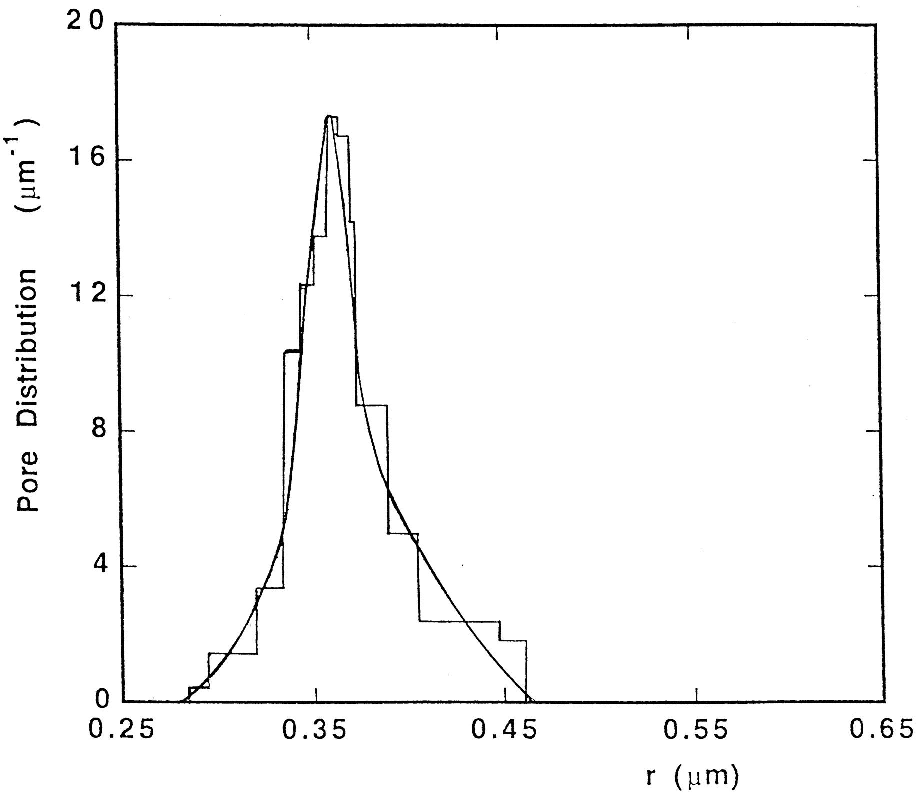

FIG. 7 Pore distribution vs pore radius plot for Durapore 450 membrane.

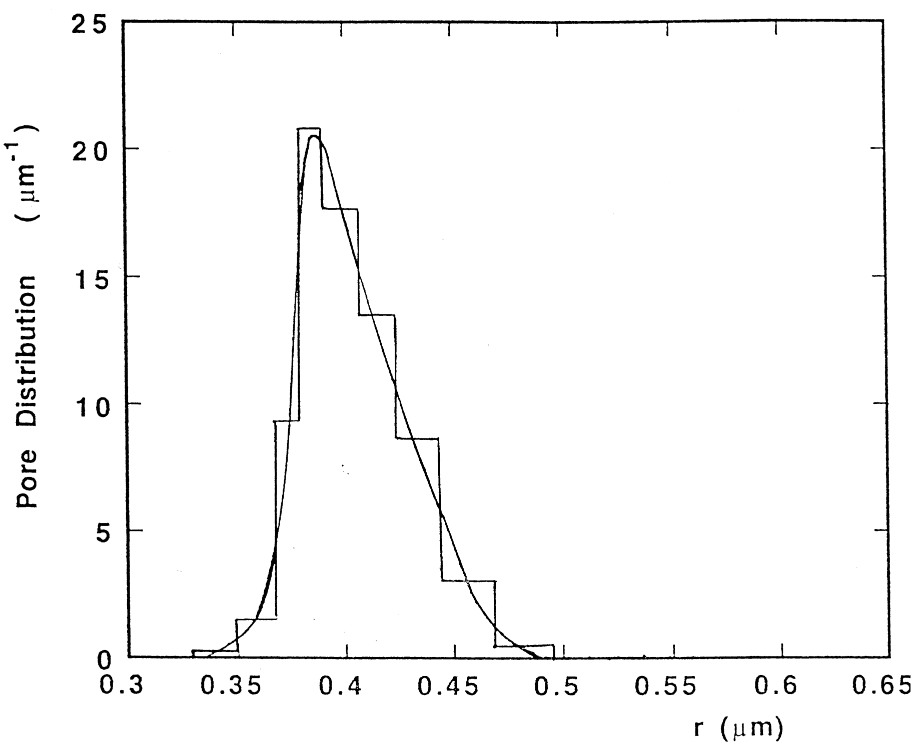

FIG. 8 Pore distribution vs pore radius plot for Inmobilon membrane.

