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Steady-State Modeling of Electroultrafiltration at Constant Concentration

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Abstract

A simple mathematical model was developed to predict the steady-state electroultrafiltration (a combination of ultrafiltration and electrophoresis) flux for processing bovine serum albumin (BSA) solutions at constant concentration. The assumption that the wall concentration is an exponential function of the electric field strength gave a linear dependence of flux on electric field strength. This dependence was experimentally confirmed for electroultrafiltration of 1–4 wt% BSA solutions at pH 7.4, using Amicon XM-50 membranes with a transmembrane pressure drop of 5 psig. The mathematical model uses the values of the solution and solvent fluxes for normal ultrafiltration plus the electrophoretic mobility of the solute to predict the electroultrafiltration flux. The difference between the model predictions and the measured performance was 7.5%.

INTRODUCTION

The flux and selectivity of the ultrafiltration process have been improved by combining it with an electrophoretic force which acts on the retained solutes to control concentration polarization when processing protein solutions (*1–4*) and colloidal suspensions (*5, 6*). During ultrafiltration, the

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steady-state solution flux occurs when the convective transport of retained solute toward the membrane (due to the bulk transport of solvent through the membrane) is balanced by the backtransport of retained solute from the membrane (due to the concentration gradient), according to the simple film theory of concentration polarization (*7*). When an electrophoretic force acts against the transmembrane pressure force for convective transport, the steady-state flux results from a balance of convective, forward transport, and diffusive *plus* electrophoretic backtransport. The one-dimensional, steady-state, solute balance in the fluid boundary layer above a membrane which completely retains the solute is

$$JC = -D\frac{dC}{dx} + uEC \tag{1}$$

where J is the solvent flux, C is the solute concentration, D is the solute diffusivity, u is the solute's electrophoretic mobility, and E is the electric field strength. The "solvent" refers to the solution of true solvent and completely permeable solutes. Assuming that u and D are constant and that electroosmosis in the membrane is negligible, integration across the boundary layer gives

$$J = k \ln (C_m/C_b) + uE \tag{2}$$

where C_m and C_b are the solute concentrations at the membrane surface and in the bulk solution, respectively, and k is an average mass transfer coefficient. Previous experimental results (*1–3, 5, 6*) indicated that J was a linear function of E, but the slope was not equal to u. Assuming that the slope of J vs E was u would mean that C_m must not depend on E. At steady-state, C_m is maintained at a value "high enough to provide a concentration boundary layer with a significant physical barrier to water transport" (*7*) to counterbalance the convection transport which is *also* balanced by the electrophoretic transport. If E changes, then C_m must change. As E increases, C_m decreases because the charged solute is transported away from the membrane by the electric field (see also Fig. 2 of Ref. *11*). A mathematical model to predict the variation of J (and C_m) with E is derived in this paper and used to analyze experimental results for the steady-state electroultrafiltration of bovine serum albumin (BSA) solutions.

MATHEMATICAL MODEL

C_m is assumed to be an exponential function of E since, experimentally, J appears to be a linear function of E. It is also assumed that the operating

conditions are such that C_m is not equal to C_g, the constant, solute gel layer concentration, or that applying E immediately decreases C_m such that it is always less than C_g. Therefore,

$$C_m = C_{m0}e^{-BE} \tag{3}$$

where B is a constant. The boundary conditions are: at $E = 0$, $C_m = C_{m0}$; at $E = E_c$, $C_m = C_b$. The first boundary condition states that the concentration at the membrane for $E = 0$ is the concentration, C_{m0}, for ultrafiltering without the electric field for the same fluid dynamic conditions. The second boundary condition indicates that at some critical electric field strength, E_c, the concentration gradient in the boundary layer, has been eliminated. Thus,

$$B = (\ln C_{m0}/C_b)/E_c \tag{4}$$

and

$$C_m = C_{m0}e^{-(\ln C_{m0}/C_b)(E/E_c)} = C_{m0}e^{-(J_{uf}/k)E^*} \tag{5}$$

where E^* is a dimensionless, electric field strength ($= E/E_c$) and J_{uf} is the solution flux for ultrafiltration without the electric field ($= k \ln C_{m0}/C_b$).

