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Critical Factors in the Determination of the Pore Size Distribution of Ultrafiltration Membranes Using the Liquid Displacement Method

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ABSTRACT

The pore size distribution of ultrafiltration membranes can be determined using the liquid displacement method developed by Munari and coworkers. However, when this technique is employed, several phenomena have to be taken into consideration in order to avoid erroneous results. In this paper three phenomena are discussed. 1) During the measurement the liquid flow is increased stepwise, resulting in pressure instabilities at the membrane surface. 2) The membrane permeability may be dependent on the pressure and has to be determined at several pressures. 3) Successive measurements of the same module show large differences between the first run and following runs. Traces of glycerol, incomplete pore filling, or long-term swelling are thought to be responsible for erroneous results in the first run.

INTRODUCTION

The pore size distribution of a membrane can be determined using the liquid-displacement technique. The liquid-displacement method was introduced by Bechold et al. (1) and Erbe (2) in 1931 and has been further developed by Munari and coworkers (3). The advantage of this technique is that the membranes are not subjected to drying which may alter the porous structure. Furthermore, by using a pair of liquids with small interfacial tension, the pore sizes can be measured at relatively low pressures.

We have found that for a correct performance of the liquid displacement measurements, several phenomena have to be taken into consideration: 1) pressure instabilities during the measurement, 2) pressure-dependent membrane permeabilities, and 3) different results from successive measurements of the same module. It is the authors' opinion that the influence of these effects has been underestimated by Munari and coworkers.

THEORY (1, 2)

For the liquid displacement method, two immiscible liquids, A and B, with a low interfacial tension are used. Liquid A, the stagnant liquid, is used to fill the pores of the membrane, while Liquid B, the displacing liquid, is present at the surface. Liquid A is the liquid that most readily wets the membrane material. In order to displace Liquid A in the pores by Liquid B, a certain pressure has to be applied. The pressure difference over the curved interface in the pores is dependent on the size of the pores. It is high for small pores (Laplace equation; Eq. 1).

During the displacement measurement the pressure is increased, hence the flux through liquid-exchanged pores increases. However, an extra increase in flux occurs due to the contribution of pores that have just responded to the displacement liquid. The flux through a membrane with a certain pore size distribution can be described by the Hagen–Poiseuille equation if a pore model consisting of parallel cylindrical pores is assumed (Eq. 2).

$$\Delta P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \cos \theta \tag{1}$$

where ΔP = pressure difference over the interface (Pa)
γ = interfacial tension (N/m)
r_1, r_2 = radii of the curved interface between the stagnant liquid and the displacing liquid (m)
θ = contact angle between the displacing liquid and the pore wall (°)

$$J = \frac{\pi \sum_i (n_i r_i^4)}{8 \eta \tau l} \Delta P \tag{2}$$

with

$$\frac{\pi \sum_i (n_i r_i^4)}{8 \eta \tau l} = p \text{ (permeability)} \tag{2'}$$

where J = flux (m/s)
p = permeability (m/Pa·s)
ΔP = pressure difference across the membrane (Pa)
r_i = pore radius (m)
n_i = number of pores of radius r_i per unit of cross section ($1/m^2$)
η = viscosity of the permeating fluid (Pa·s)
l = membrane thickness (for asymmetric membranes the thickness of the top layer) (m)
τ = tortuosity factor (—)

MATERIALS AND METHODS

The setup developed by Munari and coworkers (3) has been used for the measurements. In this setup the flux is chosen as the variable while the pressure needed to obtain this flux is registered. A HPLC pump (Waters 590) was used to enforce a certain flow through the membrane. This causes a pressure difference across the membrane. The high pressure side is in the bore of the hollow fiber. The pressure is measured using two sensors (Cerabar, 0–1 bar and 0–10 bar). The accuracy of the sensors is 0.5%.

Isobutanol (Merck, pro analysi) and distilled water were mixed and kept for one night to remove any air bubbles present and to obtain two saturated immiscible phases. The interfacial tension is 1.85 mN/m at 22°C (1). Lab-made hollow fiber membranes from the polymer blend poly(ether sulfone)–poly(vinyl pyrrolidone) (PES/PVP) were used for the measurements (4). One hollow fiber was glued at both sides in metal tubes to obtain a module with a length of 10 cm and a membrane surface of 7×10^{-4} m^2. To remove the glycerol used for storing the membranes, the modules were flushed with water at a pressure of 2 bars for 30 minutes. After this they were syringed with the most wettable liquid and then placed in the wettable liquid overnight.