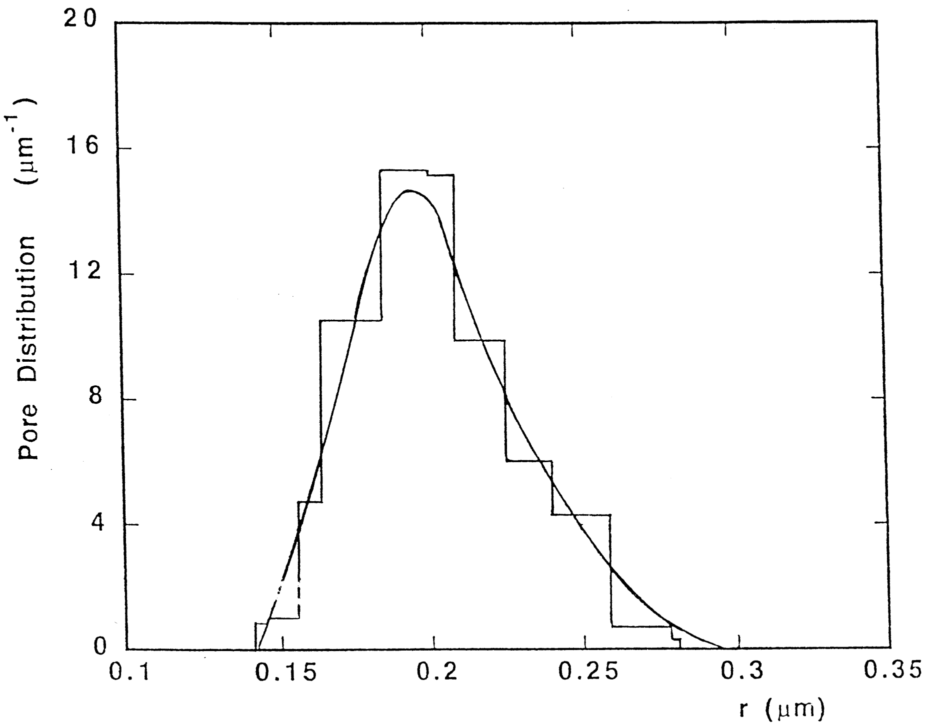

FIG. 9 Pore distribution vs pore radius plot for Durapore 200 membrane.

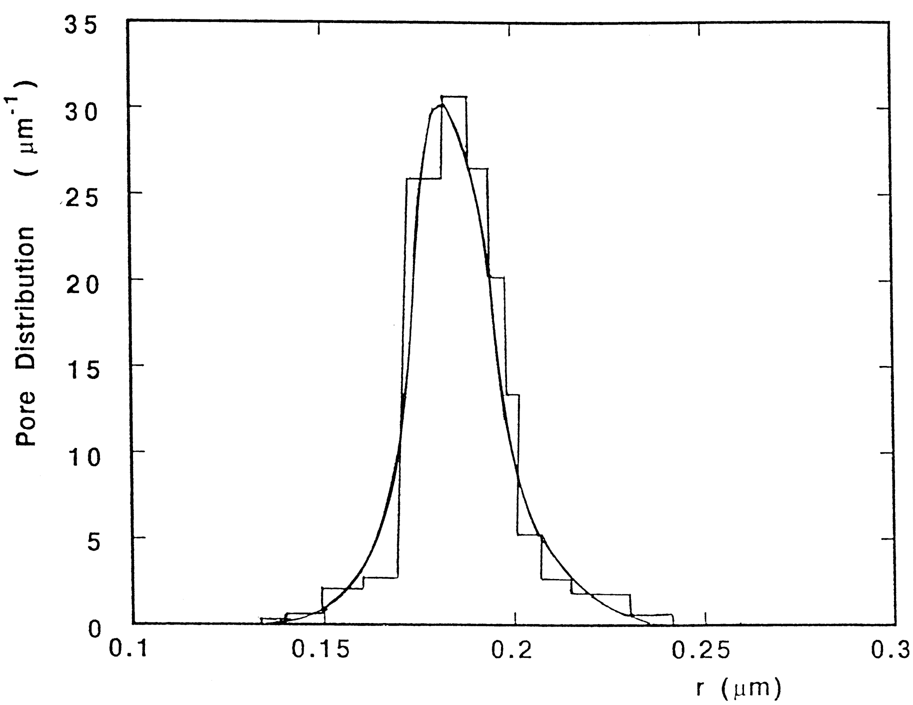

FIG. 10 Pore distribution vs pore radius plot for TF 450 membrane.