Combining Eqs. (2) and (5) leads to

$$J = k^* \ln (C_{m0}/C_b) + uE \tag{6}$$

where $k^* = k(1 - E^*)$, a modified mass transfer coefficient which varies linearly with E. Rearranging Eq. (6) to collect all terms dependent on E gives

$$J = J_{uf} + \left(u - \frac{J_{uf}}{E_c}\right) E \tag{7}$$

where

$$J_{uf} = k \ln (C_{m0}/C_b)$$

The slope of J vs E is $(u - J_{uf}/e_c)$. At $E = 0$, Eq. (7) shows that $J = J_{uf}$, and at $E = E_c$, $J = uE_c$, which defines the critical electric field strength. E_c is the field strength at which there is no net movement of solute from the bulk solution to the membrane; the concentration boundary layer has been removed. Under these conditions, E_c can be determined from

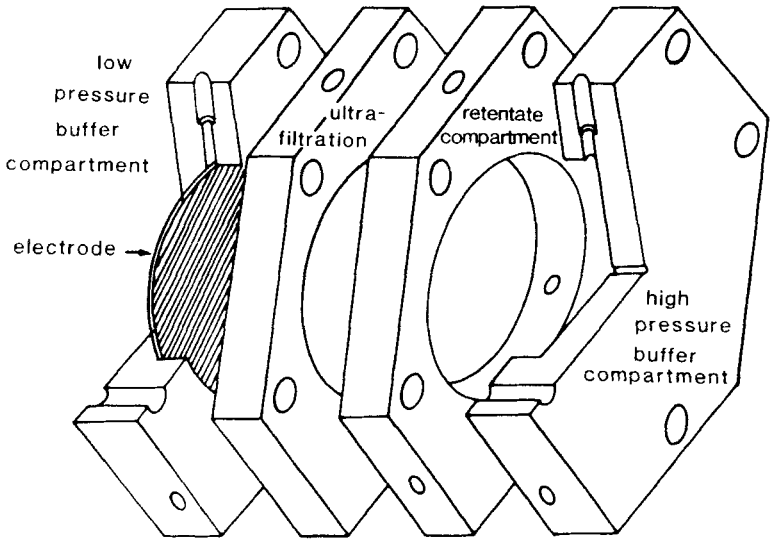

FIG. 1. Exploded view of the electroultrafiltration test cell.

$$E_c = J_s/u \tag{8}$$

where J_s is the solvent flux at a given transmembrane pressure drop; i.e., the flux that would occur if the effects of concentration polarization were eliminated.

These equations can be used to predict the flux during electroultrafiltration if the solvent flux, J_s, normal ultrafiltration flux, J_{uf}, and the solute's electrophoretic mobility, u, are known.

EXPERIMENTAL METHODS

The Plexiglas, tangential flow, ultrafiltration cells used in the experiments have been described in detail elsewhere (*6, 8*). An exploded view of the cell is shown in Fig. 1. Both electrodes were platinum. DuPont 215 PD-62 cellophane membranes separated the protein solutions from the circulating buffer solutions in the electrode compartments. The membrane surface area was 15.1 cm^2; the distance between the electrodes was 2.3 cm, and the thickness of the retentate compartment was 0.6 cm. Nitrogen was used to pressurize the cell. A Hewlett-Packard, DC Power Supply (Model 64438) supplied the voltage. The voltage drop across the retentate compartment

