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Ultrafiltration of Synthetic Polymers. Part I. Optimization of Solvent Flux during Diafiltration

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Abstract

The use of ultrafiltration as a unit operation is increasing significantly and prompts this optimization study. An exact analysis is presented which defines, as a function of the rejection coefficient, the optimum retentate concentration which minimizes the processing time for diafiltration. Three approximate solutions are also presented, and the results are compared with those from the exact solution. Experimental data are presented for the variation of ultrafiltrate flux with retentate concentration for two membrane types used with two synthetic polyelectrolytes.

INTRODUCTION

Ultrafiltration is a process which utilizes a highly specialized asymmetric porous membrane to separate species in a liquid system on the basis of molecular dimensions. Generally, macromolecules or colloids are significantly retained by these membranes while smaller solute and solvent molecules are freely transported. This unit operation is finding increasing applications in both laboratory and industrial operations. An index (*1*) of typical applications is available.

Our specific application of ultrafiltration has been the removal of low molecular weight impurities from synthetic polymer reaction mixtures to produce high purity polymeric dyes (*2*). Economically, three principal

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factors are involved in the evaluation of ultrafiltration as a viable unit operation; these are membrane lifetimes, solvent losses, and ultrafiltration fluxes.

Typically, for a chosen membrane and solvent system the problem of optimization becomes one of maximizing the solvent and low molecular weight solute fluxes while ensuring acceptable retention of the retained species. The limited choice of molecular weight cut-offs for commercial membranes requires that in some cases partial transport of the retained species is unavoidable.

The variables which affect ultrafiltrate flux are many, but here only the effect of polymer concentration will be discussed. Other variables, such as temperature, pressure, and solvent, are constrained due to the limitations of the particular membrane type and module construction.

We have previously derived an analytical expression (*3*) to determine the optimum polymer concentration that minimizes the processing time required for diafiltration. This is valid when a semilogarithmic relationship is observed between retentate concentration and ultrafiltrate flux. A recent note (*4*) has disclosed the same expression together with experimental data for one polymer–membrane combination. This prompts us to report on our more extensive theoretical examination of this problem as well as our experimental results for different polymer types and membranes.

THEORY

Many investigators have reported the dependence of ultrafiltrate flux, J, upon the concentration, C, of polymer in the retentate as following the semilogarithmic relationship (*5*)

$$J = K \ln \left[\frac{C_w - C_u}{C - C_u} \right] \tag{1}$$

where K is the ultrafiltration constant and C_w is the concentration of polymer at the membrane–solution interface (i.e., at the wall); C_u is the concentration of polymer in the ultrafiltrate. The introduction of a rejection coefficient, R, where

$$R = 1 - \frac{C_u}{C} \tag{2}$$

eliminates C_u from Eq. (1) and yields

$$J = K \ln \left[\frac{C_w/C}{R} - \frac{1}{R} + 1 \right] \tag{3}$$

Equation (3) will be used in the following to derive the optimum concentration C^*, which minimizes the process time for diafiltration.

OPTIMUM CONCENTRATION

During constant volume ultrafiltration, diafiltration, the time, t, required per diavolume performed and per unit mass of polymer processed, is given by

$$t = 1/AJC \tag{4}$$

where A is the effective membrane area.

The introduction of dimensionless groups

$$x = C/C_w \tag{5a}$$

$$y = 1/xR - 1/R + 1 \tag{5b}$$

$$\theta = tAKC_w \tag{5c}$$

yields

$$\theta^{-1} = x \ln y \tag{6}$$

Differentiating both sides with respect to x holding R constant,

$$-\theta^{-2}\frac{d\theta}{dx} = \ln y - (yRx)^{-1} \tag{7}$$

Repeated differentiation with respect to x yields

$$2\theta^{-3}\frac{d\theta}{dx} - \theta^{-2}\frac{d^2\theta}{dx^2} = -\frac{1}{R^2y^2x^3} \tag{8}$$

For critical values, $x = x^*$, $\theta = \theta^*$ at $(d\theta/dx) = 0$.

