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Steric Rejection of Polymeric Solutes by Membranes with Uniform Pore Size Distribution

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Abstract

The analysis of steric rejection by membranes with uniform pore size distribution is described. The uncharged polymeric solutes (polyethylene oxides, dextrans) are modeled as hard spheres, and the rejection in capillaries is corrected for hydrodynamic lag. The experimental data obtained with Carbowax and Dextran T solutes and track-etched Nuclepore membranes support the general validity of this model. Both single solute rejection data as well as GPC-monitored rejection data obtained with blend solutions are in good agreement with the theory.

INTRODUCTION

A key technical problem in designing and manufacturing ultrafiltration membranes is "tailoring" of membrane functional properties for the given separation process. Due to complexity of phenomena involved in membrane formation and in separation by ultrafiltration, the approach to "tailoring" is most often empirical. This involves usually high cost and slow pace of membrane development. A correlation between *functional* membrane properties (such as solute rejection and permeate flux) and *structural* membrane properties (such as pore size distribution, pore density, and chemical and electrical character of the surface) is needed for rationalization of the membrane "tailoring" process.

With these objectives in mind, we analyze in this study the situation of a purely steric rejection, i.e., rejection without possible contributions from dispersive or electrostatic interactions. We have also avoided analysis of concentration polarization effects, since this has been well described by others (e.g., Refs. *1* and *2*). Rather, we tried in our experiments to minimize concentration polarization effects by using high stirring speeds and low permeate fluxes. The solute transport is assumed to be purely convective (high Peclet number) with a negligible contribution from diffusion.

THEORY

The original Ferry formula (*3*) for rejection of a sphere by a capillary can be written as

$$R = 1 - C_p/C_f = (\lambda(\lambda - 2))^2, \qquad \lambda \leq 1 \tag{1}$$

where C_p = concentration of permeate, C_f = concentration of feed, and $\lambda = a/r$, where a = radius of sphere and r = capillary radius.

However, in an enclosed space the terminal velocity of a sphere with respect to a moving liquid is not the same as in free space, which gives rise to "hydrodynamic lag," so that the velocity of the sphere with respect to a wall is not the same as that of the liquid. The problem of hydrodynamic lag has been investigated by a number of authors (*4–8*). The viscous drag force on a solute sphere that reflects proximity of a wall can be written as

$$F = -6\pi\eta a(K_1 U - K_2 V) \tag{2}$$

where U = velocity of sphere with respect to some reference, V = velocity of liquid with respect to same, η = viscosity of liquid, and K_1 and K_2 are the drag coefficients. In a steady state:

$$U/V = K_2/K_1 \tag{3}$$

and the hindrance to convection becomes

$$W = 1 - R = \frac{C_p}{C_f} = \frac{K_2}{K_1}(1 - (\lambda(\lambda - 2))^2) \tag{4}$$

Paine and Scherr (*8*) published a table of K_1 and K_2 obtained from accurate computer calculations. Although they neglected the dependence of K_1 and K_2 on the radial position within the pore, they presented evidence to show that these were excellent approximations for calculation of hydrodynamic lag. Examination of the ratio K_2/K_1 shows that it can be fitted closely by $\exp(-\alpha\lambda^2)$, where α is a dimensionless constant. The condition for a least squares fit to Eq. (4) using this approximation is

$$\sum_i \lambda_i^2\{1 - [\lambda_i(\lambda_i - 2)]^2\}^2(f_i e^{-\alpha\lambda_i^2} - e^{-2\alpha\lambda_i^2}) = 0 \tag{5}$$

where $\lambda_i = 0.1, \ldots, 0.9$, and $f_i = (K_2/K_1)_i$. This was evaluated on an HP-29C calculator, with the result that Eq. (4) using Paine and Scherr's

TABLE 1

Steric Rejections with and without Hydrodynamic Lag

λ	R, Ferry formula	K_2/K_1, Ref. 8	$R = 1 - W$ Eq. (4)	 Eq. (6)
0	0	1.0	0	0
0.1	0.0361	0.99334	0.0425	0.0430
0.2	0.1296	0.97333	0.1528	0.1541
0.3	0.2601	0.94007	0.3044	0.3062
0.4	0.4096	0.89397	0.4722	0.4734
0.5	0.5625	0.83626	0.6341	0.6341
0.6	0.7056	0.76892	0.7736	0.7724
0.7	0.8281	0.69454	0.8806	0.8789
0.8	0.9216	0.61558	0.9517	0.9504
0.9	0.9801	0.53382	0.9893	0.9889

K_1 and K_2 was fitted by the method of least squares to give $\alpha = 0.7146$ or

$$W = 1 - R = \{1 - [\lambda(\lambda - 2)]^2\} \exp(-0.7146\lambda^2) \qquad (6)$$

Values of R from Eq. (4) using Paine and Scherr's K_1 and K_2 and from Eq. (6) are compared in Table 1. It can be seen that agreement is adequate.

