Pore Size Distributions in Microporous Membranes

II. Bulk Characterization of Track-Etched Filters by Air Porometry and Mercury Porosimetry

J. I. CALVO,* A. HERNÁNDEZ,*,1 P. PRÁDANOS,* L. MARTÍNEZ,† AND W. R. BOWEN‡

* Depto. Física Aplicada II, Fac. Ciencias, Universidad de Valladolid, 47071 Valladolid, Spain; † Depto. Física Aplicada, Fac. Ciencias, Universidad de Málaga, 29071 Málaga, Spain; and ‡ Chem. Eng. Dept., Univ. College Swansea, University of Wales, Swansea, SA2 8PP, United Kingdom

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The structure and morphology of several Cyclopore® filters, consisting of thin track-etched sheets of polycarbonate, is analyzed here through an extended bubble point method and mercury intrusion porometry. Relevant morphological parameters have been studied for six types of filters (C01, C02, C04, C06, C08, and C10). The bulk pore size distributions are directly obtained for each filter. The statistical distributions are studied thoroughly and those obtained from both methods are compared. Specific surface areas are also obtained from both methods and compared with those directly measured in BET experiments with fair agreement.

Key Words: microporous membranes; structural characterization; bubble point porometry; mercury porosimetry; BET surface areas.

INTRODUCTION

Membrane microfiltration is used for the processing of small particles, colloids, and biomaterials such as protein precipitates and microorganisms (1). Such membranes are commonly polymeric materials having pore sizes in the range from 0.1–10.0 μm. The prediction of the separation properties of microfiltration is a subject undergoing rapid progress. Such projections ultimately rest on the development and application of effective procedures for membrane characterization. A range of methods is available for assessing the physical properties of the membranes, such as porosity, surface area, pore size distribution, and pore structure (2–5). Also several models for the membrane structure are used to relate structural parameters and functional performance (6, 7).

Our aim here is to characterize a new kind of microporous track-etched membrane, the bulk structural parameters of which will be obtained from different characterization methods and compared with the previously obtained surface characteristics. In this way, we will be able to study the real structure of pores and the expected performances for these filters.

THEORY

Bubble Point Methods

Bechhold (8), was the first to measure the pressure necessary to blow air through a water-filled membrane. Bechhold et al. and Erbe (9, 10), used two different liquids instead of an air–liquid interface, reducing appreciably the surface tension. The method so developed has been thoroughly used to characterize membranes and it is called the bubble point method. Several more sophisticated characterization methods related to the bubble point measurements have been proposed. All of them use the Washburn equation, which gives the pressure needed to displace one fluid by another through a pore of diameter \(d_p\), as

\[
p = \frac{4\gamma \cos \theta}{d_p},
\]

where \(p\) is the applied pressure, \(\gamma\) is the surface tension of the liquid–liquid or air–liquid interface, and \(\theta\) is the wetting angle with the solid matrix of the membrane. If the fluid totally wets the membrane, we can assume \(\cos \theta = 1\), leading to what is commonly called the Cantor equation.

The bubble point and solvent permeability methods can be combined to yield a measure of the pore size distribution (11). The method has been recently improved for both liquid–gas interfaces (12) and liquid–liquid ones (13), allowing the evaluation of pore sizes corresponding to a range of porous materials (14, 15), and has reached the status of a recommended standard (16).

The applicability of the method and implicit assumptions...
on the air flow have been thoroughly discussed for the range of narrow micropores (17). There, it has been demonstrated that accurate results can be achieved with an air porometer if Knudsen flow is taken into account for the narrowest pores in microporous membranes.

**Mercury Intrusion Method**

Another characterization method related to the bubble point techniques is mercury intrusion porosimetry. The method (also firstly proposed by Washburn (18)) was developed by Ritter and Drake (4) and applied for the first time to characterize membrane filters by Honold and Skau (19). It has shown to be a reliable method to characterize pore size distributions, pore structure, and specific surface areas. Here an Hg–air interface is present inside each pore, thus the Washburn equation (Eq. [1]) is also followed. Nevertheless, in this case, mercury does not wet practically any kind of sample (the corresponding contact angles ranging from 112° to 150°) (4, 18).

Plots of intruded and/or extruded volumes versus pressure, usually called porograms, can show a great variety of shapes depending on the characteristics and distribution of pores, and voids if present, in the sample. But two common features are always present in porograms (4):

(i) Hysteresis is always obtained; i.e., the extrusion path does not follow the intrusion curve.

(ii) Moreover, after completion of an intrusion–extrusion cycle some portion of mercury is always retained by the sample, through pore entrapment, avoiding loop closing. This phenomenon usually ceases after the second pressurization–depressurization run.

