



Evaporometry adaptation to determine the lumen-side pore-size distribution (PSD) of hollow fiber and tubular membranes



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ARTICLE INFO

Keywords:

Hollow fiber membranes
Tubular membranes
Ultrafiltration
Pore-size distribution
Evaporometry

ABSTRACT

Determining the pore-size distribution (PSD) of ultrafiltration membranes is crucial in assessing their properties. Evaporometry (EP) characterizes the PSD based on evaporating a volatile wetting liquid from the membrane pores that permits determining the pore diameter using the Kelvin equation. EP has been applied in prior studies to determining the PSD for flat sheet and the outer surface of hollow fiber (HF) membranes. This paper adapts EP to characterizing the PSD on the lumen side of HF membranes. This required sealing the HFs to ensure that evaporation occurred only from the lumen side. A model was developed to determine the required membrane sample and test-cell dimensions. EP characterization based on remeasurements of a PES/PVP single-bore HF gave mass-based and flow-based average pore diameters of 106.2 ± 1.6 nm and 157.8 ± 4.3 nm, respectively, the latter of which was closer to the flow-based average pore diameter of 140 nm determined by liquid-displacement porometry. No pores were found larger than 300 nm, which was consistent with the known rejection properties. EP characterization based on remeasurement of a PES multi-bore HF gave mass-based and number-based average pore diameters of 26.6 ± 0.6 nm and 14.0 nm, respectively, with 90% of the pores being smaller than 20 nm, which was consistent with the known rejection properties. This study underscores the importance of understanding the basis for the PSDs obtained using different characterization methods and viewing the PSD in the form most useful to assess the relevant properties for a particular application.

1. Introduction

Hollow fiber (HF) membranes are widely used in ultrafiltration (UF) processes due to the higher packing density and larger membrane area per unit volume of the membrane module compared to flat sheet membranes [1–3]. The membrane performance depends on characteristics such as the surface charge, porosity and pore-size distribution (PSD), which dictate the key performance indicators of selectivity and permeability. Several methods have been advanced to characterize the PSD of membranes, each of which has both advantages and disadvantages [4–6].

Direct observation methods [7,8] such as scanning electron microscopy (SEM) [9–12], transmission electron microscopy (TEM) [11], environmental scanning electron microscopy (ESEM) [13], and atomic force microscopy (AFM) [14–16] give visual information for the surface of the membrane from which the number-based PSD can be

obtained. However, the shortcomings of these methods include (i) sampling a small membrane area that may not be representative; (ii) the need for coating with a conductive material in the case of SEM that can change the morphology; and (iii) the need for applying a high vacuum and an electrical voltage in the case of SEM and TEM that can damage the sample. Indirect methods for determining the membrane PSD include liquid-displacement porometry (LDP) [17,18], mercury porosimetry [19], thermoporometry [20], permoporometry [21–25] and evaporometry (EP) [26–28]. These involve relating the displacement of a liquid from the membrane pores to the membrane pore diameter using the Young-Laplace equation for LDP and mercury porosimetry, the Gibbs-Thompson for thermoporometry, and the Kelvin equation for permoporometry and EP. The disadvantages of these techniques include (i) the need for high pressure in LDP and mercury porosimetry that can change the membrane morphology; (ii) limited accuracy in measuring the heat input in thermoporometry; and (iii) demanding

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<http://dx.doi.org/10.1016/j.memsci.2016.12.024>

Received 5 October 2016; Received in revised form 12 December 2016; Accepted 12 December 2016

Available online 13 December 2016

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measurements of partial pressures and flow rates in permoporometry.

Evaporometry (EP) is a recently developed indirect method for determining the PSD by measuring the evaporation of a volatile wetting liquid from the membrane pores at ambient conditions from which the membrane pore diameter is determined using the Kelvin equation [28]. The Kelvin equation implies that the vapor-pressure depression of a volatile wetting liquid in a liquid-saturated pore is smaller for a larger pore. Therefore, when there is a distribution of pores and a saturated vapor condition is maintained at the surface of the membrane, the evaporation will progress from the largest to the smallest pores. Hence, the instantaneous evaporation rate can be used to determine the diameter and mass of the pores from which liquid is evaporating at the particular time. The seminal paper on EP was restricted to characterizing flat-sheet membranes [28]. Subsequent papers advanced EP to characterize the PSD on the outer surface of HF membranes and within the pores of fouled flat sheet membranes [26]. Recent papers focused on an improved design and protocol for obtaining enhanced accuracy in EP characterization [27] and extending EP to characterize larger pore diameters [29]. The principal advantages of EP are: (i) testing at ambient conditions; (ii) accommodating large membrane samples; (iii) ability to characterize irregularly shaped porous materials; (iv) highly accurate mass-based measurement; (v) characterization of fouled membranes; (vi) use of a variety of volatile wetting liquids including water; (vii) using simple laboratory equipment; and (viii) having a small laboratory footprint.

