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## Characterization of ultrafiltration membranes using S.T.M.

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**Résumé.** — Dans ce travail, nous avons étudié les membranes d'ultrafiltration par microscopie à effet tunnel, nous montrons que cette technique permet de les caractériser. Malgré les limites de la méthode (la forme de la pointe et la mince pellicule de carbone déposée sur ces membranes pour les rendre conductrices), nous obtenons des images reproductibles de leur surface. Ces images révèlent la forme et les dimensions des pores ainsi que la rugosité de la surface. Les valeurs moyennes de la densité des pores et de leur taille s'accordent avec les résultats obtenus par d'autres techniques.

**Abstract.** — In this report, we present the topography of ultrafiltration membranes by scanning tunneling microscopy. For making these non conducting materials to STM examinations, we have coated it by a thin carbon film. In spite of limitations induced by the coating film and by the tip shape, the STM images yield and average value of pores size and of pores density in good agreement with results achieved by other techniques.

### Introduction.

Ultrafiltration (uf) membranes are employed to retain macromolecules in solution. Because the membranes exhibit pores whose diameter is equal to or less than that of the macromolecule, they act as a sieve. Organic membranes are obtained by polymer solution coagulation [1] and solvent evaporation, resulting in pores whose size has to be dispersed as shown in the indirect characterizations carried out up to now [1-3]. Knowing the size, number and topography of the surface is important since:

- 1) pore size determines membranes selectivity;
- 2) solvent flow rate through the membrane is directly linked to the size and number of pores;
- 3) surface topography plays a part in matter accumulation at the surface following filtration.

Up to now, the values of these parameters had not been obtained by direct measurements due to, on the one hand, the small dimension of the pores whose diameter can range from the nanometer to some nanometres, and on the other, the fragile nature of this material. Indeed,

because polymers are damaged by electronic beams they do not lend themselves to conventional electronic microscopy.

We therefore tried STM [4] to characterize these membranes. *A priori*, this technique offers the advantage of providing a topography of the surface which is the active part of the membrane, with a resolution amply sufficient to address the issues of pore dimension and density.

It also features drawbacks that we will try to present and analyze. In particular, polymer membranes are seldom conductive and cannot *a priori* furnish images by STM.

### Experimental.

To observe the topography of ultrafiltration membranes using STM, the membrane surface must be conductive. To do this, several methods can be envisaged, the simplest consisting for us of depositing by evaporation at vacuum of  $10^{-5}$  torr, the thinnest possible carbon film (2 nm) to allow for the detection of a sufficient tunnel current ( $I_t = 0.1$  nA) and achievement of an image. Where required, the coated membranes were soaked in distilled water (pH = 6.3) to favour the flow of electric current at the surface.

The STM used through this work is a so-called "pocket-size" apparatus [5], operating in the air and in the constant current mode [6], since it is the best way of achieving rough surface topography.

With this operating mode, tunnel current control allows the tip to be kept at a constant distance from the sample during surface scanning. A tunnel image therefore yields the tip height  $z$  as a function of the position  $(x, y)$  on the surface. Given the major roughness of the surface, the tip-surface distance is kept as high as possible by using a tunnel current less than 0.2 nA and bias voltage in excess of 0.6 V. Typically, the observed surfaces vary from  $40 \times 40$  nm<sup>2</sup> to  $700 \times 700$  nm<sup>2</sup>. Scanning frequencies range from 1 to 0.1 Hz and image acquisition time is in the order of the minute.

The tips used in our experiment are made of 0.1 mm tungstene wires electrolytically thinned out in a NaOH solution. Magnifications are determined following voltage calibration with the help of a graphite sample on which atomic resolution is performed [7,8].

In this paper, the studied membranes are made of sulfonated polysulfone furnished by Techsep. Molecular weight cutoff is 100 kd. In other words, 90% of the macromolecules whose molecular mass exceeds  $10^5$  g/mole is retained.

For each membrane, many surface images have been recorded in different locations to confirm the statistic reproducibility of the observations made.

