Permporometry. The determination of the size distribution of active pores in UF membranes

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Abstract

Permporometry is a method by which the characteristics of the interconnecting 'active' pores of an ultrafiltration membrane can be measured It is these 'active' pores that are responsible for the actual membrane performance Application of permporometry on different membrane types, including ceramic as well as polymeric membranes, shows that the method can provide objective information on the 'active' pore sizes present

Keywords permporometry, ultrafiltration, active pore size, pore size distribution

Introduction

For the measurement of pore sizes present in mesoporous media a variety of techniques are available. The majority of these originate from ceramic materials science, where it is of particular interest to know the pore size distribution and the pore volume, irrespective whether it concerns dead-end or interconnecting pores. The characterization of UF membranes, however, is aimed at the determination of characteristic membrane properties in order to predict the transport properties and membrane performance as much as possible. To this end, it is crucial to measure the sizes of those pores which really contribute to the permeability In the case of UF membranes these so-called 'ac-

tive pores' are present in the 'active' skin layer of the membrane.

Most of the routine characterization methods cannot discriminate between the 'active' pores in the skin and 'inactive' pores present in the skin or in the supporting layer. Exceptions are the gas permeability method [1,2] and the liquid–liquid displacement technique [3,4]. These methods have other disadvantages and are not always capable of generating accurate, independent, characteristic data The significance of the gas permeability method is limited, because only mean pore sizes are measured and, as Altena et al have shown [2], the quantitative values of these pore sizes are highly ambiguous With the second method mentioned above (the liquid–liquid displacement technique), the pore size distribution of a membrane can be measured, but the results are influenced by the experimental conditions [3]. These ambiguities show the need for other

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characterization methods by which the sizes of active pores can be determined.

Permporometry, introduced by Eyraud et al. [5,6] and modified by Katz et al. [7,8], is a relatively new characterization method to evaluate the active pores of an UF membrane. It is based on the controlled stepwise blocking of pores by condensation of a vapour, present as a component of a gas mixture, and the simultaneous measurement of the gas flux through the membrane. In this paper we report on permporometry measurements using an experimental apparatus and procedure which provides a very well-defined (and easy to model) transport regime and a fast adjustment of equilibrium conditions.

Theoretical

Capillary condensation

The nature of physisorption processes of condensable vapour is usually divided in different stages [9]. In the beginning of the process, at low relative pressures, only adsorption of vapour molecules to the pore wall is assumed to occur This adsorption is restricted to the so-called 't-layer' with a maximum thickness in the order of a few molecules. At higher values of the relative pressure the adsorption process is followed by capillary condensation, i.e. the condensation of a vapour, commencing in the smallest pores. As the pressure is progressively increased, wider pores are filled until at the saturation pressure the entire system is filled with condensate. The relative pressure at which pore filling starts depends on the radius of the capillary and can be calculated from the Kelvin relation (1):

$$\ln p_r = \left(\frac{-\gamma v}{RT}\right)\cos\theta\left(\frac{1}{r_{k1}} + \frac{1}{r_{k2}}\right) \qquad (1)$$

In the application of the Kelvin reaction it is generally accepted to assume that $\theta = 0$. This

simplifies eqn. (1) and permits the direct calculation of a pore radius corresponding to a certain relative pressure [9].

During desorption a behaviour similar to adsorption is shown. Now a liquid containing pore will not empty before the vapour pressure falls below the equilibrium pressure given by eqn (1). The desorption process is pictured schematically in Fig. 1. The adsorption and desorption processes are not necessarily defined by the same curvature of the liquid–gas interface which often leads to a hysteresis phenomenon. For instance, during adsorption in a cylindrical pore the meniscus has a cylindrical shape [in eqn. (1): $r_{k1} = r_k$ and $r_{k2} = \infty$] whereas during desorption the liquid–gas interface is hemispherical [in eqn. (1). $r_{k1} = r_{k2} = r_k$], and eqn (1), with $\theta = 0$, turns into:

$$\ln p_r = (-2\gamma v/RTr_k) \qquad (1A)$$

The Kelvin radius r_k found from eqn. (1A) is the radius of curvature of the liquid–gas interface, which is equal to the pore radius minus the 't-layer' thickness of the adsorbed film on the pore wall (Fig. 1). The relationship between the true pore radius r_p and the Kelvin radius r_k thus is:

$$r_k = r_p + t \qquad (2)$$

in which t is the thickness of the adsorbed t-layer.

