Membrane Wettability

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Membrane Wettability

Studied using the Krüss Force Tensiometer – K100

Background

The term microfiltration is typically used to describe the separation of particles in the size range of 0.01 to 20 microns. Two basic types of membranes are used for such separations, screen membranes and depth membranes. The difference between the two types of membranes is their pore structure.

Screen membranes are generally thin (5 to 10 microns) and depend almost entirely on surface trapping for their effectiveness. They have void volumes of roughly 10%, and provide for little to no side-to-side flow, due to their capillary pore structure. Submicron screen membranes are typically manufactured from polycarbonate or polyester film.

Depth membranes are generally thicker (50 to 150 microns). They depend, not only on surface trapping (for larger particles), but also on trapping within their tortuous inner capillary matrices (for smaller particles). They have void volumes of greater than 75%. Depth membranes are manufactured from a variety of materials including ceramics, metallic and polymeric. However, the most frequently used polymeric materials are cellulose esters, cellulose nitrates polyvinyl halogenates, polypropylene and polysulfones.

Obviously one major criterion for a membrane material is how wettable it is with the solvent which carries the particles to be separated. The standard measure of liquid/solid wetting is the contact angle.

We have recently tested the water wettability of three polysulfone-based depth membranes using the two contact angle methods described below. The membranes are as follows:

<table>
<thead>
<tr>
<th>Membrane A</th>
<th>pure polysulfone membrane (non-permeable with pure water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane B</td>
<td>polysulfone/hydroxypropylcellulose membrane (permeable with pure water)</td>
</tr>
<tr>
<td>Membrane C</td>
<td>polysulfone/cationic cellulose membrane (highly permeable with pure water)</td>
</tr>
</tbody>
</table>
Methods

For a non-porous solid, contact angle is the angle formed when a liquid droplet is placed on the solid surface, as shown below.

![Contact Angle](image)

Fig. 1: contact angle

This angle can vary from 0° (perfectly wetting) to 180° (completely non-wetting).

For a porous solid, if the contact angle is less than 90°, and the material is homogeneous, the liquid will penetrate the pores. The specific angle is an indicator of how spontaneously the wetting will occur.

We use two methods to determine the contact angle of liquids on membranes: the Washburn Method (for penetrating liquids with contact angles of less than 90°) and the Wilhelmy Method (for non-penetrating liquids with contact angles of less than 90°). Each is described below.

Washburn Method

Washburn theory indicates that if a porous solid is brought into contact with a liquid, such that the solid is not submerged in the liquid, but rather is just touching the liquid’s surface, then the rise of liquid into the pores of the solid due to capillary action will be governed by the following equations:

\[ t = A m^2 \]  

Wherein \( t \) = time after the solid and the liquid are brought into contact, \( m \) = mass of liquid drawn into the solid and \( A \) = a constant which is dependent on the properties of the liquid and the solid in question.

Specifically,

\[ A = \frac{\eta}{c \rho^2 \cos \theta} \]  

Wherein \( \eta \) = viscosity of the liquid, \( \rho \) = density of the liquid, \( \sigma \) = surface tension of the liquid, \( \theta \) = contact angle between the solid and the liquid and \( c \) = a material constant which is dependent on the porous architecture of the solid.

Combining equation 1 and 2, followed by rearrangement, leads to equation 3 which is the useful form of Washburn’s equation.

\[ \cos \theta = \frac{m^2 \eta}{t \rho^2 A c} \]  

In setting up a Washburn experiment, a liquid with known density (\( \rho \)), viscosity (\( \eta \)) and surface tension (\( \sigma \)) should be used. An inspection of equation 3 leads to the conclusion that if this is the case, and the mass of liquid which rises into the porous solid can be monitored as a function of time (such that \( m^2/t \) is the raw experimental data), then two unknowns remain: the contact angle of the liquid on the solid (\( \theta \)) and the solid material constant (\( c \)).

