CHARACTERIZATION OF POROUS MEMBRANES VIA POROMETRY

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A Report submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the Course of
Master’s Thesis

Department of Mechanical Engineering

2012
This thesis entitled:

Characterization of porous membranes via porometry

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The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Abstract

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Characterization of porous membranes via porometry
Thesis directed by Prof. John Pellegrino

Gas-liquid porometry is the most common method for characterizing microfiltration membranes. This thesis provides a new approach to analyze data from gas-liquid porometry. Here, we combine porometry results with porosity measurement to determine the transport through the membranes. The pore size distribution and porosity measurements were performed for a range of membranes from straight through to asymmetric membranes. There was high discrepancy between the measured pore size and manufacturer data. Our study also examined the effect of asymmetry in pore size distribution of the membranes as compared to symmetric membranes. The asymmetric membranes were found to give smaller pore size compared to symmetric membranes. The orientation of asymmetric membranes provided different results for the mean pore size. A comparison between the classical approach and modified approach to analyze the data and thus in the estimation of transport parameter was made. Better correlation of measured and estimated transport parameter was found for modified approach as compared to classical approach. In addition modified approach determines the tortuosity for each pore size range during the estimation of transport parameters. The average tortuosity of the membranes under study varied from 0.707 to 6.48 with larger nominal pore membranes having higher values compared to smaller ones. This research also studied the transport of particles through the symmetric membranes. Theoretical model based on sieving was examined. The actual rejection increased for more tortuous membranes in comparison to theoretical rejection prediction with the
difference being greater for the highest tortuosity. With this study, we hope to further elucidate the characterization of membranes via porometry and hope to provide useful information regarding the development and end use of these membranes.
Acknowledgements

First of all, I would like to acknowledge my parents for guiding me in this world and teaching me the basic education and values which I still follow. I’m greatly indebted to Prof. John Pellegrino for giving me opportunity to do research and also guiding me along the way. His dedication toward the research and his emphasis on understanding the physics of process guided me a lot. I’m also very grateful to Prof. Alan Greenberg and Prof. Virginia Ferguson for their encouragements and support in my work.

I would like to give special thanks to Jason Woods and Elmira Kujundzic for guiding me in extended bubble point setup and being a great colleague to work and share ideas with. Also, I can never miss my friends and research group for helping me in every step. Lastly, I would like to thank all the people who have helped me to learn (directly or indirectly) about the world and making me a person who I’m.
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CHAPTER

I. INTRODUCTION

Overview

Membrane microfiltration (MF) is used in biotechnology, dairy, water treatment, nanomaterial industry for processing of fine particles, colloids and biological materials such as protein precipitates and microorganisms and separation of many other products [1-3]. These membranes are commonly polymeric materials having pore sizes in the range from 0.1-10 µm. In general, a membrane acts as a barrier phase between two other phases allowing selective transport of certain components between the two phases. The membranes have interconnected physical voids in their material structure called “pores” whose dimensions can vary from micron to nanometer scale. The pores vary greatly in shape, uniformity of cross-section and the degree and nature of interconnectedness (tortuosity). Transport through membranes depends on its properties as well as those of fluid mixture and hydrodynamics. The separation may be governed by size-exclusion or other interactions between the various components of the phases and the membrane materials. Despite the widespread use of these membranes, the ability to clearly define their pore-size distribution remains elusive.

This thesis focuses on characterization of MF membranes using gas-liquid displacement porometry with possible improvement of the current analysis technique. The study also includes building models of an asymmetric pore-size distribution by creating a stack of different sized but nominally uniform pore size membranes.
Classification of membranes

Membranes are generally classified as biological and synthetic membranes. Biological membranes are selective barriers within or around a living cell whereas synthetic membranes are artificial membranes fabricated for the purpose of industrial use. Here we deal with the synthetic membranes. Synthetic membranes can be classified on the basis of geometry, structure, method of fabrication and their application.

Geometrically membranes are classified as being flat sheet, spiral, tubular and hollow fiber. Based on structure, membranes are usually symmetric and asymmetric membranes. Membranes can also be classified on the basis of method of fabrication such as track etched, phase inversion, stretched films, leaching, interfacial polymerization and so on. Membranes are also classified on their applications such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis, gas separation, dialysis, pervaporation and ion exchange. This thesis focuses on the study of polymeric microfiltration flat sheet membrane structures.

Microfiltration membranes are very similar to the conventional filter with voided structure and whose pore size range are in order of 0.01 to 10 µm. Currently, polymeric membranes are most commonly used for commercial microfiltration separations. Structurally microfiltration membranes are symmetric and asymmetric.

Symmetric membranes are the membranes that have uniform pore size throughout their thickness while asymmetric membranes have pore sizes that increases from one side of the membrane to other. Asymmetric membranes are either anisotropic membrane, integrally skinned membrane or composite membranes. Anisotropic membranes exhibits gradation of pore size from one side of membrane to other, integrally skinned membranes have a thin active layer on one side of the membrane that have pores much smaller than the rest of the membrane and composite
membranes are those formed by depositing a film of the necessary characteristics onto another porous film that usually acts as a support [4].

**Membrane characterization**

Characterization, as applied to membrane systems, can have different meaning depending on the purpose for which they are applied. We should have a clear idea on when to choose the best membrane for a certain separation or when the quality of membranes in the manufacturing processes must be controlled. Thus, we can define two characteristic parameters—‘**performance related parameters**’ and ‘**morphology related parameters**’ [5]. Permeability, rejection, flux decline, diffusion coefficients and separation factors are considered to be important performance related parameters while pore size, pore size distribution, membrane thickness (and for anisotropic membranes: skin thickness), pore shape and various chemical and physical properties like adsorptive and absorptive properties and charge density are considered as morphology related parameters. The development of consistent theories on membrane structure and performance links the performance and morphology related parameters by a model. Hence, characterization involves accurate determination of porous structure, transport phenomenon and development of models to interpret the relation among the characteristic parameters. In this research, we mainly focus on the study of morphology related parameters of the membrane.

Various methods for characterization which measures one or more related parameters of the membrane structure have been developed and each method has their distinct advantage and limitations [5]. These methods may be physical methods for determining the pore size and its distribution or by means of rejection measurements using the reference molecules and particles [6]. Rejection measurements estimate solute cut-off value, which is defined as the lower limit of solute molecular weight for which the rejection is at least 90%. Though rejection measurements
can be used to estimate the pore size and its distribution [7, 8], it depends on the type of the solute, membrane and operating conditions used and varies from producer to producer. Also, the effects of particle size distribution, particle adsorption, concentration polarization and membrane fouling play an important role in the observed rejection parameter [9-12].

The physical method measures the morphology related parameters like pore shape, size, its distribution, membrane thickness and porosity[5]. There are several well established physical methods for characterization such as scanning electron microscopy (SEM), gas-liquid displacement porometry, mercury porosimetry, gas liquid equilibrium, liquid solid equilibrium [6, 13-17] and relatively new methods such as atomic force microscopy (AFM), nuclear magnetic resonance (NMR), electron spin resonance (ESR), Raman spectroscopy (RS), neutron scattering and confocal laser scanning microscopy (CLSM)[18-20]. Our focus in this work is gas-liquid porometry aka extended bubble point which is the most common method for pore size estimation [21-23]. The advantage of this method is that it characterizes only the active pores in the membrane and not the dead-end pores; tests the membrane very close to the operating condition and is a quite simple and quick method for characterization. However, the technique suffers from inaccuracies mainly due to the assumption of cylindrical pores in the analysis of the data and possible compression of gas-filled pores within the membrane [5, 6].

Morphology related parameters can be used to calculate experimental properties. For example, we may calculate porosity and pure water permeability from the pore size distribution and relate them to observed experimental values. Membrane processes cover a wide range of separation applications and hence, membrane structures vary significantly. The prediction of the process properties of the membranes for separation rests on the development of effective procedures for membrane characterization.
**Significance of research**

The focus of this work is to combine porometry and porosity measurements to draw a more complete picture of the membrane structure and correlate them to the membrane transport parameters. Various methods for analysis of data using gas-liquid porometry have been proposed [24-26]. The prediction of permeation through the membranes from morphological properties requires a model for the pore system and the assumption of transport mechanisms. The transport through the pores is governed by a combination of Knudsen flow, viscous flow, some transition flow or a single transport equation for Knudsen-viscous flow depending on the size of the pores [23, 27]. In microporous membranes gas transport through the pores is governed by Knudsen-viscous flow, while that of liquid flow is governed by viscous flow. Many modifications to these transport equations have been proposed more commonly with a slip term multiplied to the Knudsen term [23]. In a recent article by Woods et al [27], a single transport equation for Knudsen-viscous flow was used and the dependence of the transport equations on pore size was related through an exponent ‘m’ which is between zero and two. Its value was equal to two for viscous flow, one for Knudsen flow and between one and two for Knudsen-viscous flow. (It is zero for molecular diffusion, which is not relevant for the work herein presented.)