Thus the following implicit relationship [i.e., $f(C^*/C_w, R) = 0$] may be derived from Eq. (7), which allows an exact determination of C^*/C_w for any value of the rejection coefficient R:

$$C^*/C_w - [(C_w/C^* - 1 + R)\ln(C_w/RC^* - 1/R + 1)]^{-1} = 0 \tag{9}$$

By iterative calculations, values of C^*/C_w as a function of R were obtained, the latter ranging from 1.0 to 0.5. The values are plotted in Fig. 1 and fit the equation

$$C^*/C_w = -0.13R + 0.5$$

with a coefficient of determination $r^2 = 0.99$. This allows the precise calculation of C^*/C_w for any value of rejection coefficient R in the range 0.5 to 1.0.

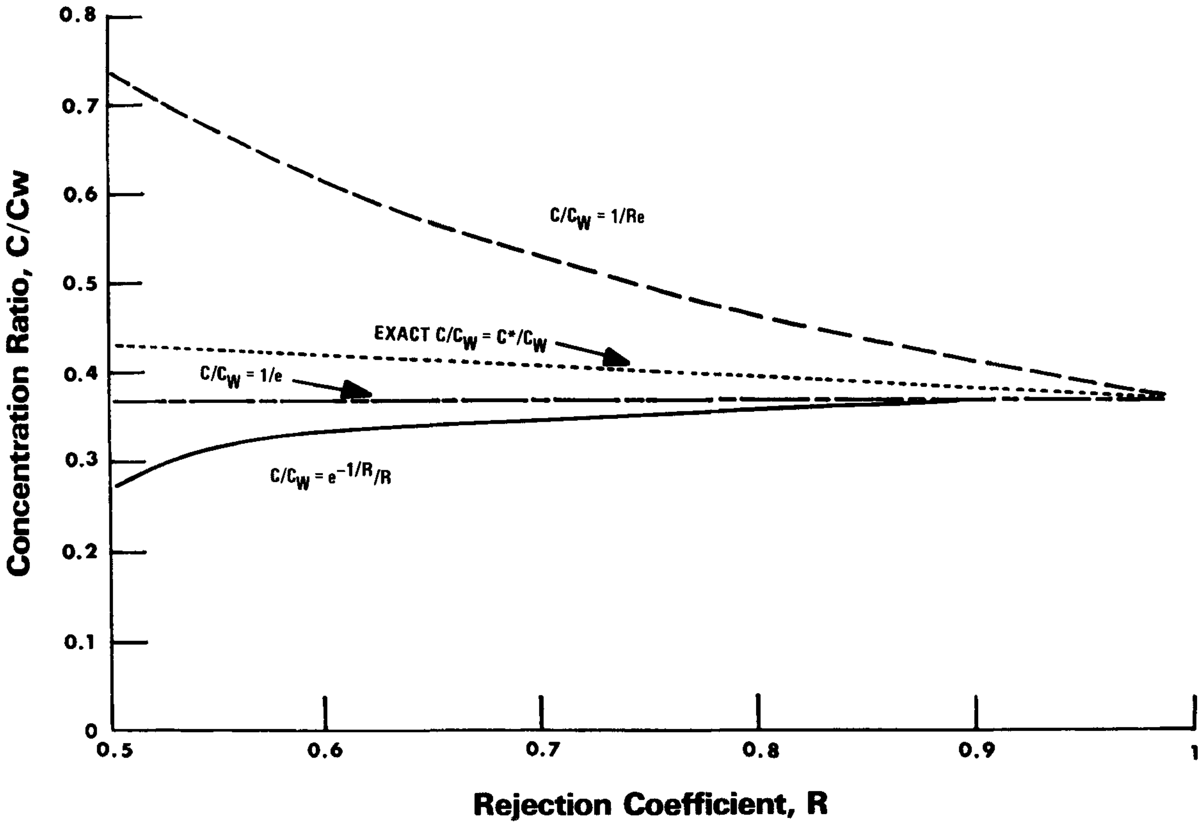

FIG. 1. Plot of concentration ratio, C/C_w, vs rejection coefficient, R.

APPROXIMATE SOLUTIONS

Since the exact solution to the problem of defining optimum operating concentrations is now available through Eq. (9), it is of interest to compare the results with approximate solutions proposed earlier (*3*, *4*).

Assuming that $C \gg C_u$ and $C_w \gg C_u$, i.e., $R \rightarrow 1$, the following approximate solution is obtained:

$$C/C_w = 1/e \tag{10}$$

By assuming only $C_w \gg C_u$, as proposed by Ng et al. (*4*), i.e., high membrane rejection, one obtains

$$C/C_w = 1/Re \tag{11}$$

Both approximations (10) and (11) are, therefore, limited to the region of high R values.