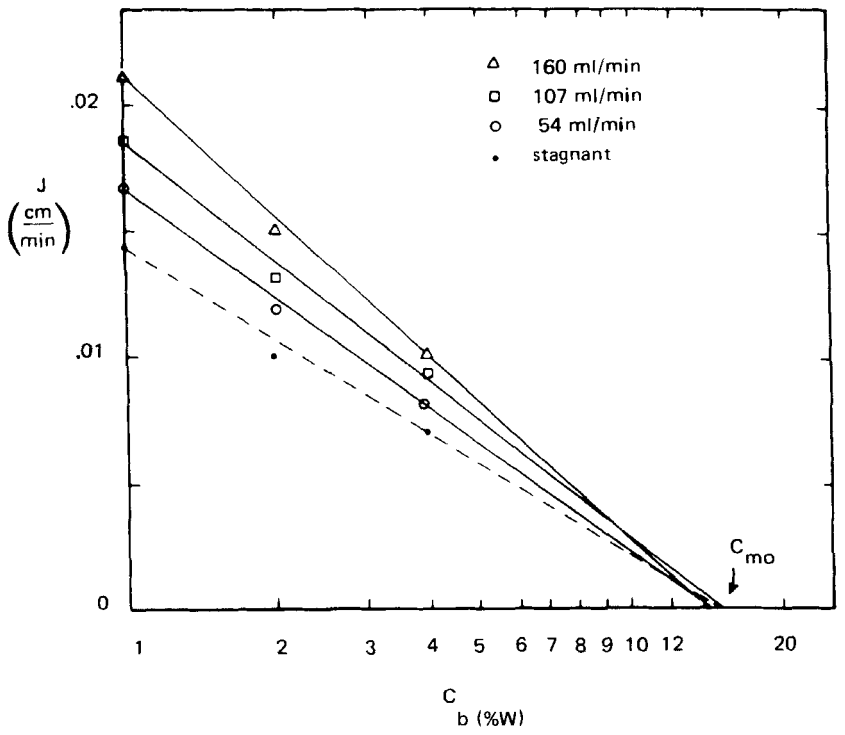

FIG. 2. Semilogarithmic relationship of ultrafiltration flux to bulk BSA concentration.

was used to calculate the electric field strength. Details of the experimental system and procedures are given by Behnam (*8*).

Amicon, Diaflo XM-50 membranes were used. Bovine serum albumin (Sigma Chemical Co., Catalogue No. A-4503, St. Louis, Missouri) was dissolved in sodium phosphate buffers with an ionic strength of 0.05 *M*. The feed concentration was kept constant. The transmembrane pressure drop (TMP) was constant at 5.0 psig. Albumin concentrations were determined by ultraviolet adsorption at 280 nm. A standard curve for the absorbance of BSA solutions of known concentrations was prepared using a Hitachi, Model 19, digital spectrophotometer.

RESULTS

The ultrafiltration flux through an XM-50 membrane at constant pressure (5.0 psig) but varying BSA bulk concentration (at pH 7.4) is shown in Fig. 2. The slope of each curve for the given tangential flow rate is

