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Dynamic Membranes. II. Concentration Effects on Reflection Coefficient and Specific Resistance of Bovine Serum Albumin "Gel" Layer

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Abstract

A comparison was made between the influence of surface concentration on the reflection coefficient of bovine serum albumin computed from experimental data and the predicted effect using a rejection model. A simple mathematical model of solute buildup during axial electrofiltration was used to determine the effect of concentration on the specific resistance of the solute layer.

INTRODUCTION

Experimental results in the literature showing the influence of the concentration of macromolecules on the reflection coefficient for membranes that are permeable to the solute are limited. A comparison between experimental results and predictions from the models that have been proposed recently (*1*, *2*) has not been possible. The first objective of this study was to fill this gap. The second objective was to obtain a better understanding of the mechanisms involved in the formation of solute layers on membrane surfaces during filtration of macromolecules by computation of the specific resistances for different concentrations.

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The experimental procedure involved the filtration of bovine serum albumin (BSA) dissolved in a solution of disodium phosphate at pH 8 in an axial electrofilter. Descriptions of the experimental set up and operating conditions are provided in Part I (*3*).

PREDICTION OF EFFECT OF CONCENTRATION ON REFLECTION COEFFICIENT

Rejection of macromolecules is said to occur by two basic mechanisms (*4*). The first of these is an equilibrium partitioning of solute between the solution just inside and outside a pore entrance. The second mechanism involves a sieving effect.

Anderson and Adamski (*1*) derived a model for the effect of concentration on the reflection coefficient when equilibrium partitioning is predominant. The flux of spherical molecules through a circular pore was computed by integrating the local unperturbed fluid velocity over the relative distribution of molecules, which is given by the Boltzmann expression. By assuming a hard sphere–pore wall interaction, laminar flow of a Newtonian liquid in the pore and negligible concentration and electrostatic effects, the following relationship was obtained for the reflection coefficient:

$$\sigma = (\lambda(2 - \lambda))^2 + 4\lambda^2(1 - \lambda)^2/3 \qquad (1)$$

where λ is the ratio of the solute radius to the pore radius. The introduction of a concentration term in the basic equations yielded the following expression:

$$\sigma_s = \sigma(1 + 0.01\psi C_s)^{-1} \qquad (2)$$

where σ_s is the reflection coefficient at a surface concentration C_s and ψ is approximated by Fig. 1. The reflection coefficient may also be computed from experimental data through the following relationship:

$$\sigma_s = 1 - C_p/C_s \qquad (3)$$

where C_p is the concentration of the solute in the permeate.

Equation (2) predicts that, in the absence of electrostatic effects, the reflection coefficient decreases with increasing solute concentration, a prediction confirmed by filtration of Dextran (*5*) and polystyrene (*6*).