Hysteresis has been frequently attributed to ‘‘ink-bottle pores’’ (20). This explanation should indicate a very spread distribution of ‘‘ink-bottle’’ pores. A possibly more realistic way to explain hysteresis and entrapment is through the assumption of a network of differently sized intersecting pores. Androutsopoulos and Mann (21), have calculated the consequences of assuming a bidimensional square network of cylindrical intersecting pores, leading to predictions not far from the actual hysteresis and entrapment behavior of catalytic materials where pelleted structure can be assumed and according to the previous observation of higher entrapments in pelleted samples than in nonpelleted specimens of the same material. Lowell and Shields (22), have shown that superimposition of the intrusion and extrusion curves is possible, at least in the second and subsequent cycles, if the contact angle θ is adjusted to distinguish between advance (θ_a) and recession (θ_r) contact angles. Nevertheless, the first cycle in the porogram cannot be totally closed due to the mercury entrapment which varies greatly (from nearly zero to almost 100%) (21).

In any case, an explanation for these facts has been proposed by Lowell and Shields (23), introducing the concept of pore potential that was previously used in gas adsorption theories (24). Pore potential acts so that the filled pores do not start emptying until a pressure lower than needed to fill them is achieved. Mercury continues leaving the pores with an extrusion angle θ_e until the interfacial free energy equals the pore potential acquired during pressurization. At this point extrusion ceases, leaving a trapped mercury portion in the pores.

**BET Isotherms**

Another method customarily used to characterize structural properties of membranes is the BET isotherm for gas adsorption, which allows one to obtain the specific surface area of porous materials (25). This surface area is a key parameter in membrane characterization as it indicates the sites for possible adsorption and/or deposition of fouling material. It is also an important parameter for different porous materials, such as found in catalysis.

The simplest theoretical model for monolayer gas adsorption is that of Langmuir (24). The model is based on some excessively simplistic assumptions (26) that cannot always be totally fulfilled. Usually it is assumed, according to the theory of Brunauer et al. for gas adsorption (24, 26), that infinite layers of molecules can be adsorbed. So we have

\[
\frac{1}{W[(P_0/P) - 1]} = \frac{1}{W_mC} + \frac{C - 1}{W_mC} \left( \frac{P}{P_0} \right), \tag{2}
\]

where \( W \) is the adsorbed mass, \( W_m \) is the maximum mass that could be adsorbed, \( P/P_0 \) is the gas pressure relative to its saturation pressure, and \( C \) is a constant related to the difference between the molar free energy of adsorption of the first layer and the liquefaction one. This simplified expression has been found to be accurate enough, provided the range of reduced pressure is restricted to 0.05 < \( P/P_0 < 0.35 \), which represents a condition where the very high energy sites have been occupied and extensive multilayer adsorption has not yet commenced.

**EXPERIMENTAL**

**Membranes**

We have used six different types of polycarbonate filters made by Cyclopore with nominal pore diameters 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 μm, which are called C01, C02, C04, C06, C08, and C10. These filters consist of a thin sheet of polycarbonate crossed by almost cylindrical parallel pores obtained by sensibilization of the raw sheets immersed in a polarized beam of heavy ions, produced by a special radio-frequency source and accelerated by a high-energy cyclotron. These high-speed ions create tracks of molecular
damage. Then the pores are made along the tracks by a precision-controlled ultraviolet exposure and chemical-etching process.

Some nominal data of these membranes are shown in Table 1. In any case, according to the process of manufacture, the filters could be portrayed as extremely regular porous media with cylindrical pores of uniform size and length. Nevertheless, as is usual with all microporous membranes, they could be described in a more realistic way by taking into account their irregular shapes and the corresponding statistical distributions for the relevant pore size parameters.

**Bubble Point Porometer**

A Coulter Porometer II manufactured by Coulter Electronics Ltd. has been used. This apparatus uses a liquid displacement technique. The sample must first be wetted with a liquid (Coulter Porofil) of low surface tension (γ = 16 × 10⁻³ N/m), low vapor pressure (3 mm Hg at 298 K), and low reactivity that can be assumed to fill all the pores given that it has a zero contact angle with virtually all materials. The wetted sample is subjected to increasing pressure up to 14 bar, applied by a compressed clean and dry air source, at 313 K. As the pressure of air increases, it will push the liquid out from the pores of diameters given by the Cantor equation.

