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Studies on Hydrophilic Polysulfone Ultrafiltration Membranes

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Ultrafiltration membranes were produced from carboxylated polysulfone polymers having different degrees of substitution (*DS*). Solute separation was found to increase with increasing *DS*. The techniques of single solute permeation and permoporometry were used to determine the pore size of these membranes. Permoporometry measurements indicated that pore size decreased with increasing *DS*. Solute separation was predicted by inserting the distribution of pore sizes obtained from permoporometry into a restricted transport model. Similar results were obtained from a nonlinear least squares fit of the restricted transport model to the experimental data. Both techniques produced similar sieving curves. It was concluded that pore size decreases were not due to the increasing repulsion of solute molecules by hydrophilic polysulfone but to changes in polymer solution properties as the *DS* increased.

On a produit des membranes d'ultra-filtration à partir de polymères de polysulfone carboxylisés ayant différents degrés de substitution (*DS*). On a trouvé que la séparation de soluté augmentait avec l'augmentation du *DS*. Des techniques d'imprégnation et de permoporométrie avec des solutés simples ont été utilisés pour déterminer la taille des pores de ces membranes. Les mesures de permoporométrie indiquent que la taille des particules diminuent avec l'augmentation du *DS*. On a prédit la séparation du soluté en intégrant la distribution de taille des pores obtenue par la permoporométrie dans un modèle de transport restreint. Des résultats similaires ont été obtenus par calage par moindres carrés non linéaires du modèle de transport restreint aux données expérimentales. Les deux techniques produisent des courbes de tamisage comparables. On a conclu que la diminution de la taille des pores n'est pas due à une augmentation de la répulsion des molécules de soluté par le polysulfone hydrophilique mais à des modifications des propriétés des solutions de polymères lorsque le *DS* augmente.

Keywords: carboxylated polysulfones, hydrophilic polysulfones, ultrafiltration membranes, permoporometry, restricted transport model.

Polysulfones are a family of high performance thermoplastics with excellent oxidative, thermal and hydrolytic stability as well as good mechanical and film forming properties. This desirable combination of properties and their availability sees polysulfones widely used in the manufacture of commercial membranes. Despite obvious advantages, polysulfones have certain drawbacks. Their hydrophobic nature is a limitation for membranes for separating low molecular weight solutes in aqueous systems. Hydrophobic properties are often cited as a reason for the protein fouling of membranes (eg. Dillman and Miller, 1973). The versatility of polysulfones is increased when their physio-chemical nature is modified.

Directed lithiation of polysulfones has been demonstrated by Guiver et al. (1988) to be a useful modification method. This general technique can be used to introduce a wide variety of functional groups onto the polysulfone backbone with good control over the degree of substitution (*DS*). Consequently, with the addition of an appropriate functional group, the properties of polysulfones can be modified. Guiver et al. (1990) reported on the chemistry and properties of carboxylated polysulfone derivatives made using the process of directed metalation. Reverse osmosis membranes made from this material have already been described by Guiver et al. (1989). The present paper will focus on the properties of ultrafiltration membranes made from carboxylated polysulfones.

The purpose of this paper is to determine the effect of the degree of substitution of carboxylated polysulfone on membrane separation. The characterization of membranes using a restricted transport model and permoporometry is described.

Theory

RESTRICTED TRANSPORT MODEL

A standard restricted transport model based on steric solute-membrane interactions was used to estimate membrane

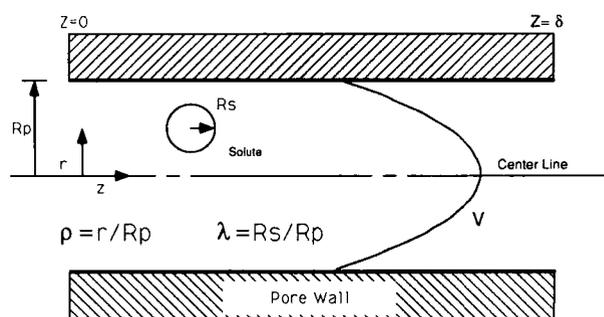


Figure 1 — Transport of a probe solute through a narrow capillary.