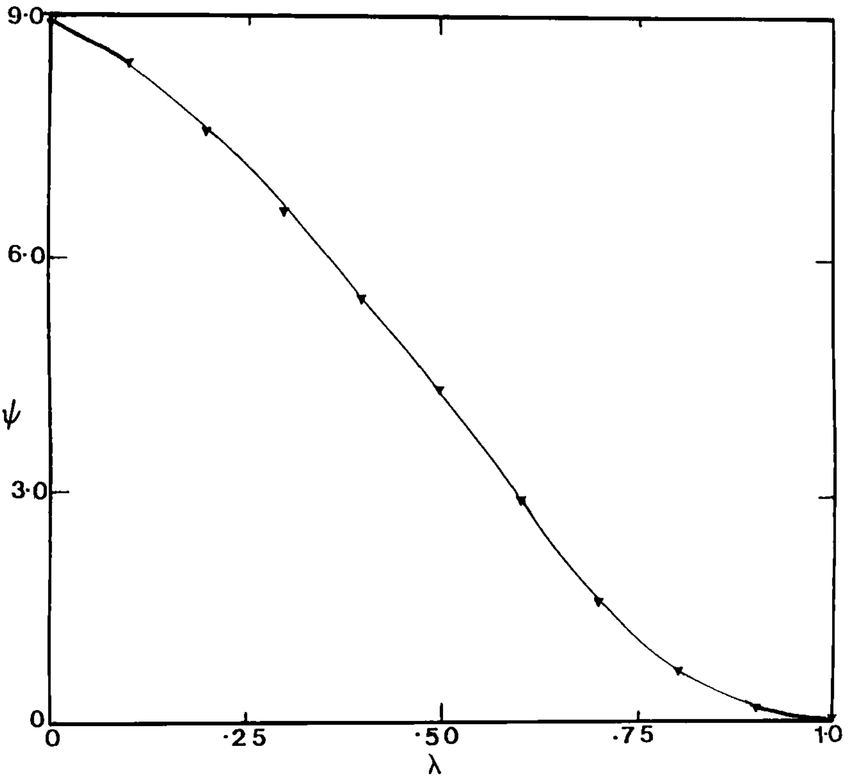

FIG. 1. Plot of ψ versus λ.

In this work, C_s was estimated by employing the thin film mass transfer model for a membrane which is permeable to the solute (*7*):

$$C_s = C_p + (C_o - C_p) \exp (J_\infty/k) \tag{4}$$

where C_o is the bulk concentration, J_∞ is the steady-state flux, and k, the mass transfer coefficient, was computed from the following empirical relationship given for a rotating cylinder in a stationary external cylinder (*8*):

$$k = 0.0791 u_i \mathrm{Sc}^{-0.644} \mathrm{Re}^{-0.30} \tag{5}$$

where u_i = peripheral velocity of the rotating inner cylinder
Sc = Schmidt number
Re = Reynolds number

CALCULATION OF THE SPECIFIC RESISTANCE OF THE SOLUTE LAYER

Assuming the resistance of the filter medium to be negligible and the resistance of the solute layer, R_c, to be proportional to its thickness, δ_c, the flux is given by

$$J = \Delta P_F / K_c \delta_c \tag{6}$$

where ΔP_F is the pressure drop causing filtration and K_c is a proportionality constant dependent on the properties of the solute layer. Applying Darcy's law to the flow of filtrate through a solute layer yields

$$J = \Delta P_F / \alpha \mu \rho_p (1 - \varepsilon) \delta_c \tag{7}$$

where α is the hydraulic resistance of the solute layer, μ is the viscosity of the filtrate, ρ_p is the density of the solute, and ε is the porosity of the solute layer. Equating the fluxes yields

$$K_c = \alpha \mu \rho_p (1 - \varepsilon) \tag{8}$$

Replacing K_c by the relationship obtained by Turkson (*9*) yields

$$\alpha = S \Delta P / 2R(1 - J_\infty / R J_0) \mu C_o \tag{9}$$

where S = the slope of a small time ($t < 90$ min plot of $(J^{-2} - J_0^{-2})$ versus time
R = rejection = $1 - C_p/C_o$
J_0 = the filtrate flux at time $t = 0$

DISCUSSION OF RESULTS

Effect of Concentration on Reflection Coefficient

The procedure for calculating the reflection coefficient of BSA involved first the computation of the diffusivity of BSA in aqueous solution from the following empirical fit to BSA diffusivity data obtained by Phillies et al. (*10*) at $T = 30°C$ and pH = 8:

$$D_c = (7.02 \times 10^{-7}) + (6.9 \times 10^{-9} C_o) \quad (10)$$

Next, the mass transfer coefficient was calculated from Eq. (5). Equation (4) was then employed to calculate the concentration of BSA at the surface of the membrane. In the absence of steady-state data, the flux and BSA concentration in the permeate after 180 min of filtration, J_{180} and C_{p180}, respectively, were used in Eq. (4) to calculate the surface concentration after 180 min, C_{s180}. Predictions of σ_s for different λ values were then calculated from Eq. (2), and Eq. (3) was used to calculate σ_s from experimental data.

Tables 1 and 2 give values of C_{s180} computed from experimental J_{180} and C_{p180} for CdS and ZrO_2, respectively. The C_{s180} values for $C_o < 0.5$ wt% are unreliable because of their sensitivity to J_{180}/k. Table 1 contains C_{s180} values computed from replicate runs for $C_o = 0.5$ wt% and $N = 2000$ rpm with Cds. The 95% confidence interval for the mean C_{s180} is 2.01 ± 0.40 wt%. Since the precision of the runs improves with declining flux (*11*), the reliability of C_{s180} is better at higher concentrations.

