Purification of Polymeric Dyes by Ultrafiltration*

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Synopsis

Ultrafiltration has been evaluated as a method for the purification of of polymeric dyes. Transport data for solvent and solutes were obtained for several polymer–impurity mixtures and different membrane types. Relatively low molecular weight impurities were found to be significantly rejected by these membranes. A critical concentration of sodium chloride or sodium hydroxide was found to be necessary to effect efficient transport of these species. Gel permeation chromatography was used to monitor these separations and characterize the purity of the polymeric dyes produced. Impurity concentrations in the final product were typically less than 500 ppm.

INTRODUCTION

The use of membranes to effect a separation in liquid systems increased dramatically following the introduction of asymmetrical membranes around 1960. These membranes possess a microscopically thin porous layer supported by a considerably thicker porous backing. This structure allows high permeation rates and good mechanical stability. The term ultrafiltration is usually applied to a membrane separation process where the solute dimensions are significantly larger than the solvent. Osmotic pressures of these solutions are small, therefore only low operating pressures are required and membrane compaction is avoided. Desirable economic features of ultrafiltration as a unit operation include low energy consumption and no change in phase. Indices of typical applications of ultrafiltration have been compiled,[1-3] and review articles are available.[4-7]

Ultrafiltration is ideally suited to the purification or concentration of macromolecules and colloids. It has also been investigated as a method for the molecular weight fractionation of lignin sulfonates,[8] dextrans,[9-11] hydrolyzed dextrans,[12] poly (vinyl pyrrolidone),[10] polyethylene glycols,[11] and proteins.[13]

We are evaluating ultrafiltration as a unit operation for the industrial scale purification of polymeric dyes.[14-16] The removal of all low molecular weight species as well as oligomers is necessary to ensure the product will be nonabsorbable following ingestion.[17] Ultrafiltration is an ideal way to achieve both these goals by selection of a membrane with appropriate molecular weight retention characteristics. This study reports our initial investigations of solute and solvent transport for a series of polymeric azo dyes with commercially available Romicon membranes (Romicon, Inc., Woburn, Ma. 01801).

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TABLE I
Polymeric Dyes and Low Molecular Weight Dyes Used in Ultrafiltration Studies

| Code | Structure | | Molecular wt. |
	Polymer	Chromophore	
A	—	Sunset Yellow	452
B	—	tartrazine	534
C	poly(aminoethylene)	tartrazine	1.9×10^4
D	poly(aminoethylene)	Sunset Yellow	1.5×10^4
E	poly(epichlorohydrin)	Sunset Yellow	1.0×10^4
F	poly(aminoethylene)	Sunset Yellow	2.6×10^4
G	—	Schaffer's salt	246

EXPERIMENTAL

Polymeric Dyes

The attachment of an azo chromophore onto a polymeric backbone has been described in detail.[14,15] The specific polymeric dyes investigated in this work were based on a polymeric backbone to which either tartrazine or Sunset Yellow

COMPOUND **STRUCTURE**

Sunset Yellow
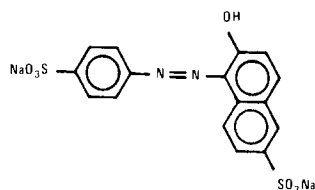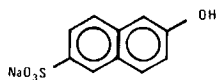

Tartrazine
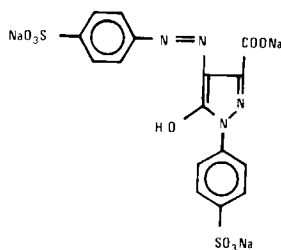
Schaffer's Salt

Fig. 1. Structural formulas for Sunset Yellow, tartrazine, and Schaffer's salt.

was covalently bonded. Details of the polymers used in this study are shown in Table I. The structures of Sunset Yellow, tartrazine, and Schaffer's salt are shown in Figure 1.