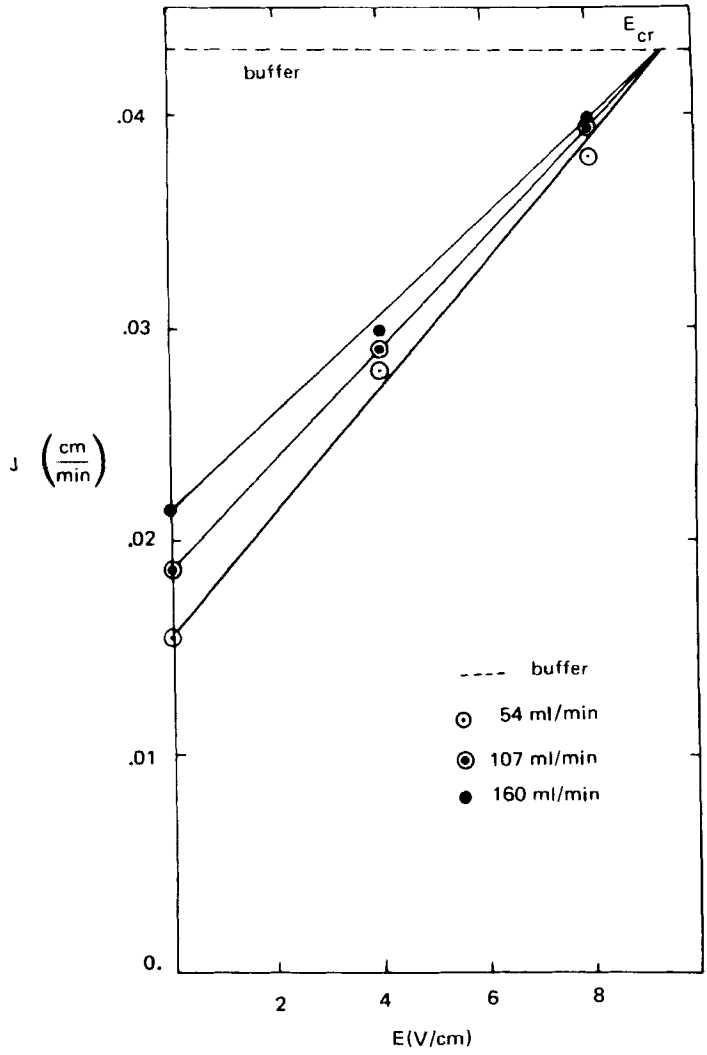

FIG. 3. Relationship between the electroultrafiltration flux and the electric field strength at different flow rates.

$-k$. k was 0.0079, 0.0069, and 0.0060 cm/min for flow rates of 160, 107, and 54 mL/min, respectively. Behnam's analysis showed that k was proportional to the velocity to the 0.213 power for our cell (*8*), compared to the 1/3 power for laminar flow in rectangular, parallel-plate flow channels (*7*). According to the film theory of concentration polarization, the intercept of the J vs ln C_b curve gives ln C_m. This method is usually used to determined C_g by plotting the limiting fluxes (pressure independent) at each bulk concentration. The fluxes in Fig. 2 are the steady-state values at 5 psig. The intercept will thus be the constant wall concentration for ultrafiltration at a TMP of 5 psig. This concentration (C_{m0}) was 15.0 wt% BSA. It is obvious that these experiments were in the pre-gel polarization region because C_{m0} is much less than the gel concentrations (40–58.5 wt%) reported in the literature (*9, 10*). Also, Behnam experimentally determined that a TMP of 12 psig was required to reach the limiting flux for a 1% BSA solution. The linear dependence of J on E is shown in Fig. 3 for different flow rates. An XM-50 membrane, 1 wt% BSA, at pH 7.4, 25°C, and a TMP of 5 psig were used.

As E increases, the effect on J of increasing the flow rate decreases. At $E = E_c$, the flux is independent of the flow rate. According to Eq. (2), increasing the flow rate at a given E would increase J because k increases. However, as E approaches E_c, C_m goes to C_b and the contribution to flux from the first term vanishes. Similar behavior was reported by Henry et al. for the electrofiltration of charged kaolin particles and oil droplets (*11*).

The change in flux as a function of E for different BSA concentrations is shown in Fig. 4. The flow rate was 160 mL/min, while other conditions were the same as those in Fig. 3. Increasing protein concentration will increase viscosity which decreases the electrophoretic mobility. A lower mobility means that the effect of a given E is less, thus the E_c should increase (as it does).

The effect of changing the pH is shown in Fig. 5, which gives J as a function of E at pH 7.4 and pH 6.2. As the pH approaches the pI of the protein (pI = 4.7 for BSA), the net charge decreases, which results in a lower electrophoretic mobility. The electrophoretic transport decreases as the mobility decreases. The slope of the J vs E curve therefore decreases, and the E_c value should increase. The data support this reasoning.

DISCUSSION

The original assumption that electroosmosis is negligible was experimentally confirmed by Behnam (*8*) for the XM-50 membranes. This assumption may not be valid for every type of membrane (*6*). The