The thickness of the t-layer depends on the relative pressure. In classical adsorption studies this thickness is calculated from separate adsorption experiments which are performed using homogeneous non-porous reference surfaces, preferably made of the same material as the porous medium This approach is very laborious and therefore an approximation, explained further on this paper, was used to calculate the t-layer thickness directly from permporometry data

Capillary condensation provides the possibility to block pores of a certain size with liquid, just by setting the relative pressure. In perm-
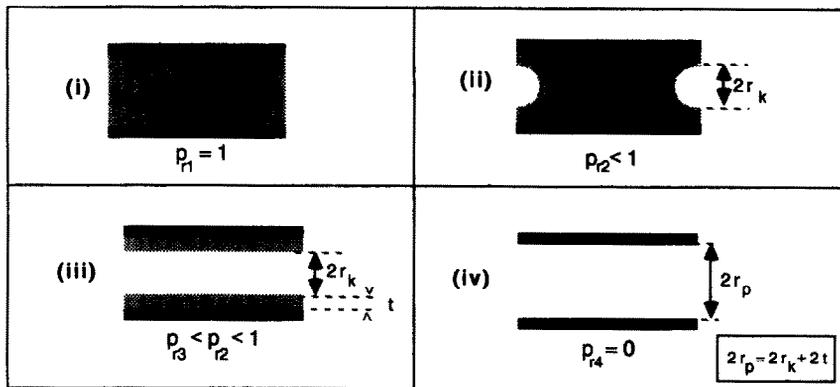
Fig. 1. Steps in the desorption process: (i) liquid filled pore, at saturation pressure, (ii) just before desorption starts, pore is still filled, (iii) just after evaporation is complete, t-layer remains, (iv) after complete desorption.

porometry this principle is combined with the measurement of the free diffusive transport through the open pores. Starting from a relative pressure equal to 1, all pores of the UF membrane are filled so that unhindered gas transport is not possible. When the pressure is reduced, pores with a size corresponding to the vapour pressure applied, are emptied and become available for gas transport. By measuring the gas transport through the membrane upon decreasing the relative pressure, the distribution of the sizes of the active pores can be found. Of course, similar measurements can be done during the adsorption process, but the equilibrium of the adsorption process is more difficult to reach and therefore quantitative analysis of the desorption process is preferred.

Counterdiffusion

In this approach, the principle of counterdiffusion of two different gases, oxygen and nitrogen, in the absence of an overall 'mechanical' pressure gradient is used to monitor the transport through the membrane. Since in our case small pores (<25 nm) are measured, whereas the driving force for the transport is a concentration gradient of the two gases, a well-defined diffusion regime can be assumed [10]. At an

overall pressure of about 100 kPa, the main transport mechanism is assumed to be Knudsen diffusion, which for a capillary structure is described by eqn. (3):

$$J_k = (\pi n r^2 D_k \Delta p) / (RT\tau l) \qquad (3)$$

in which the Knudsen diffusion coefficient D_k is:

$$D_k = 0.66 r [(8RT) / (\pi M)]^{0.5} \qquad (4)$$

Experimental

The experimental set-up (Fig. 2) is derived from those of Eyraud et al. [5,6] and Katz et
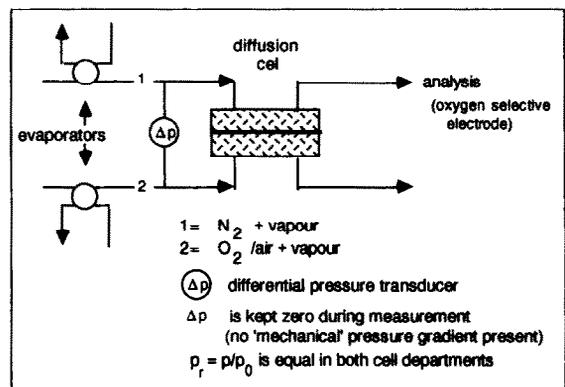
Fig. 2. Permporometry: experimental set-up.