Ultrafiltration Equipment

A Romicon[18] ultrafiltration unit, Model NO. LTCX13ST, was used in this work. The unit consists of a multistage centrifugal pump with a gate valve and pressure gauge at the inlet and outlet of the ultrafiltration membrane module. The Romicon unit was modified to incorporate a heat exchanger. The feed solution in the retentate tank is recycled through the ultrafiltration module. A level controller was used which allowed diafiltration experiments (constant retentate volume operation) to be performed. In this mode the ultrafiltrate flux rate is exactly matched by a make-up stream to the retentate tank. The membrane modules were either linear thin channel or hollow fiber units. Both of these geometries are designed to eliminate extensive buildup of polymer at the membrane surface by use of high velocities past the membrane surface. The linear

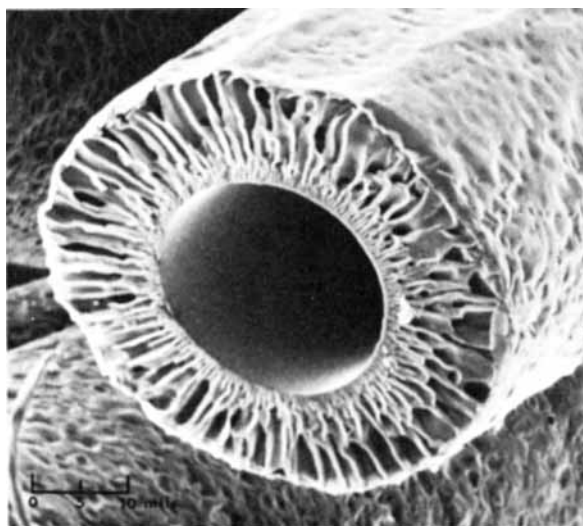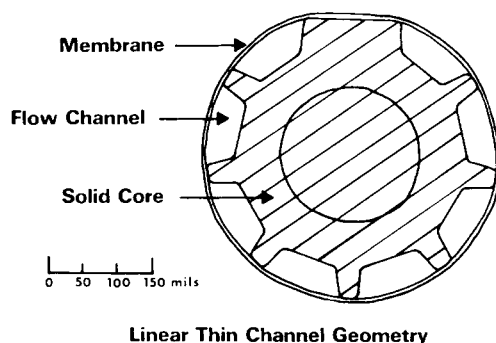**Linear Thin Channel Geometry**

Hollow Fiber Construction

Fig. 2. Membrane and module characteristics: (a) linear thin channel geometry; (b) hollow fiber structure.

TABLE II
Summary of Ultrafiltration Membranes Used in This Study

Membrane code	Romicon membrane type	Nominal mol. wt. cutoff[a]	Pore size,[a] Å	Internal fiber diam., in.	Linear thin channel depth, in.	Membrane area, ft²
A	LTC UM10	10,000	30	—	.030	1.6
B	LTC PM10	10,000	38	—	.030	1.6
C	LTC PM30 (I)	30,000	47	—	.030	1.6
D	LTC PM30 (II)	30,000	47	—	.030	1.6
E	HF PM10	10,000	38	0.017	—	25
F	HF XM50	50,000	66	0.020	—	30
G	HF XM50	50,000	66	0.045	—	15

[a] Manufacturer's data.

TABLE III
Summary of Operating Conditions for Ultrafiltrations Performed

Membrane code	Romicon membrane type	Operating Pressures, psig inlet	Operating Pressures, psig outlet	Average transmembrane pressure drop, psig	Recirculation rate,[a] gpm	Average fluid velocity in feed channels,[a] (ft/sec)
A	LTC UM10	95	20	57.5	13	23.9
B	LTC PM10	95	20	57.5	13	23.9
C	LTC PM30 (I)	95	20	57.5	13	23.9
D	LTC PM30 (II)	95	20	57.5	13	23.9
E	HF PM10	25	10	17.5	4	1.97
F	HF XM50	25	10	17.5	12	4.18
G	HF XM50	25	10	17.5	17	5.20

[a] For deionized water.

thin channel modules consist of splined core 0.5 in. in diameter, 43 in. long, forming eight flow channels 0.030 in. deep (see Fig. 2). The retentate solution is recirculated through these splined channels at 13 gpm, which corresponds to an average flow velocity past the membrane of 23.9 ft/sec. The hollow fiber modules consist of many single hollow fibers potted into a module with epoxy resin. A photomicrograph of a single fiber is shown in Figure 2. The retentate solution is recirculated through the center of the fiber which has the desired porosity. External to this surface is a more porous backing structure which gives the fiber its mechanical strength.