EXPERIMENTAL

Ultrafiltration experiments were carried out in an Amicon stirred cell, model 52. The cell was pressurized with nitrogen and the transmembrane pressure was read on a calibrated test gauge with 0.1 psi divisions. The stirring speed was kept constant in all experiments, and it was around 1000 rpm. This corresponds to a Reynolds number (angular velocity × membrane radius^2/solution kinematic viscosity) of about 48,000. Rejections were calculated from feed and permeate concentrations measured almost simultaneously. Concentrations were determined by total organic carbon analysis or from refractive index difference in the GPC-monitored experiments.

Rejection coefficients were routinely measured as a function of pressure to assess the magnitude of the concentration polarization and/or shear rate effects. The typical pore velocities were of the order of less than 0.1 cm/s. The highest pore velocity used (for the 500 Å filter at $\Delta P = 30$ psi) was about 0.32 cm/s. The rejection coefficient obtained at the lowest pressure is considered to be indicative of the intrinsic rejection value. Measured rejection coefficients were reproducible within ±3%. Clean (unused) membrane circles were used for each solute.

GPC experiments were carried out with a Waters Associates model 244 instrument. The μBondagel columns were calibrated with the Carbowax or Dextran T polymers, using their known molecular weight distributions. To avoid adsorption of Carbowax on μBondagel, Carbowax samples had to be transferred into high-purity dimethylformamide (Burdick and Jackson Laboratories) prior to GPC analysis. The transfer was effected by evaporation of water in vacuum at room temperature and redissolving the sample in the same volume of DMF. About 100 ppm hydroquinone was added to Carbowax samples prior to evaporation in order to minimize peroxide formation and possible degradation. Aqueous solutions of dextrans were directly analyzed by GPC.

Dextran polymers were purchased from Pharmacia Fine Chemicals. For the fractions used, T10, T40, and T70, the complete molecular weight distribution curves were provided by the supplier.

Carbowax (polyethylene oxide) samples were supplied by Union Carbide Corp. The molecular weight distributions were determined by GPC.

The Nuclepore filters (polycarbonate track-etched filters) were purchased from Nuclepore Corp. In our calculations we used the rated pore diameters as specified by Nuclepore Corp. These are maximum pore diameters and the actual diameters may be somewhat smaller. More definite information on the pore size range was unfortunately unavailable. According to Nuclepore literature, the actual maximum pore diameter should vary no more than +0 to −20% of rated pore size, and the size distribution should be very narrow. The nominal thickness of the filters was given by the manufacturer as 5×10^{-4} cm. A thickness calculated from weighing the circles of known area and using a value of 1.19 g/cm^3 for the density of polycarbonate was 6.51×10^{-4} cm for N150 Å, 6.21×10^{-4} cm for N300 Å, and 5.38×10^{-4} cm for N500 Å.

RESULTS

Characteristic properties of solutes used are summarized in Tables 2 and 3.

The Carbowax (single solute) rejection results are summarized in Table 4 and are presented graphically in Figs. 1, 2, and 3. Theoretical rejections were calculated using the assumption $a = (\bar{S}^2)^{0.5}$. Mean radii of gyration were calculated as described below.

The Carbowax blend rejection results are presented in Fig. 4. These results were obtained in the following way. A solution containing 0.02% each of Carbowax 1000, 1400, 1540, 4000, and 6000 (total concentration 0.1%) was ultrafiltered through the Nuclepore 150 Å filter at $\Delta P = 50$ psi.

TABLE 2

Carbowax Characteristic Properties

Carbowax	M_w[a]	M_n[a]	Intrinsic viscosity[b] $[\eta]$ (dL/g)	Radius of gyration $(\overline{S^2})^{0.5}$ (Å)[c]	Comment
600	750	630	0.05	10.8	
1,000	1,110	940	0.06	13.1	
1,400	1,580	1,360	0.07	15.5	
1,540	1,780	1,390	0.08	16.9	Blend
4,000	4,010	3,510	0.12	25.4	
6,000	7,000	6,210	0.20	36.2	
14,000	8,030	2,730	0.19	37.3	Two components, very polydisperse

[a] Weight- and number-average molecular weights determined by GPC.

[b] Calculated from M_w, $[\eta] = 0.02 + 2.4 \times 10^{-4} M_w^{0.73}$ (*9*).

[c] Calculated from the Flory-Fox equation $(\overline{S^2})^{0.5} = 3.240 \times ([\eta]\, M_w)^{1/3}$, where $(\overline{S^2})^{0.5}$ is in Å and $[\eta]$ is in dL/g.

TABLE 3

Dextran T Characteristic Properties

Dextran T	M_w[a]	M_n[a]	Stokes radius r_s (Å)[b]	Intrinsic viscosity $[\eta]$ (dL/g)[a]
10	10,500	6,400	23.8	0.098
40	39,500	29,500	44.4	0.210
70	68,500	40,300	57.5	0.260

[a] Values from Pharmacia Fine Chemicals.

[b] Calculated from $\log r_s = 0.470 \log M_w - 0.513$ (*11*).