A further approximate solution may be obtained which assumes $C \simeq C_w$ and $R \rightarrow 1$, viz.,

$$C/C_w = e^{-1/R}/R \tag{12}$$

Figure 1 shows Eqs. (10), (11), and (12) plotted as functions of C/C_w vs R, together with the exact solution, Eq. (9). The data clearly demonstrate that the simplest approximate solution, Eq. (10), is by far the best of the approximate solutions. This is rather surprising considering the assumptions involved. The approximate solution, Eq. (12), is also much better than that proposed by Ng et al. (*4*), Eq. (11).

MINIMUM PROCESS TIME

Evaluation of Eq. (8) at critical values, x^*, θ^*, i.e., $(d\theta/dx) = \theta$, yields

$$\frac{d^2\theta}{dx^2} = \frac{\theta^2}{R^2y^2x^3} \tag{13}$$

Proof that $d\theta/dx$ is a minimum at critical values of x^* and θ^* is realized by the positive nature of Eq. (13).

Substitution of the solution of C/C_w as functions of R in Eq. (6) yields the following: From Eq. (9),

$$\theta^* = C_w/C^* - 1 + R \tag{14}$$

From Eq. (10),

$$\theta = e/\ln(e/R - 1/R + 1) \tag{15}$$

From Eq. (11),

$$\theta = Re^{1/R}/\ln(e^{1/R} - 1/R + 1) \tag{16}$$

From Eq. (12),

$$\theta = Re/\ln(e - 1/R + 1) \tag{17}$$

The values of θ as a function of R for Eqs. (14), (15), (16), and (17) are plotted in Fig. 2. Again, the simplest approximation, $C/C_w = (1/e)$, Eq. (10), is seen to be better than those shown in Eqs. (11) and (12).

EXPERIMENTAL

Polymers

The polymers used in the study were synthetic polyelectrolytes. The synthetic procedures have been reported (*6*, *7*). The structures of the polymers are detailed in Table 1.

Membranes

All membrane modules were obtained from Romicon, Inc. (*8*), and were designated PM10 or PM30, nominally 10,000 and 30,000 molecular weight cut-offs, respectively. For these experiments, linear thin channel (LTC) modules were used. In this configuration the retentate is recirculated through narrow splined channels, 30 mils deep, spaced around a center core which is surrounded by the asymmetric sheet membrane.

Ultrafiltration Experiments

The ultrafiltration experiments were conducted by recycling the retentate through the ultrafiltration module back into the retentate tank with an appropriately sized pump and the usual valves and pressure gauges to adjust and monitor the inlet and outlet pressures. A heat exchanger was used on the return line from the module to the retentate tank to control the temperature. The ultrafiltrate was recycled into the retentate tank until the flux became constant, usually ~15 min. Then, some ultrafiltrate was removed to achieve a higher polymer concentration in the retentate tank and again the ultrafiltrate was recycled to the retentate tank until the flux again became constant. Typically, the concentration of polymer in the retentate was varied over the range of 1 to 8 g/dl.