al [7,8] and adapted to the conditions needed for counterdiffusion measurements. Along both sides of the membrane, a mixture of a condensable gas and a non-condensable gas is flushed The condensable gas can be any vapour, provided it has a reasonable vapour pressure and is inert with respect to the membranes to be characterized. The relative pressure of the vapour is maintained the same throughout the diffusion cell. The primary advantage of the apparatus presented here is the fact that the equilibrium between gas mixture and capillary condensate is reached faster than with the apparatus described by Eyraud et al. [5] and Katz and Baruch [8]

The measurements start at a relative pressure equal to one, which means a minimum in diffusive transport. While the membrane is equilibrated at progressively lower relative vapour pressures, the diffusive transport of oxygen through the membrane is measured with an oxygen selective electrode. After reaching a relative pressure of 0, the process is reversed and the adsorption branch is measured. Equilibration times varied from 15 to 30 min, depending on the amount of condensate that had to be adsorbed or removed. Using eqns. (1)–(4), the pore size distributions were calculated from the desorption branch.

Several membranes were characterized by the method described above. Ceramic membranes were supplied by the group of Burggraaf [11], Nuclepore 0 015 μm membranes (lot no. 86A9B14) were purchased from the Nuclepore Corporation and DDS GR61PP, manufactured by DDS Danmark, were supplied by the Dutch Institute for Dairy Research (NIZO)

A more detailed study was made of anisotropic polymeric membranes, synthesized from poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polysulfone (PSf) The PPO membranes were prepared from a 10 wt.% polymer solution in a mixture of trichloroethylene and octanol-1 in a weight ratio 78/22. The PSf

membranes were made from a 15 wt.% PSf solution in DMF In both cases the solutions were cast at room temperature to a thickness of 0.20 mm on a glass plate. The PPO films were coagulated in a methanol bath and the PSf films in a water bath. All solvents used were of analytical grade.

In principle, the condensable gas should not alter the porous matrix and the vapours must be as inert as possible. To investigate the effect of different condensable gases, four different adsorbates, i e. ethanol, methanol, tetrachloromethylene and cyclohexane (p.a quality, Merck) were used.

Results and discussion

Ceramic γ-alumina membranes

In Fig. 3 the oxygen flux through an alumina membrane during the adsorption and desorption of cyclohexane vapour is shown. This typical flux–relative pressure plot can be divided into three main areas. In the interval $1 \geqslant p_r > 0.55$ all the pores are blocked with condensate and free gas diffusion is impeded At relative pressures between 0.55 and 0.3, the flux increases with decreasing relative pressure be-
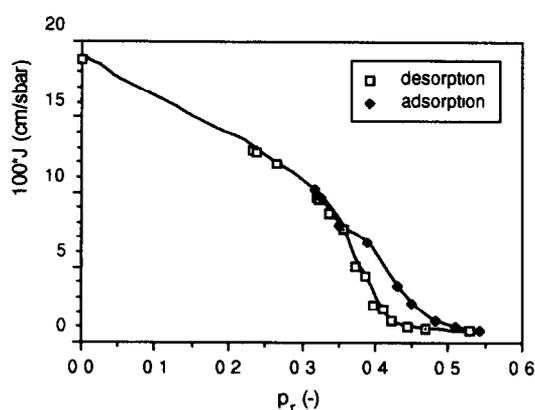
Fig 3 Permporometry adsorption and desorption curve for a γ-alumina membrane with cyclohexane used as adsorbate

cause of an increasing number of open pores. In this interval the capillary condensation process takes place. The flux–pore size plot, given in Fig. 4, was calculated from the desorption data and assuming a capillary model (eqn. 1A) From the measured diffusive flux values and the calculated Kelvin pore sizes, a number of pores was calculated using eqn (3).