TABLE 1

Variation of C_{s180} with Bulk Concentration for CdS Dynamic Membrane

C_o (wt%)	C_{p180} (wt%)	J_{180}/k	C_{s180} (wt%)
0.5	0.28	1.95	1.86
0.5	0.30	2.08	1.90
0.5	0.30	2.29	2.28
1.0	0.60	1.51	2.41
0.5	3.25	0.34	5.70
10.0	6.00	0.29	11.30

TABLE 2
Variation of C_{s180} with Bulk Concentration for ZrO_2 Dynamic Membrane

C_o (wt%)	C_{p180} (wt%)	J_{180}/k	C_{s180} (wt%)
0.5	0.28	0.87	0.81
1.0	0.58	0.35	1.18
5.0	3.00	0.25	5.60
10.0	6.00	0.20	10.90

For ZrO_2, the flux after 50 min of filtration was 4.7×10^{-3} cm/s with a rejection of 75% at $C_o = 0.1$ wt% and pH = 8 (*9*). After 50 min of filtration of BSA at $C_o = 0.1$ wt% and pH = 7.4 with Amicon XM-100 membrane, Fane et al. (*12*) obtained a flux of 4.2×10^{-3} cm/s and a rejection of 80%. In view of the similarity between the two results, the average pore diameter of ZrO_2 is probably close to 175 Å, the value obtained for Amicon XM-100 membrane (*13*). Since the Stokes-Einstein diameter of a BSA molecule is 74 Å, the ratio of solute diameter to pore diameter for ZrO_2 is probably close to 0.40.

Figures 2 and 3 show that the reflection coefficients computed from C_{s180} and C_{p180} decrease with increasing surface concentration, in agreement with the trend predicted theoretically. For ZrO_2, the effect of C_{180} on σ agrees with the theoretical prediction from Eq. (2) when λ is assumed to be 0.5, a value close to that computed on the basis of the similarity between ZrO_2 and Amicon XM-100 membrane. For CdS, the effect of C_{s180} on σ is not accounted for by a single value of λ. The poorer agreement for CdS may be due either to overestimates of C_s by C_{s180} or to factors not taken into consideration by the model of Anderson and Adamski (*1*), e.g., electrostatic forces (*2*).

At lower bulk concentrations, J_{180} values for CdS are higher than those for ZrO_2. The J_{180} values for CdS are therefore farther from the steady-state flux and the overestimation of C_s by C_{s180} is greater. The deviations of the σ_{s180} from steady-state values are therefore higher for CdS than for ZrO_2. If the steady-state flux for CdS at $C_o = 0.5$ wt% and $C_o = 1.0$ wt% is assumed to be lower than J_{180} by 20 and 15%, respectively, the corresponding surface concentrations of 1.38 and 2.05 wt% yield σ values of 0.78 and 0.7, respectively. By using these values, the variation of σ with surface concentration for CdS would be described by the theory of Anderson and Adamski with $\lambda = 0.55$.