Each module was always operated at the same values of average transmembrane pressure drop shown in Table III. As the polymer concentration is increased, therefore, the average flow velocity in the feed channels is decreased below the values shown in the table for deionized water, in proportion to the polymer solution viscosity. Since the recirculation rates or solution viscosities were not measured, it was not possible to calculate the filtration fraction per pass, i.e., the percentage of the volume of solution fed to the unit that is removed as ultrafiltrate per pass. The membranes investigated and conditions used are summarized in Tables II and III.

Solute Concentration Analysis

Sunset Yellow and tartrazine concentrations were quantitated by visible absorption spectrometry. Mixtures containing polymeric dye and Sunset Yellow or tartrazine were separated by gel permeation chromatography, and the column effluent was monitored by visible absorption spectrometry. Calibration with appropriate standards allowed quantitation of the peak areas obtained.

Gel Permeation Chromatography

The gel permeation chromatograph consisted of a Milton Roy 5000 psig minipump, a Chromatronix injection valve (HPSV-30), and two columns 2 ft × 0.180 in. I.D., packed with controlled pore glass CPG-HS-75 Å (37–44 μ particle size range). Column effluents were monitored at visible wavelengths by a Varian Techtron Model 635 spectrophotometer fitted with ISCO high-pressure cells (2850 psi rating). The solvent used was 0.1M pH 7.0 phosphate buffer, and molecular weight calibration was performed with poly(acrylic acid) fractions.

THEORY

Solvent Transport

For the ultrafiltration of polymer solutions under sufficiently high transmembrane pressures, a linear plot of solvent flux J versus logarithm of polymer retentate concentration C is predicted[4] from the concentration polarization model

$$J = -K \ln (C/C_w) \qquad (1)$$

The ultrafiltration coefficient K and the polymer concentration at the membrane wall, C_w, can be determined from such a plot. Equation (1) assumes zero polymer

transport and was the case for the polymers used in this work. The polymers used to generate flux–concentration data had been previously purified by ultrafiltration. For incomplete polymer rejection, the model predicts

$$J = -K \ln \left[(C - C_u)/(C_w - C_u) \right]$$

where C_u is the concentration of polymer in the ultrafiltrate.

Solute Transport

Solute transport for species i is given by the product of J and $(C_u)_i$, where $(C_u)_i$ is the species concentration in the ultrafiltrate stream. This concentration may vary from zero for species completely retained by the membrane to a value equal to the concentration of the species in the retentate C_i. A rejection coefficient σ_i is defined for species i:

$$\sigma_i = 1 - \frac{(C_u)_i}{C_i} \qquad (2)$$

which varies from 0 to 1 as the species are freely transported across the membrane or completely retained by the membrane.

Using a pure-solvent feed rate Q_f to the retentate tank equaling that of the ultrafiltrate flux rate Q_u, operation at constant retentate volume V_R is achieved (diafiltration). It is useful to obtain a semilog plot of the retentate concentration of solute species i, C_i, against t or the number of diavolumes N performed, where $N = Q_u t/V_R$. If the rejection coefficient varies during diafiltration, it may be determined from the slope of this plot:

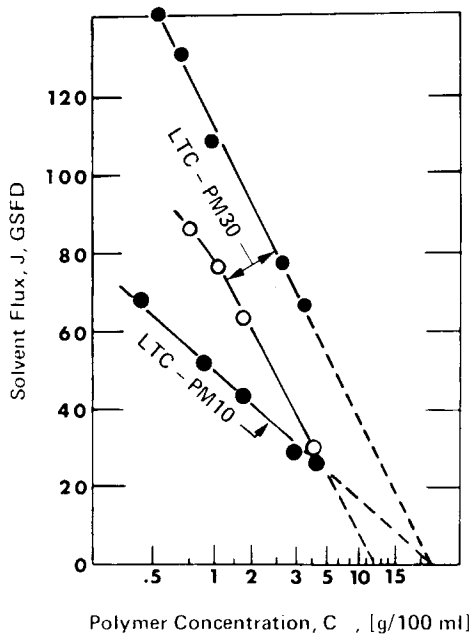$$\sigma_i = 1 + \frac{d \ln C_i}{dN} \qquad (3)$$

Fig. 3. Solvent transport in linear thin channel ultrafiltration modules with polymeric dye solutions at 20°C, solvent flux J vs polymer concentration C: g/100 ml ($\circ$) polymeric dye D, $K = 44$, $C_w = 12.6$; ($\bullet$) polymeric dye E, $K = 21$, $C_w = 22$; ($\bullet$) polymeric dye E, $K = 46$, $C_w = 22$.
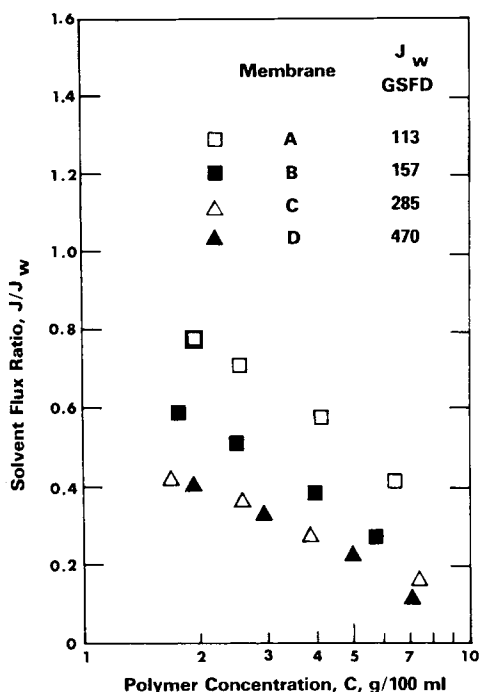
Fig. 4. Solvent transport as a function of polymer C concentration for various LTC modules at 38°C, solvent flux ratio J/J_w vs polymer concentration C: ($\square$) membrane A, J_w (GSFD) = 113; ($\blacksquare$) membrane B, J_w (GSFD) = 157; ($\triangle$) membrane C, J_w (GSFD) = 285; ($\blacktriangle$) membrane D, J_w (GSFD) = 470.

Separation Efficiency

To achieve the most efficient separations to produce high-purity polymeric dye from these reaction mixtures, the polymer should have a σ value of 1, and the low molecular weight dye and other impurities should have σ values of 0. Since the molecular weight cutoff for these membranes is not sharp, there is a transition region for lower molecular weight polymer where σ varies significantly with molecular weight. The σ–MW relationship and the ultrafiltration time define how much low molecular weight polymer is transported.