The most common pore model is the assumption of a bundle of circular capillaries representing the pore structure. In general the deviation arising from the assumption of the straight, cylindrical and non-interconnecting pores is accounted by the tortuosity factor [27]. However, the determination of this tortuosity factor is not simple and is generally an assumed value that accounts for the discrepancy between the measured and experimental transport measurements [28]. As the tortuosity is highly dependent on the porosity, the estimated porosity of the membranes differs from the actual porosity and hence results in incorrect estimation of the
effective number of flow channels involved during transport. We present an alternative approach toward the analysis of data using gas-liquid porometry that considers the actual measured porosity in the determination of transport through the membranes. Our approach determines the tortuosity for each pore size range rather than taking it as an assumed bulk parameter. Transport through the asymmetric membranes is still not well understood and various models have been developed to establish the transport regime. In this research, we also try to develop the asymmetric model by creating a stack of two different sized but nominally uniform pore size membranes and study their relative effects on the measured pore size distribution, number of pores and predicted permeability as compared to a single membrane. With this study, we hope that a simple physical model for asymmetric membranes can be established and may provide useful information regarding the development and end use of these membranes. This research also studied the effects of measured membrane properties on the transport of particles through the membranes. Since the ultimate goal of the membrane technology is effective and selective transport through the membrane, the accurate estimation of membrane morphology helps us understand the reasons for observed transport and ultimately provides the recipe for improvement.

**Research tasks**

The tasks supporting this research focus on:

1. Perform measurements on a range of symmetric and asymmetric membrane structures using gas-liquid displacement porometry.
2. Investigate different analytical models for interpreting experimental data.
CHAPTER

II. LITERATURE REVIEW

Overview

This chapter provides the necessary background knowledge relating to the project. The background information includes various methods to characterize the membranes, their relative advantages and disadvantages, and current state of research in terms of characterization of membranes using gas-liquid porometry.

Membrane characterization

Various methods for characterization of microfiltration and ultrafiltration membranes have been reviewed [5, 6]. Each method has distinct advantages and disadvantages over each other. Scanning electron microscopy (SEM) provides the visual representation of the membrane structure. In SEM, the membrane sample is struck with a narrow beam of electrons and these electrons cause the sample to release secondary electrons which are then detected and an image of the surface is formed. The backscattered electrons from the sample can also be detected to provide an image [5]. This method is very useful in the direct estimation of surface porosity. A major drawback is that microscopic analysis is very local and that the resolution is insufficient to study finely porous structures. Villa et al [29] studied the surface morphology along with the computerized image analysis of various track-etched membranes while Zeman et al [30, 31] studied the cellulosic microfiltration membranes in great detail. On the other hand Dietz et al [32] studied the track-etched microfiltration membranes between 100 nm to 10 nm using atomic force microscopy (AFM) instead of SEM. Recently, Husson et al [20] developed cross-sectional confocal laser scanning microscopy (CLSM) methods to characterize asymmetry in thick
microporous membranes and to quantify sub-surface porosity as a function of depth. They also worked to identify the limits of resolution and penetration depth, which depend on the specific system, but are nominally ~0.2 µm and 20 µm, respectively.

Rejection measurements using reference molecules and particles [6] have also been used to estimate the pore size and its distribution [7, 8]. Aimar et al [7] calculated the retention curves corresponding to a given pore size distribution by transport of dextran molecules through polysulphone membranes. Their analysis involved transport through capillaries according to sieving and Poiseuille flow models. Similar study was also conducted by Wickramasinghe et al [33] where the experimentally determined rejection curves were compared with calculated rejection curves obtained from field emission scanning electron microscopy (FESEM). The rejection measurement depends on the type of the solute, membrane and operating conditions used. Also, the effects of particle size distribution, particle adsorption, concentration polarization and membrane fouling play an important role in the rejection parameter [9-12].

Thermoporometry is based on the micro-calorimetric analysis of solid–liquid transformations in pore structure [5]. The principle is based on the lowering of the triple point temperature of a liquid filling a porous material which depends on the curvature of the solid/liquid interface that relates to the pore size. Zeman et al [34] studied the ultrafiltration membranes using thermoporometry. They used low speed differential scanning calorimeter and found that thermoporometry provided means of characterizing porous sub-layers of ultrafiltration membranes.

Khulbe et al [18] reviewed some relatively new methods such as atomic force microscopy (AFM), nuclear magnetic resonance (NMR), electron spin resonance (ESR), Raman
spectroscopy (RS), and neutron scattering. However, each characterization method has certain limitations and their applicability depends on the purpose for which they are used.

Our focus in this work is gas-liquid porometry which is the most common method for pore size estimation [21-23].

**Gas-liquid displacement porometry**

Bechhold in 1908 was the first to use the gas pressure to evaluate pore sizes by measuring the pressure necessary to blow air through a water filled porous membrane [35]. However, this method only gave the maximum pore size present in the pore distribution corresponding to the minimum pressure necessary to blow the air through the membrane. The bubble point and solvent permeability method was combined to give the pore size distribution [36] and was later improved to take into account the surface energy at the liquid-gas interface [37]. The method has been modified a number of times ever since [24-26].

As previously discussed many different transport models have been assumed to represent the flow through the membrane pores. The membrane pores are usually assumed to be bundle of capillaries. Although use of the wet/dry flow has been widely accepted [15, 23], the study conducted by P. Schneider et al. [24] criticized the theoretical basis for using wet/dry flow for determination of the pore size distribution, showing that it will cause erroneous results since it did not take into account of the varying transport mechanisms of the gas flow in the pores. It was found that the contribution of Knudsen flow partly decreased during the wet flow as the mean free path of the gas is inversely proportional to the gas pressure and the smallest pores open at the highest pressure difference. However, during dry flow no suppression of the Knudsen flow takes place as all pores are active in gas permeation. We are using the model formulation which uses only the wet flow curve for the determination of pore size distribution.
In the study conducted by Martinez et al [26], it was shown that the pore number and the magnitudes in which it influences are calculated as a relation to the tortuosity-thickness product. The classical method of analysis assumes the tortuosity value to be equal to 1 [21, 23] or some arbitrary value [38, 39]. In the article by Kong et al [40], improved gas permeation method was proposed where the pore size distribution has been taken into account and the membrane morphological parameters such as pore size, pore size distribution, and effective surface porosity was determined through the regression analysis of gas permeation data. The effective surface porosity was taken as porosity per unit pore length (i.e. tortuosity-thickness product). Hence, the actual porosity as well as the actual measured pore size was not taken into account. They were just estimated values to fit the gas permeation data.

The analysis of flux versus pressure drop curve, commonly referred to as flow-pressure curve [25], generally results in a histogram or a common statistical distribution assumed to fit the statistical parameters obtained [41]. Many researchers have used log-normal distribution to fit their data [6, 7] while others have used the Gaussian distribution to fit their data [23]. In the research article by Zydney et al [41], the use of log-normal distribution function in the characterization of the membrane was analyzed. The study showed that the previous studies have employed several different forms of the log-normal distribution function and there had been a number of inconsistencies and errors in the definition and interpretation of the parameters that appear in the equations. As shown in their study, these different forms for the log-normal distribution were in fact completely equivalent, although the parameters involved in those expressions had very different physical and/or statistical interpretations. Thus, this study [41] was used as the basis for fitting the pore size distribution obtained into a log-normal distribution.
CHAPTER

III. Theory

Overview

This chapter describes the details of the theoretical formulations used in the analysis of data using gas-liquid porometry, porosity measurement using ‘pat and weigh’ method and solute sieving calculations. An overview of different approaches for analysis of porometry data is presented. A modified method of analysis which uses the independent measure of porosity in combination with air permeability is developed to determine a more realistic number of pores indicative of the tortuous porous media. The expression for theoretical solute sieving through the porous media accounting the effects of the pore size and particle size distributions is also developed.

Gas-liquid displacement porometry

In gas-liquid displacement porometry, a non-reacting gas is applied to remove the wetting liquid, that is initially filling the pores, from the pores and, thereby, permitting gas flow. The solid/liquid surface free energy \((\gamma_{s/l})\) is less than the solid/gas surface free energy \((\gamma_{s/g})\). Therefore, the wetting liquid spontaneously fills the pores but work must be done to remove the liquid from the pores. The work done by the gas must be equal to the increase in surface free energy [42].

\[
pdV = (\gamma_{s/g} - \gamma_{s/l})dS \tag{3-1}
\]

\[
p = \gamma \cos \alpha \frac{dS}{dV} \tag{3-2}
\]
here, $p$ is the pressure, $dV$ is the increase in volume of gas displacing the liquid in pore, and $dS$ is the increase in surface area associated with $dV$, $\gamma$ is the surface tension of liquid, and $\alpha$ is the contact angle.

Pore diameter, $d$, of a pore at any location along its path is defined such that $(dS/dV)$ at that location is equal to the $(dS/dV)$ of a cylindrical opening of diameter, $d$, i.e.

$$
\left( \frac{dS}{dV} \right)_{\text{pore}} = \left( \frac{dS}{dV} \right)_{\text{cylindrical-opening}}
$$

If a gas is used to displace the wetting liquid from the pore, the differential pressure required is given by the Young-Laplace equation [42],

$$
\Delta p = \frac{4 \gamma \cos \theta}{d}
$$

Figure 1-Schematic diagram illustrating principle of gas-liquid displacement porometry [43]

Each increment of pressure opens another interval of pores, and the volumetric flow increase providing measure of total number of pores with that diameter by application of the appropriate mass transfer equation. The stepwise increment of pressure allows calculating the number of pores corresponding to each pore diameter by equation 3-4.

Depending on the relation between the mean free path of the permeated gas and the pore size, the mass transport through the pores are predominantly governed by either Knudsen flow, Hagen-
Poiseuille flow, (or molecular diffusion if there is insignificant pressure gradient) or some transition flow. In our case, the volumetric flux for each pore diameter in the distribution is given by the full description of Knudsen-Poiseuille flow, which approaches the limits of viscous or Knudsen flow depending on dimensionless Knudsen number, Kn) [27].