TABLE 4

Rejection of Carbowax by Nuclepore Filters

Carbowax	Radius of gyration (Å)[a]	Nuclepore radius (Å)	Theoretical rejection (%)[b]	Rejection (%) measured at ΔP (psi)[c]							
				5	10	15	20	25	30	40	50
CW 1540	16.9	75	19.0	—	—	—	—	11.9	11.7	0	—
		150	5.4	9.9	0	0	4.3	—	10.2	—	—
		250	2.0	3.0	0	3.5	1.3	—	4.4	—	—
CW 4000	25.4	75	37.1	—	36.5	—	40.0	—	40.0	38.5	38.0
		150	11.4	—	19.9	—	12.7	—	14.1	11.0	7.5
		250	4.4	—	3.8	3.3	4.9	—	3.1	—	—
CW 6000	36.2	75	60.6	—	—	—	60.1	—	57.2	52.5	51.2
		150	21.3	—	16.5	—	7.0	—	6.0	0.8	0.7
		250	8.6	8.3	0	—	0	—	0	—	—
CW 14000	37.3	75	63.0	—	—	—	62.4	—	63.3	61.0	61.0
		150	22.5	—	18.1	—	11.0	—	6.1	—	3.8
		250	9.1	8.4	0	0	0.4	—	0	—	—

[a] Based on actual M_w measured by GPC.

[b] Calculated from Eq. (6).

[c] Measured in Amicon cell, model 52, with 0.1% Carbowax solution.

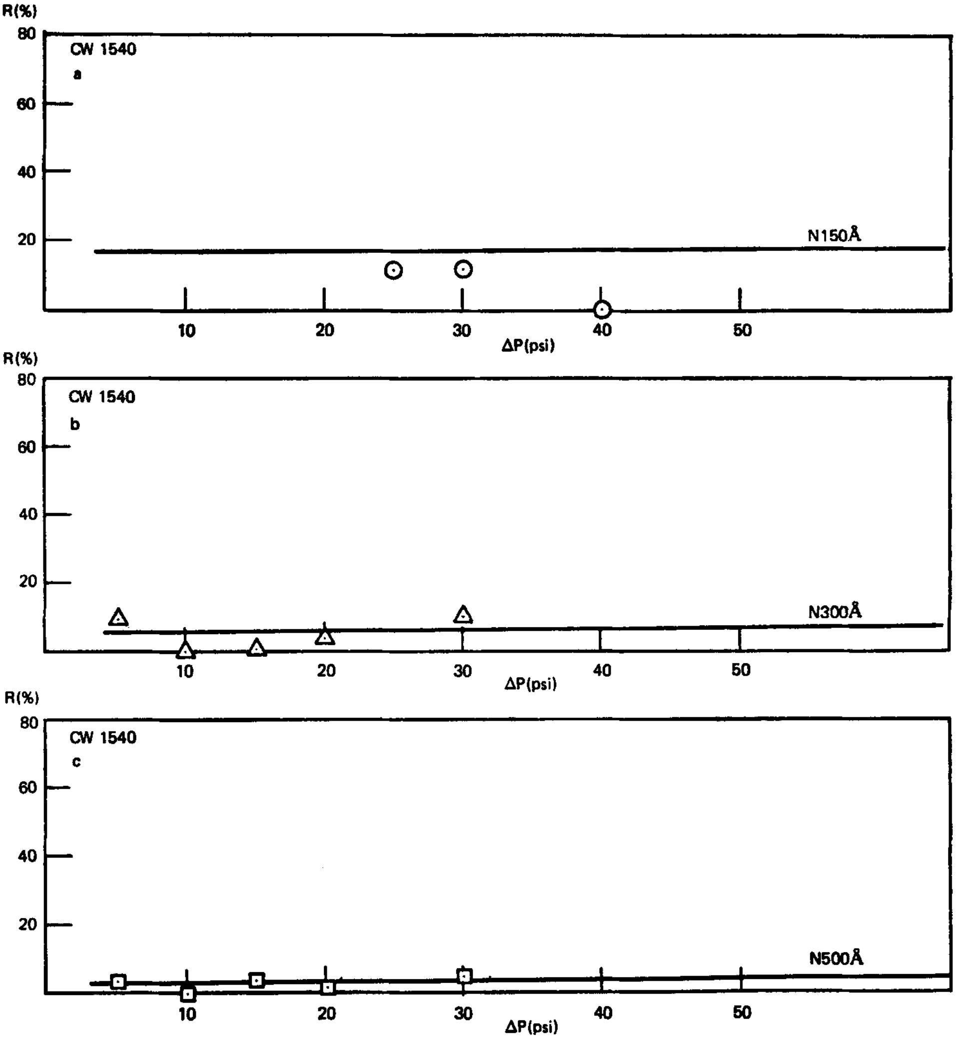

FIG. 1. Measured apparent rejection coefficients R (%) as a function of transmembrane pressure ΔP for 0.1% Carbowax 1540, and (*a*) Nuclepore 150 Å, (*b*) Nuclepore 300 Å, and (*c*) Nuclepore 500 Å. Solid lines show theoretical predictions according to Eq. (6).