In order to find the real pore size the Kelvin radii should be corrected for the adsorbed t-layer. Figure 3 shows that upon lowering the relative pressure beneath 0.3, the flux through the membrane increases slightly It can be argued that in this region all pores with radii r_k are already empty and available for transport, but still the size of the pores increases a little as the result of the desorption of the t-layer. When a uniform t-layer (with a thickness t) in all pores is assumed at $p_r = 0$ 3, the effective pore size will increase from r_k to $r_p = r_k + t$ (eqn 2) upon decreasing the relative pressure from 0.3 to 0 So, by using the calculated pore size distribution (Kelvin radii) and the experimental values of the oxygen flux at relative pressures 0 3 and 0, an estimation of the t-layer thickness can be made From the data found for cyclohexane on alumina a mean t-layer thickness of 0 5 nm (at $p_r = 0.3$) was calculated.
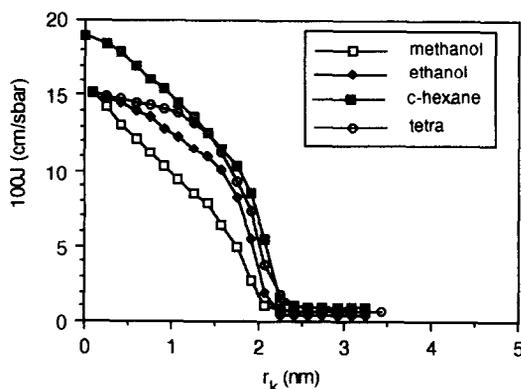
Fig 4 Oxygen flux as a function of the Kelvin radius measured with different adsorbates found for γ-alumina membranes

In principle also the adsorption curve can be used for the pore size evaluation. However, the combination of the adsorption data with a capillary model gave substantially lower pore sizes than the desorption data. This may indicate that the pore shape of the alumina membrane is not cylindrical. Leenaars [12] concluded from classical adsorption–desorption studies that the alumina membranes contain slit-shaped pores. If the ratio of the length to the width of these slits is not too high, this slit-shaped pore model indeed is a better approximation.

To investigate the influence of different absorbates on the quantitative analysis, measurements using ethanol, methanol and carbon tetrachloride as the condensable gas were carried out. Carbon tetrachloride and cyclohexane are considered as so-called Van der Waals gases which implies that their gas molecules are assumed to act as non-interacting hard spheres (similar to an ideal gas) with a finite volume Their physical behaviour is described by the Van der Waals equation. Methanol and ethanol are considered to be less ideal which may influence the permporometry measurements [13]

In Fig 4 the resulting J–r_k plots for the different vapours used, are shown The nominal Kelvin radii found with ethanol, tetrachloride and cyclohexane, differ only slightly When methanol is used, lower values of the Kelvin radii are found. This shift can be attributed to the difference in t-layer thickness. For ethanol, cyclohexane and carbon tetrachloride the calculated t-layer thicknesses (Table 1) are about the same (~ 0.4 nm). This value corresponds to about one molecular layer, which is in good agreement with literature data on physical adsorption of organic molecules [9,14] In case of methanol the t-layer is significantly thicker: 0 7 nm, which is an unexpectedly high value especially when compared with ethanol. In physical adsorption only Van der Waals forces account for the interaction, which means that when the

TABLE 1

Pore sizes (r_p) and t-layer thicknesses (t) found for γ-alumina membranes and using different adsorbates

Adsorbate	r_p (nm)[a]	t (nm)
Cyclohexane	2 3	0 5
Ethanol	2 2	0 4
Methanol	2 3	0 7
Carbon tetrachloride	2 2	0 4

[a]Nominal pore size

size of the molecules of the different adsorbates is comparable, the thickness of t-layers of these adsorbates is expected to be same. It follows therefore that the interaction between the alumina pore wall and the methanol molecules is substantially stronger than it is for the other condensable gases. This interaction has also been shown in other studies in which γ-alumina is used as catalyst in the oxidation of methanol [15].