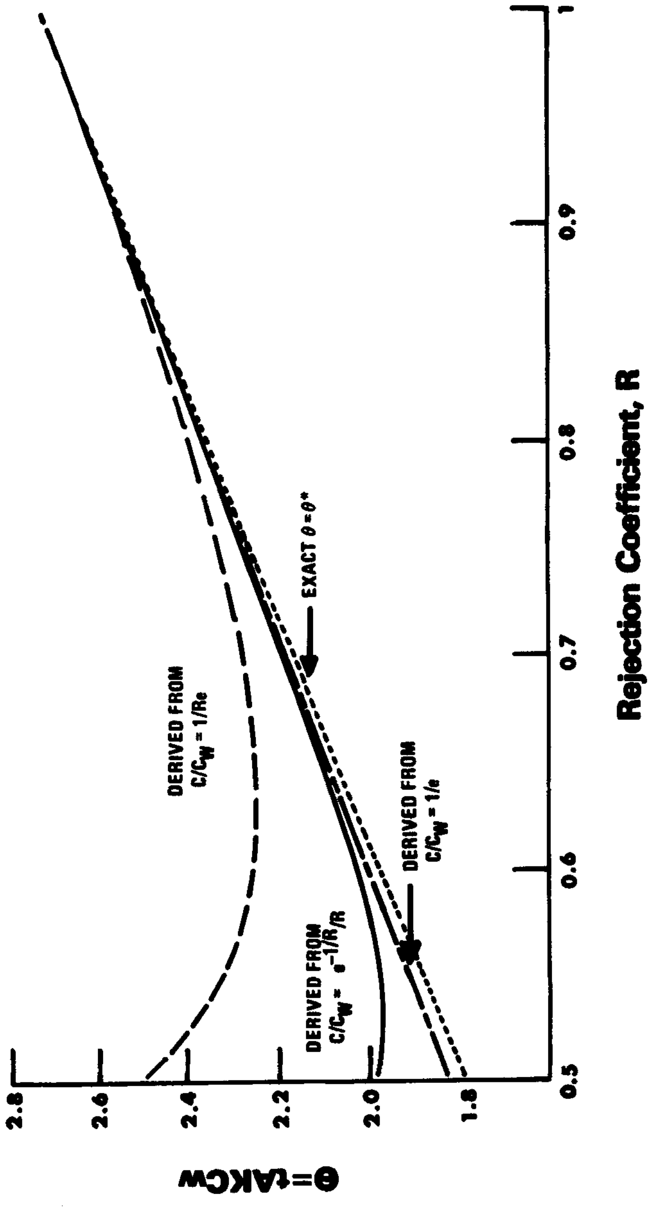

FIG. 2. Plot of $\theta = tAKC_w$ vs the rejection coefficient, R.

TABLE 1

Polymer code	Polymer backbone	Attached chromophore
A	Poly(epichlorohydrin)	Sunset Yellow
B	Poly(aminoethylene)	Sunset Yellow

RESULTS AND DISCUSSION

Experimental values of ultrafiltrate flux, J, for different values of the retentate concentration, C, were obtained for linear thin channel modules at 22°C. Two membrane types and two synthetic water-soluble polymers were used in these experiments. Figure 3 shows the data plotted on semilog coordinates. The linearity of the plots suggests that the gel model is appropriate. Hence

$$J = K \ln C_w/C$$

applies, since both polymers are totally rejected at the membrane surface (i.e., $R = 1$). It is interesting to note that the values of K are similar for the same membrane and the values of C_w are similar for the same polymer. The values are listed in Table 2. The K values are, of course, the values for the ultrafiltrate flux rate when operating at optimum polymer concentration, C^*.

The process time is relatively insensitive to polymer concentrations, as can be seen from the shallow nature of the curves in Fig. 4. For example, in Run 2, polymer retentate concentrations ranging from 60 to 115 g/l yield a 5% or less change in the process time.

The processing time versus concentration curves becomes steeper as the value of C_w decreases, thus operating closer to C^* becomes more critical.

CONCLUSIONS

An exact solution for the optimization of solute flux in the diafiltration mode has been presented. The results from three approximate solutions have been compared with this exact solution. Results for synthetic polyelectrolytes and linear thin channel modules with PM10 or PM30 membranes have been presented. The optimum values of retentate concentration, C^*, for these systems are in the range 45 to 85 g/l. For a given polymer, C^* is relatively independent of membrane type. The value of C^*, however, is highly dependent upon polymer type for a given membrane.