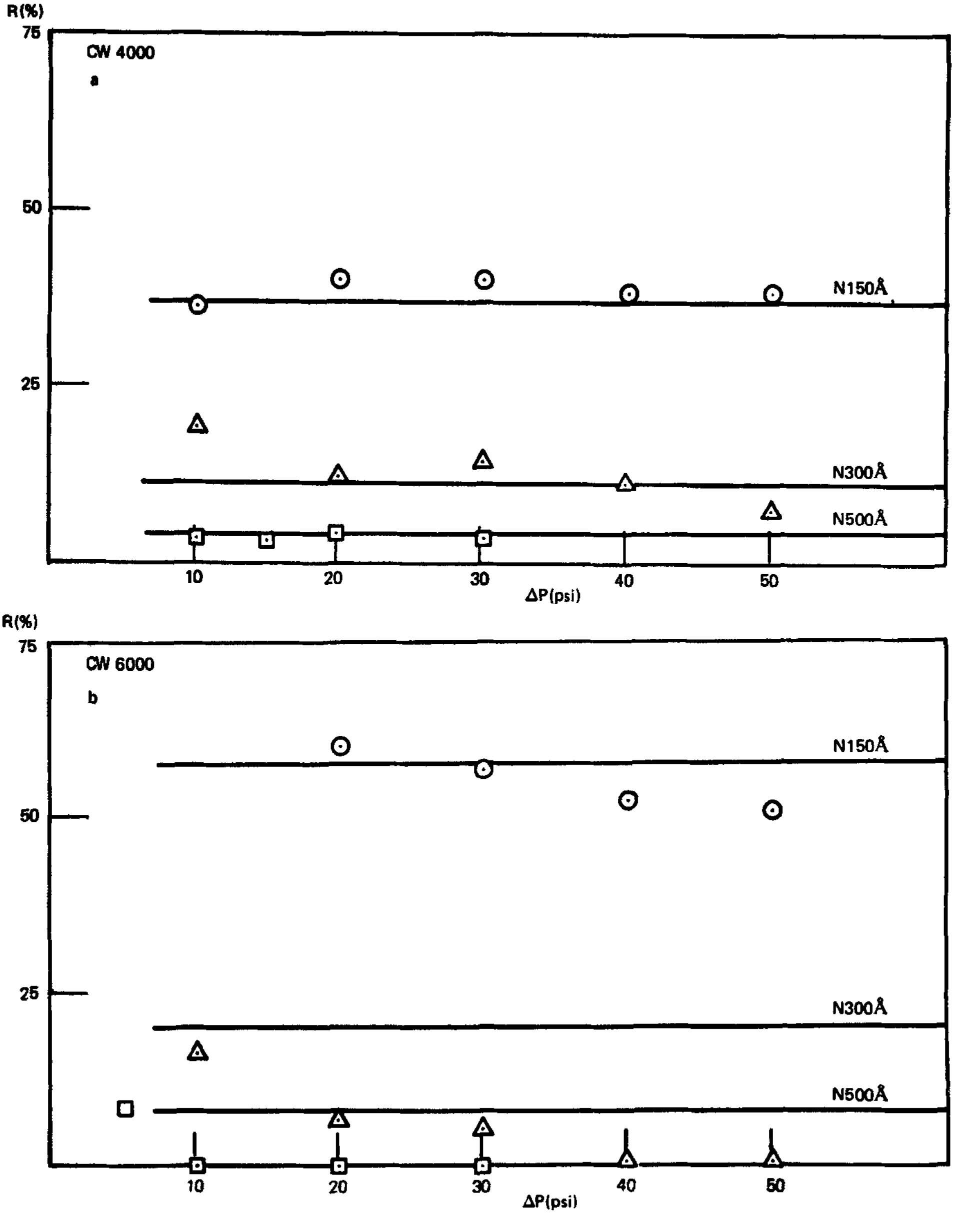

FIG. 2. Measured apparent rejection coefficients R (%) as a function of transmembrane pressure ΔP for Nuclepore 150 Å (⊙), Nuclepore 300 Å (△), Nuclepore 500 Å (▣), and (*a*) 0.1% Carbowax 4000, (*b*) 0.1% Carbowax 6000. Solid lines show theoretical predictions according to Eq. (6).