By monitoring the applied pressure and the flow of gas through the sample when liquid is being expelled, during the wet run, and thereafter for the dried membrane, the pore size distributions can be evaluated (27–29), if the gas transport through the pores is conveniently analyzed and corrections for Knudsen–Poiseuille transition regimes are taken into account (17).

In essence, the cumulative flow for the pores with sizes below \( d_p(j) \) is

\[
f_c(j) = \frac{J^c_p(j)}{J^c_p(j)}
\]

and the differential flow through pores in the \( j \)th class \((j = 1, \ldots, n)\), \( f_d(j) \), can be obtained from numerical differentiation. Moreover, by taking into account that flow is proportional to pore area, the relative number of pores with size \( d_p(j) \), \( n_d(j) \), along with the cumulative relative number distributions, \( n_c(j) \), can be evaluated.

Nevertheless, if the water permeability and porosity are to be evaluated, the absolute number of pores has to be known and a model for the gas flow through the pores must be assumed. In effect, if it is accepted that for pores until those in the \( m \)th class \( (d_p(m) = 0.96 \mu m) \) for a downstream pressure of 1 atm and an experimental temperature of 313 K (17), the transport is of the Knudsen type while for diameters over \( d_p(m) \) there exists a viscous flow, the total number of pores per surface unit, \( N_T(j) \), is

\[
N_T(j) = \frac{L_p(j)}{l_p}, \quad [4]
\]

where \( L_p(j) \) is the air permeability of the porous matrix at the \( j \)th pressure, while \( l_p \) is

\[
l_p = \frac{\pi}{\Delta x} \left[ \frac{2}{3p} \left( \frac{RT}{8\pi M_w} \right)^{1/2} \sum_{j=1}^{m} n_d(j) d_p^3(j) \right]^{1/2} + \frac{1}{128\eta} \sum_{j=m}^{n} n_d(j) d_p^4(j). \quad [5]
\]

Due to some nonidealities, the air permeability of the dry membrane is not constant. Thus, Eq. [4] leads to different \( N_T(j) \) for each pressure. Hence, the absolute distributions of pores per surface unit can be obtained as

\[
N_a(j) = n_d(j) N_T(j) \quad [6]
\]

for the differential distribution and

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Table 1. Nominal Data for the Six Cyclopore Filters

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Diameter (µm)</th>
<th>Thickness (µm)</th>
<th>Pore density ((10^{12} \text{ Pores/m}^2))</th>
<th>Mean porosity (%)</th>
<th>Min. water bubble point ((10^5 \text{ Pa}))</th>
<th>Typical water flow rate ((l/s \text{ m}^2))</th>
<th>Typical air flow rate ((10^6 \text{ l/s m}^2))</th>
<th>Typical burst strength ((10^5 \text{ Pa}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C01</td>
<td>0.1</td>
<td>10</td>
<td>6.0</td>
<td>4</td>
<td>&gt;6.9</td>
<td>0.50</td>
<td>2.17</td>
<td>&gt;1.38</td>
</tr>
<tr>
<td>C02</td>
<td>0.2</td>
<td>10</td>
<td>4.5</td>
<td>14</td>
<td>5.1</td>
<td>4.00</td>
<td>10.83</td>
<td>&gt;0.69</td>
</tr>
<tr>
<td>C04</td>
<td>0.4</td>
<td>10</td>
<td>1.0</td>
<td>5</td>
<td>2.5</td>
<td>12.17</td>
<td>20.83</td>
<td>&gt;1.03</td>
</tr>
<tr>
<td>C06</td>
<td>0.6</td>
<td>9</td>
<td>0.3</td>
<td>8</td>
<td>1.8</td>
<td>14.67</td>
<td>20.83</td>
<td>&gt;2.07</td>
</tr>
<tr>
<td>C08</td>
<td>0.8</td>
<td>9</td>
<td>0.3</td>
<td>15</td>
<td>1.1</td>
<td>33.33</td>
<td>36.67</td>
<td>&gt;2.07</td>
</tr>
<tr>
<td>C10</td>
<td>1.0</td>
<td>9</td>
<td>0.2</td>
<td>16</td>
<td>0.95</td>
<td>36.67</td>
<td>33.33</td>
<td>&gt;2.07</td>
</tr>
</tbody>
</table>

Note. The filters are track-etched hydrophilic polycarbonate films.

\^ Initial flow rate per unit of filter area with prefiltered water at 25°C and 0.7 × 10^5 Pa.