As stated previously, we are using the analytical approach that uses only wet flow curve for the determination of pore size distribution. The novelty we are proposing is a modified approach, which incorporates the independently, measured porosity, and that allows us to calculate a unique tortuosity for each pore size by regression analysis with the measured air permeability (aka the "dry" flow). Table 1 shows the overview of differences between the various approaches of analysis we considered in this thesis.

Table 1- Overview of different approaches for analysis of porometry data

<table>
<thead>
<tr>
<th>attributes</th>
<th>classical wet and dry flow method</th>
<th>classical wet flow only method</th>
<th>modified method</th>
</tr>
</thead>
<tbody>
<tr>
<td>accounts full description of flow</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>calculates number of pores</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>assumes bulk tortuosity</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>calculates tortuosity for each pore size</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>uses the measured porosity</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>uses the difference in wet and dry flow</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>fits the air permeability</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

**Classical porometry analysis**

**Wet and dry flow method**

The wet and dry flow method uses the difference in the wet and dry flow curves in the determination of the pore size distribution and consequently the number of pores.

For the pores below the diameter \(d_i\), i.e. for the pores in class \(i^{th}\) \((i=1,2,3\ldots)\), the cumulative flow can be written as [23],
The differential flow through the pores with diameter $d_i$ is given by:

$$f_{d,i} = \frac{f_{a,i+1} - f_{a,i-1}}{2}$$  \hspace{1cm} (3-6)$$

Taking into account that the flow is proportional to the pore area, the number of pores with size $d_i$ is:

$$N_{d,i} = K \frac{f_{d,i}}{d_i^2}$$  \hspace{1cm} (3-7)$$

Where $K$ is the normalization factor and,

$$K = \frac{\sum_{i=1}^{n} f_{a,n}}{\sum_{i=1}^{n} \left( \frac{f_{a,i}}{d_i^2} \right)}$$  \hspace{1cm} (3-8)$$

Finally, the cumulative distribution for the number of pores is given by,

$$N_{a,i} = \sum_{j=1}^{i} N_{d,j}$$  \hspace{1cm} (3-9)$$

If the absolute number of pores and porosity is to be evaluated, a model for the gas flow must be assumed. Assuming that the transport through the pores follows full description of the flow, the total number of pores per surface unit is given by

$$N_{l,i} = \frac{J_i}{l_p}$$  \hspace{1cm} (3-10)$$

Where,

$$l_p = \frac{\pi}{\Delta x} \left[ \frac{2}{3} p \left( \frac{RT}{8\pi M_w} \right)^{\frac{1}{2}} \sum_{i=1}^{n} N_{d,i} d_i^3 + \frac{1}{128\eta} \sum_{i=1}^{n} N_{d,i} d_i^4 \right]$$  \hspace{1cm} (3-11)$$

Hence, the absolute distribution per unit macroscopic surface area can be obtained as:
\[ N_{d,i} = N_{d,i} N_{i,i} \]  \hspace{1cm} (3-12)

**Wet flow only method**

Assuming cylindrical pores, the Knudsen-Poiseuille equation for air flux through a cylindrical conduit is \([23, 27, 44]\),

\[
J_i = \frac{\pi N_i \Delta p_i}{\tau_i \delta^m} \left[ \frac{d_i^4}{128 \eta} + \left( \frac{2}{3} \right) \left( \frac{RT}{8 \pi M_w} \right)^{1/2} \frac{d_i^3}{p_i} \right] + \Delta p_i \frac{J_{i-1}}{\Delta p_{i-1}} \]  \hspace{1cm} (3-13)

Here, the first term in right hand side represents the viscous contribution whereas the other term represents the Knudsen contribution.

The first increment of pressure causes flux through \(N_1\) pores of diameter \(d_1\). The next increment in pressure causes additional flux through the pores of diameter \(d_1\), as well as, flux through the newly opened pores of diameter \(d_2\). This progressive increase in flux with the opening of new pores corresponds to the pressure increments and the flux through \(i^{th}\) pore is given as,

\[
J_i = \frac{\pi N \Delta p_i}{\tau_i \delta^m} \left[ \frac{d_i^4}{128 \eta} + \left( \frac{2}{3} \right) \left( \frac{RT}{8 \pi M_w} \right)^{1/2} \frac{d_i^3}{p_i} \right] + \Delta p_i \frac{J_{i-1}}{\Delta p_{i-1}} \]  \hspace{1cm} (3-14)

The number of pores of a given diameter can be calculated when the experimental determination of flux versus pressure through a wet membrane is made. The number of pores of a given diameter is given as,

\[
\frac{N_i}{\tau_i} = \frac{J_i - J_{i-1}}{\Delta p_i K} \]  \hspace{1cm} (3-15)

Where,

\[
K = \frac{\pi}{\delta^m} \left[ \frac{d_i^4}{128 \eta} + \left( \frac{2}{3} \right) \left( \frac{RT}{8 \pi M_w} \right)^{1/2} \frac{d_i^3}{p_i} \right] \]  \hspace{1cm} (3-16)
The classical wet flow analysis assumes that the tortuosity of the membrane is equal to one (or it can be set to any arbitrarily convenient value). The fractional number distribution is then given as

\[ f_i = \frac{N_i}{\sum_{i=1}^{n} \frac{N_i}{\tau_i}} \approx \frac{N_i}{\sum_{i=1}^{n} N_i} \]

(3-17)

**Modification to standard porometry analysis for improvement**

The analysis of gas liquid porometry data determines the number of pores per unit tortuosity of the membrane as shown in equation 3-15. The straight through cylindrical pore approach of standard porometry analysis assumes a tortuosity value of 1. Hence, the calculated number of pores using standard porometry is the number of pores per unit tortuosity and not necessarily the actual number of pores. This means that the total number of pores involved in the transport may not be correct for all further transport processes. The modified method of analysis uses the independent measure of porosity in combination with air permeability ‘dry flow’ as calculated using standard gas-liquid porometry to determine a more realistic number of pores indicative of the tortuous porous media.

If one assumes a distribution of right cylindrical pores with diameter, \(d_i\), nominal length (the membrane's thickness) \(\delta_m\), and a number (in the given projected membrane area, \(A_m\)), \(N_i\), then the overall porosity for non-tortuous pores would be

\[ \theta = \frac{\pi}{4} \sum_i N_i d_i^2 \]

(3-18)

where \(N_i\) is the number of pores of diameter \(i\) per unit projected area of the membrane.

The porosity \(\theta_i\) due to any bin "i" of pore diameters is then
\[
\theta_i = \frac{n_i \pi d_i^2 \delta_m}{4 A_m \delta_m} = \frac{\pi}{4} N_i d_i^2
\]  
(3-19)

and the fraction of porosity, \( f_i \), due to pores in any bin "i" of pore diameters is then

\[
f_i = \frac{\theta_i}{\theta} = \frac{N_i d_i^2}{\sum_i N_i d_i^2}
\]  
(3-20)

If we now include tortuosity as a real indication of the increased volume of certain pores, we can make the assumption

\[
f_i = \frac{N_i d_i^2}{\sum_i N_i d_i^2} \approx \frac{N_i d_i^2}{\sum_i \frac{N_i}{\tau_i} d_i^2}
\]  
(3-21)

Then we can calculate \( f_i \) (and the subsequent \( \theta_i \)) for each bin "i" using the total measured porosity as the \( \theta \).

The air permeability is given as

\[
L_{p, \text{air}} = \sum_{i=1}^{n} \left[ \frac{\theta_i d_i^2}{32 \eta_a \tau_i \delta_m} + \left( \frac{RT}{8 \pi M_w} \right)^{1/2} \frac{8 \theta_i d_i}{3 \tau_i \delta_m p_i} \right]
\]  
(3-22)

The modified approach uses the fractional porosity and measured porosity which calculates a unique \( \tau_i \) and \( N_i \) for each i by regression analysis with the measured air permeability. Two cases of constraints- tortuosity to be greater than one and tortuosity to be greater than zero were considered.

Once we know the tortuosity value for each pore size range, we can calculate the actual number of pores of that size range. The actual number density of the pores is then given as

\[
f_{i, \text{actual}} = \frac{N_i}{\sum_i N_i}
\]  
(3-23)
The mean pore size based on actual number density is given as

$$d_{\text{mean}} = \frac{\sum_{i=1}^{n} f_{i,\text{actual}} d_i}{\sum_{i=1}^{n} f_{i,\text{actual}}}$$

(3-24)

The solvent permeability can be calculated as a function of fractional porosity, tortuosity and pore diameter i.e.

$$L_{p,sol} = \sum_{i=1}^{n} \frac{\theta_i d_i^2}{32 \eta_f \tau_i \delta_m}$$

(3-25)

Where, $\eta_f$ is the viscosity of the fluid. For water, isopropanol, and n-butanol permeability $\eta_w$ is replaced with the respective viscosity of the fluids (Table 2).

