Journal of Membrane Science 470 (2014) 219–228

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Fitting approach to liquid–liquid displacement porosimetry based on the log-normal pore size distribution

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ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form
16 July 2014
Accepted 17 July 2014
Available online 24 July 2014

Keywords:
Membrane characterization
Ultrafiltration (UF) membranes
Liquid–liquid displacement porosimetry (LLDP)
Log-normal pore size distribution
Permeance distribution

ABSTRACT

Liquid–liquid displacement porosimetry (LLDP) has been used to characterize several UF membranes in a wide range of molecular weight cut-offs (MWCO). A new method to convert porosimetric data into pore size distributions and related information has been developed based on assuming log-normal pore size distributions. The results of this are in good agreement with those from the customary data conversion algorithm (as derived by Grabar and Nikitine). The proposed method can also be used when a reduced number of experimental data points is available, leading to a significant reduction of data acquisition time needed to complete a reliable analysis.

1. Introduction

For most of the membrane separations, especially those based on the application of a pressure gradient across the membrane (namely microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF)) sieving is the main separation mechanism and therefore, the relative size of the membrane pores/interstices and the molecules to be retained, is the key factor to control separation.

A proper knowledge of the porous structure of a membrane (usually consisting of a section which controls separation or active layer, supported on a more open porous substructure or support) is very important to assess its separation capabilities.

This kind of knowledge is the target of multiple characterization methods that can be grouped under the term porometries. These methods are based on very different physical principles but all of them try to obtain information about the pore size distribution (PSD), from which important separation parameters such as mean, maximum and minimum pore sizes, porosity or pore density can be calculated. Methods based on the bubble point test have been gaining recognition due to their unique capabilities. For example, these methods test the membrane in wet state, very close to the real operation conditions. In addition, the information given refers only to active layer pores (even when the support is not detached from the whole membrane).

There are two methods based on the bubble point: the gas–liquid displacement porosimetry (GLDP) and the liquid–liquid displacement porosimetry (LLDP), whose main difference relies on the state of the fluids used for displacing the inner liquid. Both techniques have been indistinctly named as capillary flow porometry [1], liquid extrusion porometry [2], or even combined bubble pressure and solvent permeance method [3,4], but all of them refer to the same principle [5].

Both LLDP and GLDP are well-known and very similar in concept and even in operation mode. Nevertheless GLDP has gained general recognition while LLDP is still scarcely used, because it is more difficult to operate and less reproducible. Some of the authors have been working over in the last years to improve LLDP in an effort to show the potential of the method, especially for tight UF and NF membranes where other methods have strong difficulties to get reliable results. One of the features of the LLDP that makes it less attractive than GLDP is the shape of the distributions it provides. Certainly the good aspect of the GLDP results is a consequence of a continuous measurement procedure. Commercial GLDP apparatuses usually divide the experimental range in 256 data points and determine corresponding data pairs (flux, pressure), resulting in a very smooth Gaussian distribution. The same procedure is not accomplished in LLDP because liquid–liquid equilibrium usually takes longer time (the whole experiment should take some hours) and there is no guarantee of obtaining superior results to GLDP.

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http://dx.doi.org/10.1016/j.memsci.2014.07.035
0376-7388/

Different algorithms are used to process data from GLDP and LLDP experiments. Gas–liquid experiments need to account for different gas flow regimes, namely Knudsen molecular flow along with Hagen–Poiseuille convective transport [6]. Moreover, the dependence of the gas permeance with applied pressure requires a different experimental procedure (wet run followed by dry ones) and different algorithms to convert experimental results into pore size information. The algorithms which could be used for processing data from LLDP experiments have been reviewed by Morison [7], who found that all of them are very sensitive to experimental errors requiring some smoothing to get reasonable distributions. Some authors have performed spline smoothing to get better results from LLDP [8,9], based on a polynomial fitting that somehow loses the physical meaning.

The approach in this work is to begin assuming a log-normal PSD and then fit the experimental results to such model function. A similar approach was used by Aimar et al. [10] to fit log-normal distributions from retention data, sometimes combined with moment theory to get more insight into theoretical distributions [11,12]. Most of the membranes found in the market are well described by a log-normal distribution of pore sizes [13], with a continuous range from many very small pores to few much bigger ones. This should lead to a right skewed distribution which is better described by a log-normal function.

2. LLDP theory

2.1. Traditional methods to determine pore number distribution

The final aim of LLDP characterizations is to determine the PSD of a porous sample, in this case a membrane. This technique is based on the Young–Laplace equation which relates the surface tension of a fluid inside a capillary with the radius of such capillary. The experimental procedure consists in forcing a liquid to enter the pores of a membrane previously filled with another immiscible liquid (wetting liquid).