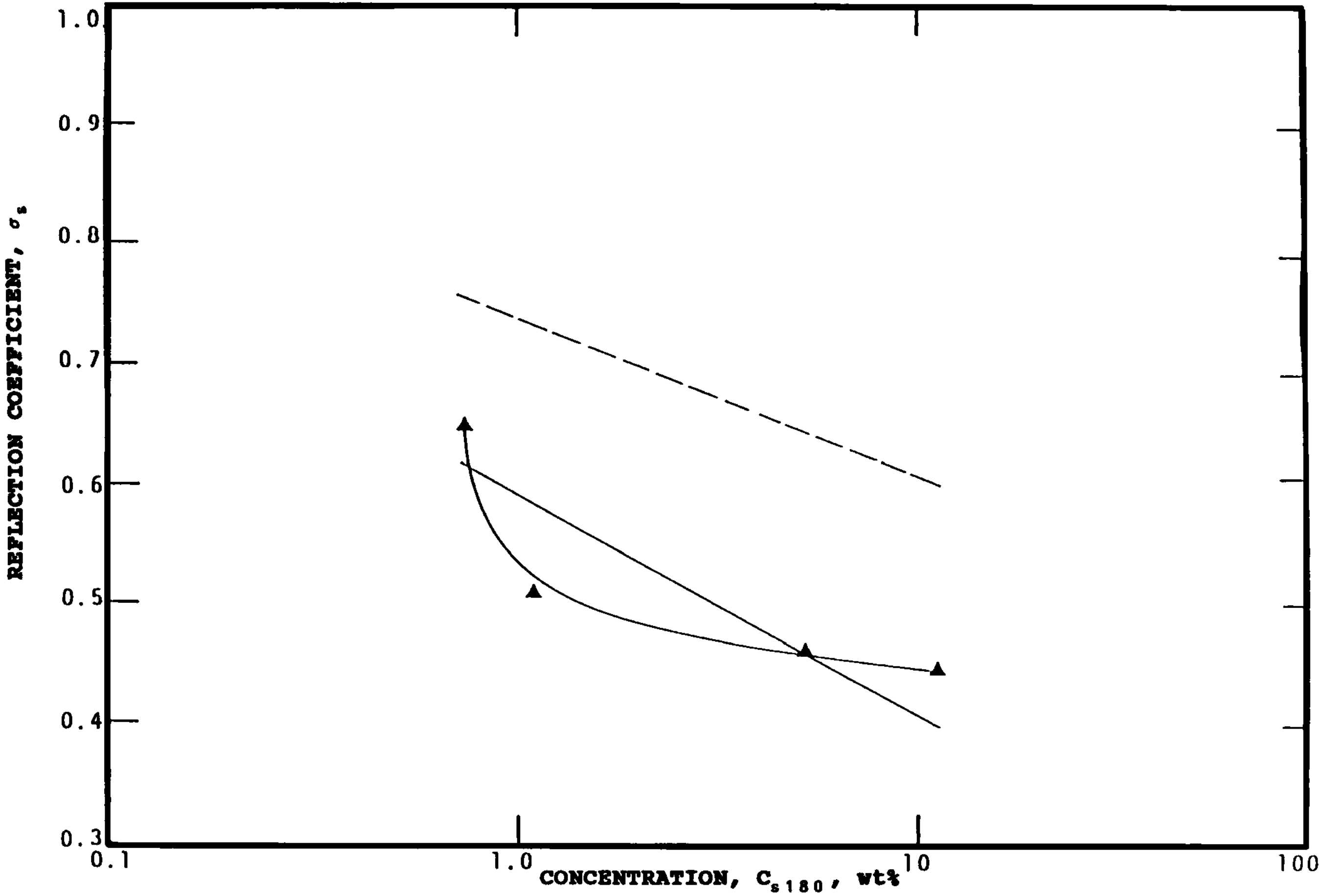

FIG. 2. Effect of BSA concentration at surface of ZrO_2 dynamic membrane on reflection coefficient. Theoretical predictions of λ: (——) 0.5, (— —) 0.6. (▲) Experimental points. $N = 2000$ rpm, pH = 8, $\Delta P = 138$ kPa, $T = 30°C$.