\^ Initial flow rate per unit filter area with prefiltered air at 25°C and 0.7 × 10^5 Pa.
The data acquisition software allows one to use appropriate derivation algorithms to smooth the resulting curves. In our case a moving ninth-point average has been used in calculations. The relative population of pores in each class is obtained from

\[ n_d(j) = \frac{(D_v(d_p)[d_p(j) - d_p(j - 1)]/\{[d_p(j) + d_p(j - 1)]/2\}^2)}{\sum_{i=1}^{n} (D_v(d_p)[d_p(i) - d_p(i - 1)]/\{[d_p(i) + d_p(i - 1)]/2\}^2)}. \tag{9} \]

The question of what contact angle should be used in the Washburn equation remains open, moreover if it is taken into account that errors of one degree out of 140 should lead to errors in all pore radii of 1.4% (4). Here we have used the customary value \( \theta \) Å140 7, which seems to be valid for a wide range of materials (4). While the Hg–air surface tension, \( \gamma \), is 0.474 N/m (30). Nevertheless, some authors calibrate porosimetric results in order to reproduce previous independent calculations on the pore size distributions. This approach has been followed by Liabastre and Orr (18), for nuclepore membranes, comparing with computerized image analysis of scanning electron microscopy (SEM-CIA) pictures, leading to a contact angle of 126.3°. This method can induce very inexact estimations of pore size distributions if the reference method is not adequately chosen. In this way SEM photographs seem an unfortunate choice as far as they refer to surface characteristics of the membrane that should be necessarily different from those referring to bulk structure (31). In any case, as will be shown below, a contact angle of 140° leads to pore size distributions very close to the other bulk structure characterization method used here, bubble point porometry.

To assure satisfactory accuracy, a great number of samples (at least 30) was used. The samples were dried for 24 h (in an oven at 100°C) prior to analysis. Each group of membrane samples, previously weighted, was introduced into the sample cell and air was evacuated for 10 h, at a vacuum pressure of 10−3 mm Hg. Then highly purified (triplly distilled) mercury was intruded into the cell and pressure was increased steeply to introduce the mercury into all the sample pores and voids. Pressures until 3300 psia were enough to include all expected pore sizes (>0.032 μm), higher pressures being neglected in order to avoid damage to the samples. A typical pattern for the directly measured intrusion and extrusion curves is shown in Fig. 2 for the C04 membrane. Note the common features previously pointed out, hysteresis and entrapment. In our case entrapment was always low, as it corresponds to very cylindrical pores (21, 24).

**BET Measurements**

Surface areas of membranes were determined using a Micromeritics ASAP (Accelerated Surface Area and Porosime-
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mentioned validity range, allowing one to obtain \( W_m \) from the slope and the intercept and, consequently,

\[
S_a = \frac{W_m N_A A_a}{M_w W_s},
\]  

[10]

where \( N_A \) is Avogadro's number, \( A_a \) is the cross-section area of the adsorbate molecule, \( M_w \) is its molecular mass, and \( W_s \) is the sample mass.

Measurements have only been performed for C01 and C02 membranes. The great number of samples necessary to obtain an accurate evaluation (a number which increases with the pore size, as will be demonstrated below) constrained us to the membranes with the narrowest pores. The apparatus gave us values of specific adsorbed volume instead of absorbed weights. So the corresponding BET transformative must be \( 1 / \left[ \frac{1}{v_0} \left( \frac{P}{P_0} \right) - 1 \right] \). Representative curves for the directly measured BET data and linear fitting are shown in Fig. 3 for the C01 membrane.

RESULTS

Pore Size Distributions

Using the corrected calculations for the extended bubble point method, the resulting differential and cumulative pore distributions were obtained for all the membranes studied (an example is shown in Fig. 4 for the C01 membrane). All of them fairly fit the Gaussian curves with very narrow dispersions. This has been confirmed by nonlinearly fitting the corresponding experimental distributions to Gaussians, which is also shown in Fig. 4. The so-obtained values for
FIG. 4. Pore diameter distribution for the C01 membrane, obtained with the air porometer.

FIG. 5. Pore diameter distribution for the C01 membrane, obtained with the mercury porosimeter.

the mean diameters along with the corresponding standard deviations are shown in Table 2.

Similarly, the resulting pore size distribution for the C01 membrane, as obtained from the mercury porosimetry, is presented in Fig. 5. Data in Fig. 5 and that corresponding to the rest of the membranes (not shown here) have also been fitted to Gaussian distributions and the resulting parameters are also presented in Table 2.

The corresponding cumulative distributions are compared in Figs. 6 to 11. Agreement is considerable, as is also shown by the distribution parameters presented in Table 2, allowing us to state that a value of 140° for the contact angle was a reasonable election. In general, mean pore diameters are lower for the Hg porosimetry curves, which are also broader, corresponding to higher standard deviations. In these figures, the corresponding pore size cumulative distributions for the surface structure as previously obtained from SEM-CIA (31) are shown too.