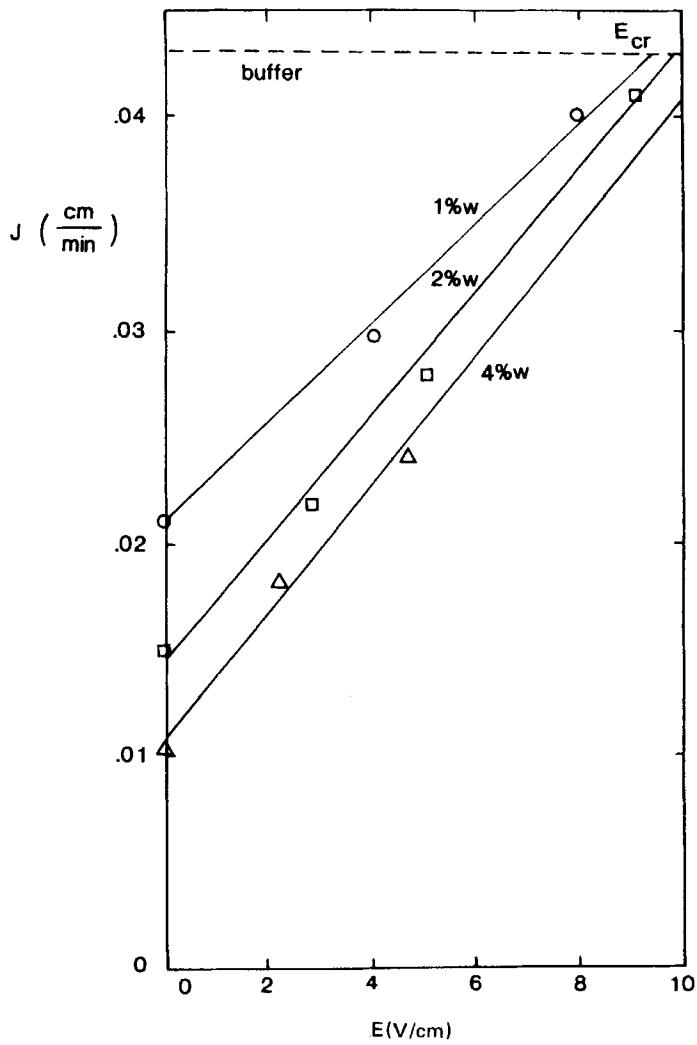

FIG. 4. Relationship between the electroultrafiltration flux and electric field strength at different bulk BSA concentrations.

