Porosimetric characterization of polysulfone ultrafiltration membranes by image analysis and liquid–liquid displacement technique

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HIGHLIGHTS

- LLDP offers a valuable tool for membrane structural characterization.
- Comparison of LLDP and FESEM results gives good accordance except for cut-off values.
- FTIR-ATR information helps to increase membrane wettability improving LLDP analysis.

ARTICLE INFO

ABSTRACT

Structural and surface properties of two commercial polysulfone ultrafiltration membranes have been evaluated by different techniques. Pore size distributions have been determined by Liquid–Liquid Displacement Porosimetry (LLDP) as well as by image analysis performed onto Field Emission Scanning Electron Microscopy (FESEM) images of the membrane surfaces. Fourier Transform Infrared Spectroscopy (FTIR) has been used to investigate membrane composition, and in particular, to obtain proper information on the presence of an additive within the membrane structure.

Porosimetric results obtained by the two independent techniques compared reasonably well and the Molecular Weight Cut Off (MWCO) of the two membranes estimated from LLDP pore size distribution was found to be in good agreement with the nominal values given by manufacturers.

1. Introduction

Ultrafiltration (UF) is a pressure driven process where membranes are used to separate macromolecules from fluid streams. In such process, the selectivity is mainly determined by the porous structure, since retention is determined for these membranes by a sieving mechanism.
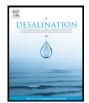
In that sense, sieving curves are the usual way to evaluate the selectivity of UF membranes. These curves are obtained by plotting the retention of some selected solutes, called tracers, versus their molecular mass and the analysis of such plots leads to define the so-called Molecular Weight Cut-Off (MWCO), a key parameter in selecting membranes for given applications. This parameter has reached the category of a "de facto" standard [1] not only for the characterization of UF membranes, but also for the nanofiltration (NF) ones [2].

In effect, for membrane manufacturers and end-users as well, MWCO value is a very valuable parameter because it gives an idea about the molecular weight of species being separated by such membrane.

Manufacturers generally specify for their membranes a nominal MWCO defined as the molecular mass of the solute that is (or would be) 90% retained by the membrane. However, it has been often pointed out [3–8] that the reported values of a cut-off for a given membrane may be strongly dependent on the different methodologies and/or experimental test conditions used. Effectively, the influence of important experimental factors as, for example, device configuration and operational parameters as channel geometry or feed turbulence degree on the membrane surface, which prevent concentration polarization and fouling phenomena, is quite often neglected. Moreover, these factors are not always controlled or clearly stated [1].

Moreover the results of retention tests cannot be really considered as a characteristic parameter of the membrane because they also depend on the shape, flexibility and molecular weight distribution of the

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macromolecules used for these tests [9] and their interaction with the membrane materials. So, it can be concluded that the results from retention tests could be sometimes far from what might be expected from the actual membrane pore size [10].

Another aim when determining MWCO is to evaluate the pore size distribution of membranes in order to know, from such structural information, which molecules can be retained or passed through the membrane pores. Once a unique relationship between retention results and the actual structural characterization of the membrane is assumed, the knowledge of the actual structure of the pores in the membrane will be really informative because it could be translated into retention characteristics for each particular solute.

Many characterization methods like permporometry, thermoporometry, mercury porosimetry, gas adsorption–desorption, nuclear magnetic resonance, gas–liquid porosimetry and liquid–liquid porosimetry along with several microscopic techniques, both electronic as scanning and transmission electron microscopies and atomic as atomic force microscopy, have been used to analyze the pore structure and pore size distribution of the membrane [11]. Each of these methods has different features and principles of operation and needs different theoretical considerations to convert the direct results into pore sizes. In any case, the information given by all these methods must not be considered as competitive but rather complementary, since all results should contribute to a complete picture of the pore characteristics.

UF membranes usually present pores in the range from some nanometers to 50 nm (0.05 μm) and a proper knowledge of the size distribution of those pores actually open for the flux (active pores) is of great interest to estimate the sort of macromolecules retained. Techniques, such as those based on the bubble point test that have gained enormous relevance for the characterization of microfiltration membranes, cannot be properly applied to UF membranes due to the high pressure (more than 10 bars) to be applied in order to evaluate pore sizes below 0.1 μm, owing to the high value of the surface tension ($\gamma = 72$ mN/m) between air and the wetting liquid (water) [11]. On the contrary Liquid–Liquid Displacement Porosimetry (LLDP), because it uses a pair of immiscible liquids with very low interfacial tension, is very suitable for characterizing UF membranes at relatively low applied pressures. Tung et al. [12] consider the technique as relatively new although, in fact, it comes from earlier works of Erbe [13] who proposed the principles of the methodology as an extension of the well-known bubble point technique previously proposed by Bechhold [14]. After several years of scarce attention, in recent times, more and more research groups are getting interesting results using LLDP for the characterization of ultrafiltration membranes [15–18].