If a perfect wetting of the membrane by the wetting fluid is assumed, the needed pressure to empty a given cylindrical pore is related to the radius of such pore through the so called Cantor equation (Eq. (1)) [14].

$$\Delta P = \frac{2\gamma}{r} \tag{1}$$

where ΔP is the applied pressure and γ the interfacial tension (N/m) between both liquids and r the equivalent pore radius.

This technique accounts for the narrowest section of the pores, because these pore-throats effectively govern the fluid transport and the retention capabilities of the membrane, no matter how complicated the membrane structure is.

The increase in the applied pressure is linked to an increase in the flow due to the opening of new smaller pores. Therefore, by measuring the equilibrium pressure drop corresponding to each increment of flux, the basic experimental information from LLDP is obtained.

A transport model inside the pores is then required to get the PSD. The Hagen–Poiseuille equation through capillary cylindrical pores is regularly used for convective transport of liquids inside pores. This geometry assumption is not as restrictive as it may look; since many membrane geometries can be simplified to a group of more or less straight cylindrical pores having a radius equal to the narrowest section of the actual pores found in the membrane structure. Therefore, the flux J_i (m^3/m^2 s) associated to the pores of radius r_i (m) of the membrane, when a transmembrane pressure ΔP (Pa) is applied, is given by the Hagen–Poiseuille equation (Eq. (2)).

$$J_i = \frac{N_i \pi r_i^4}{8\eta l}\Delta P \tag{2}$$

where N_i (pore/m^2) is the pore number density of pores having a radius r_i, η (Pa s) is the viscosity of the displacing liquid and l (m) is the length of the pores (usually the active layer thickness). This term should include a tortuosity factor for not so regular geometries.

However, the experimental flow values obtained are not associated to a single pore size, but to those pores with radii higher or equal to the radius obtained through the Cantor equation (Eq. (1)) for the given applied pressure. Thus, Eq. (2) cannot be directly applied to obtain the number of pores of a given pore size and then, more complex mathematical procedures have to be carried out in order to discriminate the contribution of each pore size to the global flux. Different methods have been developed for that purpose, such as the original method of Erbe [15], based on a graphical evaluation, and the method of Grabar and Nikitine [14], which has been selected for this work, and it will be briefly explained below

The volumetric flux for a given ΔP ($J(\Delta P)$) is defined in terms of the number of pores per unit area through Eq. (3).

$$J(\Delta P) = N\int_r^{r_{max}} F_V(r,\ \Delta P) f_n(r)\mathrm{d}r \tag{3}$$

where N is the total number of pores per unit area (pore/m^2), $F_V(r, \Delta P)$ is the volumetric flow (m^3/s) through a single pore of radius r at ΔP and $f_n(r)$ is the probability distribution function value for a pore of radius r.

The pore number distribution ($n(r)$) is defined as the number of pores per unit area and per unit radius, and can be calculated using Eq. (4) which is based on the distribution function $f_n(r)$.

$$n(r) = N f_n(r) \tag{4}$$

Therefore, the number of pores per unit area with radii between r_A and r_B (N_{AB}) is given by Eq. (5). Note that if the limits of integration are 0 and ∞ the result of the integral is the total pore population, N.

$$N_{AB} = \int_{r_A}^{r_B} n(r)\mathrm{d}r = \int_{r_A}^{r_B} N f_n(r)\mathrm{d}r \tag{5}$$

Taking into account the Hagen–Poiseuille equation and Eq. (4), it is possible to rewrite Eq. (3) to obtain the volumetric flux, as long as the variables are assumed to be independent of pressure.

$$J(\Delta P) = \frac{\pi \Delta P}{8\eta l}\int_r^{\infty} r^4 n(r)\mathrm{d}r \tag{6}$$

where the limits of integration are the lowest radius which is opened at the applied transmembrane pressure ΔP (given by Cantor equation) and the highest radius of the membrane which is denoted as ∞, because the probability distribution is 0 for $r > r_{max}$.

According to Grabar and Nikitine method [14], Eq. (6) has to be differentiated, substitute radius by pressure using the Cantor equation, and then, calculate the number of pores per unit area and per unit radius for a given differential of pressure through Eq. (7).

$$n(r) = \frac{8\eta l \Delta P^5}{\pi (2\gamma)^5}\left[\frac{\mathrm{d}J}{\mathrm{d}(\Delta P)} - \frac{J}{\Delta P}\right] \tag{7}$$

The algorithm derived by Grabar and Nikitine is, essentially, a differential algorithm which requires the continuous curve of permeance variation for its derivation. However, experimental procedures only give discrete values of flow and pressure, so Eq. (7) has to be