RESULTS AND DISCUSSION

Solvent Transport

Solutions of polymeric dyes were ultrafiltered at various concentrations with a series of membranes. In all cases, complete rejection of the polymeric dyes was obtained and the ultrafiltrate flux rates were measured. In Figure 3 the same polymeric dye E was studied with two membranes. The values of the ultrafiltration coefficient K are significantly different because of the differing membrane porosity. However, C_w obtained by extrapolation is identical for each membrane. As predicted by the model, the C_w values depend only on the polymer and not the membrane. For a given membrane, the value of C_w is found to be very dependent upon the polymer structure and molecular weight. The solvent flux is higher for the PM30 than the PM10 membrane at the same polymer concentration over the range of concentration investigated.
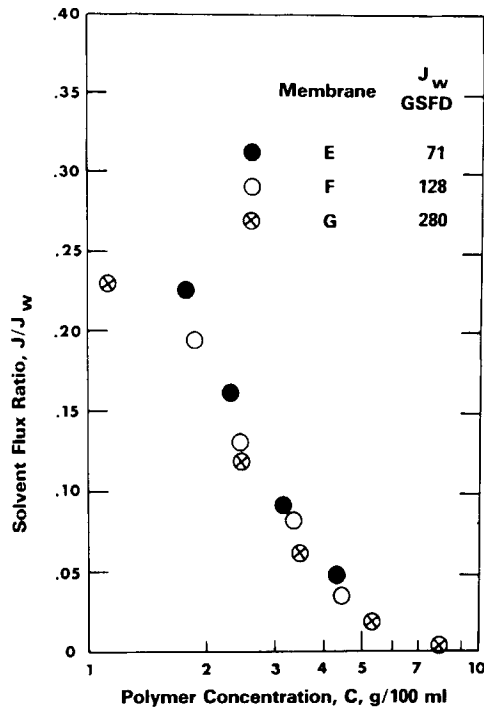
Fig. 5. Solvent transport as function of polymer C concentration for various hollow fiber modules at 38°C, solvent flux ratio J/J_w vs polymer concentration C: (●) membrane E, J_w (GSFD), 71; (O) membrane F, J_w (GSFD), 128; (⊗) membrane G, J_w (GSFD), 280.

Figures 4 and 5 show the solvent flux rate relative to the flux rate for deionized water, J_w, as a function of polymer C concentration for a series of different membranes. In Figure 4 the solvent flux ratio is plotted as a function of polymer concentration for LTC modules with three membranes, UM10, PM10, and PM30. It is evident that the solvent flux ratio decreases with increasing pore size. Since the ultrafiltrations were performed under identical conditions of temperature, flow velocity, and average transmembrane pressure, the gel layer should be similar at a given polymer concentration for all membranes. Expressed in terms of a series resistance model,

$$\text{flux for pure water feed } J_w = \frac{\Delta P}{R_m}$$

For polymer solution at a given concentration,

$$J = \frac{\Delta P}{R_m + R_g}$$

where R_m is the resistance of the membrane, R_g is the resistance of the gel layer, and ΔP is the average transmembrane pressure drop.

Thus, at fixed values of polymer concentration and ΔP,

$$\frac{J}{J_w} = \frac{R_m}{R_m + R_g}$$

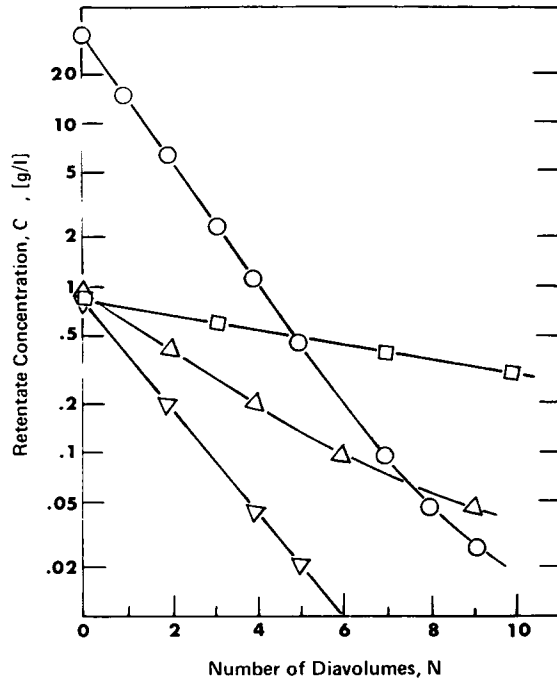The flux-versus-polymer concentration data should not, therefore, be capable