However, if a Washburn experiment is performed with a liquid which is known to have a constant angle of \( \theta \) 0° (\( \cos \theta = 1 \)) on the solid, then the solid material constant is the only remaining unknown in equation 3 and can thus be determined. N-hexane is typically a good choice as the liquid for determining material constants, because of its low surface tension (18.4 mN/m) at room temperature.

Once the material constant (\( c \)) has been determined for a particular solid, a second sample of the solid can be tested for wettability by another liquid. The material constant determined by the n-hexane test is simply used in the Washburn equation, in combination with \( m^2/t \) data obtained during testing with the second liquid and the solid.

Washburn adsorption experiments can be easily and automatically performed on a variety of porous materials using a Krüss Force Tensiometer – K100 in combination with Krüss Windows based Laboratory Desktop software in the Sorption mode. The porous solid is placed in an appropriate sample holder and suspended from the balance in the Force Tensiometer just above the surface of a test liquid (see figure 2).

![Washburn Method Principle](image)

Fig. 2 Washburn method principle
The Force Tensiometer performs the whole experiment automatically. The liquid is raised until it just touches the bottom of the porous sample. Mass versus time data is then collected as liquid penetrates into the solid. The rate and interval over which this data is collected is user selectable in the Laboratory Desktop software. At the end of the experiment data can be reduced to either graphical or tabular format. It is also automatically converted to mass versus time data from which a slope is taken and used in the Washburn equation to calculate either the material constant “c” or a contact angle “θ” depending on the experiment.

Wilhelmy Method

The Wilhelmy method involves dipping a membrane into a non-penetrating liquid while measuring the force on the sample due to wetting. The advancing (wetting) contact angle of the liquid on the membrane is determined from force data obtained during submersion of the membrane into the liquid. The receding (dewetting) contact angle is likewise determined from force data pertaining to removal of the solid from the liquid. (Receding contact angles are not obtainable for penetrating liquids by the Washburn technique.) See figure 3.

Contact angles are calculated from force data using the Wilhelmy equation:

\[
\cos \theta = \frac{F - F_b}{l \sigma}
\]  

wherein \( \theta \) = the contact angle, \( l \) = the membrane’s wetted length (perimeter), \( \sigma \) = the surface tension of the liquid, \( F \) = the total force felt by the membrane at any submersion position and \( F_b \) = the buoyant component of the force on the membrane at any submersion position. \( F_b \) is due to the membrane displacing liquid as it is submerged and removed. It is, in general, a distraction to Wilhelmy contact angle experimentation, since the contact angle depends on the Wilhelmy force (\( F_W \)) only, which is the wetting force, or the total force felt by the solid (\( F \)) less the buoyant force (\( F_b \)). Hence \( F_W = F - F_b \) as used in the Wilhelmy equation above.

Polysulfone membrane results

Figure 4 shows raw force versus submerged position data from a Wilhelmy experiment done with pure water and a very hydrophobic polysulfone membrane (membrane A). Membrane A was found to have an advancing contact angle of 103° against pure water from this data.

Figure 5 shows raw mass versus time data from Washburn experiments done with pure water and the hydroxypropylcellulose-containing polysulfone membrane (membrane B) and the cationic cellulose containing polysulfone membrane (membrane C). It is obvious from the raw data that both membranes imbibe water. However, the cationic membrane imbibes water more quickly than the membrane containing only non-ionic hydroxypropylcellulose. The respective constant angles were 79° for the hydroxypropylcellulose membrane and 50° for the cationic cellulose membrane.
Conclusions

(1) The addition of hydrophilic cellulose to polysulfone-based membranes increases their wettability with pure water. This is expected, since celluloses are more hydrophilic than polysulfones.

(2) The addition of ionic (charged) celluloses has an even greater effect in wettability.

(3) There are two techniques for the determination of contact angle for liquids on membranes: a technique for penetrating liquids and a technique for non-penetrating liquids.

(4) The contact angle techniques can, of course, be used for other liquids beside pure water.

(5) The contact angle techniques are very useful characterization tools for the study, manufacture and modification of membranes.

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