pore size. The derivation of this model is given by Anderson and Quinn (1974) and Tremblay (1989). The active separation layer of a membrane is represented by an array of capillaries of cylindrical cross-section. Two simplifying assumptions are used in the derivation of this model. First, the solvent inside the pore is assumed to form a continuous phase; therefore the usual equations of continuum mechanics are applicable. Second, the physio-chemical interactions between the membrane material and probe solutes are assumed to be negligible. The restricted transport model only accounts for steric interactions in evaluating membrane pore size. The transport of solute through a membrane pore is represented schematically in Figure 1.

Estimates of membrane pore size can be obtained by relating solute separation (*f*), test conditions and steric parameters to standard fluid transport equations. Solute separation, as a function of λ , (the ratio of solute radius (R_s) to pore radius (R_p)) is given by,

$$f(\lambda) = 1 - \{ \chi / [1 - \exp(-Pe)(1 - \chi)] \} \dots \dots (1)$$

where *Pe* is the pore Peclet number defined as follows,

$$Pe = (\chi \langle V \rangle \delta) / (\xi D_\infty) \dots \dots \dots (2)$$

$\langle V \rangle$ is the average velocity within the pore. δ is the length of the membrane pore. ξ is the ratio of restricted diffusivity of the solute in the pore (D) and the bulk diffusivity of the solute in solution (D_∞). χ is a global steric parameter associated with restricted convective transport within the pore.

Both ξ and χ are global parameters determined from the integration of functions that are dependent on λ and the radial position of the solute across the pore (ρ). ξ and χ are defined as follows,

$$\xi = D/D_\infty = \int_0^{1-\lambda} [2\rho K^{-1}] d\rho \dots\dots\dots (3)$$

$$\chi = \int_0^{1-\lambda} [4\rho(1-\rho^2)G] d\rho \dots\dots\dots (4)$$

K^{-1} is the local enhanced friction term. G describes the local lag coefficient which accounts for the retarding effect of the pore wall. A summary of transport parameters obtained from various sources has been reviewed by Deen (1989). Bungay and Brenner (1973) derived numerical values of ξ and χ for a sphere translating through a quiescent fluid. These values were used throughout this work since they are valid for a broad range of λ , ($0 \leq \lambda < 1$).

The average pore size of a membrane can be estimated by performing a regression on the restricted transport model using experimentally obtained separation data. In this work, the criteria of the minimum sum of squares of residuals was used to determine average pore sizes.

PERMOPOROMETRY

Permoporometry, including the bubble point and mercury intrusion method, is a well documented technique for characterizing porous materials. The bubble point method using air to displace water in membrane pores is widely used to characterize microfiltration membranes. The surface tension of the air-water interface is too great in order to characterize the smaller pores of ultrafiltration membranes. Two immiscible liquids, having a lower surface tension, can be used in this case. This method was used by Bechold et al. (1931), Erbe (1935) and Grabar and Nikitine (1936) for analyzing the pore size and pore size distribution of microfilters. The technique, as applied to ultrafiltration membranes, is described in detail by Capannelli et al. (1983) and Kesting (1985).

In this method, a fluid "A", which completely wets the membrane is used to fill the pores. A second fluid "B", immiscible in the former, is then permeated through the membrane. The trans-membrane pressure is measured at various permeate flowrates. This process is represented in Figure 2. The pore size and the pore size distribution can be obtained by using Cantor's equation.