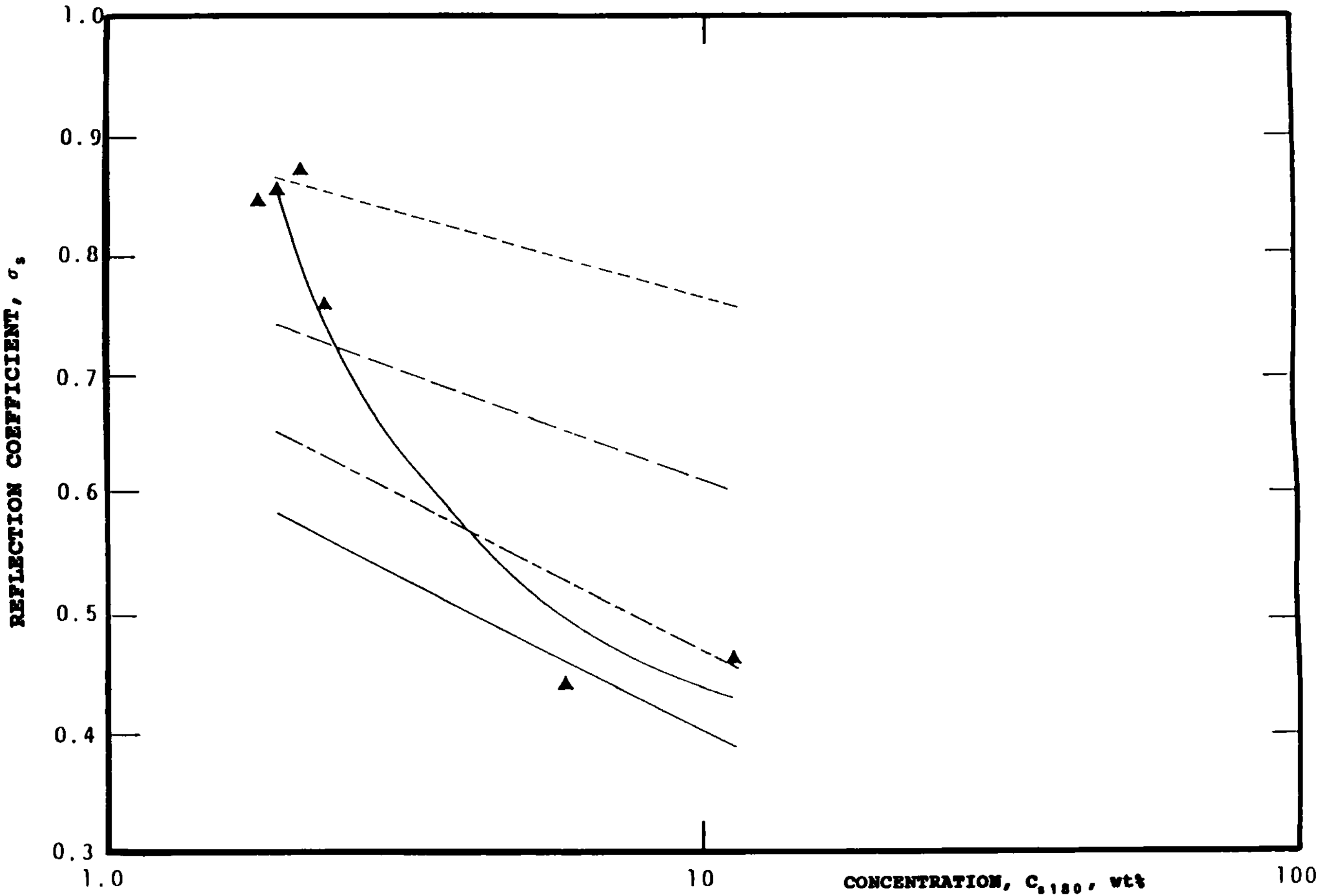

FIG. 3. Effect of BSA concentration at surface of CdS dynamic membrane on reflection coefficient. Theoretical predictions of λ: (——) 0.50, (— -) 0.55, (— —) 0.60, (- -) 0.70. (▲) Experimental points. N = 2000 rpm, pH = 8, ΔP = 138 kPa, T = 30°C.

The presence of electrostatic forces may affect the reflection coefficient and cause the relationship between σ and surface concentration to be different from that predicted by Eq. (2) in which only steric interaction was considered. For example, if the total interaction energy is attractive, then, as pore closure due to adsorption increases at higher concentration, the decline in reflection coefficient with increasing surface concentration will be more severe than predicted by concentration effects alone. A confirmation of this expectation is provided by the data of Fane et al. (*12*), which showed a decrease in BSA rejection when the pH was decreased from 9, where the solute is negatively charged, to pH = 5, which is close to the isoelectric pH of 4.7, where BSA is neutral. Without considering concentration effects, the rejection decreased as adsorption increased due to reduction in repulsion between the solute and the membrane.

The mobility of BSA was measured in the presence of dynamic membrane-forming additives in a microzone electrophoresis cell. The negative charge on the BSA molecule at pH = 8 was reversed in the presence of both CdS and ZrO_2. The results with CdS were similar to those reported by Schilling (*14*). Since CdS is negatively charged at pH = 1.2, the pH of formation, the interaction between the CdS dynamic membrane and the BSA layer with which it is in direct contact is probably attractive. For ZrO_2, the interaction is probably repulsive because ZrO_2 is positively charged at the pH of formation of 3.5. The decline in reflection coefficient with increasing surface concentration for CdS is therefore expected to be worse than that predicted by concentration effects alone. For ZrO_2, the reflection coefficient is not deleteriously affected by electrostatic effects, and concentration effects account for the decline in reflection coefficient.