Table 2- Viscosity of various fluids at 20 °C

<table>
<thead>
<tr>
<th>Fluid</th>
<th>Viscosity, Pa.s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>1.75E-05</td>
</tr>
<tr>
<td>water</td>
<td>8.94E-04</td>
</tr>
<tr>
<td>iso-propyl alcohol</td>
<td>2.07E-03</td>
</tr>
<tr>
<td>n-butyl alcohol</td>
<td>2.95E-03</td>
</tr>
</tbody>
</table>

Determination of actual porosity using pat and weigh

The membrane porosity is the total void volume present within the membrane and is commonly defined as the pore volume divided by the total volume of the membrane:

$$\text{porosity} = \frac{\text{volume of the pores}}{\text{total volume of membrane}} \times 100\%$$

(3-26)

The porosity of the membrane was calculated using the average mass of the polymer material and the mass of liquid in the membrane. The volume of the membrane was determined gravimetrically by weighing a sample of known area and thickness. The density of the membrane polymer material was estimated from the literature. The membrane thickness was determined by a digital micrometer. The overall porosity was calculated using both the physical dimensions and
mass and density of the polymer. The porosity of the membranes was calculated using the equation:

\[
\text{porosity}(\theta) = \left[1 - \frac{\left(\frac{m_f}{\rho_f}\right)}{\left(\frac{m_m}{\rho_m} + \frac{m_f}{\rho_f}\right)}\right] \times 100\% \quad (3-27)
\]

**Solute sieving**

The particles along with the membranes have a size distribution. So instead of using a nominal particle size for rejection calculation we are taking into account the particles size distribution (PSD), as well.

The solute flux of diameter \(d_s\) (i) through the membrane pores is given by [45]

\[
N(j) = K_c v C_s - K_d D \frac{dC_s}{dz} \quad (3-28)
\]

It is assumed that the pore is straight through, non-tortuous, and non-interconnected. Basically, this approach says that any particles which get into the pore structure come out the other side. They are carried along by a convection velocity and diffusion and but experience a "friction" that slows them down.

Using the centerline approximation [46], the solute partition coefficient is given as

\[
\phi(j) = (1 - \lambda(j))^2 \quad (3-29)
\]

where, \(\lambda\) is the ratio of solute \(d_s\) (i) to pore radius \(d_p\) (j).

The values of \(K_c\) and \(K_d\) are given as
\[ K_c(j) = \frac{(2-\phi(j))K_s}{2K_t(j)} \]  \hspace{1cm} (3-30)

\[ K_d(j) = \frac{6\pi}{K_s(j)} \]  \hspace{1cm} (3-31)

where, \( K_s \) and \( K_t \) are defined as

\[ K_s(j) = \frac{9}{4} \pi^2 \sqrt{2}(1-\lambda(j))^{-5/2} \left( 1 + \sum_{n=1}^{2} a_n (1-\lambda(j))^n \right) + \sum_{n=0}^{4} a_{n+5} \lambda(j)^n \]  \hspace{1cm} (3-32)

\[ K_t(j) = \frac{9}{4} \pi^2 \sqrt{2}(1-\lambda(j))^{-5/2} \left( 1 + \sum_{n=1}^{2} b_n (1-\lambda(j))^n \right) + \sum_{n=0}^{4} b_{n+5} \lambda(j)^n \]  \hspace{1cm} (3-33)

The values of \( a_n \) and \( b_n \) are taken from literature [33, 45] (Table 3)

The Peclet number, \( Pe \), which is defined as the ratio of rate of convection to diffusion is given as,

\[ Pe = \left( \frac{K_c}{K_d} \right) \left( \frac{v\delta_m}{d} \right) \]  \hspace{1cm} (3-34)

<table>
<thead>
<tr>
<th>n</th>
<th>( a_n )</th>
<th>( b_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-73/60</td>
<td>7/60</td>
</tr>
<tr>
<td>2</td>
<td>77,293/50,400</td>
<td>-2,227/50,400</td>
</tr>
<tr>
<td>3</td>
<td>-22.5083</td>
<td>4.018</td>
</tr>
<tr>
<td>4</td>
<td>-5.6117</td>
<td>-3.9788</td>
</tr>
<tr>
<td>5</td>
<td>-0.3363</td>
<td>-1.9215</td>
</tr>
<tr>
<td>6</td>
<td>-1.216</td>
<td>4.392</td>
</tr>
<tr>
<td>7</td>
<td>1.647</td>
<td>5.006</td>
</tr>
</tbody>
</table>

The classical base case assumes that since the applied pressure drop causes significant convective flow through the membrane, the \( Pe \gg 1 \), and thus, we can ignore the diffusional portion in equation 3-28. The rejection coefficient in this case is given as

\[ R(j) = 1 - \phi(j)K_c(j) \]  \hspace{1cm} (3-35)
The weighted rejection coefficient for pore size distribution is given as

$$R(i) = \sum_{n=1}^{j} f_p(j)R(j)$$

(3-36)

where $f_p(j)$ is the fractional pore distribution of size $d_p(j)$.

The overall rejection coefficient considering both particle as well as pore size distribution is then given as

$$R_T = \sum_{n=1}^{i} f_s(i)R(i)$$

(3-37)

with $f_s(i)$ as the fractional distribution of particle size $d_s(i)$. 
CHAPTER

IV. Experimental Methods

Overview

This chapter describes the details of the experimental methods used for the characterization of membrane morphology. Gas-liquid displacement porometry was used to measure the pore size distribution, porosity and permeability of the membranes. The porosity of the membranes was also measured using a gravimetric analysis aka “pat and weigh”. The pure water permeability, isopropanol permeability, n-butanol permeability and solute transport through the membranes were also measured to determine self-consistency with the results obtained from the characterization methods. The influence of asymmetry was measured by layering two membranes with relatively uniform pore size throughout their thickness as well as making measurements on an inherently asymmetric membrane.

Membranes and chemicals

All membranes were nominal microfiltration (MF) rated. Nine sets of symmetric and six sets of model asymmetric membrane (Figure 2 shows the model asymmetric orientation), and an intrinsically asymmetric one (operated in two orientations) were used for characterization and solute rejection measurements (Table 4).

For the gas-liquid porometry experiments, ultra high purity nitrogen gas was used for gas pressure. De-ionized (DI) water and n-butanol were used as wetting liquids. Each condition was repeated three times. The liquid permeation rates through the membranes were carried out using DI water, isopropanol and n-butanol. The porosity of the membranes was measured using the pat and weigh method.
For the solute rejection experiments, 0.5 mg/mL of 250 nm silica particles from Fiber Optics Center Inc. in 0.05% (m/m) FL-70 surfactant solution (Sigma Aldrich) in DI water was used as the challenge.

Table 4- List of membranes used for study

<table>
<thead>
<tr>
<th>symmetric membrane</th>
<th>model asymmetric membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 µm polycarbonate Isopore®</td>
<td>0.22-0.8 µm MCE</td>
</tr>
<tr>
<td>0.22 µm MCE (SCWP04700)</td>
<td>0.8-0.22 µm MCE</td>
</tr>
<tr>
<td>0.45 µm MCE MCE(SMWP04700)</td>
<td>0.22-1.2 µm MCE</td>
</tr>
<tr>
<td>0.65 µm MCE (SSWP04700)</td>
<td>1.2-0.22 µm MCE</td>
</tr>
<tr>
<td>0.80 µm MCE (RAWP04700)</td>
<td>0.8-1.2 µm MCE</td>
</tr>
<tr>
<td>1.2 µm MCE (AAWP04700)</td>
<td>1.2-0.8 µm MCE</td>
</tr>
<tr>
<td>3.0 µm MCE (DAWP04700)</td>
<td></td>
</tr>
<tr>
<td>5.0 µm MCE (HAWP04700)</td>
<td></td>
</tr>
<tr>
<td>8.0 µm MCE (GSWP04700)</td>
<td></td>
</tr>
<tr>
<td>inherently asymmetric membrane</td>
<td>0.65 µm polyethersulphone, SSU &amp; SSD</td>
</tr>
</tbody>
</table>

Figure 2- Schematic showing the orientation of model asymmetric membranes
Methodology

Gas-liquid porometry

The schematic diagram for the experimental setup for the gas-liquid porometer is shown in Figure 3. The porometer consisted of a pressure controller, mass-flow meter, membrane cell module and two pressure transducers. The pressure was supplied through a compressed nitrogen gas in a cylinder. The automatic pressure controller (Alicat Scientific Model No: PC-125PSIG-D-V125, range 0-62.5 psig and maximum resolution 0.1 psig) was used to control the pressure supplied from the cylinder. A digital mass flow meter (Omega Model No: FMA1728, range 0-50 SLPM and maximum resolution of 0.1 SLPM) was used to measure the flow through the membrane. The upstream pressure transducer (range of 0-200 psig (0-1.35MPa)) and the downstream pressure transducer (range of 0-15 psig (0-0.1MPa)) were used to measure the differential pressure across the membrane. The membrane cell was fabricated from aluminum [4]. A National Instruments data acquisition device (Model No: USB 6008) was used to interface the pressure controller, flow indicator and pressure transducers to the computer. Labview© data acquisition software (Version 8.5) was used to record the data from the porometer. A screenshot and logical description of the Labview© program is shown in the Appendix A.
The membrane was placed in the membrane cell (Figure 4) with a porous metallic support with sufficient strength on the downstream side. Once the membrane was secured in the membrane cell, the pressure was set at a predetermined value and was termed as starting pressure in the Labview© program. The pressure was then allowed to stabilize for some time (for these
experiments the time was set at 60 s). The pressure was then slowly increased at a predetermined rate of 0.2 psig per 5 s until the termination pressure was reached, which was set at a sufficiently high value over the nominal bubble point such that all the pores would be open in the wet-flow test. By measuring the pressure and corresponding flow at every increasing pressure step, the wet-flow curve for the membrane was obtained. The pressure rate specified above was chosen because it is the smallest pressure rate that can be reproducibly detected by the high pressure transducer (maximum resolution of the DAQ was ~0.02 volts). Once the wet flow curve was obtained, the pressure was again ramped up at the same rate used for the wet-flow measurements. The pressure versus flow rate was measured at every positive increase in pressure to obtain the dry curve.