The Bubble point method allows an evaluation of the total number of pores (per surface unit). This cannot be achieved with Hg porosimetry where the volume of mercury intruded into each class of pores is difficult to correlate with the corresponding absolute number of pores in this class. The values of \( N_T \) obtained from air porometry are presented in Table 3 along with those obtained by SEM-CIA.

![Table 2](image)

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Air Porometry</th>
<th>Mercury Porosimetry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean, ( \mu )</td>
<td>St. dev., ( \sigma )</td>
</tr>
<tr>
<td>C01</td>
<td>0.134</td>
<td>0.005</td>
</tr>
<tr>
<td>C02</td>
<td>0.265</td>
<td>0.011</td>
</tr>
<tr>
<td>C04</td>
<td>0.462</td>
<td>0.019</td>
</tr>
<tr>
<td>C06</td>
<td>0.680</td>
<td>0.033</td>
</tr>
<tr>
<td>C08</td>
<td>0.988</td>
<td>0.042</td>
</tr>
<tr>
<td>C10</td>
<td>1.162</td>
<td>0.059</td>
</tr>
</tbody>
</table>

Note. The corresponding Hg porosimetric results for the C10 membrane are not presented due to the high imprecisions obtained in that experiment.

![Figure 6](image)
Porosities and Water Permeabilities

The bulk porosity $\epsilon$ has been evaluated from air porometer curves as

$$\epsilon = \frac{\pi}{4} \sum_{j=1}^{n} N_d(j)d_p^2(j)$$  \[11\]

and can be obtained by using $N_d$ from Eq. [6]. Also mercury porosimeter experiments can lead to an evaluation of membrane porosities, by a more indirect method, as

$$\epsilon = 1 - \frac{V_{\text{intr}} \rho_{\text{Hg}}}{[(W_{c,\text{Hg}} - W_c) - (W_{c,\text{Hg}} - W_{c,s})]}$$  \[12\]

where $V_{\text{intr}}$ is the volume intruded into the pores, and $W_c$, $W_{c,\text{Hg}}$, $W_{c,s}$, $W_{c,\text{s,\text{Hg}}}$ are the weights of the cell, emptied, filled with mercury, filled with the sample, and filled with the
Table 4

<table>
<thead>
<tr>
<th>Membrane</th>
<th>( \epsilon ) (Air–Por.) (%)</th>
<th>( \epsilon ) (Hg–Por.) (%)</th>
<th>( \epsilon ) (SEM–CIA) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C01</td>
<td>13.1</td>
<td>13.0</td>
<td>10.5</td>
</tr>
<tr>
<td>C02</td>
<td>22.5</td>
<td>24.5</td>
<td>9.6</td>
</tr>
<tr>
<td>C04</td>
<td>13.4</td>
<td>24.2</td>
<td>14.2</td>
</tr>
<tr>
<td>C06</td>
<td>8.7</td>
<td>3.9</td>
<td>8.9</td>
</tr>
<tr>
<td>C08</td>
<td>12.2</td>
<td>13.2</td>
<td>11.3</td>
</tr>
<tr>
<td>C10</td>
<td>8.7</td>
<td>—</td>
<td>8.5</td>
</tr>
</tbody>
</table>

\[
L_{p,w} = \frac{\pi}{128\eta_w} \sum_{j=1}^{n} \left[ N_d(j) [d_p(j)]^4 \right],
\]

using a value of \( \eta_w = 8.937 \times 10^{-4} \text{Kg/m} \cdot \text{s} \) (water viscosity at 298 K). Water permeabilities calculated through Eq. [13] can be compared with those obtained in a similar way from SEM-CIA, but also with the nominal values and the experimental ones as measured in typical permeation experiments. This comparison is made in Table 5.

**Specific Surface Areas**

Results from nitrogen BET isotherms for membranes C01 and C02 are shown in Table 6. The mercury intrusion technique can also be used to evaluate surface areas of porous samples. In effect, Rootare and Prenzlow (20), developed a method of evaluation of the specific surface area, independently of the shape and structure assumed for the pores. This method relies on integration of the intrusion curve, leading to

\[
S_a = \frac{-1}{\gamma \cos \theta} \int_0^{v_{\text{max}}} pdv,
\]

with \( v_{\text{max}} \) being the maximal specific volume of mercury intruded. They found good agreement for several common powders between their measurements and BET results. Nevertheless, others have found more discrepancies in such comparisons. Lowell and Shields (4), attributed them to the existence of pores narrower than those corresponding to the porosimeter pressure limit (up to 60,000 psia or 18 Å) and to the wall roughness.