The pore size distributions of the alumina membranes, corrected for the t-layer thickness agree very well with each other (Fig. 5). This indicates that, at least for such porous system, the pore size analysis is not dependent on the nature of the vapour used. It is clear that the γ-alumina membranes used, exhibit a very well-defined structure which is in agreement with results found with other characterization techniques. For instance, a very sharp pore size distribution ($r \sim 2$ nm) was also found with the gas adsorption–desorption technique and thermoporometry (Fig. 6) [12,13]. Also, the thickness of the active layer is known accurately (5 μm) [11,12], which all together, should make the membrane a well-suited system to be used in a model study.

Using the experimentally determined Kelvin radii and the number of pores, a surface porosity and a volume porosity can be calculated. When the capillary model is applied with a tortuosity factor, $\tau = 1$, the data result in a surface and volume porosity of 0.9–1.2% (Fig. 5) The
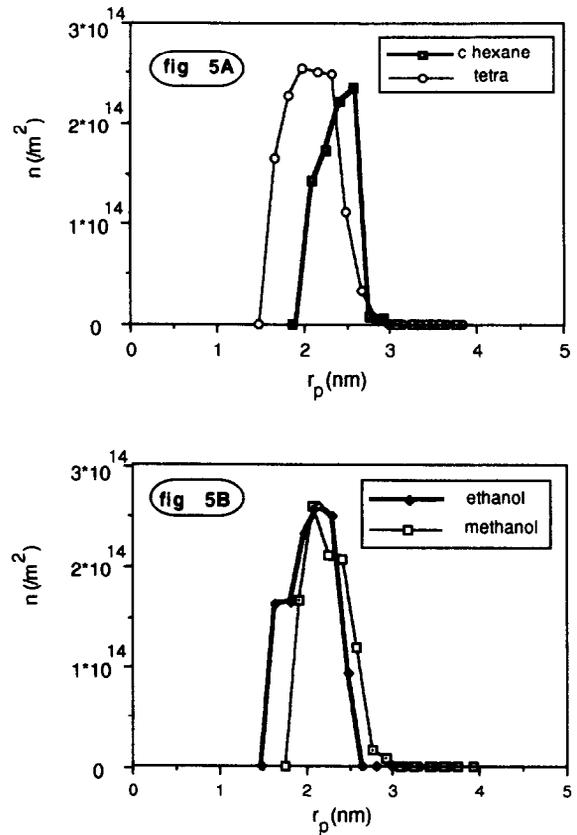
Fig 5 Pore size distributions of active pores of alumina membranes measured with different adsorbents in permporometry ($\tau = 1$) When corrections for tortuosity and resistance of the supporting layer are made, the number of pores (n) is increasing by a factor of about 40 (see text)

other techniques already mentioned indicate a much higher value for the volume porosity ($\sim 45\%$) [11,12]. One of the reasons for this large deviation is the extremely high tortuosity factor of the alumina membranes For many porous media the tortuosity factor has a value of 2–3, but for the alumina system a value of 13 was found [12]. Another point is that, due to the very thick sublayer of the alumina membranes, the effective driving force across the top layer is only 30% of the total [11]. This means that, when the corrections for the tortuosity (so $\tau = 13$ instead of 1) and the resistance of the
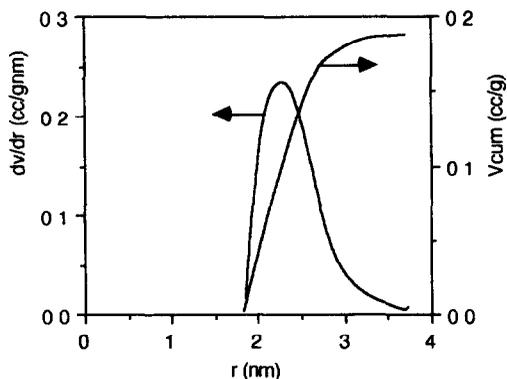
Fig 6 Pore size distributions for γ-alumina membranes using thermoporometry

Fig 7 Oxygen flux as a function of the Kelvin radius measured with different adsorbates found for a Nuclepore 0 015 μm membrane (calculated flux value using data given by Nuclepore $r=7\,5$ nm, $n=6\times10^{12}/m^2$, tortuosity$=1$)

sublayer are used, the volume porosity is calculated to be 35–50%.