**Porosity measurement**

Porosity of the membranes was measured using a gravimetric aka ‘pat and weigh’ method. In pat and weigh method, the membrane was immersed in wetting fluid for 24 h and was weighed immediately after removing fluid by patting off the surface. The process was performed repeatedly (3 repetitions) and the weight of the wet and dry membrane was measured. By comparing the mass of the wet and dry membranes, the porosity of the membranes was calculated.

**Liquid permeance**

The liquid permeation experiments were performed in the three cell apparatus for DI water permeance and a single cell apparatus was used for the n-butanol and isopropanol experiments. The effective membrane area in case of DI water permeance was 35 mm diameter (ie approx. 9.62x10^{-4} m^2) while that for n-butanol and isopropanol permeance was 25 mm diameter (ie approx. 4.90x10^{-4} m^2). The transmembrane pressure was maintained between 10-15 psig while
the time for the measurements were varied based on the nominal size of the membrane. A fixed volume of approx. 2 litres of DI water was used for the measurements while that for the n-butanol and isopropanol permeance measurements approx. 1 litre of solvent was used.

**Solute sieving**

The solute sieving experiments were performed for the symmetric membranes. The constant flux cross-flow filtration experiments were performed. The details of the experimental set up are explained in Appendix B. The feed solution was 0.5 mg/mL of silica particles suspended in 0.05 % (m/m) of FL-70 in DI water. The centrifugal pump (Fluid O Tech Model: TMFR-TSFR at 1100 rpm) was used to pump the feed and generate the cross-flow across the membrane interface. The Cole Parmer® magnetic stirrer was used to create additional vortex across the membrane interface. The permeate rate was maintained at approximately 5 g/min. The constant permeate flux was maintained using the peristaltic pump (Cole Parmer® Model: 7523-70, 1.6-100 rpm, 0.1 hp). This initial backpressure of approximately 50 psig was created using a manual back pressure valve (Go Inc. 0-750 psig). The change in transmembrane pressure during the experiment was measured using Omega Engineering Inc. (Model: PX313-1kg10V, 0-1000 psig) pressure transducers connected to a personal computer. The dynamic light scattering equipment (Malvern Zetasizer Nano Model: ZEN1690) was used to analyze the feed, permeate and retentate solutions.
CHAPTER

V. Results and discussion

Overview

This chapter provides the results of the modified approach to analyze data from gas-liquid porometry. The effect of asymmetry in calculation of pore size distribution of the membranes as compared to symmetric membranes is presented. The result for the measurement of tortuosity and transport through the membrane using the modified approach is shown. A comparison of the theoretical and actual liquid permeances for various approaches of data analysis is made. The result of the solute transport through the membranes is also presented.

Porometry results

Figures 5-7 shows the examples of the porometer results (nominal 0.22, 0.65 and stacked 0.8-1.2 µm MCE membranes) showing the pores gradually opening with each pressure increment (indicated as wet flow) and after all of the pores have been opened (indicated as dry flow). The results for other membrane combinations are shown in Appendix A. It was observed that at low transmembrane pressure, \( \Delta p \) the gas permeation velocity through the membrane is practically zero (below our detection limit). At a certain value of \( \Delta p \) corresponding to the bubble point of the membrane, the largest pores will be opened and the gas permeation velocity starts to increase. Smaller membrane pores are opened as \( \Delta p \) increases according to the Young-Laplace equation 3-4. Finally, at the pressure corresponding to the minimum pore size, all the pores become empty. When \( \Delta p \) is higher than this pressure the flow rate versus \( \Delta p \) returned is that which is obtained with a membrane dry sample.
Figure 5- Wet and dry flow for 0.22 µm MCE membrane

Figure 6- Wet and dry flow for 0.65 µm MCE membrane
Figure 7: Wet and dry flow for 0.8-1.2 µm MCE membrane

The pore size distribution (PSD) for all of the membranes were determined using the calculations described previously. The analysis of flux versus pressure drop curve commonly referred to as a flow-pressure curve [25] generally results in a histogram or a common statistical distribution assumed to fit the statistical parameters obtained [41]. The PSD were presented as pore fraction versus the pore diameter and were fitted as a log-normal distribution to provide a simple visual representation. The rationale behind fitting to log-normal distribution is that it is defined only for positive pore diameter pores and it provides easier graphical representation [41]. The histogram plot fitted to log-normal distribution for 0.22 µm MCE membrane is shown in Figure 8 and the goodness of fit analysis for the log-normal distribution was performed using Minitab© statistical software. The Figure 9 shows that the goodness of fit for log-normal distribution at 95% confidence interval for the 0.22 µm resulted in a p-value = 0.008. This indicates that log-normal distribution is not a good fit as p-value is less than 0.05 at 95% confidence interval. It was also found that PSD did not have good fit for any of the distribution under study. In any case, the actual histogram was used to make the predictions of permeance and particle transport.
Figure 8- Histogram plot for PSD of 0.22 µm MCE membrane and fitted to log-normal distribution.

Figure 9- Goodness of fit test-probability plot for 0.22 µm MCE membrane fitted to log-normal distribution.
Symmetric membrane results

Figure 10 shows the result of log-normal pore size distribution (PSD) for various symmetric MCE membranes under study. The obtained values for the mean (arithmetic) pore size ($\mu$) and its standard deviation ($\sigma$) has been tabulated in Table 5. The measured mean pore size for the straight-through pores of the Isopore® membrane is much closer to its nominal rated value than for MCE nitrocellulose membranes. There was high discrepancy between the measured mean pore size and manufacturer's rating for the MCE nitrocellulose membranes. This indicates that their rating is based on some other basis, which we will not consider in this study. Figure 11 shows the comparison between the measured and nominal pore size diameter.

Figure 10- PSD for monolithic MCE membranes. Here, PSD curves 1-8 represents nominal (1) 0.22 \(\mu\)m; (2) 0.45 \(\mu\)m; (3) 0.65 \(\mu\)m; (4) 0.8 \(\mu\)m; (5) 1.2 \(\mu\)m; (6) 3 \(\mu\)m; (7) 5 \(\mu\)m; and (8) 8 \(\mu\)m MCE membranes respectively.
Table 5- Summary table showing the mean, standard deviation, number of pore/m² and estimated tortuosity, using the modified analysis for gas-liquid porometry. The measured thickness and overall porosity of the individual membranes are also listed.

<table>
<thead>
<tr>
<th>membrane (µm rating)</th>
<th>mean μm</th>
<th>sd μm</th>
<th>number of pores/m² (x10¹¹)</th>
<th>thickness μm</th>
<th>porosity %</th>
<th>τ&gt;1</th>
<th>τ&gt;0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopore®</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>0.282</td>
<td>0.002</td>
<td>39.8</td>
<td>20±2</td>
<td>25.4±1.6</td>
<td>1.037</td>
<td>1.037</td>
</tr>
<tr>
<td>MCE</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>0.22</td>
<td>0.552</td>
<td>0.090</td>
<td>30.5</td>
<td>148±3</td>
<td>74.8±0.3</td>
<td>1.63</td>
<td>1.63</td>
</tr>
<tr>
<td>0.45</td>
<td>1.008</td>
<td>0.027</td>
<td>10.9</td>
<td>130±2</td>
<td>79.6±0.2</td>
<td>1.87</td>
<td>1.87</td>
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<tr>
<td>0.65</td>
<td>1.446</td>
<td>0.046</td>
<td>4.9</td>
<td>110±1.5</td>
<td>79.1±0.01</td>
<td>2.55</td>
<td>2.55</td>
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<td>0.8</td>
<td>1.817</td>
<td>0.019</td>
<td>3.7</td>
<td>142±4</td>
<td>83.2±0.1</td>
<td>2.75</td>
<td>2.75</td>
</tr>
<tr>
<td>1.2</td>
<td>2.306</td>
<td>0.068</td>
<td>2.3</td>
<td>134±2.4</td>
<td>82.1±0.8</td>
<td>3.83</td>
<td>3.83</td>
</tr>
<tr>
<td>3</td>
<td>2.355</td>
<td>0.015</td>
<td>2.0</td>
<td>113±1.8</td>
<td>82.5±0.1</td>
<td>4.31</td>
<td>4.31</td>
</tr>
<tr>
<td>5</td>
<td>2.426</td>
<td>0.071</td>
<td>2.3</td>
<td>99.5±2.3</td>
<td>83.2±0.04</td>
<td>4.25</td>
<td>4.25</td>
</tr>
<tr>
<td>8</td>
<td>2.611</td>
<td>0.066</td>
<td>2.1</td>
<td>115.3±1.2</td>
<td>83±0.05</td>
<td>5.02</td>
<td>5.02</td>
</tr>
<tr>
<td>0.22-0.8</td>
<td>0.529</td>
<td>0.007</td>
<td>37.3</td>
<td></td>
<td></td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td>0.8-0.22</td>
<td>0.532</td>
<td>0.006</td>
<td>33.4</td>
<td></td>
<td></td>
<td>1.08</td>
<td>1.08</td>
</tr>
<tr>
<td>0.22-1.2</td>
<td>0.518</td>
<td>0.007</td>
<td>37.8</td>
<td></td>
<td></td>
<td>1.00</td>
<td>0.94</td>
</tr>
<tr>
<td>1.2-0.22</td>
<td>0.521</td>
<td>0.007</td>
<td>30.9</td>
<td></td>
<td></td>
<td>1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>0.8-1.2</td>
<td>1.603</td>
<td>0.053</td>
<td>4.8</td>
<td></td>
<td></td>
<td>1.70</td>
<td>1.70</td>
</tr>
<tr>
<td>1.2-0.8</td>
<td>1.637</td>
<td>0.024</td>
<td>4.0</td>
<td></td>
<td></td>
<td>1.79</td>
<td>1.79</td>
</tr>
<tr>
<td>PES</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.65, SSU</td>
<td>0.633</td>
<td>0.003</td>
<td>28.9</td>
<td>124±3</td>
<td>75.1±0.5</td>
<td>1.00</td>
<td>0.94</td>
</tr>
<tr>
<td>0.65, SSD</td>
<td>0.800</td>
<td>0.012</td>
<td>17.6</td>
<td></td>
<td></td>
<td>1.05</td>
<td>1.05</td>
</tr>
</tbody>
</table>
Asymmetric membranes

