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MATERIALS AND INTERFACES

Variations in the Pore Size of Charged and Noncharged Hydrophilic Polysulfone Membranes†

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Changes affecting carboxylated polysulfone (CPS) membranes were studied in relation to membrane porosity. The pore size of CPS membranes containing COOH substituents was measured after exposure to acidic and basic environments. Membrane pore size was found to be dependent on the form of the carboxyl group. Pore size decreased by 10–25% on exposure to acid. The conversion from the COOH form to the ionic COO^-Na^+ form, by exposure to base, increased the pore size of the membrane by 30–100%. These changes were fully reversible on conversion to the COOH form. Membranes were exposed to aqueous ethanol and chlorine to determine their resistance to these environments. Aqueous ethanol had no measurable effect on membrane pore size. For membranes in the COOH form, a 24-h exposure to chlorine resulted in a small increase in membrane pore size, while no significant change was observed for membranes in the COO^-Na^+ form.

Introduction

Aromatic polysulfones are commonly used in the manufacture of synthetic membranes. They have outstanding oxidative, thermal, hydrolytic, and dimensional stability. The inherent hydrophobic nature of polysulfone is often cited as a disadvantage in using this polymer as a membrane material. Hydrophilicity can be imparted into polysulfone by the addition of carboxyl functional groups. These groups are added to the polymer backbone with the implicit assumption that the polymer will retain many of its favorable characteristics. The lithiation/carboxylation process described by Guiver et al. (1990a) is one method of adding pendant carboxyl groups onto the polysulfone backbone, resulting in the production of carboxylated polysulfones (CPS). The use of these materials has been demonstrated in the manufacture of reverse osmosis (Guiver et al., 1990b) and ultrafiltration membranes (Tremblay et al., 1991).

The carboxyl groups present in CPS membranes can exist either in the COOH form or in the ionized COO^-Na^+ form, depending on the pH environment. The change of pore size was studied after exposure to acidic and basic media. The effects of exposure to chlorine and aqueous ethanol were also studied. Data were collected from single solute permeation experiments in order to generate a molecular weight separation curve for the membranes. A restricted transport model was then used to analyze the separation data and produce an average pore size, characteristic of membrane morphology. Changes in membrane morphology were interpreted from differences in the average membrane pore size.

Theory

The average pore size of the membranes studied in this work was estimated with a restricted transport model. The derivation of this model was described by Bungay and Brenner (1973) and Anderson and Quinn (1974). In this model, the surface of the membrane is represented as an array of capillaries of equivalent cylindrical cross section. The usual assumptions of continuum mechanics are believed to be valid. Only steric interactions are assumed to exist between the solute and pore wall. The translation of a solute molecule through a membrane pore is represented schematically in Figure 1. Separation experiments were carried out with dilute solutions which had a negligible osmotic pressure compared to the operating pressure used in the characterization test. They were performed at high cross-flow velocities and low pore fluid velocities.

On the basis of momentum and mass balances, solute separation ($f(\lambda)$) was defined as

$$f(\lambda) = 1 - \frac{\chi}{1 - e^{-Pe}(1 - \chi)} \tag{1}$$

where λ is the ratio of solute radius (r_s) to pore radius (r_p). The pore Peclet number (Pe) is given by

$$Pe = \frac{\chi\langle V\rangle\delta}{\xi D_\infty} \tag{2}$$

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

With the application of the Hagen–Poiseuille equation

$$\langle V\rangle = \frac{r_p^2\Delta P}{8\delta\eta} \tag{3}$$

where r_p is the pore radius, ΔP is the system pressure, and η is the viscosity of water. The Peclet number can be

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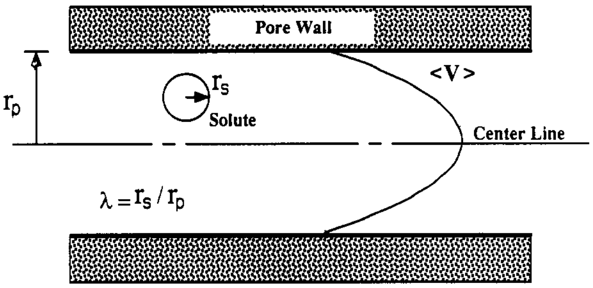

Figure 1. Probe solute translating through a membrane pore.

defined without explicit knowledge of the pore length by substituting eq 3 into eq 2

$$Pe = \frac{\chi}{\xi D_\infty} \frac{r_p^2 \Delta P}{8\eta} \quad (4)$$

Numerical values for ξ and χ as a function of λ are given in Bungay and Brenner (1973).