Nuclepore membranes

Nuclepore membranes are claimed to have a very well-defined capillary structure with a uniform pore size and thus a tortuosity equal to one ($\tau=1$) can be assumed. Consequently these membranes should be very suitable for model studies. In this work membranes with a claimed pore radius of 7 5 nm were used.

The resulting pore size values found by permporometry (Fig 7) are indeed in reasonable agreement with the expected values. The experimental flux, however, appears to be 7 times higher than the value calculated from the data given by Nuclepore (number of pores: $6\times10^{12}/m^2$, tortuosity: 1, pore radius 7.5 nm)

Using electron microscopy (EM), the number of pores of similar membranes have been investigated by a number of researchers [16,17]. Their results appeared to correlate very well with the Nuclepore values (also determined by EM) The only possibility to explain the apparent discrepancy is the tortuosity factor, which is suggested to be too high. A tortuosity factor lower than 1 can be related to a widening of the pores inside the membrane,

which accounts for a lower resistance for transport. From the experimental fluxes, the effective pore size (for water and gas transport[1]) is estimated to be twice the size of the pore opening. Altogether this means that pores of a Nuclepore membrane have a narrow pore mouth with a size claimed by the manufacturer and a larger effective pore size inside the membrane which accounts for the main transport resistance

Since the pores of the Nuclepore membrane are relatively large, the thickness of the t-layer is of minor importance (Fig. 7) A remarkable effect, however, is that the t-layer thickness appears to be unchanged at very low relative pressures, which might be due to specific interaction (instead of only Van der Waals interactions). Going from a relative pressure of ~0.7 to 0 2, the flux through the membrane is constant but when the relative pressure is decreased to 0, a 10% increase in flux is found. This increase corresponds with a t-layer thickness of about 0 5 nm which is the thickness of about one monolayer of ethanol molecules [14].

PPO membranes

Pore size distributions of PPO membranes were determined using methanol and ethanol

as the condensable component In Fig. 8 results
for different samples of PPO membranes are
given. It appears that the largest interconnect-
ing pores present in PPO membranes have a
size of about 15 nm, although a large number of
small pores are present too. Despite their low
number, the larger pores mainly determine the
performance of the membrane. Consequently
the thickness of the adsorbed t-layer is not of
significance; it is sufficient to know that it is
very small. Using the same approach as before,
the thickness for methanol was found to be 0.25
nm. For ethanol the thickness was estimated to
be 0 5 nm.

In order to calculate the number of pores
present in the membrane skin, all characteris-
tic parameters in eqn (3) are needed. With the
gold sol method [18] the skin thickness has
been determined to be 0.2 μm and (assuming
the tortuosity factor equals one) the number of
pores can be estimated. From the number of
pores and their sizes the surface porosity is cal-
culated to be 0.5%, a very low value, as is also
found for other UF membranes [19,20]

From thermoporometry and the gas adsorp-
tion–desorption technique it was found that
PPO membranes possess a very sharp pore size
distribution, with a characteristic mean pore

size of 2 nm. This result is in strong contrast
with the permporometry data mentioned above.
Furthermore, the value of the total pore volume
calculated from permporometry is 2000 times
smaller than the value found by thermoporo-
metry (about 1.5×10^{-4} cm^3/cm^2 [21]) This
can be explained by the fact that in the case of
gas adsorption–desorption and thermoporo-
metry the membrane is characterized as a whole
(top- and sublayer) and small pores, which may
be present in the sublayer, are measured too In
the case of PPO membranes, the ratio between
the porosity related to active pores (deter-
mined by permporometry) and the overall po-
rosity (determined by thermoporometry) in-
dicates that 99 95% of the pores are present in
the sublayer and consequently do not influence
membrane performance. On the other hand,
from permporometry it is suggested, that the
pore volume of the larger active pores present
in the skin, is so small that their presence can-
not be detected by, e g. thermoporometry