Figure 12 shows the result of PSD for model asymmetric stacked MCE membranes and the inherently asymmetric PES membrane. The asymmetric PES membrane had pores closer to its nominal rating while that of stacked MCE membrane was close to that of smallest pore diameter. The model asymmetric membranes had a smaller pore size as compared to the symmetric membrane. The exact reason for this discrepancy is unknown and needs further research for proper explanation, which is beyond the scope of this thesis. However, a possible explanation could come from the assumption that it takes higher pressure for a liquid to penetrate a sharp edged pore than to make a liquid penetrate a cavity making the apparent pore size for model asymmetric membranes is lower than symmetric membranes [47].

The orientation of the asymmetric membranes provided different results for the measured mean pore sizes. When the tight side of the asymmetric membrane was facing the gas pressure, it provided smaller pore diameter as compared to the reverse orientation when the tight side was facing away from the gas pressure. The reason for this observed deviation needs further study and is also beyond the scope of this thesis.
Figure 11- Comparative figure showing measured mean pore diameter to nominal pore diameter
Figure 12- PSD for asymmetric PES membranes and asymmetric MCE membranes made by stacking two membranes of different pore sizes. Here, PSD curves 1-8 represents the (1) 0.22 µm; (2) 0.8 µm; (3) 1.2 µm; (4) 0.22-1.2 µm; (5) 1.2-0.22 µm; (6) 0.8-1.2 µm; (7) 1.2-0.8 µm MCE membranes; and (8) 0.65 µm PES skin side up (SSU) and (9) skin side down (SSD) membranes.

*Estimation of tortuosity*

The results of the porosity measurements from "pat and weigh" method is tabulated in Table 5. Figure 14 shows the tortuosity for each pore size range for 0.2 µm Isopore, 0.22 µm MCE, 0.65 µm MCE and 3 µm MCE membranes. The straight-through Isopore® membrane has average tortuosity of 1.037 indicating that our approach towards quantifying tortuosity is reasonable. The average tortuosity values calculated for each of the membrane is shown in Table 5. The average tortuosity range for the membranes under study varied from 0.707 to 6.48 with larger nominal pore size membranes having higher values compared to smaller ones. It indicated that nominally larger pore size membranes were more tortuous than the smaller pore sized membranes.

A tortuosity value larger than one indicates an increased resistance during the transport relative to a cylindrical pore with the constant diameter, d, and length equal to the thickness of the membrane. Although a pore length cannot be lower than the thickness of the membrane, a tortuosity less than one indicates the presence of pore constriction with the diameter, d (Figure 13). It indicates that the porometer tests (straight-through pore assumption) overestimated the number of pores, making the calculated porosity greater than the independently measured porosity. Thus, the tortuosity value less than one is observed.

We considered both cases of constraint \( \tau \geq 0 \) and \( \tau \geq 1 \). When the constraint is set as \( \tau \geq 1 \) we see that the average tortuosity of some of asymmetric membranes (Table 5) is forced to be 1. In
contrast when the constraint is set $\tau \geq 0$, the average tortuosity is lower than one. This is because we were measuring the throat diameter of the pore at the skin layer and considered the thickness of the skin layer equal to the overall thickness of the membrane which over estimated the number of pores involved in the transport. This caused the calculated porosity to be larger than the actual porosity and hence a tortuosity value was lower than 1. The measured tortuosity value for each pore size would allow us to better estimate the actual number of pores and hence more realistic pore size distribution. The total number of pores calculated from this approach is tabulated in Table 5.

Figure 13- A pore with constriction (left) and without constriction (right)
Comparison with the transport properties

As the transport properties are a result of interplay of pore size distribution, tortuosity and thickness of active part of the membrane [5], a comparison of the functional performances in the actual experiments with the theoretical predictions allows us to determine how well the measurements predict performance. We used the actual water, isopropanol and n-butanol permeability measurements in comparison to the theoretical prediction as a basic metric to determine the effectiveness of the characterization technique under study.
Figure 16 shows the comparative chart of the predicted and actual water permeability measurements using the modified analysis ($\tau \geq 0$), classical wet/dry flow analysis and classical wet-flow-only analysis for all the membranes (and configurations) under study. It can be seen that the predicted water permeability using the modified analysis fits closer to the 45 degree line in comparison to the classical wet/dry flow and wet-flow-only analysis. However, the predicted water permeability using classical porometry is closer to our values when tortuosity values are closer to one. The classical porometry technique is unable to correctly predict the water permeability as the tortuosity increases. Figure 15 shows the variation of the predicted permeability using our approach and classical porometry with respect to the actual permeability as the average tortuosity factor for the different membrane changed from lower to higher values.

In classical approach ($\theta/\tau$) is always constant in contrast to modified analysis where $\theta$ is measured independently and $\tau$ is estimated through regression analysis such that the SSE between the predicted and experimental permeability is near zero. This means that the contribution of each pore size bin to the total flow is constrained by the measured porosity, actual flow and estimated tortuosity. Hence, there is improvement in prediction of permeability as compared to classical approach. We see that the variation using our approach is less as compared to classical method. The goodness of fit test, F-test (Appendix A) also indicates that the modified method had better predictions as compared to the classical method.

It can also be seen in Figure 17 and 18 that the theoretical and actual isopropanol and n-butanol permeability using the gas liquid porometry for monolithic membranes matches well to each other. Figure 15 shows the variation of the predicted permeability using our approach and standard porometry with respect to the actual permeability as the average tortuosity factor for the different membrane changed from lower to higher values. As in DI water permeability, we see
that the variation using our approach is less as compared to standard method. The improvement using the modified approach as compared to standard method as indicated by the goodness of fit i.e. F-test (Appendix A) provides further validity for improvement. It also indicates that there is minimal effect of wetting liquid towards the swelling of the membranes. Hence, our approach seems to give consistent results and can be used as a more accurate method for determination of transport properties using gas-liquid porometer.

Figure 15- Ratio of predicted to measured liquid permeances through the MCE monolithic membranes against their mean tortuosity using DI water (smallest symbols), isopropanol (middle-sized symbols), and n-butanol (largest symbols); wherein predictions were made using PSDs derived with the different data analysis methods.
Figure 16- Comparative figure showing the calculated (both modified (τ≥0) and classical porometry) and actual experimental DI water permeability
Figure 17- Comparative figure showing the calculated (both modified ($\tau \geq 0$) and classical porometry) and actual experimental isopropanol permeability for monolithic membranes.
Figure 18- Comparative figure showing the calculated (both modified (τ≥0) and classical porometry) and actual experimental n-butanol permeability for monolithic membranes

*Solute sieving*

The actual and theoretical prediction of solute rejection through monolithic polycarbonate and MCE membranes is shown in Table 6. The particle size distribution for permeate and feed solutions for 0.22 µm MCE membrane is shown in Figure 19. It can be seen that the actual solute rejection matches close to theoretical prediction in case of 0.2 µm Isopore® membrane and the less tortuous MCE membranes. However, the actual rejection increases for the more tortuous MCE membranes in comparison to the theoretical rejection prediction, with the difference being greater for the highest tortuosity (Figure 20).
The theoretical model is based on sieving [46], however, the MCE membranes have varying tortuous paths that incorporate depth filtration[48]—a mechanism not included in the theoretical model previously described. The solute has to navigate through the tortuous path where it may have to pass around an obstacle, turns and twists that diverts it momentum from the flow path. This increases the probability that it can be "captured" by a variety of scenarios, and probably underlies the higher solute rejection values for more tortuous membranes. It is also consistent with the deviation between measured pore throat and nominal rating based on the manufacturer's challenge tests.