The radius of poly(ethylene glycol) (r_s) was calculated on the basis of a predictive equation (Tremblay, 1989) for r_s as a function of molecular weight. This equation was obtained by combining data from Amu (1982) and Sourirajan (1983). This relation is expressed as follows

$$r_s/\text{nm} = 0.02607(\text{PEG molecular weight})^{1/2} - 0.015 \quad (5)$$

The correlation has a regression factor of 1.00 and is based on 13 data points for poly(ethylene glycols) ranging from 200 to 40000 molecular weight.

The diffusion coefficient of PEG can be obtained using the Stokes–Einstein relationship (e.g., Reid et al., 1987):

$$D_\infty = \frac{RT}{6\pi\eta r_s} \quad (6)$$

where R is the gas constant, T is the temperature, η is the viscosity of water, and r_s is the solute radius.

The average pore size of a membrane was 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.

Experimental Section

Carboxylated polysulfone (CPS) having a degree of substitution (DS) of 0.88 was made via the lithiation procedure illustrated in Figure 2. The degree of substitution was verified using ^{1}H-NMR spectroscopy. All membranes were cast from carboxylated polysulfone in its acidic form (COOH). In a basic environment, the carboxylic acid groups are converted to the salt form (COO^-Na^+).

Membranes were cast from a 28 wt % polymer solution in *N*-methylpyrrolidinone (NMP) onto a nonwoven polyester backing and gelled directly into water at 0 °C. Seven sheets of membranes were cast, and coupons were cut from these sheets. Test coupons were divided into three groups. Each set was subjected to different exposure histories as follows:

(a) Set A was not exposed to acid or base. These coupons were used to verify the reproducibility of the characterization procedure.

(b) Set B was first characterized, exposed to acid, and recharacterized. These membranes were then exposed to base and characterized once more.

(c) Set C was first characterized, exposed to base, and recharacterized. Finally the coupons were exposed to acid and characterized once more.

Table I. Average Pore Size and 95% Confidence Interval (CI) for All Membranes from Set A

membrane	no. of tests	av pore size/nm	95% CI/nm	95% CI ± % of av pore size
A1	4	1.83	±0.26	14.2
A2	4	1.65	±0.13	7.9
A3	4	1.81	±0.20	11.0
A4	5	1.90	±0.17	8.9

Table II. Initial Pore Size, Obtained from a Single Characterization Run, for All Membrane Coupons

set	membrane designation	pore size/nm
A	A1	1.77
	A2	1.75
	A3	1.94
	A4	2.08
B	B1	1.66
	B2	1.87
	B3	2.41
	B4	1.52
C	C1	2.09
	C2	1.91
	C3	1.93
	C4	1.71
		av: 1.89

After this series of alternating exposure to acid and base, selected membranes from each set were exposed to ethanol and chlorine. The membranes were rinsed with pure water after each exposure. Membranes were recharacterized using pure water and dilute PEG solutions.

The acidic treatment was performed by exposing the membranes to 2 M HCl (pH 0.5) for 24 h. The base treatment was performed by immersing the membrane for 24 h in 2 M NaOH (pH 13). Membranes were also exposed to 20% aqueous ethanol for 24 h. Tolerance to chlorine was determined by immersing membranes in an aqueous solution of 0.05 wt % NaOCl for 24 h.

Ultrafiltration experiments were carried out at 347 kPa (50 psig) in test cells having an effective surface area of 14.50 cm^2. The feed solution was circulated in the system at a rate of 3 L/min. This feed flow rate provided a cross-flow velocity of 0.8 m/s over the surface of the membrane. Membranes were characterized by the successive permeation of water-soluble polymers. A series of PEG's of various molecular weights and narrow molecular weight distribution were used as "probe" solutes. The PEG feed concentration was 200 ppm. At this low feed concentration and high cross-flow velocity, effects of concentration polarization are negligible. One complete characterization run involved a series of five individual permeation tests. PEG concentration was determined using total organic carbon analysis. A complete membrane characterization run, including PEG analysis, took 24 h.