This operating mode supported the recording of images as shown in figure 1. In figure 1a the observed area is equal to  $75 \times 75$  nm<sup>2</sup> and the roughness defined as the tip height variation between the highest and the lowest points equals 4 nm. This image allows characterization of a pore. In figure 1b the scanned area is equal to  $194 \times 208$  nm<sup>2</sup>, roughness equals 10 nm. This image allows the pore density to be estimated and defined as the number of pores per unit area.

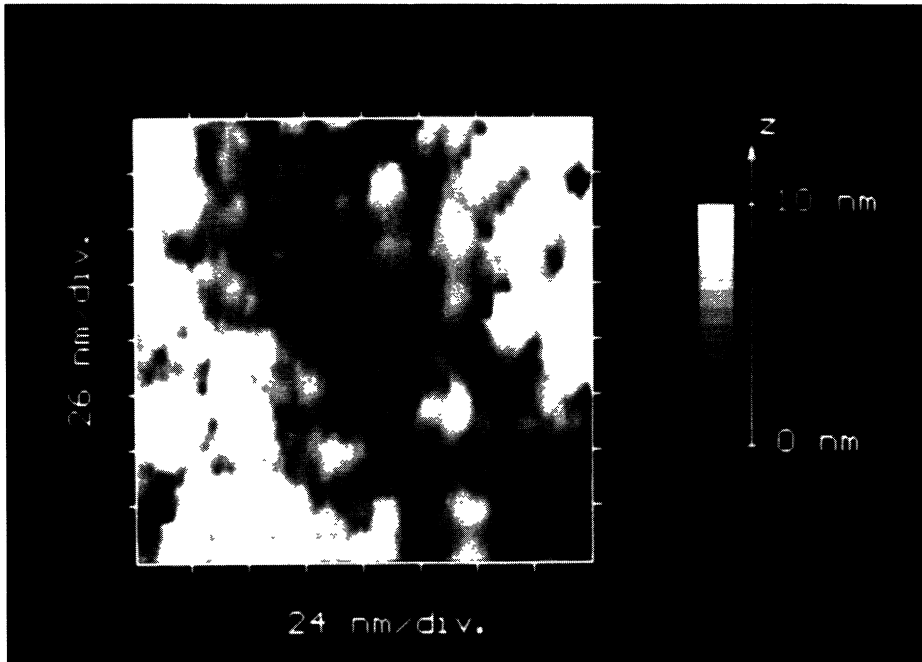
Analysis of these images permits characterization of the uf membranes.

### Results and discussion.

Handling of these images turns out to be difficult and the results obtained are prone to errors. Basically, two problems hinder the method used. On the one hand, the carbon layer deposited on, the membrane partly masks the surface and, on the other, the tip may adversely affect observations. To overcome these two limitations, the following provisions have been made which define our method of analysis.



a)



b)

Fig. 1. — a) STM image of a sulfonated polysulfone uf membrane showing a great pore whose depth is about 4 nm, surrounded by two smaller ones. The scanned area is  $75 \times 75 \text{ nm}^2$  while the Tunneling current is kept at a value of 0.2 nA. Bias voltage and corrugation are 0.6 V and 4 nm respectively. b) Image at high scale of a sulfonated polysulfone uf membrane. This topography shows pores size dispersion and gives the porosity of the membrane skin layer. The scanned area is  $192 \times 208 \text{ nm}^2$ . Tunneling conditions: 0.2 nA, 0.6 V. The maximum corrugation is about 10 nm.

**ROLE OF THE CARBON LAYER.** — It is considered that the adverse effect resulting from the carbon layer deposition cannot exceed the thickness of said layer. In other words, only a surface roughness with a magnitude in excess of the deposited carbon layer thickness is considered as significant.

**TIP ROLE.** — Although the part played by the tip in tunnel image formation remains partly unclear, its influence can be confirmed experimentally since, among other things, all observed pores exhibit a bottom part [9,10].