For reliable measurements the lowest pressure that could be applied accurately was 0.1 bar. Measurements were stopped at a maximum of 5 bars to prevent the fiber from breaking. Using the saturated liquid pair isobutanol/water (interfacial tension 1.85 mN/m) (1) implies that pores with radii between 370 nm (0.1 bar) and 7 nm (5 bar) can be measured.

After the displacement measurement, when the stagnant liquid has been displaced in all pores, the pump is stopped and the pressure difference reduces to zero. Then the flux of the membrane for the displacing liquid is measured at different pressures in order to verify whether the permeability is independent of pressure.

Water saturated with isobutanol was found to be the best wetting phase for the PES/PVP membrane, and it was used as the stagnant liquid. The diameter of the dry fiber was compared with the diameters of the fibers swollen in the two saturated liquids; the swelling was 7% for both liquids. Therefore, it was assumed that the swelling of the membrane structure does not change during measurement.

RESULTS AND DISCUSSION

Pressure Instability during the Measurement

While performing the displacement measurements it appeared that each stepwise increase of the liquid flow through the membrane was immediately followed by an increase of the pressure (P_{max}) in the bore of the fiber. Next, the pressure decreased until it became constant after a few minutes (P_{end}). In Fig. 1 both pressures are plotted as a function of the flux through the membrane. To calculate the *permeability*, the imposed flow was divided by P_{end} because this indicates the equilibrium pressure. However, for a few moments the pressure in the membrane was higher than P_{end} and the smaller pores (related to P_{max}) already responded. Therefore P_{max} was used to calculate the *pore size distribution* of the

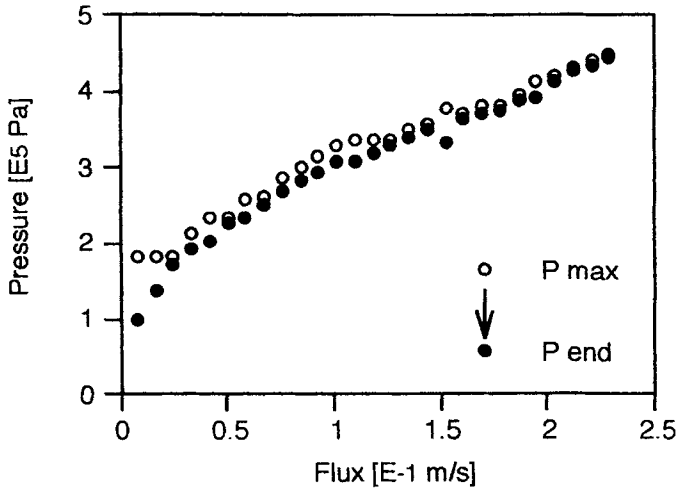

FIG. 1 Results of a displacement measurement of a hollow fiber PES/PVP membrane. For each stepwise increase of the flux through the membrane (by an increase of the flow of the HPLC pump), pressure first increases to P_{max} and then reaches the equilibrium pressure P_{end}.

membrane. Neglecting this pressure instability results in overestimation of the pore sizes. The difference between P_{max} and P_{end} was about 0.2 bar. In this case the overestimation of the pore radius is 10 nm at P_{max} of 1 bar. The effect can be diminished by a more gradual increase of flow.

Effect of Pressure on Membrane Permeability

The cumulative permeability is plotted versus the pressure in Fig. 2. The open circles shown in Fig. 2 are the data of the displacement measurement. The straight line represents the isobutanol permeability of the membrane when it is completely filled with the isobutanol phase. For an ideal situation this permeability must be independent of the pressure, as indicated by the dashed line. The increased isobutanol permeability might be caused by expansion of the fiber as pressure increases.

To find the real permeability dependence on opening of the pores, the data of the displacement measurement have to be corrected for the influence of the pressure. To do so, each value of the permeability has to be diminished with the pressure times the slope of the upper line. Without this correction the number of pores is overestimated, especially in the small pore radius region. In their experiments, Munari and coworkers did not check whether the permeability of the membranes is pressure-dependent.