![Feed and permeate particle size distribution for 0.22 µm MCE membranes](image)

Figure 19- Feed and permeate particle size distribution for 0.22 µm MCE membranes
Table 6- Comparative table showing theoretical and actual rejection coefficient for various monolithic membranes under study

<table>
<thead>
<tr>
<th>Rejection coefficient (%)</th>
<th>Theoretical</th>
<th>Actual</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 µm Isopore</td>
<td>95.06</td>
<td>97.97</td>
</tr>
<tr>
<td>0.22 µm MCE</td>
<td>53.16</td>
<td>41.97</td>
</tr>
<tr>
<td>0.45 µm MCE</td>
<td>21.82</td>
<td>19.02</td>
</tr>
<tr>
<td>0.65 µm MCE</td>
<td>11.73</td>
<td>17.19</td>
</tr>
<tr>
<td>0.8 µm MCE</td>
<td>7.72</td>
<td>13.53</td>
</tr>
<tr>
<td>1.2 µm MCE</td>
<td>5.01</td>
<td>13.00</td>
</tr>
<tr>
<td>3 µm MCE</td>
<td>4.75</td>
<td>14.29</td>
</tr>
<tr>
<td>5 µm MCE</td>
<td>4.63</td>
<td>12.05</td>
</tr>
<tr>
<td>8 µm MCE</td>
<td>3.97</td>
<td>10.23</td>
</tr>
</tbody>
</table>

Figure 20- (Measured/ Theoretical) rejection with average tortuosity of the monolithic membranes
CHAPTER

VI. CONCLUSION

An extension to the current method of analysis of the data using gas-liquid porometer for characterization of microfiltration membranes have been developed. The method takes into account the actual measured porosity of the membranes during analysis and determines the tortuosity values for each pore size range. The measurements were performed for the symmetric and asymmetric membranes. There was discrepancy between the measured and nominal rating for the symmetric MCE membranes which indicates that manufacturer used some other basis for their ratings. The measured pore size for the asymmetric membranes were influenced by the orientation of the membrane. Further study needs to be performed to better understand the effects of orientation in the measurement using gas liquid porometry. It should also be noted that the membranes that were tested had insignificant number of smaller pores hence the limited pressure range for our apparatus didn’t have much impact on the measurement of pore sizes. However, if one intends to measure PSD in the membranes that have more of smaller pores then they will have to use much higher pressure range.

The measured porosity and tortuosity in combination with the measured pore size values from gas-liquid porometer was used to determine the theoretical performance parameters and was compared with actual measured values. Good agreement of measured and theoretical values was found. It indicates that the modified method was able to better predict the geometry of the membranes under study.

The solute rejection experiments using the monolithic membranes were also performed. It was found that the actual rejection increased for more tortuous MCE membranes in comparison to the theoretical rejection prediction. The capture of particles via depth filtration mechanism could be
possible reason for increased actual rejection for more tortuous membranes. This can be taken as the basis for further research.

Thus, the current work provides a new insight into the analysis of data using gas-liquid porometry and we hope that our work will provide a further simplification in the field of membrane characterization.
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172-198.


List of acronyms

\( \gamma_{s/l} \) = solid/liquid surface free energy, dynes/cm

\( \gamma_{s/g} \) = solid gas surface free energy, dynes/cm

\( dV \) = increase in volume of gas displacing the liquid in pore, cm\(^3\)

\( dS \) = increase in surface area associated with \( dV \), cm\(^2\)

\( \Delta p \) = differential transmembrane pressure, Pa

\( \gamma \) = surface tension, dynes/cm

\( \alpha \) = contact angle, radians

\( d \) = pore diameter, \( \mu \)m

\( f_{a,i} \) = cumulative flow through pores below diameter, \( d_i \)

\( f_{d,i} \) = differential flow through the pores with diameter, \( d_i \)

\( N_{d,i} \) = number of pores with size \( d_i \)

\( N_{a,i} \) = cumulative number of pores

\( K \) = normalization factor, m\(^2\)

\( N_{t,i} \) = total number of pores per surface unit evaluated at \( i^{th} \) pressure, m\(^2\)

\( l_p \) = gas permeability assuming the total number of pores to be 1, m\(^3\)/s.Pa

\( J_i \) = air flux through pores of diameter \( d_i \), m/s.Pa

\( N_i \) = number of pores/m\(^2\) of diameter \( d_i \)

\( \tau_i \) = tortuosity factor for \( i^{th} \) pore

\( \delta_m \) = thickness of membrane, \( \mu \)m

\( \eta \) = viscosity of fluid, Pa.s

\( R \) = molar gas constant,

\( M_w \) = molecular weight
\( T = \) temperature, K

\( p_i = \) average pressure across the membrane, Pa

\( \theta_a = \) apparent porosity

\( \theta = \) actual porosity

\( f_i = \) fractional number distribution

\( f_{i,\text{actual}} = \) actual number density of the pores of size \( d_i \)

\( d_{\text{mean}} = \) arithmetic mean pore size, \( \mu m \)

\( L_{p,\text{sol}} = \) solvent permeability, m/s.Pa

\( L_{p,\text{air}} = \) air permeability, m/s.Pa

\( m_m = \) mass of membrane, g

\( m_f = \) mass of fluid in the membrane, g

\( \rho_m = \) density of membrane, g/cm\(^3\)

\( \rho_f = \) density of fluid, g/cm\(^3\)

\( N(j) = \) solute flux, mol/m\(^2\)s\(^{-1}\)

\( K_c = \) convective hinderance factor

\( K_d = \) diffusive hinderance factor

\( K_t = \) hydrodynamic function

\( K_s = \) hydrodynamic function

\( D = \) diffusivity, m\(^2\)s\(^{-1}\)

\( C_s = \) radially averaged solute concentration in the pores, mol/m\(^3\)

\( Z = \) distance through the pore

\( Pe = \) peclet number

\( \Phi = \) solute partition coefficient
\( \lambda = \) ratio of solute to pore radius

\( a_n = \) coefficient

\( b_n = \) coefficient

\( R(j) = \) rejection coefficient

\( R_T = \) overall rejection coefficient

MCE = mixed cellulose ester

PES = poly ether sulphone
APPENDIX
A. Gas-liquid porometry

The porometer equipment used is shown in figure. The description of the equipment and its operating protocol was described in Chapter III.

![Apparatus used for gas-liquid porometry measurements](image)

Selection of wetting liquid

In order learn the limitations of current bubble point technique, we chose three different wetting fluids viz. isopropanol (21.4 dynes/cm), n-butanol (24.4 dynes/cm) and a commercial wetting fluid porefil® (16 dynes/cm). Assuming that the wetting fluid completely wets the membrane, the calculated pressure required to open pores of various sizes are as follows
Table 1- Pressure required opening up the pores of various sizes using various wetting liquids

<table>
<thead>
<tr>
<th>Diameter of the pores, µm</th>
<th>iso-propanol</th>
<th>n-butanol</th>
<th>Porefil®</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.42</td>
<td>14.16</td>
<td>9.28</td>
</tr>
<tr>
<td>0.9</td>
<td>13.79</td>
<td>15.73</td>
<td>10.31</td>
</tr>
<tr>
<td>0.8</td>
<td>15.52</td>
<td>17.69</td>
<td>11.60</td>
</tr>
<tr>
<td>0.7</td>
<td>17.74</td>
<td>20.22</td>
<td>13.26</td>
</tr>
<tr>
<td>0.6</td>
<td>20.69</td>
<td>23.59</td>
<td>15.47</td>
</tr>
<tr>
<td>0.5</td>
<td>24.83</td>
<td>28.31</td>
<td>18.56</td>
</tr>
<tr>
<td>0.4</td>
<td>31.04</td>
<td>35.39</td>
<td>23.21</td>
</tr>
<tr>
<td>0.3</td>
<td>41.38</td>
<td>47.19</td>
<td>30.94</td>
</tr>
<tr>
<td>0.2</td>
<td>62.08</td>
<td>70.78</td>
<td>46.41</td>
</tr>
<tr>
<td>0.1</td>
<td>124.15</td>
<td>141.56</td>
<td>92.82</td>
</tr>
<tr>
<td>0.09</td>
<td>137.95</td>
<td>157.29</td>
<td>103.14</td>
</tr>
<tr>
<td>0.08</td>
<td>155.19</td>
<td>176.95</td>
<td>116.03</td>
</tr>
<tr>
<td>0.07</td>
<td>177.36</td>
<td>202.22</td>
<td>132.61</td>
</tr>
<tr>
<td>0.06</td>
<td>206.92</td>
<td>235.93</td>
<td>154.71</td>
</tr>
<tr>
<td>0.05</td>
<td>248.30</td>
<td>283.11</td>
<td>185.65</td>
</tr>
<tr>
<td>0.04</td>
<td>310.38</td>
<td>353.89</td>
<td>232.06</td>
</tr>
<tr>
<td>0.03</td>
<td>413.84</td>
<td>471.86</td>
<td>309.41</td>
</tr>
<tr>
<td>0.02</td>
<td>620.76</td>
<td>707.78</td>
<td>464.12</td>
</tr>
<tr>
<td>0.01</td>
<td>1241.52</td>
<td>1415.57</td>
<td>928.24</td>
</tr>
</tbody>
</table>
Since the range of the current pressure controller was only 62.5 psig, and we used n-butanol as the wetting liquid, the upper limit of current system would be around 0.2 µm assuming the contact angle between the liquid/solid interfaces is zero degree. For larger pore diameter pores we used DI water as the wetting liquid as the pressure necessary to open up the pores were in workable range in that case. We preferred to use n-butanol instead of isopropanol as n-butanol is less volatile compared to isopropanol, hence the evaporation of wetting liquid is minimized. We chose n-butanol over Porefil® as it was convenient and economical to purchase.