Results

Reproducibility. Set A was used to verify the reproducibility of the characterization method. Figure 3 represents a typical sieving curve and shows the reproducibility of characterization tests performed on coupon A4.

The average pore size based on 4–5 successive characterizations are summarized in Table I. The confidence interval (CI) is a measure of the uncertainty in evaluating the average pore size. These values represent the combined experimental errors involved in concentration determinations as well as possible membrane performance changes over time. The individual confidence intervals obtained in estimating membrane pore size ranged from ±0.13 to ±0.26 nm, as shown in Table I.

Table II lists the initial characterization for pore size generated using the restricted transport model for all

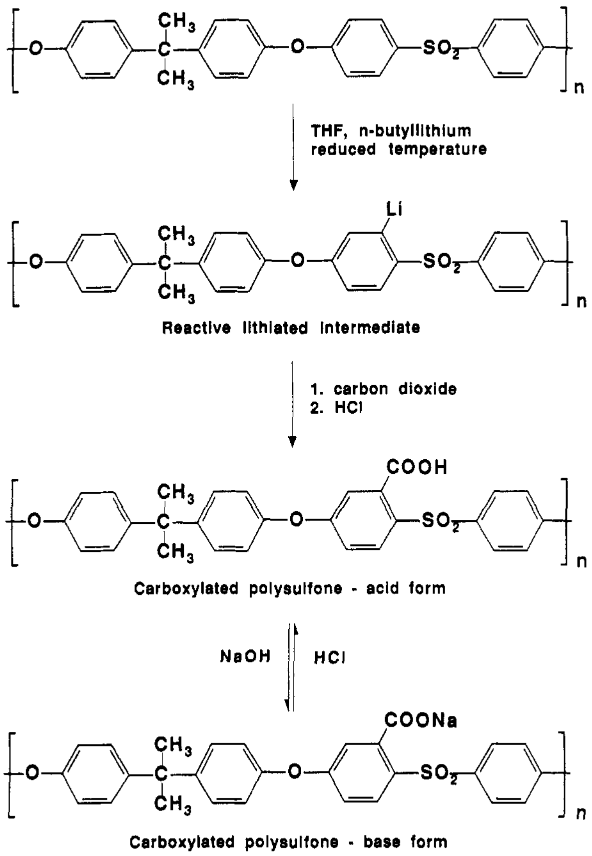

Figure 2. Synthesis route to carboxylate polysulfone.

Table III. Average Pore Size for Set B Membranes in the COOH Form before and after Exposure to Acid

membrane	initial pore size (in COOH form)/nm	pore size after exposure to acid/nm	difference/nm	% change from initial pore size
B1	1.66	1.34	-0.32	-19.3
B2	1.87	1.61	-0.26	-13.9
B3	2.41	1.80	-0.61	-25.3
B4	1.52	1.35	-0.17	-11.2

membranes used in this study. The average pore size of these membranes after the initial characterizations was 1.89 ± 0.15 nm (95% CI), as seen in Table II. This average pore size accounts for the uncertainty associated with the reproducibility of individual membrane sheets and the location of a coupon on a sheet.

Effect of Acid on the COOH and COO^-Na^+ Membranes. A comparison of the separation curve for a membrane before and after exposure to acid is shown in Figure 4. Solute separation increased slightly after the membrane, already in the COOH form, was exposed to acid. Table III lists the change in average pore size of all membranes in set B after exposure to acid. Accounting for experimental uncertainties, the change in average pore size was significant but small, in the order of -0.3 nm.

The effect of acid on the COO^-Na^+ form membrane was determined by examining the results obtained for set C.

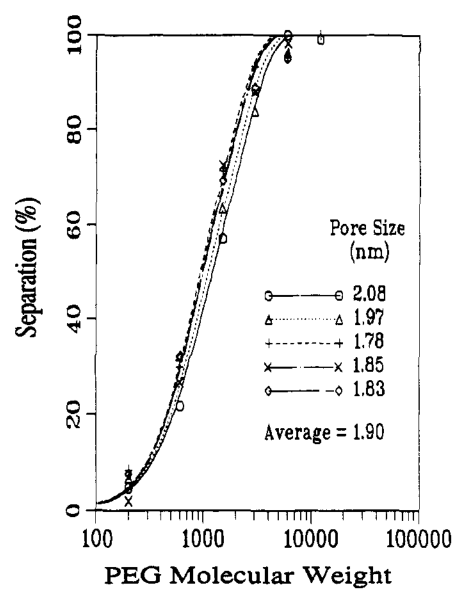

Figure 3. PEG separation and average pore sizes for five repeat characterizations performed on membrane A4. Curves represent a least squares fit of eq 1 to the separation data generated in a characterization run.