PSf membranes

Pore size distributions of two PSf mem-
branes are given in Fig 9 Methanol and
ethanol, used as the condensable gases, showed
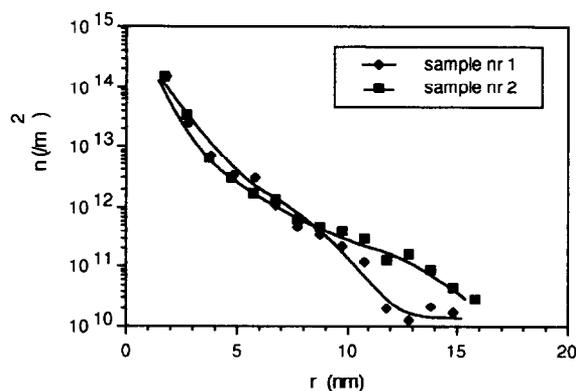
Fig 8 Pore size distribution using permporometry found
for two samples of the same PPO membrane (lab-made),
methanol was used as the adsorbate
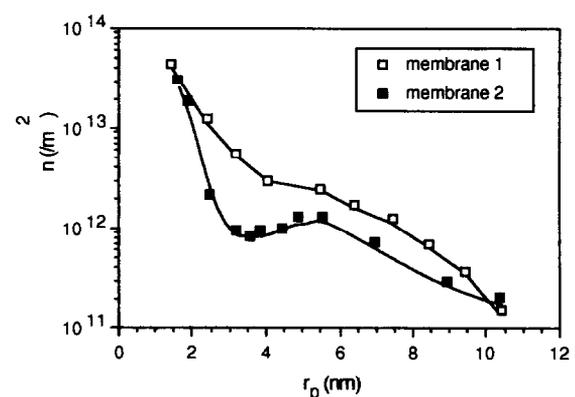
Fig 9 Pore size distribution using permporometry found
for two lab-made PSf membranes (cast from the same
polymer solution), ethanol was used as the adsorbate

a similar t-layer thickness as in the case of PPO.
Also for PSf membranes a broad pore size dis-
tribution is calculated (skin thickness 0.2 μm,
determined with the gold sol method [18],
$\tau=1$), with the largest pore size being approx.
10 nm. Compared to PPO membranes, the
number of the smaller pores (<5 nm) is sub-
stantially lower. In Fig. 9 is shown, that despite
the fact that the two membranes presented here
were cast from the same polymer solution, their
pore size distributions differ somewhat. One of
the membranes appears to have a certain dip in
the distribution at a pore size of about 3 nm.
This altogether indicates that, even for mem-
branes made at nearly the same time and from
the same polymer solution, differences in pore
structure can be present. This sort of anoma-
lies have also been shown by Nilsson [22].

The low surface porosity (calculated value
~0.3%) is probably the main reason that the
pore size distribution of PSf membranes could
not be determined by one of the methods al-
ready mentioned. This independence of pore
volume, and its high resolution for open inter-
connected pores is another advantage of perm-
porometry, in particular when UF membranes,
which are known to have a low skin porosity,
are evaluated.

DDS GR61PP

GR61PP membranes, manufactured by DDS,
have a claimed cut-off of 20 kDa. The pore size
distribution as determined with permporome-
try is remarkably sharp (Fig. 10). Most of the
pores have sizes between 1.5 and 5 nm, al-
though a few pores with a size larger than 10
nm were found. Estimating the thickness of the
top layer of the membranes, hence the length
of the pores (with $\tau=1$), to be 0.2 μm, and us-
ing the number of pores calculated (Fig. 10),
the surface porosity was calculated to be about
1%.

The pore sizes (Fig. 10) found in this work
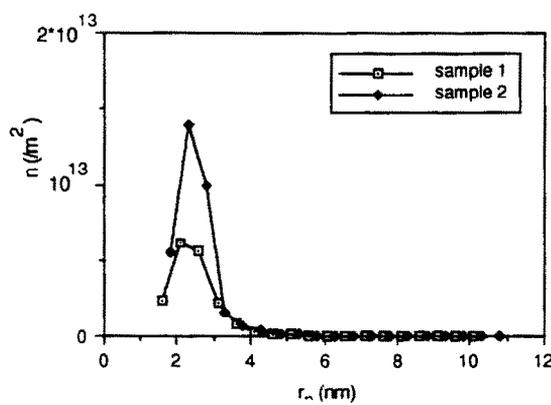
Fig. 10. Pore size distribution using permporometry found
for two samples of the same DDS GR61PP membrane,
ethanol was used as the adsorbate.