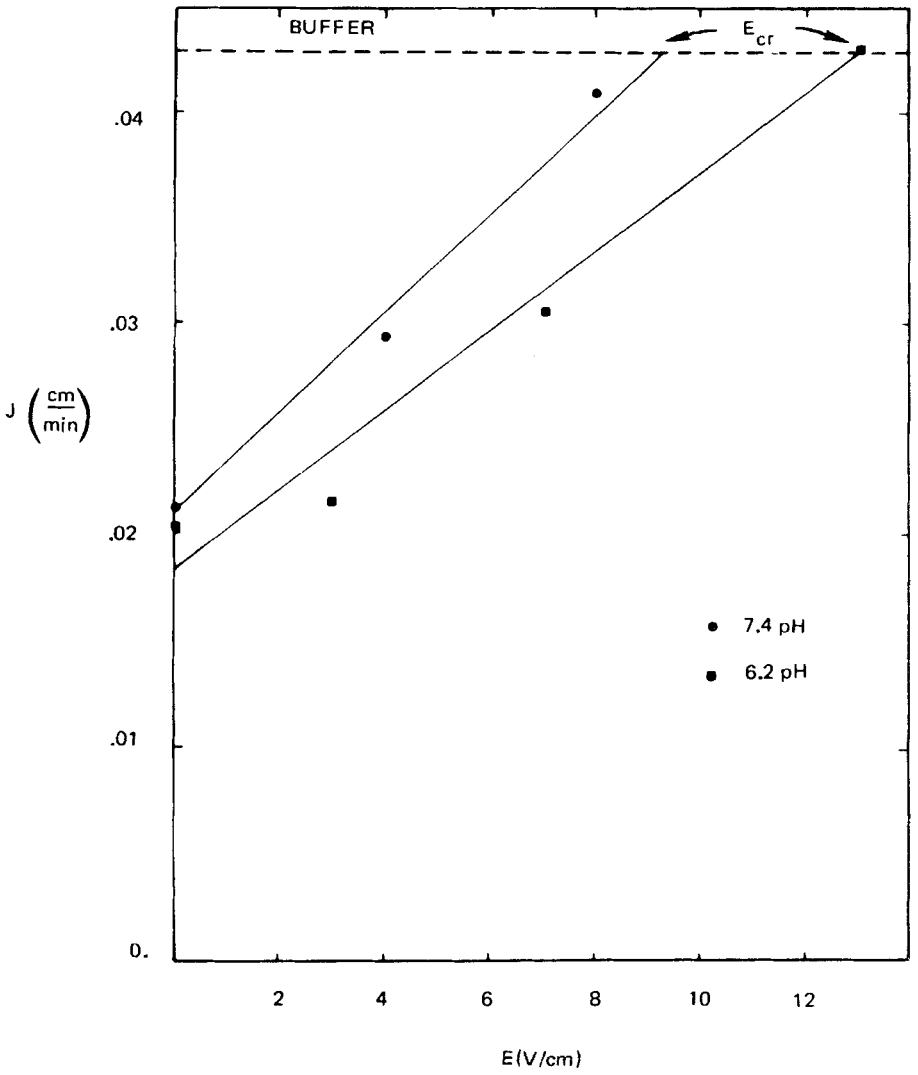

FIG. 5. Dependence of the electroultrafiltration flux on the electric field strength at different pH.

TABLE 1
A Comparison of Slopes of J vs E Curves

Flow rate (mL/min)	J_{uf} (cm/min)	Slope: $cm^2/V \cdot min$, $u - (J_{uf}/E_c)$	k (cm/min)	Slope: $cm^2/V \cdot min$ $u - (k \ln (C_{m0}/C_b)/E_c)$	Slope: $cm^2/V \cdot min$, measured
160	0.0215	2.48×10^{-3}	0.0079	2.47×10^{-3}	2.31×10^{-3}
107	0.019	2.77×10^{-3}	0.0069	2.78×10^{-3}	2.58×10^{-3}
54	0.016	3.12×10^{-3}	0.0060	3.09×10^{-3}	2.90×10^{-3}
Ref. *2*	0.01	4.35×10^{-3}	—	—	4.53×10^{-3}

assumption that the membrane is impermeable to BSA was also validated by Behnam's experiments (*8*). The retention coefficients for BSA were 0.98 when the electric field was applied; 0.95 for normal ultrafiltration. Radovich (*12*) earlier measured retentions of 0.89 without and 0.96 with the electric field. Reihanian et al. (*13*) report lower retentions (0.82) for higher TMP (7–21 psig) and lower BSA concentrations (0.6 wt%).

The data presented in the Results section can be used to predict the total flux during electroultrafiltration by applying Eqs. (8) and (7). Equation (8) can be used to predict E_c or u if J_s or one of the other variables is known. An experimental E_c of 9.3 V/cm was obtained from Fig. 3 by extrapolation. Using the experimental $J_s = 0.043$ cm/min gave a value of 4.62×10^{-3} $cm^2/V \cdot min$ for u. A value of $5.12 \times 10^{-3} cm^2/V \cdot min$ for u was obtained by interpolating the measurements of Schlessinger (*14*) at 0°C, pH 7.4, $\Gamma/2 = 0.05\ M$; correction for the temperature effects by ratioing the dielectric constant ε and viscosity η, according to Van Oss (*15*) ($u \propto \varepsilon/\eta$), and adjusting for the effect of protein concentration on viscosity by using the equation (*10*):

$$\eta = 0.01e^{0.00244C^2} \tag{9}$$

where C is g protein/1000 cm^3. Using the literature value of u, the predicted E_c is 8.4 V/cm. A similar analysis of the data reported by Radovich and Sparks (*2*) gave a u of 5.16×10^{-3} $cm^2/V \cdot min$ for the experimental $E_c = 15.5$ cm. The accuracy of the corrections to the u obtained from Schlessinger is uncertain since there are no reported values of u at our experimental conditions. An average of the three values for u, 4.97×10^{-3} $cm^2/V \cdot min$, will be used for predicting E_c in subsequent analyses.

A comparison of the predicted and measured slopes of the J vs E curves in Fig. 3 is summarized in Table 1. u was 4.97×10^{-3} $cm^2/V \cdot min$ and E_c was 8.65 V/cm for the slope prediction using Fig. 1 data, but E_c was 16.1 V/cm for the Ref. *2* predictions. These predicted slopes are about 7.5% higher than the measured values. The slopes can also be predicted by obtaining k from Fig. 2 (the slope) and C_{m0}. These predicted values were also within 7.5% of the measured slopes. The near equality of the slopes predicted by either method indicates that our method for determining C_{m0} is valid since it can be used to predict J_{uf} accurately.