Indeed, the emitter atom on the tip, which in atomic resolution remains unchanged during an image can be altered in the case of a topographic image. With respect to extremely rough surfaces, this can seriously affect recorded topographies [11].

Hence, the recorded topography is the surface topography convoluted by the tip shape [12-14], as shown in figure 2. Given the reproducibility of our images, an approximation was attempted by first ruling out this effect. The operating mode based on positioning the tip as far away as possible from the surface (low tunnel current, high bias voltage) supports this approximation.

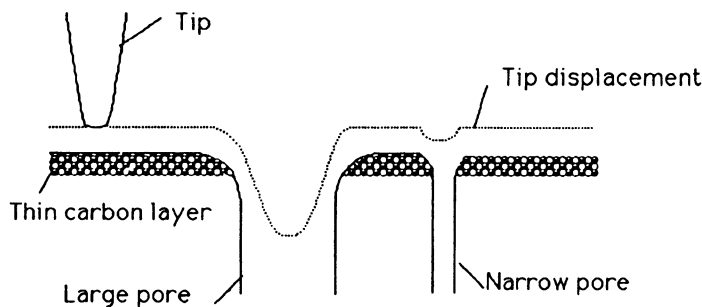


Fig. 2. — This scheme shows the effects of the tip shape on the recorded topography. Dotted line gives the displacement of the STM tip on the sample.

**PORE DEFINITION.** — Any variation in  $z$  in excess of the evaporated carbon thickness has been regarded as significant. It will therefore be assumed that a pore exists whenever a relative variation of the tip height higher than the carbon layer thickness is found in a given area. In practice, this is confirmed as pores sometimes are three or four times deeper than this thickness (even 80 times and more).

**DEFINITION OF A PORE SIZE.** — To define a pore size, measurements were carried out on images yielding the tip height as a function of the displacement. As diameter of the hole making up the pore we selected the distance from the total height variation of the tip.

Since the observed holes were not circular, two characteristic diameters were chosen, i.e., the highest diameter  $D$  and the smallest one  $d$ .

Repeated measurements on a single membrane supported a statistical study of the recorded scatterings on these measurements.

RESULTS. — All recorded tunnel images show the pore size to be highly dispersed, ranging from 1 nm to 35 nm.

Figure 3 illustrates high magnification images of different pores. Large surfaces were also investigated as shown in figure 1b. These two types of images supported our tentative measurement of the pore size and density. The pictures show that the pores may greatly vary in shape and are seldom the circular type depicted in theoretical models.

In these findings (see Fig. 3), the deposited carbon layer is 2 nm thick and the relative variations of the tip height range from 4 to 6 nm. According to our criteria, these three 4, 6 and 6 nm deep-surface corrugations were considered as the pore holes.

Using the same criteria defined above, these pore diameters were measured, yielding the following values:

for a)  $D = 20$  nm and  $d = 7.5$  nm

for b)  $D = 17$  nm and  $d = 9$  nm

for c)  $D = 24$  nm and  $d = 10$  nm

Averaging out these values on 17 pores, an average high diameter of 15 nm was found with a root mean square of 7 nm and a small diameter of 6 nm with a root mean square of 3 nm. Figure 4 lists all our results and the related dispersion.

Similarly, using the topographies analogous to that of Fig. 1b) the pore density was measured on the surface.