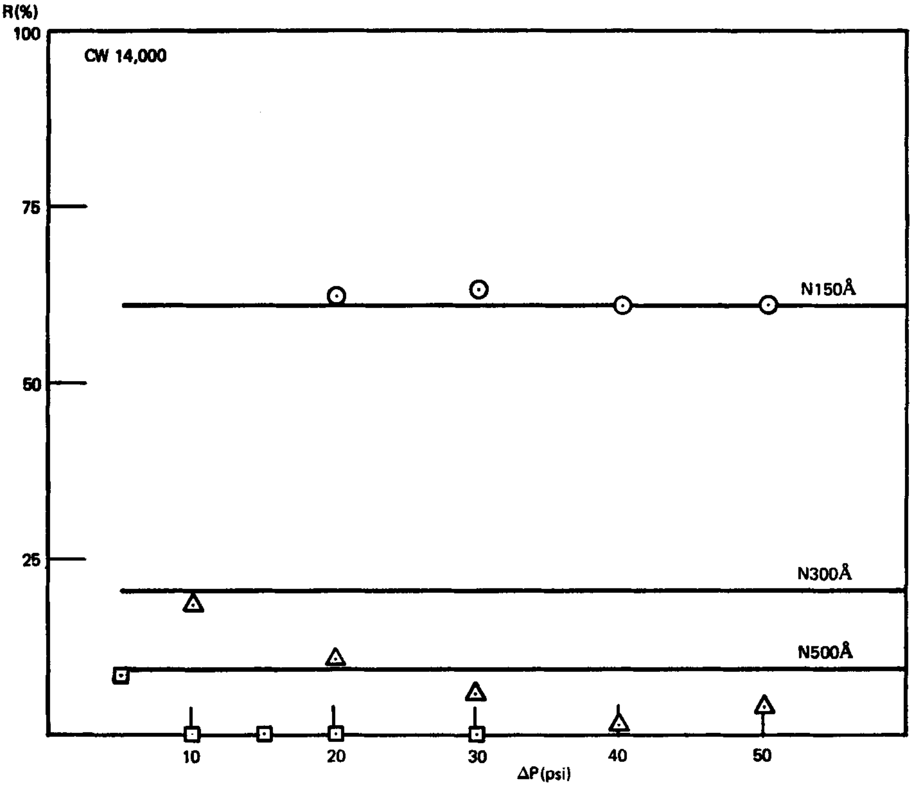

FIG. 3. Measured apparent rejection coefficients R (%) as a function of transmembrane pressure ΔP for 0.1% Carbowax 14000 and Nuclepore 150 Å (⊙), Nuclepore 300 Å (△), and Nuclepore 500 Å (▣). Solid lines show theoretical predictions according to Eq. (6).