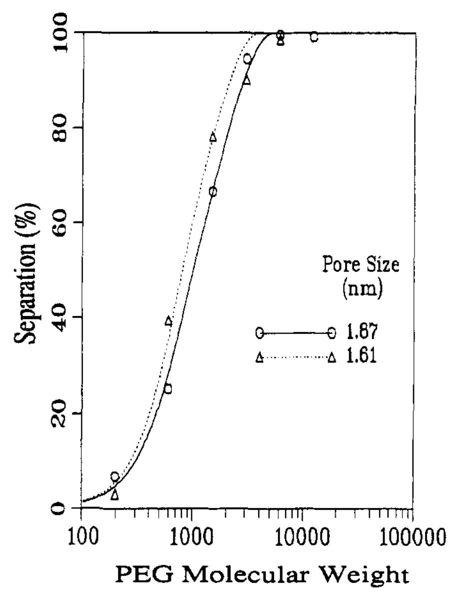

Figure 4. PEG separation and average pore sizes for membrane B2 in the COOH form (solid line, pore size = 1.87 nm) and as a result of exposure to acid (dotted line, pore size = 1.61 nm). Curves represent a least squares fit of eq 1 to the separation data generated in a characterization run.

Membranes in the COOH form were first converted to the COO^-Na^+ form by exposure to NaOH and then characterized. The larger pore COO^-Na^+ form membranes were then converted to the COOH form by exposure to acid. The final characterizations for this set showed an initial slight increase in membrane pore size, as seen in Table IV. However, after a 2-day period of testing, the pore size

Table IV. Average Pore Size for Set C Membranes in the COO^-Na^+ Form before and after Exposure to Acid

membrane	time after treatment/day	pore size of COO^-Na^+ membrane/nm	pore size after exposure to acid/nm	difference from COO^-Na^+ form/nm	% change
C1	1	2.89	3.28	+0.39	+13.5
	2		1.66	-1.23	-42.6
	3		1.70	-1.19	-41.2
C2	1	2.97	1.65	-1.32	-45.0
	2		1.72	-1.26	-42.7
C3	1	2.64	3.94	+1.30	+49.2
	2		1.72	-0.92	-34.9
C4	1	2.51	3.34	+0.83	+33.1
	2		1.57	-0.94	-37.5

Table V. Pore Sizes for Set C Membranes in the COOH Form before and after Exposure to Base

membrane	initial pore size of COOH form/nm	pore size after exposure to base/nm	difference/ nm	% change from initial pore size
C1	2.09	2.89	+0.80	+38.3
C2	1.91	2.97	+1.06	+55.5
C3	1.93	2.64	+0.71	+36.8
C4	1.71	2.51	+0.80	+46.8

decreased to values below those initially obtained in the first characterization. In general, membranes in the COO^-Na^+ form had a 1-nm decrease in average pore size after immersion in acid. This decrease in pore size is clearly illustrated in Figure 5.

Effect of Base on the COOH Membranes. Table V contains a summary of the change in pore size as a result of exposure to base. This increase in pore size is shown in Figure 5. A substantial increase of at least 0.7 nm in the average pore size was observed after the COOH membranes were exposed to NaOH.

The same increase in membrane pore size was observed for acid membranes from group B. Table VI shows that membranes first exposed to acid and then to base have a larger increase in average pore size (at least 1 nm).

Ethanol. One coupon was selected from each membrane set and immersed in 20 wt % aqueous ethanol. The results, summarized in Table VII, show that ethanol treatment had no effect on CPS in either the COOH or COO^-Na^+ forms.

Chlorine. One coupon was selected from each membrane set and immersed in a solution of 0.05 wt % NaOCl for 24 h. No sign of physical deterioration of the membrane in either form was apparent. The change in average pore size after exposure is shown in Table VIII. The pore size increased by 0.63 and 0.89 nm for the polymer in the COOH form (sets A and C), which are greater than the limits of experimental uncertainty. In the COO^-Na^+ form (set B) the average pore size showed a negligible change with exposure to chlorine.