The dependence of J on E in Fig. 4 for different wt% BSA solutions can also be predicted by the mathematical model as shown in Tables 2 and 3.

The measured and average values for u were corrected by Eq. (9) for the change in protein concentration. The change in measured u with increased concentration cannot be completely accounted for by the viscosity

TABLE 2
A Comparison of E_c and u for Different BSA Concentration

		E_c (V/cm)		u (cm^2/V · min)		
BSA (wt%)	J_{uf} (cm/min)	Measured	Predicted	Measured	Corrected average	Corrected measured
1.0	0.0215	9.3	8.4	4.62×10^{-3}	4.97×10^{-3}	4.62×10^{-3}
2.0	0.0145	9.7	8.5	4.43×10^{-3}	4.93×10^{-3}	4.58×10^{-3}
4.0	0.0111	10.6	8.7	4.06×10^{-3}	4.79×10^{-3}	4.45×10^{-3}

TABLE 3
Comparison of Slopes for J vs E Curves at Different BSA Concentrations

		Slopes ($cm^2/V \cdot min$)		
BSA (wt%)	J_{uf} (cm/min)	$u-(J_{uf}/E_c)$	$u-\frac{k \ln (C_{m0}/C_b)}{E_c}$	Measured
1.0	0.0215	2.48×10^{-3}	2.47×10^{-3}	2.31×10^{-3}
2.0	0.0145	3.22×10^{-3}	3.06×10^{-3}	2.94×10^{-3}
4.0	0.0111	3.53×10^{-3}	3.59×10^{-3}	3.01×10^{-3}

correction. The differences between the measured u and corrected average u increases from 7.0% at 1 wt% BSA to 15.2% at 4 wt% BSA. The predicted E_c were determined from Eq. (8) using the corrected average u.

The measured and predicted slopes for J vs E at different BSA concentrations are compared in Table 3. The corrected average u and the predicted E_c were used to predict the slopes. A k of 0.0079 cm/min was used in these calculations because the trangential flow rate was 160 mL/min. The measured and predicted (by either method) slopes differ by 4 to 10%.

The effect of pH on the electroultrafiltration flux is shown in Fig. 5. The value of u calculated from the experimental E_c (13 V/cm) for pH 6.2 was 3.31 $cm^2/V \cdot min$ while the interpolated and adjusted literature value (*14*) is 3.73 $cm^2/V \cdot min$, a difference of 11.3%. This mobility predicts $E_c = 11.5$ V/cm. The measured slope was 1.90×10^{-3} cm/min while the predicted slope using the literature u and $J_{uf} = 0.0205$ cm/min was 1.97×10^{-3} cm/min, a difference of 3.6%.

The assumption that C_m was an exponential function of E (see Eq. 3) can be checked by calculating the value of $B = J_{uf}/kE_c$ for different conditions. These results are shown in Table 4.

The greatest difference between the calculated B values using the predicted (8.65) or experimental (9.3) E_c is 3.5%. The greatest difference between any value of B and the average value is 2%. This close agreement indicates that C_m has the same exponential dependence on E for our experimental conditions.

CONCLUSIONS

A simple mathematical model, assuming an exponential dependence of the wall concentration on the electric field strength, was able to predict the

TABLE 4
Prediction of the E Dependence of C_m

Flow rate (mL/min)	k (cm/min)	J_{uf} (cm/min)	B (E_c = 8.65) (cm/V)	B (E_c = 9.3) (cm/V)
160	0.0079	0.0215	3.15	2.93
107	0.0069	0.019	3.18	3.96
54	0.0060	0.016	3.08	2.86
			av 3.14	av 2.92

steady-state electroultrafiltration flux. The solution and buffer fluxes from normal ultrafiltration and the protein's electrophoretic mobility are the only parameters necessary for this prediction. The predicted and experimental results were in close agreement for BSA solutions operating in the pre-gel polarized regions using a membrane which was essentially impermeable to BSA. The model can probably not predict the effect of operating under gel polarized conditions and using membranes which are partially permeable or have appreciable electroosmotic flow. Consideration of those cases would be an interesting next step in the development of the model.

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