Influence of Concentration on Specific Resistance of BSA Layer

The specific resistance of the BSA layer, α, was computed from Eq. (9) with the slope at small time ($t < 90$ min) obtained by least-squares fit to a plot $(J^{-2} - J_0^{-2})$ versus time. The effect of concentration on viscosity was accounted for by applying the following relationship (*15*):

$$\mu_{BSA} = 0.01 \exp (2.44 \times 10^{-3} C_o^2) \qquad (11)$$

Figures 4 and 5, which contain plots of α versus C_o for ZrO_2 and CdS, respectively, show α first remains unchanged and then increases to a maximum value before declining again with increasing concentration. Pro-

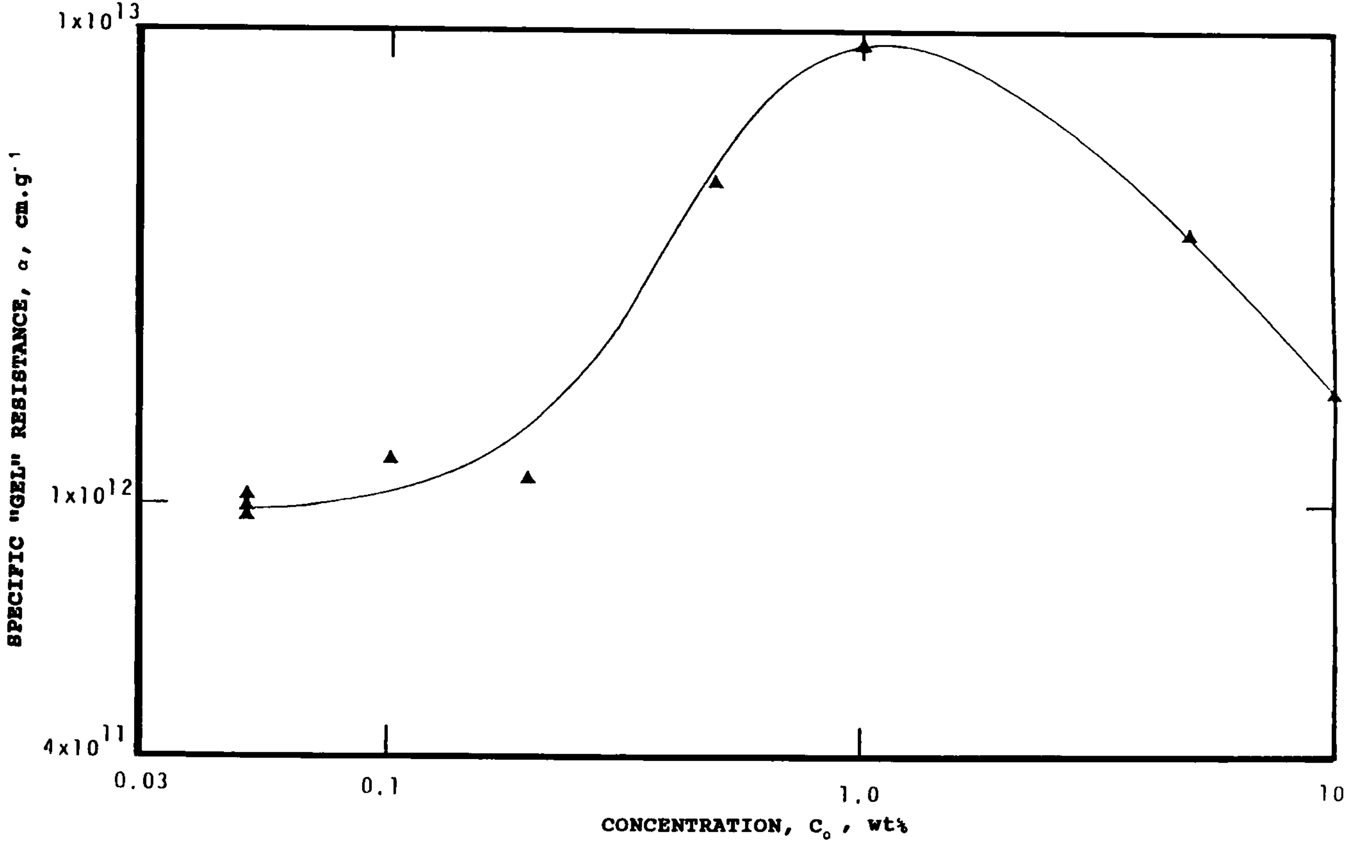

FIG. 4. Variation of specific "gel" resistance with concentration for BSA with ZrO_2 dynamic membrane. BSA conditions: $N = 2000$ rpm, pH = 8, $\Delta P =$ 138 kPa, $T = 30°C$.

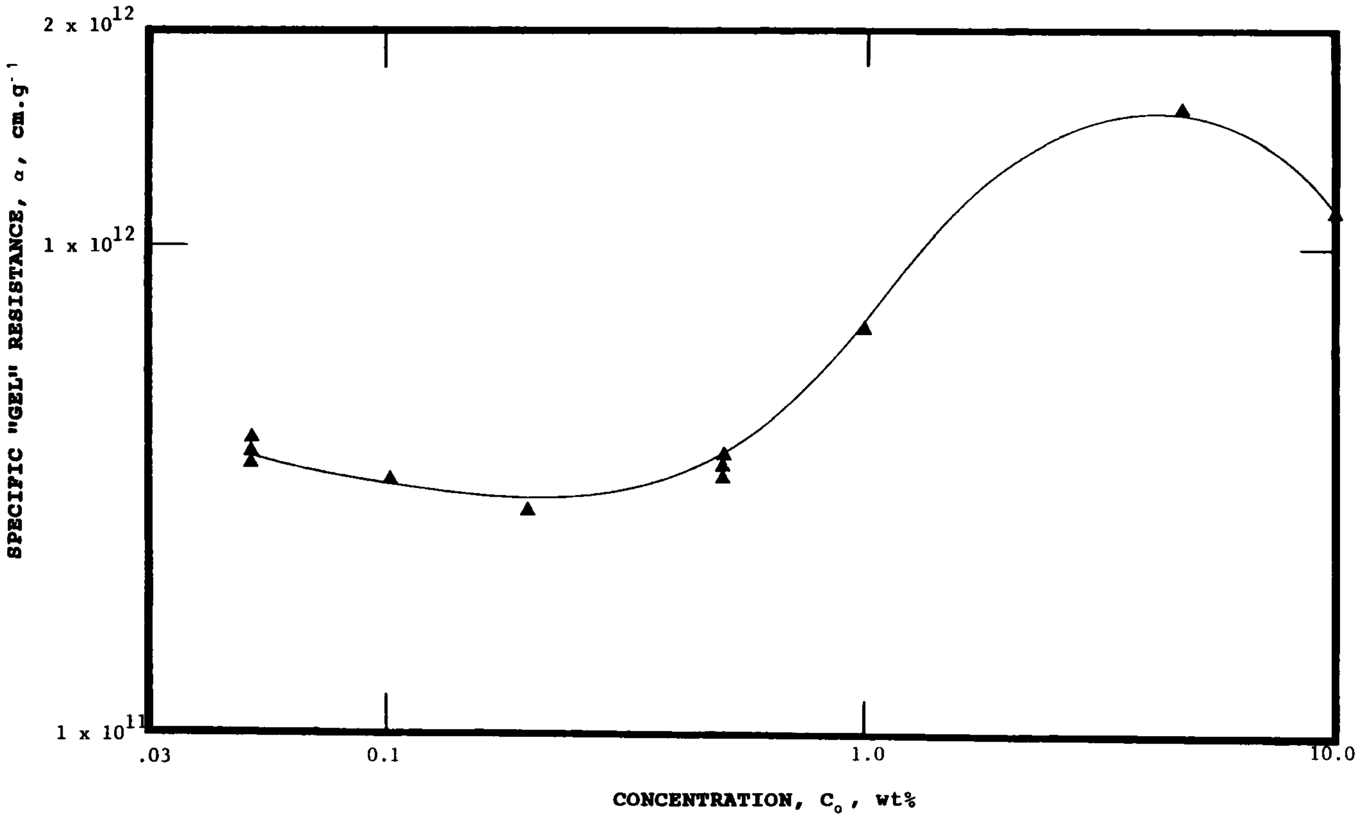

FIG. 5. Variation of specific "gel" resistance with concentration for BSA with CdS dynamic membrane. BSA conditions: N = 2000 rpm, pH = 8, ΔP = 138 kPa, T = 30°C.