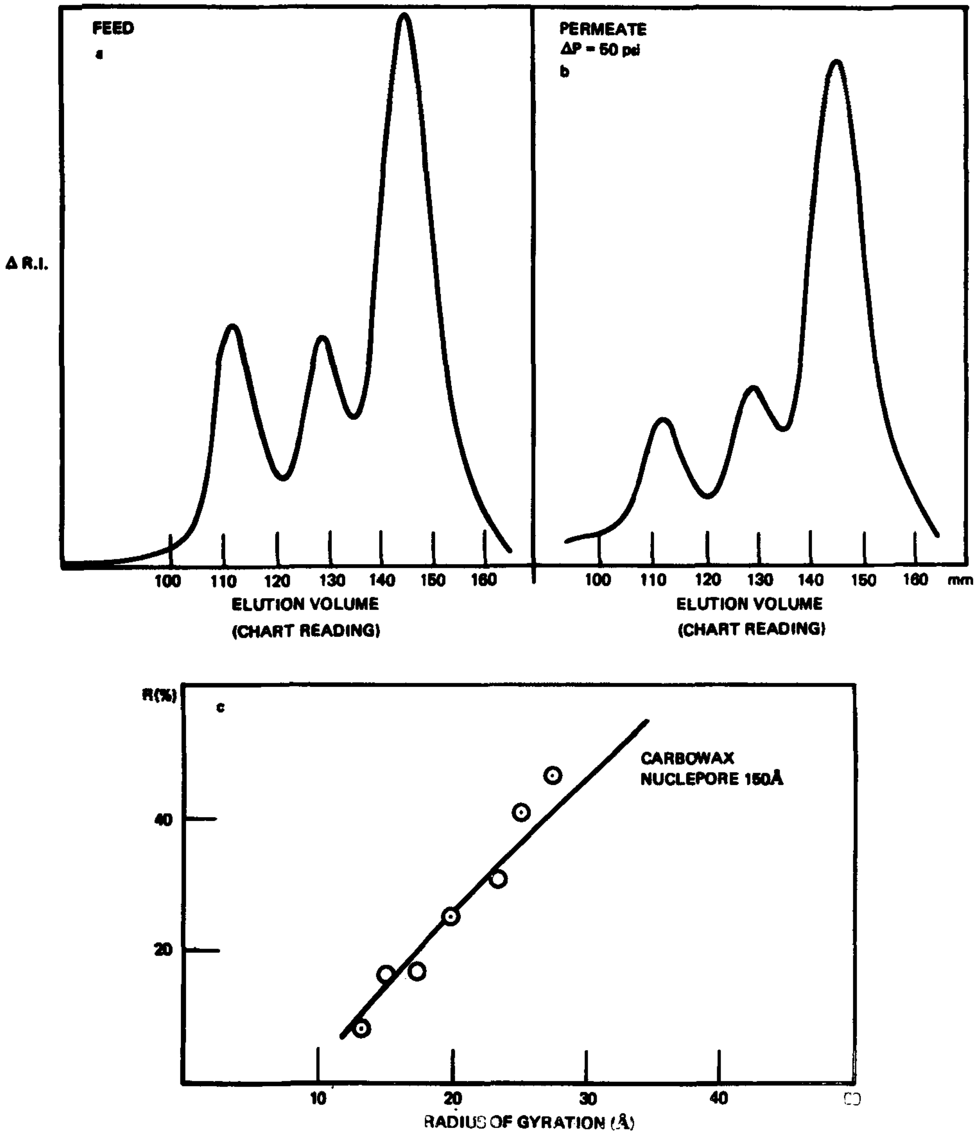

FIG. 4. Measured apparent rejection of polyethylene oxide (Carbowax) at $\Delta P = 50$ psi. (*a*) GPC trace of a blend solution containing 0.02% of each Carbowax 1000, 1400, 1540, 4000, and 6000. (*b*) GPC trace of a permeate obtained by ultrafiltration at $\Delta P = 50$ psi through Nuclepore 150 Å membrane. (*c*) Apparent rejection calculated from GPC traces shown in *a* and *b*, (⊙) as a function of solute radius of gyration. Solid line shows theoretical prediction according to Eq. (6).

Feed and permeate samples were analyzed by GPC (chromatograms are shown in Figs. 4*a* and *b*).

For different elution volumes v, the rejections $R(v)$ were calculated according to

$$R(v) = \frac{h_f(v) - h_p(v)}{h_f(v)} \tag{7}$$

where $h_f(v)$ and $h_p(v)$ are chromatogram heights at elution volume v for feed and permeate, respectively. For the two μBondagel columns used, the calibration curve for Carbowax was determined from peak maxima and known M_w values of Carbowax samples:

$$M_w = 10^{(-0.0246v+6.5984)} \tag{8}$$

where v is the elution volume in mm (chart reading) and the radius of of gyration was calculated from

$$(\bar{S}^2)^{0.5} = 3.240 \times (0.02M_w + 2.4 \times 10^{-4}M_w{}^{1.73})^{0.333} \tag{9}$$

Equation (9) is a combination of a published (*9*) Mark-Houwink equation (footnote *b*, Table 2) and the Flory-Fox equation

$$(\bar{S}^2)^{0.5} = \frac{1}{\sqrt{6}}\left(\frac{[\eta]M_w}{\Phi}\right)^{1/3} \tag{10}$$

where the Flory-Fox constant Φ for a polymer in a good solvent is assumed to be 2×10^{21} mol^{-1}. The molecular weights of our Carbowax samples were rather low and therefore we had to ascertain that the Flory-Fox relation held true for this region of molecular weights. This was done along the lines of analysis suggested by Kurata and Stockmeyer (*10*, pp. 220, 257–258), using the published data of $[\eta]$ and M_w (*9*). We found that for polyethylene oxides in water at 25°C, the "end effects" become important only at molecular weights below 1000, i.e., below the range used in this work.

Using Eqs. (7), (8), and (9), rejection was calculated as a function of $(\bar{S}^2)^{0.5}$ (Fig. 4).

Dextran solution containing 0.06% Dextran T70, 0.06% Dextran T40, and 0.12% Dextran T10 (total dextran concentration 0.24%) was ultrafiltered through Nuclepore filters 150 Å (ΔP = 50 psi), 300 Å (ΔP = 10 psi), and 500 Å (ΔP = 10 psi). Feed and permeate solutions were analyzed by GPC (Fig. 5) and rejections calculated as a function of the corresponding dextran Stokes radii. This was done in a way analogous to the treatment of the Carbowax data. First, the GPC columns were calibrated by fitting the experimentally determined chromatograms of Dextran T10,