Some of us in the frame of a long-term collaboration have designed and built-up powerful LLDP devices, fully automated and very precise, for obtaining an exhaustive porosimetric characterization of UF membrane with different MWCO and configuration [19–25].

In this work, porosity and pore size distribution of two different kinds of commercial polymeric UF membranes evaluated by LLDP will be used to estimate their MWCO according to a procedure previously developed [26].

In addition to LLDP experiments, FESEM pictures will be obtained and used to get information on pore size distributions. Image analysis of several microscopic images is frequently used because it gives a good view of the membrane surface that can be used to study surface membrane modifications [27–29]. In this case such image analysis was performed in order to obtain independent information on the porosimetric characteristics of the membrane.

Finally FTIR combined with Attenuated Total Reflectance (ATR) and Photoacoustic Spectroscopy (PAS) allows analyzing the membrane composition and provides useful help for a better understanding of some anomalous results we obtained at the initial steps of LLDP measurements.

2. Experimental

2.1. Membranes and chemicals

Two commercial UF membranes (GR61PP and GR70PE) were kindly supplied by Alfa-Laval. Both membranes are made from polysulfone and have a MWCO of 20 kDa, according to the manufacturer [30].

All membrane discs were bathed in Milli-Q water for 24 h to eliminate any previous soaking of preservative agent, before being used for LLDP analysis.

Isobutanol from Scharlab (analysis grade, purity >99.5%) was used as received without further purification. Water was bidistilled and Milli-Q treated freshly prior to use.

2.2. Liquid–Liquid Displacement Porosimetry

The porosimeters used in the analysis consist of two twin automated devices developed in parallel with SMAP (University of Valladolid) and DCCI (University of Genoa) laboratories [19,20]. A detailed description of the equipment and the experimental procedure can be seen elsewhere [20] while a scheme of the experimental setup has been published in several previous papers, see for example [26]. The main feature of the equipment is the use of a precise syringe pump ISCO-250D, allowing accurate and very stable fluxes without fluctuations that make unnecessary any sort of dampening. The experimental procedure allows relating the applied pressure and the corresponding pore radius opened at a given applied pressure according to the Cantor equation [31] provided that the contact angle between the liquid–liquid interface and the membrane material could be assumed to be zero,

$$\Delta p = \frac{2\gamma}{r_p} \tag{1}$$

where Δp is the applied pressure, γ the interfacial tension (1.9 mN/m in our experimental conditions) and r_p the equivalent pore radius.

By increasing the applied pressure stepwise, corresponding pore radii and flux values, represented as the permeability of the membrane (flux/pressure ratio), are obtained and form what we call porogram. Therefore, by measuring the equilibrium pressure drop corresponding to each increment of flux, a pore size distribution of the membrane can be evaluated.

For it is supposed that pores are cylindrical and normal, then Hagen–Poiseuille equation for convective flow applies to correlate the volumetric flow, F, and the number of pores, n_k, having a pore radius, r_k. For each pressure step, p_i, the corresponding flow measured, F_i, can be correlated in such a way with the number of pores opened in that and all previous steps by:

$$F_i = \sum_{k=1}^{i} \frac{n_k \pi r_k}{8\eta l} p_i \tag{2}$$

where η is the dynamic viscosity of the displacing fluid (aqueous phase of liquid mixture, then a value of 0.89 mPa·s, for water at 25 °C, was used in calculations), l is the pore length (membrane thickness for symmetric membranes while for asymmetric ones must be evaluated as the active layer thickness). n_k and r_k are, respectively, the number of pores and the radius of such pores opened up during the k-th step (for $k = 1, \ldots, i$).

It should be noted that this pore size corresponds to the narrowest section along the pore found across the whole membrane. Even with membranes having a so complicated pore structure (hourglass like) as those studied here, this technique focuses the part of the pores which presents the narrowest section. This section is what effectively governs fluid transport and also retention capabilities.

The liquid mixture used to perform the LLDP measurements has been a 1:1 w/w mixture of water/isobutanol. The mixtures were