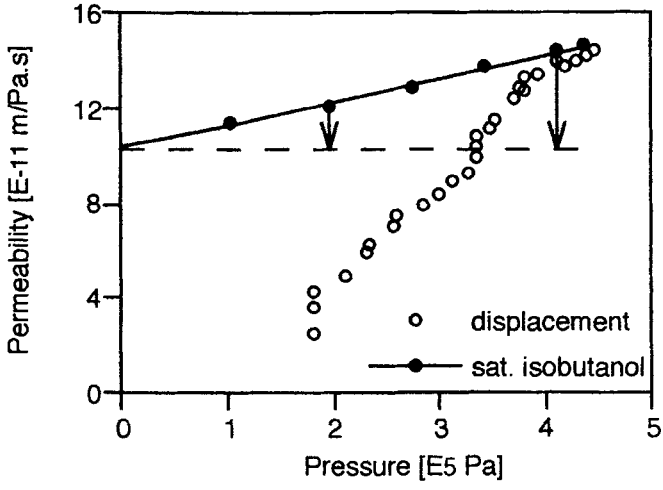

FIG. 2 Permeabilities of the displacement measurement (lower curve) and of the fully liquid displaced membrane (upper curve) for saturated isobutanol. The arrows indicate the correction for the pressure dependency of the permeability.

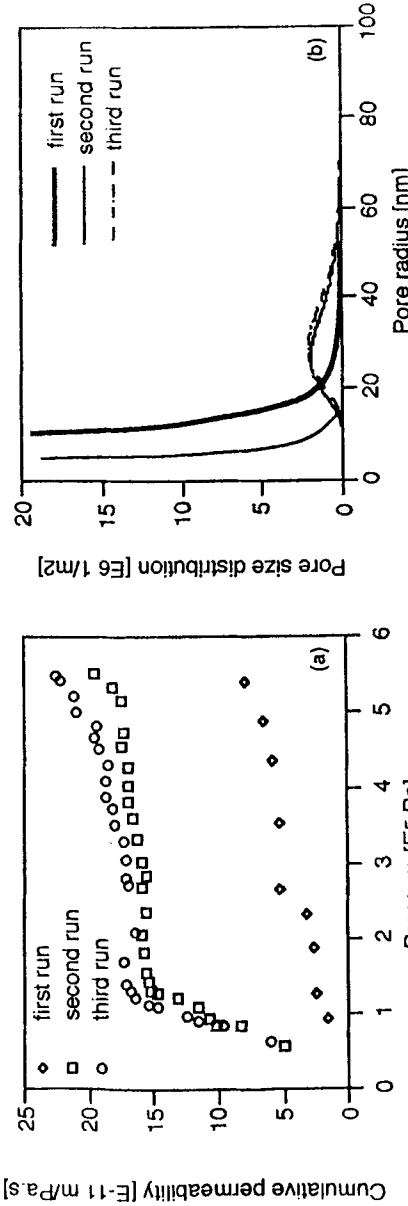

FIG. 3 Corrected cumulative permeability versus the applied pressure (a) and pore size distribution (b) for three successive measurements of the same module.

Successive Measurements of the Same Module

In Fig. 3(a) the corrected cumulative permeability for *one* module in three successive measurements is given. Between the measurements the module was removed from the setup, syringed with and stored in the aqueous phase. The pore size distribution curves resulting from these measurements are shown in Fig. 3(b). For the first measurement the maximum of the pore size distribution curve is at a pore radius smaller than 10 nm. In the second run, however, the total permeability of the membrane is 2.5 times as high as in the first run due to the appearance of larger pores. The difference between the second and third runs is not very profound.

The low permeability found in the first run is probably caused by traces of glycerol or by incomplete filling of the pores by the stagnant liquid. The expansion of the fibers at increasing pressure is too little to cause such a strong increase in permeability. Also, the time between two measurements was usually 24 hours, during which relaxation of the expansion would occur. The small difference between the second and third runs could be a result of the expansion. Another reason for the increase of permeability might be long-term swelling of the membrane material. The bubble point technique (Coulter porometer) was used to verify whether any large holes were present; however, no pores larger than 100 nm were found.

CONCLUSIONS

In order to correctly determine the pore size distribution of ultrafiltration membranes using the liquid displacement method, several phenomena have to be taken into consideration. Pressure instabilities caused by a stepwise increase of flow can be corrected for when both the maximum pressure and the equilibrium pressure are measured. The membrane permeability may be dependent on the pressure, and therefore it has to be determined at several pressures. Traces of glycerol, incomplete pore filling, or long-term swelling may cause erroneous results in the first run. Successive measurements of the same module give more reliable information on the actual pore size distribution of the membrane.

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