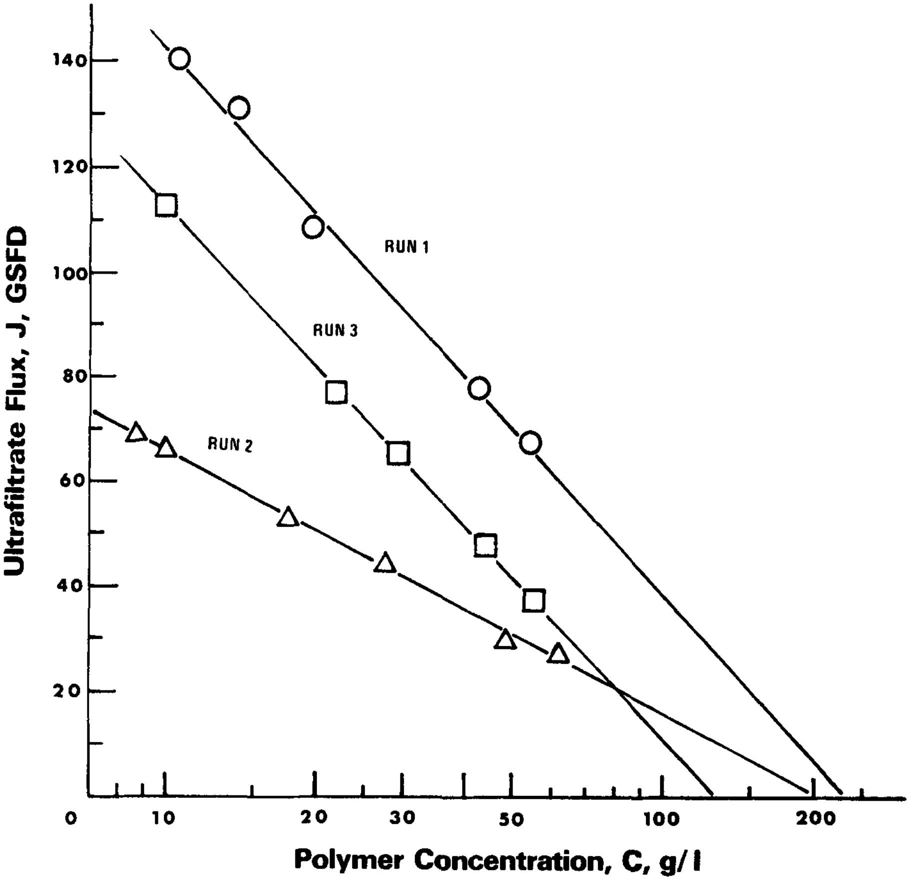

FIG. 3. Ultrafiltrate flux as a function of polymer concentration for various polymers and linear thin channel membranes at 22 °C. (For conditions see Table 2.)

TABLE 2

Experimental Results at 22 °C for Linear Thin Channel Membranes (1.6 ft^2 Modules). Inlet Pressure 100 psig, Outlet Pressure 15 psig

Run no.	Membrane type	Retentate material	K (GSFD)	C_w (g/l)	C^* (g/l)	Process time[a] t^* (min/lb/diavolume)
1	PM30	Polymer A	45.4	232	85	72
2	PM10	Polymer A	21.7	202	74	171
3	PM30	Polymer B	44.2	126	46	136

[a] Process time is determined from $t^* = (AKC^*)^{-1}$ with $A = 1.6$ ft^2.

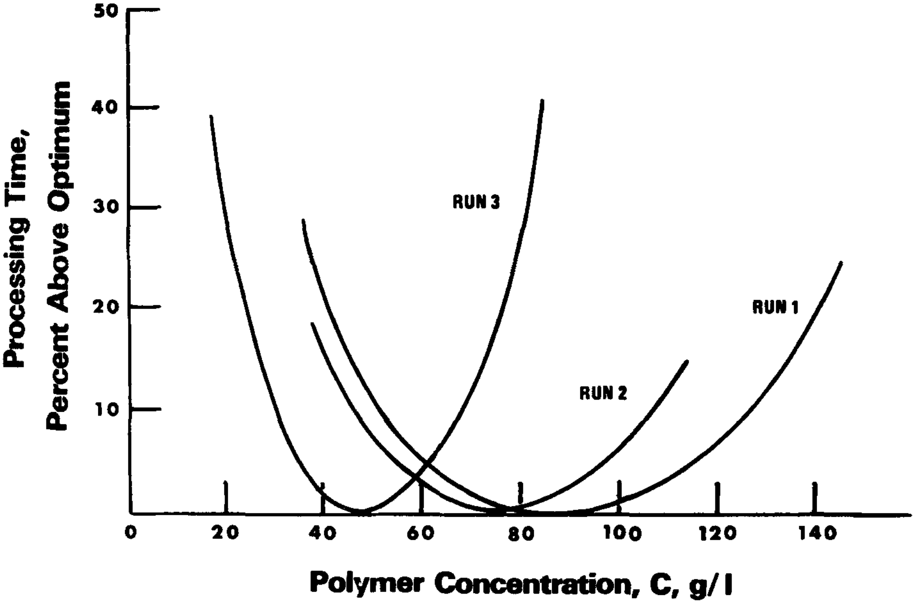

FIG. 4. Processng time expressed as a percentage above the optimum at different polymer concentrations. (For conditions see Table 2.)

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