**Labview© program**

National Instruments Labview© progam, version 8.5 was used to automate the porometer. The step by step logic diagram and screenshot for working of Labview© program is shown in Figure 2-10. The Labview© program is enabled to measure the wet flow and dry flow subsequently. The Labview© program comprises of two windows: front panel and block diagram. The input to the program is given in front panel while the execution of the program is defined in the block diagram window. The input to the program is startup pressure, rate of pressure increment, time interval between the pressure increments and the terminal pressure. The front panel window also comprises of the destination file in which the measured data is stored. There are separate data files in which the dry and wet flow measurements are stored. The startup pressure is the initial pressure input to the program and the terminal pressure is the highest pressure to which the experiment is conducted. Generally, the terminal pressure is maintained much higher than the pressure at which the smallest pore opens up. The pressure increments are made at the rate of 0.2 psig per 5 sec. This pressure increment was chosen because it is the smallest pressure that could be reproducibly increased by the pressure controller.
Figure 2- Logical diagram showing the working of gas-liquid porometry in Labview© program
The block diagram window contains the sequential steps for the working of the program. In step 0, the pressure is set at the initial starting pressure and maintained at that pressure for certain time (Figure 4, 5). The purpose of it is to stabilize the pressure controller. In the next step (figure 6-9), the wet flow test is carried out. The wet flow test has three sequential steps: pressure increment step, time delay step to stabilize the pressure and the data collection step. The final step (figure 10) is the termination step where the program automatically stops the data collection after the termination pressure is reached. The same procedure is applied in case of dry flow as well.

Figure 3- Screenshot of front panel of Labview© program
Figure 4- Screenshot of block diagram of Labview© program for startup pressure

Figure 5- Screenshot of block diagram showing time delay step
Figure 6- Screenshot of block diagram showing pressure increment step

Figure 7- Screenshot of block diagram showing time delay between pressure increments
Figure 8- screenshot of block diagram showing data acquisition step

Figure 9- Screenshot of block diagram showing pressure controlling step
Figure 10- Screenshot of block diagram showing termination of program

**Statistical analysis**

We used the F-test (or variance ratio test) to determine if the modified approach had some improvement in predicting the performance parameters (water, isopropanol and n-butanol permeability). F-test is usually applied to test the significant difference between the variances of two independent normal populations. It can also be applied to test whether the two samples are taken from a normal population having same variance or not. In our case, we tested whether the variance or improvement we got from modified approach were significant or were just due to randomness.

Hypothesis setting:

Null hypothesis: the two estimates of variance do not differ significantly

Alternative hypothesis: the two estimates of variance differ significantly

Level of significance: 5 %
Test statistics: F-test

Computation:

We are taking DI water as an example

Variance for modified method: $S_1^2 = 31.258$

Variance for classical wet flow only method: $S_2^2 = 170.73$

Variance for classical wet and dry flow method: $S_3^2 = 1523.10$

$F_a = \frac{S_1^2}{S_2^2} = 5.46$

$F_b = \frac{S_1^2}{S_3^2} = 48.67$

Degree of freedom for modified method: 17

Degree of freedom for classical wet flow only method: 17

Degree of freedom for classical wet and dry flow method: 17

Tabulated value of F at 5 % level of significance for d.f.1 (17-1) and d.f.2 (17-1) is 2.33

Tabulated value of F at 5 % level of significance for d.f.1 (17-1) and d.f.3 (17-1) is 2.33

Decision: Since the calculated value of F is larger than the tabulated value, the null hypothesis is rejected i.e. there is significant difference in variance estimated between the two methods.

Also, the tabulated p-value in this case is 0.000533 (wet flow only method) and 0.000210 (wet and dry flow method) which is significantly lower than 0.05 indicating the improvement.

Similarly, p-value in case of isopropanol and n-butanol permeability was 0.000027 and 0.000066 (wet flow only method) and 0.0000012 and 0.0000014 (wet and dry flow method) respectively.

**Supplementary figures**

This section provides all of the supplementary figures for the tests conducted using the gas-liquid porometry.
Figure 11: Wet and dry flow for 0.2 µm Isopore membrane

Figure 12: Wet and dry flow for 0.45 µm MCE membrane
Figure 13- Wet and dry flow for 0.8 µm MCE membrane

Figure 14- Wet and dry flow for 1.2 µm MCE membrane
Figure 15 - Wet and dry flow for 3 µm MCE membrane

Figure 16 - Wet and dry flow for 5 µm MCE membrane
Figure 17- Wet and dry flow for 8 µm MCE membrane

Figure 18- Wet and dry flow for 0.22-0.8 µm MCE membrane
Figure 19 - Wet and dry flow for 0.8-0.22 µm MCE membrane

Figure 20 - Wet and dry flow for 0.22-1.2 µm MCE membrane
Figure 21- Wet and dry flow for 1.2-0.22 µm MCE membrane

Figure 22- Wet and dry flow for 1.2-0.8 µm MCE membrane
Figure 23- Wet and dry flow for 0.65 µm PES-SSU membrane

Figure 24- Wet and dry flow for 0.65 µm PES-SSD membrane
Figure 25- Goodness of fit test-probability plot for 0.45 µm MCE membrane fitted to log-normal distribution

Figure 26- Goodness of fit test-probability plot for 0.65 µm MCE membrane fitted to log-normal distribution
Figure 27- Goodness of fit test-probability plot for 0.8 \( \mu m \) MCE membrane fitted to log-normal distribution

Figure 28- Goodness of fit test-probability plot for 1.2 \( \mu m \) MCE membrane fitted to log-normal distribution
Figure 29- Goodness of fit test-probability plot for 3 µm MCE membrane fitted to log-normal distribution

Figure 30- Goodness of fit test-probability plot for 5 µm MCE membrane fitted to log-normal distribution
Figure 31- Goodness of fit test-probability plot for 8 µm MCE membrane fitted to log-normal distribution

Figure 32- Goodness of fit test-probability plot for 0.22-0.8 µm MCE membrane fitted to log-normal distribution
Figure 33- Goodness of fit test-probability plot for 0.8-0.22 µm MCE membrane fitted to log-normal distribution

Figure 34- Goodness of fit test-probability plot for 0.22-1.2 µm MCE membrane fitted to log-normal distribution
Figure 35- Goodness of fit test-probability plot for 1.2-0.22 µm MCE membrane fitted to log-normal distribution

Figure 36- Goodness of fit test-probability plot for 0.8-1.2 µm MCE membrane fitted to log-normal distribution
Figure 37- Goodness of fit test-probability plot for 1.2-0.8 µm MCE membrane fitted to log-normal distribution

Figure 38- Goodness of fit test-probability plot for 0.65 µm PES SSU membrane fitted to log-normal distribution
Figure 39- Goodness of fit test-probability plot for 0.65 µm PES SSD membrane fitted to log-normal distribution
B. Solute rejection

Sample preparation

The challenge solution for the solute rejection experiments was 0.5 mg/ml of 250 nm silica particles suspended in 0.05% Fl-70 in DI water. The procedure for the sample preparation for solute rejection experiment is described below.

1. Take 1500 mg of powdered silica particles
2. Take 500 g of 0.05 % Fl-70 in DI water and add the powder silica particles while stirring the DI water. This will prevent the formation of large agglomerates of the particles.
3. Sonicate the solution for around 30 minutes to completely disperse the particles.
4. Take 2500 g of fresh surfactant-DI water solution and add the concentrated particle solution into it. Continuously stir the solution for effective dispersion.
5. Then, the solution prepared was used during the filtration.

Constant flux experiments

The constant flux experiments were performed for the rejection measurements. The schematic diagram for the filtration apparatus is shown in Figure 40. The feed solution was prepared as explained above. A liter or approximately 1000g of the feed sample was taken as feed. The back pressure regulator was set at 50 psig. The permeate flux was maintained approximately 5 g/min (membrane area 35 mm diameter). The constant flux was monitored using the sartorious® mass balance connected to the computer. The change in transmembrane pressure was also monitored using the computer. The experiment was run such that equal mass of permeate was collected (approx. 300 g). Small volume of permeate, feed and retentate were collected for further analysis with DLS.
Dynamic light scattering (DLS)

We performed the dynamic light scattering measurements for the characterization of the particles. The dynamic light scattering measures the Brownian motion of the particles and relates it to the particle diameter. The DLS measurement was performed for the feed and the permeate solutions from the filtration experiments. To get the concentration figures of the feed and permeate solutions, known concentration of the sample solutions were prepared and run in the DLS. DLS has inbuilt program that gives the measure of the concentration from the scattering intensity. The measured concentration from DLS and the actual concentration were used to get the calibration curve to determine the concentrations in feed and permeate solutions. The obtained calibration curve is shown in figure 50. It was seen that the maximum concentration that the DLS was able to detect in the linear range was 0.5 mg/ml. The figure 51-58 shows the measured feed and permeates particle size distribution in terms of concentration.
Figure 41- Calibration curve for silica particles suspended in 0.05 % FL-70 in DI water using DLS

\[ y = 16973x + 560.1 \]
\[ R^2 = 0.9811 \]

Figure 42- Feed and permeate particles size distribution for 0.2 µm Isopore membrane
Figure 43- Feed and permeate particles size distribution for 0.45 µm MCE membrane

Figure 44- Feed and permeate particles size distribution for 0.65 µm MCE membrane
Figure 45- Feed and permeate particles size distribution for 0.8 µm MCE membrane

Figure 46- Feed and permeate particles size distribution for 1.2 µm MCE membrane
Figure 47- Feed and permeate particles size distribution for 3 µm MCE membrane

Figure 48- Feed and permeate particles size distribution for 5 µm MCE membrane
Figure 49- Feed and permeate particles size distribution for 8 µm MCE membrane