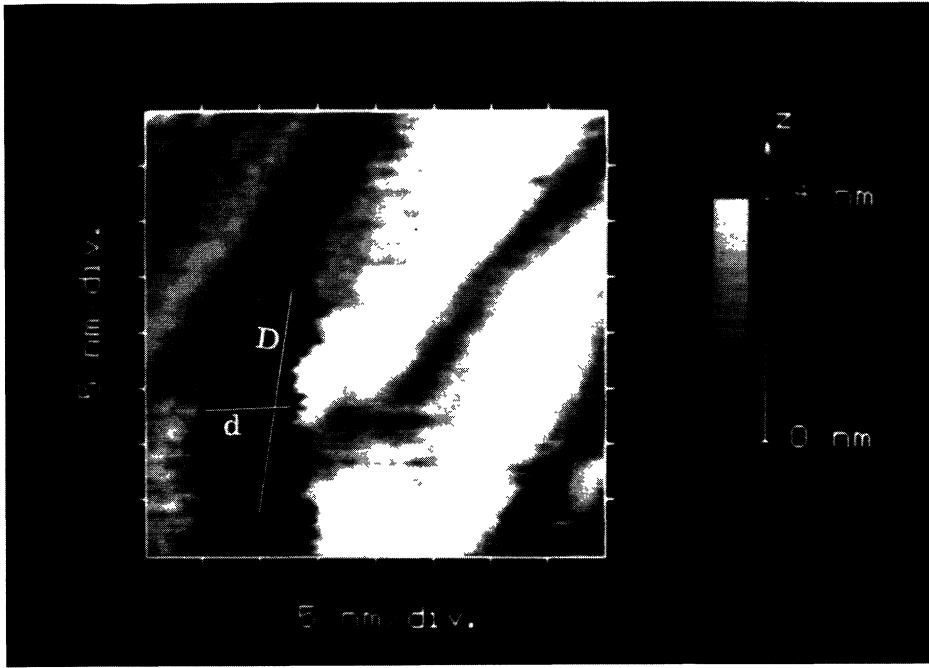
Following measurements carried out on about ten images, an average value of pore density equal to  $4 \times 10^{14}$  p/m<sup>2</sup> was found with root mean square of  $1.5 \times 10^{14}$  p/m<sup>2</sup>. These measured pore size and density yield a porous surface in the order of 4%. This is rather consistent with the values usually given for this type of organic membranes (between 5 and 10%).

## Conclusion.

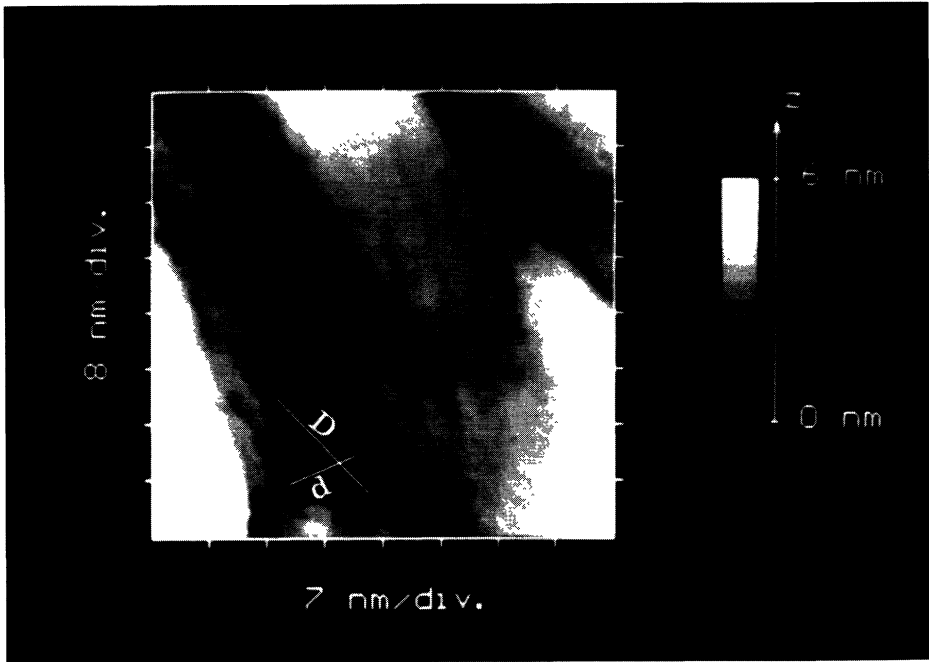
In this paper, we intended to show that tunnel imagery could be used to carry out measurements of the ultrafiltration membrane surfaces. By improving this technique through use of increasingly thinner depositions, an enhanced definition of the tip will result, leading to more accurate measurements and an improved approach.