Fig. 6. Solute transport of nonpolymeric species through membrane B, retentate concentration C vs number of diavolumes N: (O) NaCl; (□) Sunset Yellow; (△) Schaffer's salt; (▽) tartrazine + NaCl (>20 g/l).
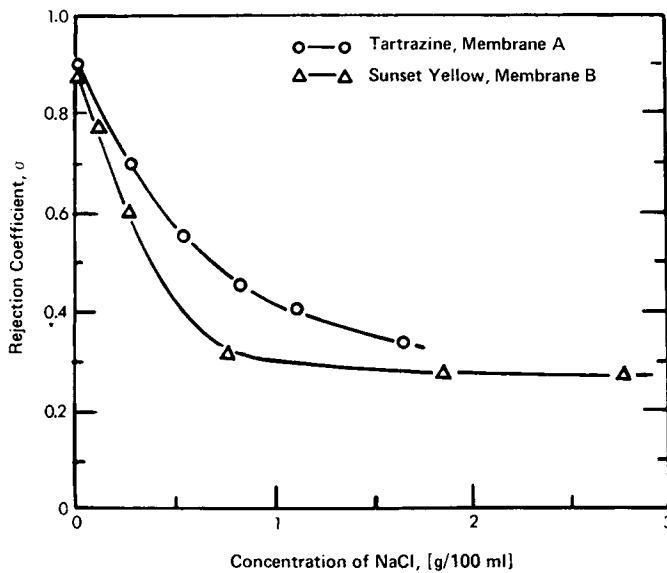

Fig. 7. Rejection coefficient σ of tartrazine and sunset Yellow as function of sodium chloride concentration.

of being normalized with respect to pure water flux for various membranes. This is seen to be the case for the different membranes used in Figure 3. However, the unexpected observation was made that the two PM30 modules which ex-
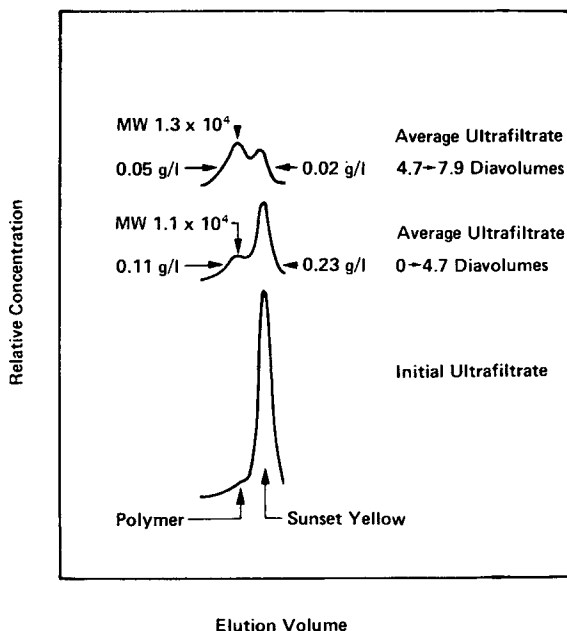
Fig. 8. Gel permeation chromatographic analyses of the purification of polymeric dye F containing Sunset Yellow using membrane D, relative concentration vs elution volume.

hibited large differences in pure-water flux could be normalized on this plot. This could arise from the polymer blocking the larger pores which are responsible for the major differences in deionized water flux.

If the gel layer resistance for these systems at a given polymer concentration is back-calculated from J/J_w and R_m, the values obtained are not constant. This would suggest that a simple series resistance model is not applicable and some interaction between the gel layer and the membrane surface occurs.

The results for the hollow fiber modules are shown in Figure 5. These results were all obtained at the same average transmembrane pressure, but the fluid velocities in the channels were different for all three membranes because of the differing fiber internal diameters. The gel layer resistance would therefore be expected to be different and decrease as the fiber internal diameter increases.

These results demonstrate that membranes with the highest solvent fluxes will not necessarily give the highest ultrafiltrate fluxes when moderately concentrated polymer solutions are used. The increased retention characteristics of the UM10 or PM10 membranes should not be sacrificed in favor of the higher solvent fluxes reported for a PM30 membrane or XM50, for example.