Bubble point porometry gives the total population of pores of each diameter which are present in the membrane. Thus, if straightforward cylindrical capillaries are assumed, the specific surface areas can also be evaluated as

\[
S_a = \left( \frac{A_s}{W_s} \right)^2 \sum_{j=1}^{n} \pi [N_d(j)d_p(j)] \Delta x + 2 \epsilon.
\]
where $\Delta z$ is the membrane thickness and $A_s$ is the sample area.

The specific surface areas evaluated from mercury porosimetry and air porometry are presented in Table 6. Along with them is presented a similar evaluation from the previous SEM-CIA distribution results.

**CONCLUSIONS**

We have used two common methods of membrane bulk characterization to obtain several structural and morphological parameters. These methods, air porometry and mercury porosimetry, lead to results more or less concordant, depending on the parameter evaluated and the extra assumptions used.

First, we compared pore size distributions obtained from both techniques. Comparison of them shows that agreement is fine between bulk methods. In general (see Figs. 4 and 5) the curves are reasonably Gaussian, broader and with lower peaks for the mercury intrusion method (see also Table 2). This can be related to the increasing number of samples required to obtain accurate results with mercury porosimetry as pore size augments. In effect, accordance is better for both characterizations when pore size decreases.

**TABLE 5**

<table>
<thead>
<tr>
<th>Membranes</th>
<th>$L_{p,w}$ (Air porometry) $(\times 10^{-7}$ m$^2$/s/Kg)</th>
<th>$L_{p,w}$ (SEM–CIA) $(\times 10^{-7}$ m$^2$/s/Kg)</th>
<th>$L_{p,w}$ (Experimental) $(\times 10^{-7}$ m$^2$/s/Kg)</th>
<th>$L_{p,w}$ (Nominal) $(\times 10^{-7}$ m$^2$/s/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C01</td>
<td>0.08</td>
<td>0.13</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>C02</td>
<td>0.56</td>
<td>0.13</td>
<td>0.49</td>
<td>0.57</td>
</tr>
<tr>
<td>C04</td>
<td>0.97</td>
<td>0.86</td>
<td>1.62</td>
<td>1.74</td>
</tr>
<tr>
<td>C06</td>
<td>1.43</td>
<td>1.06</td>
<td>1.80</td>
<td>2.10</td>
</tr>
<tr>
<td>C08</td>
<td>4.55</td>
<td>2.87</td>
<td>2.35</td>
<td>4.76</td>
</tr>
<tr>
<td>C10</td>
<td>4.51</td>
<td>2.31</td>
<td>4.29</td>
<td>5.24</td>
</tr>
</tbody>
</table>

Referring to the SEM-CIA distributions, they are much broader with average sizes systematically below those corresponding to bulk distributions (see Table 2), with the exception of that of the C08 membrane, whose mercury porosimetry experiment presents a considerable discrepancy as compared to the rest of the distributions.

Moreover, all SEM-CIA distributions show a clear asymmetry, which is usually attributed to double and multiple pores (31, 32). The corresponding cumulative distributions (see Figs. 6 to 11) show that bulk intrusion distributions do not exhibit these asymmetries. Nevertheless, they certainly present slight asymmetries to lower pore sizes (i.e., the left part of the total distribution, instead of the right part, as found in SEM-CIA).

Distributions obtained from mercury porosimetry are always affected by the high pressures used. Then a slight compression on the analyzed material can be translated into a significant change in volume–pressure derivatives and, due to the very small pore diameters corresponding to the last steps in the program, to a high number of pores. So, the left side of the distributions, clearly due to this fact, can be affected by undesired experimental artifacts. Similarly, air porometry distributions show an even slighter left asymmetry. This fact, even though it does not lead to significant changes in the Gaussian behavior of the distributions, could be due to small experimental differences on the last part of the wet and dry curves (see Fig. 1). The absence of significant tails to the higher pore sizes in bulk distributions shows that the double and multiple pores present in the surface distributions do not exist in the actual bulk structure of the membrane.