The focus of this study was to adapt EP to enable characterizing the PSD of the pores on the lumen-side of HF and tubular membranes. The specific objectives were the following: (i) to design an appropriate way to seal the outside surface of HF or tubular membranes to permit evaporation of the volatile wetting liquid only from the lumen side; (ii) to develop a model to determine the appropriate dimensions of the membrane sample and test cell to enable accurate EP characterization; (iii) to use the modified EP design to characterize the PSD of the lumen side for a HF membrane with a known nominal pore diameter; and (iv) to use the modified EP design to characterize the PSD on the lumen side for multi-bore HF membranes.

2. Principles of Evaporometry

Evaporometry (EP) can be used to determine the PSD by measuring the evaporative mass loss from membrane pores that have been pre-saturated with a volatile wetting liquid [26–28]. This is based on the Kelvin equation that relates the vapor-pressure depression due to the curvature of the air-liquid interface to the pore diameter (d_{pore}):

$$\ln \frac{P_A}{P_A^\circ} = -\frac{4\gamma V \cos \theta}{d_{pore} RT} \quad (1)$$

where P_A is the vapor pressure of the volatile wetting liquid in the pores, P_A° is the vapor pressure of the same liquid over a flat surface in the absence of any vapor-pressure depression, γ is the interfacial tension, V is the liquid molar volume, θ is the contact angle of the volatile wetting liquid at the walls of the pores, R is the gas constant, and T is the absolute temperature. Eq. (1) becomes inaccurate for pores smaller than 4 nm, which determines the lower bound of EP. Since for a completely wetting liquid $\theta=0$, the pore diameter can be obtained from Eq. (2):

$$d_{pore} = -\frac{4\gamma V}{RT \ln \frac{P_A}{P_A^\circ}} = -\frac{4\gamma V}{RT \ln \frac{x_{A0}}{x_{A0}^\circ}} \quad (2)$$

where x_{A0} is the gas-phase mole fraction of the volatile wetting liquid above its interface in the pores, and x_{A0}° is the gas-phase mole fraction of the same liquid above a flat interface. Since x_{A0} and x_{A0}° are not directly measurable, Eq. (2) can be expressed in terms of the evaporation rates that can be measured [28]:

$$d_{pore} = -\frac{4\gamma V}{RT \ln \frac{W_A}{W_A^\circ}} \quad (3)$$

where W_A is the evaporation rate of the volatile wetting liquid from the pores and W_A° is the evaporation rate of the same liquid over a flat interface in the absence of any vapor-pressure depression. The liquid evaporates progressively from the largest pores to the smallest pores, since the vapor pressure decreases with decreasing pore diameter. If saturation conditions are maintained in the gas phase above the membrane, at any instant of time the volatile wetting liquid will be evaporating from just the pores having a particular diameter, since the vapor will be supersaturated above all the pores smaller than this particular diameter pore and all the volatile wetting liquid will have completely evaporated from any pores larger than this particular pore.

3. Experiment design

3.1. Design considerations

EP characterization of the PSD requires determining the evaporation rates (i.e., W_A and W_A°) in Eq. (3) of the membrane samples placed in an appropriately designed test cell. Proper implementation of EP characterization requires careful consideration of the test cell, microbalance used to determine the evaporation rate, membranes, test liquid, and data analysis and procedure. The test cell must accommodate a sufficiently large sample to be representative of the membrane. Evaporative mass loss must be avoided from all surfaces of the membrane sample other than the one whose PSD is to be determined. The test cell must provide the principal resistance to mass transfer to ensure that the vapor pressure at the surface of the membrane sample is that above the pores from which liquid is evaporating at any instant of time. The microbalance must have sufficient resolution to determine the evaporation rate accurately and be capable of accurate gravimetric measurement over the time required for characterizing the PSD. It has to be capable of taring the weight of the test cell and membrane sample. The temperature in the microbalance must be carefully controlled owing to its effect on the vapor pressure. Room vibrations must be minimized to ensure accurate gravimetric measurement. Electrostatic charging effects on the microbalance in dry environments must be eliminated. The test liquid should be nontoxic, volatile, and must wet but not swell the membrane sample. Preparing the samples for using EP to characterize the PSD on the lumen side of HFs or tubular membranes requires special considerations that will be described in Section 3.2 after which a description of the complete EP apparatus and materials will be given in Section 3.3. The design of the membrane sample and test cell had to satisfy dimensional constraints dictated by the condition that the controlling mass-transfer resistance is that of the test cell. These constraints were determined from a mathematical model for the mass transfer that is described in Section 3.4.

3.2. HF membrane sample preparation

Sample preparation for flat-sheet membranes in prior EP studies involved sealing the periphery of the circular disk membrane sample to avoid any evaporation from the underside [27,28]. Sample preparation for EP characterization of the outer surface of HFs in prior EP studies involved sealing both ends of the fibers to avoid any evaporation from the lumen side [26]. EP characterization of the lumen-side of HFs in the present study required a substantively modified sample preparation to avoid any evaporation from the outer surface of the fibers that will be described here.

EP characterization was done for both a Pentair Xiga PES/PVP blend single-bore HF membrane (Norit Filtrix) and a SevenBore™ PES multi-bore HF membrane (General Electric Co.). Pentair claims that their PES/PVP single-bore HF membranes give a 6-log reduction of *Pseudomonas diminuta*, a bacterium whose diameter is 300 nm, thus

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