spline in Eq. (8). In the present work we have followed this idea and used the commercial application JMP for Apple Macintosh. The fitting technique used in this program applies a cubic polynomial to the interval between points; the polynomial is joined in such a way that the curve meets at the same point with the same slope to form a continuous and smooth curve. The smoothing spline, S, is obtained by adding a curvature penalty to the optimization that minimizes the sum of squares error. So the spline S is found in a way that

$$\int_{\Delta p_{\min}}^{\Delta p_{\max}} S''(x)^2\, dx + \frac{1}{\lambda}\sum_{i=1}^{m} (S(\Delta p_i) - J_i)^2 \tag{9}$$

is minimum (7). Here, S'' is the second derivative of S, m is the number of experimental data points $(\Delta p_i, J_i)$, and λ is the smoothing parameter. To obtain the smoothed spline for the flow–pressure data, a smoothing parameter must be specified. A smoothing parameter of zero will give a natural spline fit to the data that goes through every data point, and any experimental errors in the data will be reflected by spikes in the resulting distribution. With more sophisticated experimental apparatus than that used in this study, the errors in the data could be reduced and smaller smoothing parameters could be used without the appearance of spikes in the distributions. A low smoothing parameter is desired, so that the smoothing spline closely approximates the experimental data. Therefore, the smoothing parameter was adjusted as low as possible without giving erratic spikes. McGuire et al. (1) proved in their work that only minor differences appear between pore distributions corresponding to different smoothing parameters. So, for the smoothing parameter chosen, we have obtained the smoothing spline and its derivative. Finally, the pore size distributions shown in Figs. 7–10 were obtained by using Eq. (8).

In the mentioned figures, both histogram and pore size distribution f(r) have been normalized to make the area under the curve unity. The average pore sizes

$$\langle r_{\mathrm{a}} \rangle = \sum_{j=1}^{m-1} R_j n_j \tag{10}$$

and

$$\langle r_{\mathrm{b}} \rangle = \int_{r_{\min}}^{r_{\max}} r\, f(r)\, dr \tag{11}$$

have been calculated. The results obtained are shown in Table 2.

As can be see in Figs. 7–10 and Table 2, there is a good qualitative and quantitative agreement between the pore size distributions determined by both methods for all the membranes studied. So, as indicated by McGuire et al., continuous pore size distributions for microporous membranes can be deter-

TABLE 2
Average Pore Sizes of Membranes Used

Membrane	$\langle r_a \rangle$ (μm)	$\langle r_b \rangle$ (um)
Durapore 450	0.371	0.356
Inmobilon	0.398	0.393
Durapore 200	0.203	0.199
TF 450	0.185	0.184

mined from liquid permeation data following the method indicated. As can be seen, all the membranes studied exhibit broad pore size distributions. These are in good agreement with the values we obtained from gas–liquid displacement porometry measurements (8). Obviously the characterization of these membranes by their nominal pore size as indicated by the manufacturer is insufficient. In addition, and in order to compare the pore size distributions here obtained with the "nominal" data of catalogue (Table 1), a knowledge of the meaning of this term and of the characterization technique used by the manufacturer is necessary.

CONCLUSIONS

Continuous pore size distributions for microporous membranes can be determined from liquid permeation data without the need of a priori assumptions about the distribution shape. In this paper we have shown that this can be made with a commercial program using a smoothing spline that quickly converts the liquid permeation data into pore size distributions. The continuous distributions obtained for all the membranes studied show good agreement with the results obtained from the classical graphical method.

NOMENCLATURE

J	volume flux of water through membrane (volume/time)
L	thickness of membrane (length)
Δp	applied transmembrane pressure drop (force/area)
Δp_{max}	pressure at which all of the pores are flooded (force/area)
Δp_{min}	pressure at which the first pores are penetrated (force/area)
R	center radius of a class in the discrete distribution (length)
r	radius of a pore (length)
r_{max}	largest pore radius (length)
r_{min}	smallest pore radius (length)
γ	surface tension of water (force/length)

η	viscosity of water [mass/(length time)]
ϑ	contact angle of water with membrane (degrees)
λ	smoothing parameter for the smoothing spline [(abscissa units)^3]
τ	tortuosity of the membrane pores (dimensionless)

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