Cantor's equation relates the pressure drop across a capillary (ΔP) to the surface tension (σ) and the radius (r) of the capillary,

$$\Delta P = 2\sigma/r \dots\dots\dots (5)$$

Membranes have a distribution of pore sizes ranging from R_{\min} to R_{\max} . The pressure required for the immiscible fluid ("B") to flow through the largest pore is given by,

$$\Delta P_{\min} = 2\sigma/R_{\max} \dots\dots\dots (6)$$

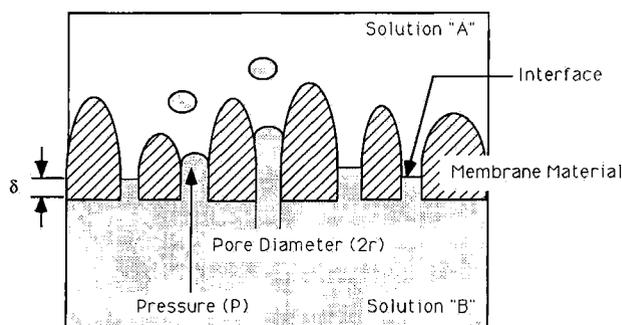


Figure 2 — Description of permoporometry.

As the pressure of "B" is increased, smaller pores are available for permeation. When the permeate rate becomes proportional to pressure, all the fluid "A" in the pores has been displaced by "B". At this point the smallest pores (R_{\min}) are contributing to flow. Therefore,

$$\Delta P_{\max} = 2\sigma/R_{\min} \dots\dots\dots (7)$$

The pore size distribution can be determined graphically (Kesting (1985)) from a plot of permeation rate as a function of pressure or numerically (Capannelli et al. 1983). The numerical version of this technique was used in this study.

Experimental

Udel P-3500 polysulfone was obtained from Amoco Performance Products and used as the starting material in all carboxylations. Carboxylic acid polysulfone derivatives with a DS of 0.25, 0.46, 0.60, 0.70 and 1.06 were prepared as previously described by Guiver et al. (1990). A DS of 0.0 refers to the unmodified Udel polymer. The value of DS for modified polymers was determined using 1H -NMR. The solvent, 1-methyl-2-pyrrolidinone (NMP), was obtained from Aldrich and used as received.

Ultrafiltration membranes made from Udel polysulfone were cast from 20 weight percent solutions of polymer in NMP. Since the repeat units of the modified polymers had different molecular weights, casting solutions were made up to have the same mole ratio of polymer to solvent as the 20 weight percent Udel solution. Polymer solutions at room temperature were cast on a glass plate using a doctor blade having a 250 μm gap. The cast solutions were gelled directly into de-ionized water at 0°C. Membranes were left in fresh water for 24 hours to remove all traces of solvent.

Membrane testing procedures for determining molecular weight cut-off curves have been previously described by Hazlett et al. (1989). Ultrafiltration experiments were performed in cross-flow test cells having a 508 μm gap using a feed flowrate of 3 L/min which provided a cross-flow velocity of 0.85 m/s. These thin channel ultrafiltration test cells had an effective surface area of $10.75 \times 10^{-4} m^2$. All test runs were performed at an operating pressure of 275.8 kPa. The probe solutes were polyethylene glycols (PEG) of various molecular weights obtained from Fluka. Gel permeation chromatography was used to verify that the PEG's used in this work had a narrow molecular weight distribution. Feed concentration for all characterization runs was 200 mg/L. Feed and permeate concentrations were determined using an automated Beckmann Total Organic Carbon analyzer. A period of 24 hours was required to perform a series of characterization tests.