Discussion

The basic premise of this work is that the change in solute separation is a direct measure of the change in morphology of the membrane. This premise is based on two initial assumptions: (1) Concentration polarization has been minimized so that bulk solution concentration is approximately the same as the concentration at the membrane solution interface, and (2) only steric interactions exists between PEG and the membrane. The validity of these initial assumptions can be supported from both experimental data and theoretical considerations.

Concentration polarization is the result of the accumulation of solute on the high-pressure side of the membrane. Consequently, the bulk concentration may not be representative of the actual pore inlet concentration. Concentration polarization effects can be minimized by increasing the mass-transfer coefficient of the test cell. Long and Anderson (1984) used the mechanical action of a Teflon bar to eliminate concentration polarization. In their experiment, they used a stirring speed of 240 rpm over a track-etched mica membrane of 1.6 cm in diameter. This translated to a maximum surface velocity of 0.2 m/s. The cross-flow velocity of 0.8 m/s in our test cell is 4 times greater. The average pore fluid velocity in Long and Anderson was reported to be 5.5×10^{-5} cm/s. On the basis of a conservative estimate of 0.25 μm for the selective layer of the membranes used in this work, the average pore fluid velocity for a 1.89-nm pore radius was calculated to be 3.02×10^{-6} cm/s. This velocity is 1 order of magnitude lower than that reported in Long and Anderson. The cross-flow velocity and pore fluid velocity are comparable to that of Long and Anderson. Accordingly, we can justify the assumption of negligible concentration polarization.

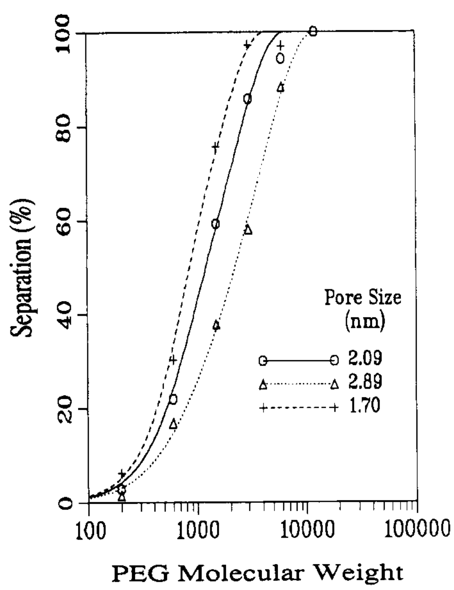

Figure 5. PEG separation and average pore sizes for membranes C1 in the COOH form (solid line, pore size = 2.09 nm) and as a result of exposure to base (dotted line, pore size = 2.89 nm) and then acid (dashed line, pore size = 1.70 nm). Curves represent a least squares fit of eq 1 to the separation data generated in a characterization run.

Tremblay et al. (1991) compared the pore size of hydrophilic polysulfone membranes evaluated using solute sieving experiments and permoporometry. Excellent agreement was obtained between sieving curves predicted from permoporometry and those obtained by fitting the separation data. The experimental test conditions of high cross-flow velocity and low pore fluid velocity and agreement between both characterization techniques indicates that concentration polarization had a negligible effect. Purely steric solute–membrane interactions are adequate to determine the membrane pore size in these experiments.

In this work, no apparent physical deterioration of the membrane occurred in the alternating exposure to acid or base environments. However, changes in membrane performance linked to membrane morphology were observed. The pore size of CPS membranes was affected by the ionization of the carboxylate groups on the polymer backbone. CPS membranes in the COO^-Na^+ form had

Table VI. Average Pore Size for the Acidified Set B Membranes before and after Exposure to Base

membrane	time after treatment/days	pore size after exposure to acid/nm	pore size after exposure to base/nm	pore size change/nm	% change
B1	1	1.34	2.42	+1.08	+80.6
	2		2.54	+1.20	+89.6
B2	1	1.61	2.43	+0.82	+50.9
	2		1.80	+0.19	+11.8
B3	1	1.80	2.85	+1.05	+58.3
	2		2.48	+0.68	+37.8
B4	1	1.35	2.76	+1.41	+104.4
	2		2.33	+1.00	+72.6
	3		2.77	+1.42	+105.2