Referring to the total number of pores per surface unit, surface and bulk methods lead to similar results that are also in fair agreement with nominal ones (see Tables 1 and 3). Nevertheless, note that for small nominal pore sizes, air porometry values are higher than those from SEM-CIA, while they are closer as pore size increases. This means that possibly for small pore sizes most of the double pores are, in fact, two simple ones that follow, into the membrane,

**TABLE 6**

<table>
<thead>
<tr>
<th>Membrane</th>
<th>$S_{a}$ (Air) (m$^2$/g)</th>
<th>$S_{a}$ (Hg) (m$^2$/g)</th>
<th>$S_{a}$ (SEM) (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C01</td>
<td>3.977</td>
<td>2.984</td>
<td>2.216</td>
</tr>
<tr>
<td>C02</td>
<td>3.898</td>
<td>6.461</td>
<td>1.979</td>
</tr>
<tr>
<td>C04</td>
<td>1.332</td>
<td>3.647</td>
<td>1.482</td>
</tr>
<tr>
<td>C06</td>
<td>0.491</td>
<td>0.333</td>
<td>0.542</td>
</tr>
<tr>
<td>C08</td>
<td>0.494</td>
<td>1.185</td>
<td>0.439</td>
</tr>
<tr>
<td>C10</td>
<td>0.286</td>
<td>—</td>
<td>0.318</td>
</tr>
</tbody>
</table>

Note. The BET results are $S_a = 3.213$ m$^2$/g for C01 and $S_a = 3.744$ m$^2$/g for C02.
close but different paths. Whereas, as pore size increases, these double pores probably merge into single pores corresponding to a higher probability of coalescence of tracks as etching time augments.

As far as porosities are concerned, it is seen that all porometry and SEM-CIA data are close, possibly this could be due to their similar dependence on the assumption of cylindrical pores. Nevertheless none of them reproduce the manufacturer’s values (see Tables 1 and 4), which was foreseeable given that nominal porosities seems to refer to the density of tracks, which possibly is the actual control parameter in the production process, more than to the effective density of pores after etching.

The comparison of water permeabilities data shown in Table 5 is probably the most conclusive test of the quality of each technique. Excepting the mercury intrusion method, which do not allows hydraulic permeability evaluations, the results of bulk characterization are almost always closer to the nominal ones and especially to the experimentally measured values. So air porometry presents an advantage over SEM-CIA analysis in the prediction of experimental performance, which is a major reason to consider this method the most complete for membrane characterization, at least among those here studied.

Finally, we can consider the results obtained for specific surface area evaluations. These results are shown in Table 6 and present a considerable agreement between air porometry data and BET results (for the only two membranes for which we have such results). This agreement is more relevant if the usually assumed error of the BET measurements is taken into account. It is customarily estimated that this technique leads to errors over 10% (20) or even higher (between 20–25% according to Ruthven (26). The SEM-CIA predictions are not far from BET results when comparison is possible and follow the air porometry results in the rest of the cases, usually leading to lower values of $S_a$. Finally, mercury porosimetry, which could be considered more accurate to measure surface areas than other indirect methods (based on extra assumptions about pore geometry) are only in good accordance for the first membrane considered, C01. The rest of the results are quite inconsistent, probably due to the presence of a portion of dead-end pores contributing to the calculated specific surface area and, especially for the highest nominal pore sizes, to the already mentioned imprecisions linked to the low porous volumes of these membranes. In effect they have lower pore densities (see Table 3) and consequently the total volume intruded into the samples is lower. These error sources can also superimpose on the significant contributions of the intersample voids, which could be on the order of 0.5–1 $\mu$m. This is why C08 gives such bad distributions and C10 has not been measured. In any case, the refinement of the experimental or calculation procedures seem unnecessary since air porometry gives sufficiently good results that are in excellent agreement with those from porosimetry when they have been made in the best conditions (small nominal pores).

Altogether it seems that referring to porosities, permeabilities, and specific surface areas, air porometry gives the best results when compared with experimental and nominal data. Thus, the slipping of the central peaks in the air porometry distributions to the right of the SEM-CIA ones cannot be attributed to experimental errors. This fact can be related to a certain internal widening of the pores, as was previously proposed as a hypothesis (31). The assumption of internal widening of the pores is here tested in Fig. 12, where the mean values of the corresponding distributions are presented versus the average pore size from air porometry. The values for each characterization method have been fitted to straight lines whose slopes give a measure of the mean widening found according to each characterization method. Note that for the SEM-CIA data (considered here as the correct representation of the surface structure), two average pore sizes are included, one of them corresponding to the total populations and the other to the isolated group of single pores (31).

The final conclusion that arises from this study is that bulk characterization offers complete coverage of the gap between surface and bulk features of membranes (31). In this way, if total populations are taken the corresponding internal widenings are 119% of the surface values and a 131% if only the single pores are considered (very close to the previously assumed widening of 120% (31).