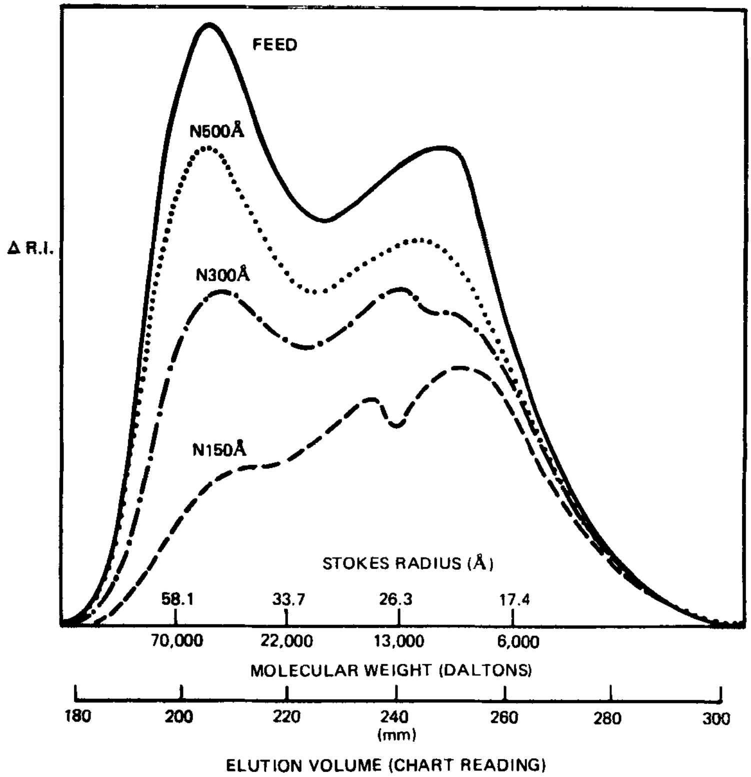

FIG. 5. GPC trace of a blend solution containing 0.06% Dextran T70, 0.06% Dextran T40, and 0.12% Dextran T10 (——) and of permeates obtained by ultrafiltration at $\Delta P = 50$ psi through Nuclepore 150 Å membrane (· · ·), at $\Delta P = 10$ psi through Nuclepore 300 Å membrane (- ·), and at $\Delta P = 10$ psi through Nuclepore 500 Å membrane (- -).

T40, and T70 to the known molecular weight distributions (supplied by Pharmacia). Then molecular weights were converted into Stokes radii, using the relation determined by Granath and Kvist (*11*) for dextrans (*Leuconostoc mesenteroides*, strain B512):

$$r_s = 10^{(0.47 \log M_w - 0.513)} \tag{11}$$

We found that Stokes radii rather than $(\bar{S}^2)^{0.5}$ had to be used for nonlinear dextrans in order to obtain correct estimates of rejection. The use of Eq. (10) would not have been justified since it is valid for linear polymers only. The results obtained with the three different Nuclepore filters were combined into a single graph (Fig. 6). The theoretical rejection curve was

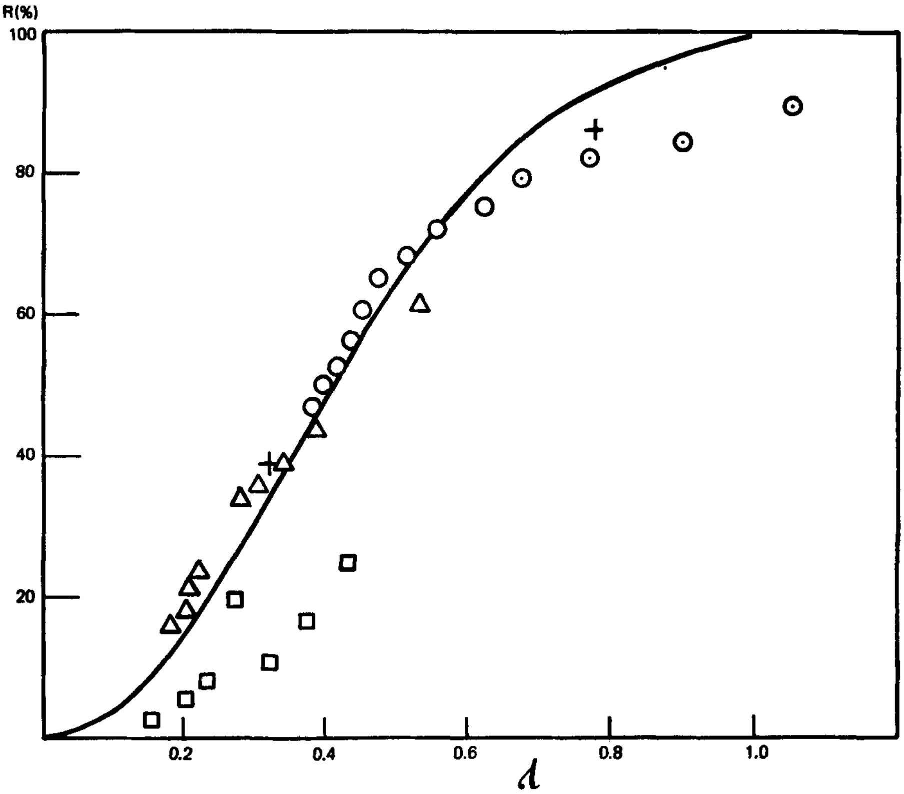

FIG. 6. Measured apparent rejection of dextrans by Nuclepore filters calculated from GPC traces shown in Fig. 5 as a function of λ (see Eq. 1). Points calculated from Nuclepore 150 Å (○), 300 Å (△), and 500 Å (□) traces. Solid line shows theoretical prediction according to Eq. (6). Rejection coefficients measured for single Dextran fractions (T10 and T70) and Nuclepore 150 Å filter are also shown (+).

calculated with the assumption $a = r_s$ and using Eq. (6) with the membrane pore radii specified by Nuclepore Corp. In this graph, rejections were plotted against the ratio of solute to pore radius (λ). The results are also shown in a numerical form in Table 5.