files similar to Figs. 4 and 5 were obtained by Rushton et al. (*16*) for calcium sulfate and magnesium carbonate.

According to Heertjes (*17*), specific resistance is influenced by the relative effects of bulk concentration and flux, two parameters which are not necessarily independent. As the concentration is increased, the specific resistance is predicted to increase if the decline in flux is predominant over the increase in solute concentration at the membrane and to decline if the reverse is true. If the two effects balance each other, the specific resistance remains invariant with concentration At low bulk concentraion, molecules move separately and easily follow the flow streamlines. The result will be that the molecule, depending on λ, will either enter a pore or block the pore opening. As the concentration is increased, more molecules will arrive near the pores at the same time and pore blocking will increase. The same type of effect observed with decreasing concentration occures when the flux decreases. As the flux decreases, the molecules will follow the flow streamlines causing the packing density and the specific resistance to increase.

For CdS and ZrO_2, the effects of increasing concentration and declining flux initially canceled out, causing the specific resistance to remain constant. With further increases in feed concentration, the decline in the flux became predominant, causing the specific resistance to increase. The specific resistance attained a maximum value and started to decline when the flux changed only marginally with an increase in concentration. For CdS, the flux changed only marginally beyond C_o = 5.0 wt%, and α was therefore at a maximum at this concentration, whereas for ZrO_2 the flux changed only marginally after C_o = 1.0 wt%, and the maximum α was attained at this value.

CONCLUSIONS

(1) The reflection coefficient computed from experimental data decreased with increasing BSA concentration at the surfaces of ZrO_2 and CdS dynamic membranes, in general agreement with the trend predicted by a model based on equilibrium partitioning of macromolecules.

(2) For both CdS and ZrO_2 dynamic membranes, the computed specific resistance of the BSA layer first remained invariant, then increased to a maximum value, and then declined as the bulk concentration was increased. The maximum value of the specific resistance coincided with the concentration level beyond which the flux changed only marginally.

SYMBOLS

C	solute concentration (wt%)
D	diffusion coefficient (cm^2/s)
D_c	concentration-dependent diffusivity for BSA given by Eq. (10)
J	filtrate flux (cm/s)
k	mass transfer coefficient (cm/s)
K_c	constant in Eq. (8)
N	rotation rate (rpm)
R	fractional rejection = $(1 - C_p/C_o)$
R_c	hydraulic resistance of solute layer on membrane surface (kPa/cm · s)
Re	Reynolds number = $2R_i\rho u_i/\mu$
R_i	outside radius of inner cylinder (cm)
S	small time ($t < 90$ min) slope of plot of $(J^{-2} - J_0^{-2})$ versus time (s/cm^2)
Sc	Schmidt number, $\mu/\rho D$
t	time (s)
u_i	peripheral velocity of rotating inner cylinder = $2\pi NR_i/60$ (cm/s)
α	specific resistance of the solute layer (cm/g)
δ_c	thickness of solute layer (cm)
ΔP	measured pressure difference (kPa)
ΔP_F	pressure difference causing filtration (kPa)
ε	porosity
λ	ratio of solute to pore diameters
μ	fluid viscosity (g/cm · s)
μ_{BSA}	viscosity relationship for BSA given by Eq. (11) (cm/g · s)
ρ	fluid density (g/mL)
ρ_p	density of dispersed phase (g/mL)
σ	reflection coefficient at zero concentration given by Eq. (1)
ψ	parameter given in Eq. (2)

Subscripts

o	of the feed
p	of the permeate
s	of the solute at the surface of the filter medium
0	at the beginning of experimentation ($t = 0$ s)
180	after 180 min of filtration
∞	at steady state

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