are somewhat lower than the values found by
Hanemaaijer et al. [23] and Nilsson [22]. Ha-
nemaaijer et al. used rejection measurements of
low molecular weight sugar molecules [23],
whereas Nilsson [22] determined the pore size
distribution of the same type of membranes
with the liquid–liquid displacement technique.
Although their results are not comparable, both
found that a considerable number of large po-
res were present. The 'characteristic pore size'
of Hanemaaijer was about 10 nm (radius),
the pore sizes of Nilsson ranged from 25 nm to 100
nm. Nilsson also found that the porosity (num-
ber of pores) of membranes is inhomogeneous:
the pore number on one part of the membrane
differs significantly from another part. The lat-
ter is confirmed by permporometry measure-
ments (Fig. 10), but pore sizes larger than 10
nm were not detected. The large differences in
pore size might be due to the use of the different
characterization techniques. The liquid–liquid
displacement technique, used by Nilsson can
cause swelling of the polymer, an effect that may
induce larger pore sizes [3]. Such swelling ef-
fects might also play a role in permporometry
measurements, but this was not found in the
analysis of previous experiments using PPO and
PSf membranes [19,21].

Some comments on the pore size distribution determination by permporometry

The distributions determined for the different polymeric membranes are characterized by an asymmetric shape. For all the membranes, it appears that a relatively large number of small pores ($r<2$ nm) are present. The question arises whether this porosity really corresponds to such small pores or is an artefact induced by the characterization technique itself.

One should realize that in the concept used here, the discrimination between t-layer desorption (or adsorption) and the capillary condensation is only an estimate. In case of the ceramic membranes the adsorption and desorption branch can be separated easily, as shown in Fig. 3. The lowest relative pressure where the adsorption and desorption process meet, is directly related to the point were capillary condensation and adsorption processes merge. For these membranes this transition is sharp because the pore size is well-defined. The question, however, is what happens when a wider pore size distribution and a relatively large number of small pores are present. In such a case the t-layer analysis proposed in this work neglects the presence of these small pores in favour of a larger t-layer thickness.

The range over which the Kelvin relation is valid is not strictly defined, but it is generally agreed that for pores with radii smaller than 1.5 nm, the equation is not valid. This can be rationalized because in these very small pores (about the size of a few molecules), the concept of a meniscus becomes meaningless [9]. In very small pores (micropores), the interaction between molecules and pore wall will be much higher than in mesopores. In such small pores adsorption already occurs at very low pressures and molecules present inside the pores can only be removed by using very low relative pressures ($p_r=0$ or in vacuum) This is not only true for

the adsorbates used in this study, but also when such membranes are used in actual applications. This means that the transport of molecules in such pores is hindered very much. Together with the fact that in UF membranes the larger pores will mainly determine transport properties and hence the performance of the membrane, it can be concluded that even when small pores are present permporometry indeed gives relevant data on the structure of the membrane [21].

Conclusions

Permporometry is a method by which the active pore size distribution can be calculated accurately. Characteristic data found by permporometry, sometimes deviate substantially from the characteristics determined by other methods. These discrepancies can be fully understood from the pore structure itself.

The pore size distribution of ceramic γ-alumina membranes is very narrow, whereas the distributions of polymeric UF membranes are substantially broader. From the latter it can be concluded that the actual performance of polymeric membranes is governed by the larger pore sizes.

List of symbols

p_r	relative pressure (-)
θ	contact angle (°)
γ	interfacial tension (N/m^2)
r_{k1}	(Kelvin) radius describing the curvature of the liquid–gas interface (m)
v	molar volume (m^3/mol)
J_k	diffusive flux (mol/sec-Pa-m^2)
n	number of capillaries per unit membrane area (1/m^2)
r	pore radius (m)
Δp	partial pressure difference (Pa)
l	thickness of the porous medium (m)

M molar mass of the gas (g/mol)

τ tortuosity (-)

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