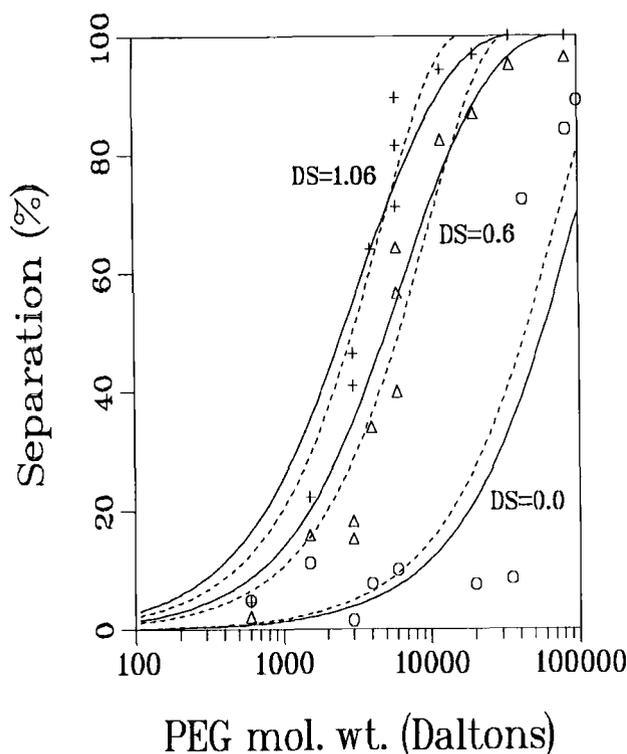


Figure 3 — Solute separation vs. molecular weight for various *DS* of carboxylated polysulfone.

----- Calculated from a least squares fit of the restricted transport model to the separation data.

————— Calculated using permoporometry data.

- + *DS* = 1.06.
- Δ *DS* = 0.60.
- *DS* = 0.00.

Details of the porosimeter are given in Capanelli et al. (1988). The main components of the porosimeter used in this work were: a Waters 590 programmable HPLC pump, pressure transducer (Validyne model P305D), data acquisition system (CHROM card from Metrabyte) and an IBM-compatible computer. The computer functioned as a data logger and controller. Isobutanol, methanol and ultrapure water were mixed in a volume ratio of 15:7:25. This mixture separated into two stable phases. The aqueous phase of this solution, defined as "A", was used to fill the membrane pores. The alcohol phase, "B", was introduced at various flowrates to obtain the membrane pore size. Capanelli et al. (1988) reported the surface tension of the non-aqueous phase to be 3.5×10^{-4} Pa · m and a viscosity of 3.4 mPa · s (at 20°C).

Results

Molecular weight cut-off experiments were performed on membranes made from six polysulfones each having different degrees of substitution. The results of three membranes having a *DS* of 0.0, 0.6 and 1.06 are plotted in Figure 3. Solute separation was found to increase with higher *DS* values.

The average pore size for each membrane listed in Table 1 was calculated from the restricted transport model. These pore sizes, generated from the separation data, decrease with increasing degree of substitution. Model predictions of the separation using pore sizes obtained from solute permeation was plotted as a dashed line in Figure 3.

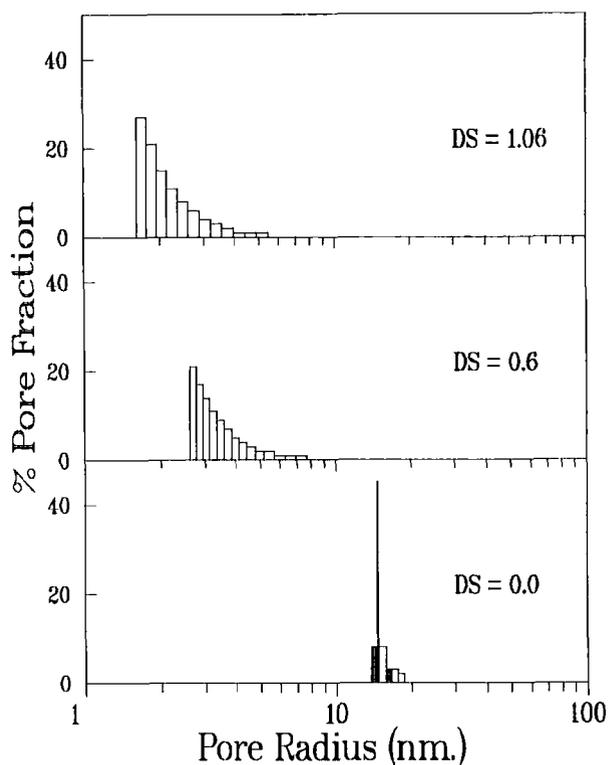


Figure 4 — Membrane pore size distribution obtained from permoporometry.