Table VII. Pore Size of Membranes after Immersion in 20 wt % Aqueous Ethanol

membrane designation	pore size before ethanol/nm	pore size after ethanol/nm	difference/ nm	% change
A2 (initial)	1.65	1.64	−0.01	0.0
B2 (base)	1.80	1.75	−0.05	+2.8
C4 (acid)	1.57	1.58	+0.01	+0.6

Table VIII. Pore Size of Membranes Tested after Immersion in Chlorine

membrane designation	pore size before NaOCl/nm	pore size after NaOCl/nm	difference/ nm	% change
A1 (initial)	1.83	2.46	+0.63	+34.5
B1 (base)	2.54	2.39	−0.15	−6.3
C3 (acid)	1.72	2.61	+0.89	+51.7

larger pore sizes than CPS membranes in the acid COOH form. This change in pore size was found to be completely reversible. Reversible changes in pore size suggest that the polymer networks which form a membrane have some degree of mobility. Immersion of CPS membrane in base results in a localization of charge on the polymer chain. We believe the negatively charged carboxyl groups on the polysulfone backbone induce an electrostatic repulsion to neighboring groups. This is an equivalent effect to swelling, as the distance between polymer chains of the polymer network forming the membrane pores increased. Osmotic pressure effects may also have a role in polymer swelling. Upon exposure to base, the concentration of cations within the polymer network is greater than in the bulk solution due to the attracting power of the fixed anionic charge. Thus, the osmotic pressure within the network is greater than the external solution which swells the polymer network. The effects of the carboxylate group in polysulfone can be compared to the behavior of charged groups in a space network polyelectrolyte gel, as described by Flory (1953).

Aromatic polysulfones are not soluble in nor attacked by aqueous acids (Johnson, 1969). Udel polysulfone is extremely tolerant to strong alkaline conditions, remaining stable in 40% NaOH solution at 70–80 °C for 300 h with no sign of cracking (Zschocke and Quellmalz, 1985). Such physical properties have been attributed to a combination of the ether linkage and the rigid phenyl sulfone portion of the polymer backbone (Cheryan, 1986). Additions of carboxylate groups onto the phenyl rings should have little effect on chain rigidity. Carboxyl functional groups provide additional sites for hydrogen bonding and consequently increase the hydrophilicity of the material.

Udel itself is resistant to both chlorine and aqueous ethanol. Our results indicate that chlorine had a small effect on the CPS membrane in the COOH form. A negligible change in pore size was observed on exposure to chlorine when the membrane was in the COO^-Na^+ form.

Conclusion

The pore size of membranes cast from carboxylated polysulfone were compared to the COOH and COO^-Na^+ forms. Acid treatment led to a slight decrease in pore size while the base treatments led to large increases in pore size. The changes in pore size were completely reversible, implying that membranes in the COOH form could be subjected to caustic cleaning cycles and re-acidified with minimal change in separation characteristics. This reversibility could eventually be exploited in areas where the pore size of a membrane must be changed in situ, such as application in sensors and controlled release devices.

The performance of carboxylated polysulfone membranes was not affected by aqueous ethanol solutions. This property is important in the separation of certain organics from water and in applications such as pervaporation. There is a demand for membrane materials which can tolerate exposure to chlorine, especially in point of use potable water treatment. Carboxylated polysulfone membranes were found to have resistance to chlorine, making this material a potential candidate for use in reverse osmosis and nanofiltration applications.

Nomenclature

D = diffusivity of solute in the pore
D_∞ = diffusivity of solute in solution
$f(\lambda)$ = solute separation
ΔP = system pressure
Pe = pore Peclet number
R = gas constant
r_p = pore radius
r_s = solute radius
$\langle V \rangle$ = velocity inside the pore

Greek Letters

δ = length of the membrane pore
η = viscosity of water
λ = ratio of solute radius to pore radius
ξ = ratio of restricted diffusion within the pore to free diffusion in bulk solution
χ = global steric parameter

Registry No. PEG, 25322-68-3; NaOH, 1310-73-2; EtOH, 64-17-5; NaOCl, 7681-52-9; $(-OC_6H_4\text{-}p\text{-}SO_2C_6H_4\text{-}p\text{-}OC_6H_4\text{-}p\text{-}C(CH_3)_2C_6H_4\text{-}p-)$, 25135-51-7.

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