A simple test was carried out to evaluate the possible effect of solute adsorption (fouling) on the results presented above. If irreversible adsorption in the membrane pore occurs, the pore radius is decreased from its initial value r_1 to some lower value r_2. A ratio r_2/r_1 can be determined from the values of water flux measured before ($J_{w,1}$) and after ($J_{w,2}$) the UF test. Assuming validity of Poiseuille's law, we can write

TABLE 5

Dextran Rejection by Nuclepore Filters

Dextran M_w	Dextran Stokes radius[a]	Rejection with Nuclepore filter radius (Å) 75 Theory	75 Expt	150 Theory	150 Expt	250 Theory	250 Expt
1.90×10^5	92.9	100	95.7	80.0	69.2	42.5	16.7
7.00×10^4	58.1	92.8	82.7	46.0	44.3	20.0	8.2
3.40×10^4	41.4	71.0	72.5	27.5	34.1	10.5	4.8
2.20×10^4	33.7	56.0	61.0	18.0	23.9	7.0	0
1.55×10^4	28.6	44.5	46.8	13.5	17.6	5.0	0

[a] Calculated from eq. (11).

TABLE 6

Evaluation of Adsorption Effects

Membrane	Solute	$J_{w,2}/J_{w,1}$[a]	r_2/r_1[b]
Nuclepore 150 Å	0.1% Carbowax 4000	1.006	1.001
Nuclepore 300 Å	0.1% Carbowax 4000	1.039	1.010
Nuclepore 150 Å	0.24% Dextran T10	0.884	0.970
Nuclepore 150 Å	0.24% Dextran T70	0.918	0.979

[a] Obtained by a least-square correlation between $J_{w,2}$ and $J_{w,1}$.
[b] Calculated from Eq. (12).

$$\left(\frac{J_{w,2}}{J_{w,1}}\right)^{0.25} = \frac{r_2}{r_1} \tag{12}$$

Our way of obtaining the ratio $J_{w,2}/J_{w,1}$ was to measure the initial water flux at several pressures, then to measure the second water flux (after the UF test) at the same pressures, and to obtain the straight-line least-square correlation between $J_{w,2}$ and $J_{w,1}$. The results obtained for four different membrane–solute combinations are presented in Table 6.

The largest effect was observed for Dextran T10 and Nuclepore 150 Å. In this case the estimated pore radius reduction (due to adsorption) was about 3% ($r_2/r_1 = 0.970$). This amounts to about 4% change in the determined rejection coefficient. Thus the contribution from irreversible adsorption was comparable to the experimental error of our measurements (about ±3% of the measured value).

DISCUSSION

Results presented above demonstrate a very satisfactory power of Eq. (6) in predicting rejections of relatively small uncharged polymers by an uncharged (polycarbonate) membrane. Equation (6) is valid only for membranes with a uniform pore size distribution and for solutes with reasonably narrow molecular weight distributions. It does not account for effects of concentration polarization, solute adsorption (fouling), solute deformation in the pore, or nonsteric (e.g., electrostatic) mechanisms of rejection.

The Carbowax rejection data (Figs. 1 to 3) show quite often a decrease in R with an increase in ΔP. This decrease may reflect both the concentration polarization effects and/or the shear-induced solute distortion at higher transmembrane pressures (fluxes). Our data do not allow us to distinguish between these two alternatives.

The discrepancy between the curves calculated from Eq. (6) and the dextran rejection data shown in Fig. 6 at high values of λ could be significant. In the absence of more definite information on the membrane pore size, we refrain from attempts to interpret this feature of our results. Nuclepore nominal pore densities are not known with sufficient accuracy (for filters used in our work) to allow calculation of pore radii from measured permeabilities.

We feel that our data are not necessarily in conflict with those published recently by Munch et al. (*12*) who found lower than expected rejections of Separan AP273 (a partially hydrolyzed linear polyacrylamide of molecular weight $0.25\text{–}1.0 \times 10^7$) by track-etched filters. Our polymers are nonionic and with molecular weights that are lower by about three orders of magnitude in comparison with Separan AP273. Recently, Schultz et al. (*13*) determined reflection coefficients (from measured osmotic flow rates) for Dextran T70 and T500 by Nuclepore filters with 300 and 500 Å pore diameters. Their data are difficult to compare with ours because a different (albeit related) methodology was used in each case.

SYMBOLS

a	radius of a rigid macromolecule (sphere), (Å)
C_p	concentration of permeate (g/cm^3)
C_f	concentration of feed (g/cm^3)
f	K_2/K_1 (dimensionless)
F	viscous drag force (dyn)
$h_f(v)$, $h_p(v)$	height of a GPC trace at elution volume v for the feed and permeate (cm)
J_w	water flux (cm/s)
K_1, K_2	drag coefficients of Ref. *8* (dimensionless)
M_n	number-average molecular weight (dalton)
M_w	weight-average molecular weight (dalton)

ΔP	transmembrane pressure (psi)
r	capillary radius (Å)
r_s	Stokes radius (Å)
R	rejection coefficient (dimensionless)
$(\bar{S}^2)^{0.5}$	root-mean-square radius of gyration (Å)
U	velocity of sphere (cm/s)
v	GPC elution volume (chart reading), (mm)
V	velocity of liquid (cm/s)
W	hindrance to convection (dimensionless)
α	constant in Eq. (5) (dimensionless)
η	shear viscosity of liquid (poise)
$[\eta]$	intrinsic viscosity (dL/g)
λ	a/r
Φ	Flory-Fox constant (mol^{-1})

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