TABLE 1
Average Pore Size of Membranes with Different Degree of Substitution Calculated Using the Restricted Transport Model and from Permoporometry

| Degree of Substitution | Average Pore Radius from Probe Solutes (nm) | Average Pore Radius from Permoporometry (nm) |
|------------------------|---|--|
| 0.00 | 13.08 | 15.4 |
| 0.25 | 6.94 | — |
| 0.46 | 5.14 | — |
| 0.60 | 4.86 | 3.77 |
| 0.70 | 3.82 | — |
| 1.06 | 3.37 | 2.44 |

Figure 4 shows the pore size distribution of the same membranes generated by permoporometry. The average pore size of these membranes are given in Table 1. As observed from Figure 4 and Table 1 the average pore size decreases as the *DS* increases. The pore size distributions obtained from the porosimetry experiments were used to predict solute separations with the restricted transport model. These results have been plotted as solid lines in Figure 3.

Discussion

Membrane morphology and solute-membrane material interactions are two major factors affecting solute separation and permeation. The addition of carboxylic acid groups onto the polysulfone back-bone changes the solution and surface properties of the polymer. The significance of interfacial effects could be determined if it were possible to produce membranes having exactly the same pore size from different polymers. However, when the polymer structure is changed,

solution properties are also altered. This could result in the production of membranes of having different pore sizes.

In order to decouple these two effects, independent methods were used to characterize membranes produced from polymers having various DS . The permeation of solutions containing probe solutes through membranes is a standard characterization technique. The separation data obtained with this technique reflects the influences of solute-membrane material interactions and pore size. The technique of permoporometry generates a pore size distribution which is independent of solute-membrane material interactions. Comparing the pore sizes obtained with these two methods can therefore verify the assumption of minimal material interactions advanced in the restricted pore flow model.

The dashed lines in Figure 3 represents least squares predictions of the restricted transport model to the separation data based on a single average pore size. The solid lines in Figure 3 were produced by inserting the pore size distribution obtained with permoporometry into the restricted transport model. The fit is excellent considering the permoporometry curve is based on a distribution of pore sizes and that of the probe solute is based on a single pore size. These results indicate that, compared to the restricted diffusion and convection contributions, the effects of PEG-polysulfone material interactions on solute separation are negligible with respect to solute transport. They also indicate that increases in solute separation are due to a physical decrease in membrane pore size.

Changes in the polymer solution properties with the addition of carboxylate groups is a probable explanation for the reduction of membrane pore size. As the DS is increased, the polymer is more hydrophilic and the polymer's affinity for NMP decreases. This increases the exchange rate of NMP and water during the gelation process thereby changing gelation dynamics. This results in increased membrane separation.

Conclusion

Increasing the degree of substitution of carboxylated polysulfone produced membranes having smaller pores for the same casting solution concentration. For unmodified polymer, a pore size of 13.08 nm was obtained, while carboxylated polymer having a DS of 0.60 and 1.06 had a pore size of 4.86 nm and 3.37 nm respectively. This behavior was attributed to an increased rate of solvent exchange during the gelation process.

Two methods of membrane characterization, solute permeation and permoporometry, were used to evaluate membrane pore size. Solute permeation results were analyzed by a restricted transport model based on negligible solute-membrane material interactions. Both methods predicted similar pore sizes for a given membrane thus confirming the assumptions made in the restricted transport model. This simple model adequately represents the transport of solute through polysulfone ultrafiltration membranes and provides a realistic estimate of membrane pore size. The model is useful for fitting membrane sieving curves and provides a quantitative measure of pore size instead of the qualitative value of molecular weight cut-off.

Nomenclature

D = diffusivity of solute in the pore (m^2/s)
 D_∞ = diffusivity of solute in solution (m^2/s)
 DS = degree of substitution

f = separation
 K^{-1} = local enhanced friction term
 G = local lag coefficient
 Pe = Peclet number
 r = radial position of solute in pore (m)
 $\langle V \rangle$ = velocity inside the pore (m/s)
 z = pore axial direction (m)

Greek

δ = length of the membrane pore (m)
 λ = ratio of solute size to pore size
 ξ = ratio of restricted diffusion within the pore to free diffusion in bulk solution
 ρ = radial position across the pore (m)
 σ = surface tension ($Pa \cdot m$)
 χ = global steric parameter
 ΔP = pressure drop across the pore (kPa)

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