From now on, scanning tunneling microscopy will allow images of uf membranes to be accessed at scales never reached before and may result in better membrane characterization.

Finally, it can never be fully stated that the observed pores really traverse the membrane. To address this issue, further studies using this observation technique are still needed.

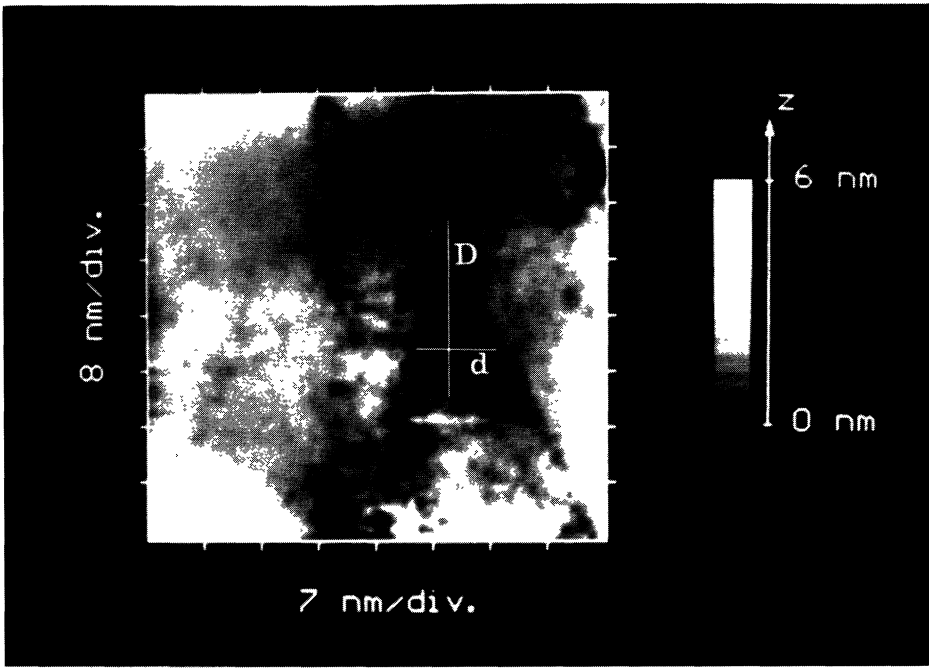


a)



b)

Fig. 3. — Images of pores indicating their size and shape dispersion on sulfonated polysulphone of membrane surface. Scanned Areas a)  $38 \times 41 \text{ nm}^2$  b)  $56 \times 61 \text{ nm}^2$  c)  $56 \times 61 \text{ nm}^2$  and corrugations a) 4 nm b) 6 nm c) 6 nm. The size of the greater pores are respectively a)  $D = 20 \text{ nm}$ ,  $d = 7.5 \text{ nm}$  b)  $D = 17 \text{ nm}$ ,  $d = 9 \text{ nm}$  c)  $D = 24 \text{ nm}$ ,  $d = 10 \text{ nm}$ . (Tunneling current 0.2 nA, Bias voltage 0.6 V).



c)

Fig. 3. — (continued)

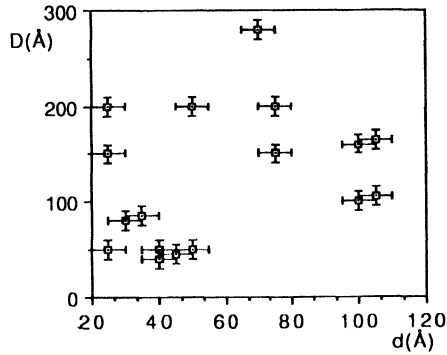


Fig. 4. — Dispersion of pores size “d” and “D” as deduced from STM measurements on the sulfonated polysulfone uf membrane surface.

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