FIG. 12. Mean values of the pore size Gaussians for mercury porosimetry and image analysis (both total and simple pores populations) versus those for air porometry.
functional parameters (with only the assumption of cylindrical shape for the pores). For other noncylindrical microporous membranes, this characterization method could give good results with the aid of an adequate model for the pore structure. Another advantage is that air porometry do not results in membrane damage and needs only one membrane for each test (reducing costs of characterization). In any case more functional measurements of rejection of different kinds of molecules could be used to strengthen the validity of these conclusions, in conditions of effective separation.

ACKNOWLEDGMENTS

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APPENDIX: NOMENCLATURE

\[ A_s \] Cross section area of the adsorbate molecule (m²).
\[ A_t \] Sample area (m²).
\[ C \] BET constant (dimensionless).
\[ d_p \] Pore diameter (m).
\[ d_p(j) \] Diameter of the \( j \)th pore (m).
\[ D_s(d_p) \] Specific volume distribution for each pore diameter (m³/g).
\[ f_s(j) \] Flow cumulative frequency for a diameter \( d_p(j) \) (dimensionless).
\[ f_s(d_p) \] Flow differential frequency for a diameter \( d_p(j) \) (dimensionless).
\[ J_v^C(j) \] Volume flow through the dry membrane at the \( j \)th pressure (m/s).
\[ J_v^O(j) \] Volume flow through the open pores of a wet membrane at the \( j \)th pressure (m/s).
\[ J_v \] Volume flow through the pores with diameter \( d_p \) (m/s).
\[ l_p \] Gas permeability assuming a total number of pores of 1 (m²/s·Pa).
\[ L_p(j) \] Gas permeability at the \( j \)th pressure (m²/s·Pa).
\[ L_{p,w} \] Water permeability of the membrane (m³/s·Pa).
\[ M_w \] Molecular weight of the gas (kg/mol).
\[ n \] Total number of classes in the pore size distributions (dimensionless).
\[ n_s \] Cumulative number of pores, (dimensionless).
\[ n_s(j) \] Cumulative number frequency of pores (dimensionless).
\[ n_d \] Differential number of pores below \( d_p(j) \) (dimensionless).
\[ n_d(j) \] Differential number frequency of pores (dimensionless).
\[ n_d(j) \] Differential number frequency for a diameter \( d_p(j) \) (dimensionless).
\[ N_A \] Avogadro’s number (molecules/mol).
\[ N_o(j) \] Cumulative number of pores, per surface unit, with a diameter \( d_p(j) \) (m⁻²).
\[ N_o(j) \] Differential number of pores, per surface unit, with a diameter \( d_p(j) \) (m⁻²).
\[ N_f \] Pore density per surface unit (pores/m²).
\[ N_f(j) \] Total number of pores per surface unit evaluated at the \( j \)th pressure (m⁻²).
\[ p \] Applied pressure (Pa).
\[ P \] Pressure applied to the adsorbed gas (Pa).
\[ P_a \] Saturation pressure of the adsorbed gas (Pa).
\[ R \] Gas constant (J/K·mol).
\[ S_s \] Specific surface area (m²/Kg).
\[ T \] Temperature (K).
\[ v \] Specific intruded volume of mercury (m³/Kg).
\[ u_a \] Specific adsorbed volume (m³/Kg).
\[ v_{max} \] Maximum specific intruded volume (m³/Kg).
\[ V_{m} \] Volume of mercury intruded into the pores (m³).
\[ W \] Weight of absorbed gas (Kg).
\[ W_c \] Weight of the porosimeter cell, totally empty (Kg).
\[ W_{c,s} \] Weight of the porosimeter cell, filled with the sample (Kg).
\[ W_{c,Hg} \] Weight of the porosimeter cell, filled with mercury (Kg).
\[ W_{c,Hg} \] Weight of the porosimeter cell, filled with sample and mercury (Kg).
\[ W_m \] Weight of absorbed gas in a complete monolayer (Kg).
\[ W_i \] Weight of the membrane samples (Kg).
\[ \Delta x \] Membrane thickness or capillary length (m).
\[ \epsilon \] Membrane bulk porosity (dimensionless).
\[ \gamma \] Surface tension (N/m).
\[ \mu \] Mean pore diameter (m).
\[ \rho_a \] Mercury density (Kg/m³).
\[ \sigma \] Standard deviation of pore diameters (m).
\[ \theta \] Contact angle (radians).
\[ \theta_c \] Contact angle during mercury extrusion (radians).
\[ \theta_i \] Contact angle during mercury intrusion (radians).
\[ \eta \] Air viscosity (Pa·s).
\[ \eta_w \] Water viscosity (Pa·s).

REFERENCES