Solute Transport

Initial experiments showed that Sunset Yellow, Schaffer's salt, and tartrazine were not being removed from these systems at the rates predicted for unretained solutes. Model experiments were conducted to measure the transport of these low molecular weight materials in the absence of polymeric dye. These experiments were performed in constant volume mode. The results are shown in Figure 6. Sodium chloride follows the relationship expected for an unretained

solute $\sigma = 0$ and is therefore the reference slope on the graph. In the absence of sodium chloride, Sunset Yellow and Schaffer's salt transport at significantly slower rates than an unretained solute. It is known that dye molecules of this type can associate in solution. However, this association should decrease in the presence of salts. The phenomenon of dye association is therefore not responsible for the retention of these materials. Most neutral species in this molecular weight range are essentially unretained by these materials. It seems probable that the dye molecules themselves are capable of adsorbing on the membrane surface and make it an effective anionic membrane. Thus, an ionic rejection mechanism may operate until a sufficiently high solvent ionic strength is reached which effectively screens the charge on the membrane. The rejection coefficient for tartrazine in the presence of 20 g/l. sodium chloride is 0.23.

In order to determine the minimum concentration of sodium chloride required to obtain the lowest σ possible, experiments were performed to measure σ for various solutes as a function of sodium chloride concentration. These results are shown in Figure 7 and demonstrate that maintaining a sodium chloride concentration of at least 15 g/l. is necessary for efficient transport of these solutes. At lower salt concentrations these solutes are highly retained such that the separation becomes impractical. The σ values at sodium chloride concentrations > 15 g/l. are not zero but are sufficiently low to allow the separation to be feasible.

Similar experiments demonstrated that maintaining the retentate at high pH, ~12, had an exactly similar effect on solute transport as sodium chloride at > 15 g/l. concentration. Several reaction mixtures of polymeric dyes having the structure F were successfully purified by maintaining the pH of the retentate at 12.0.

Gel permeation chromatography is an extremely useful technique to monitor ultrafiltration processes. The separation of polymeric and nonpolymeric species allows the amounts of each to be quantitated and the molecular weight of the polymer to be assigned. Typical chromatograms of ultrafiltrates are shown in Figure 8. The initial ultrafiltrate has a high concentration of Sunset Yellow relative to polymer. Analysis of the chromatogram of the average ultrafiltrate collected during the first 4.7 diavolumes shows 0.23 g/l. Sunset Yellow and 0.11 g/l. low molecular weight polymeric dye with molecular weight 1.1×10^4. The average ultrafiltrate collected from the last 3.2 diavolumes shows 0.02 g/l. Sunset Yellow and 0.05 g/l. polymeric dye with molecular weight 1.3×10^4. The molecular weight of the polymeric dye in the retentate was 2.6×10^4. The polymeric dye produced in this experiment contained less than 500 ppm Sunset Yellow, which was the limit of the analytical method.

CONCLUSIONS

Ultrafiltration has been demonstrated to be an excellent method for the large-scale purification of polymeric dyes. The polymers investigated were highly retained using commercial membranes with molecular weight cutoffs in the range of 10,000–50,000. Low molecular weight organic impurities were found to be significantly rejected by these membranes. This could be alleviated by maintaining a critical level of sodium chloride or adjusting the pH of the solution to ~12. Gel permeation chromatography is an extremely effective way to characterize these separations.

References

1. *Reverse Osmosis and Ultrafiltration and Their Practical Applications,* Publ. No. 77, 1972, The British Food Manufacturing Industries Research Association, Leatherhead, Surrey.

2. *Literature References to the Use of Amicon Ultrafiltration Systems,* Publ. No. 428D, 1976, Amicon Corp., Lexington, Mass.

3. *Reverse Osmosis Bibliography: Abstracted and Indexed,* Plastic Report R45, 1973, Plastics Technical Evaluation Center, Picatinny Arsenal, Dover, New Jersey.

4. A. S. Michaels, *Chem. Eng. Progr.,* **64,** 31 (1968).

5. G. F. Fallick, *Proc. Biochem.,* 7 (1969).

6. A. R. Thomson, *Proc. Biochem.,* 35 (1971).

7. J. Melling, *Proc. Biochem.,* 7 (1974).

8. J. L. Gordon and S. G. Mason, *Can. J. Chem.,* **33,** 1477, (1955).

9. K. C. B. Wilkie, J. K. N. Jones, B. J. Excell, and R. E. Semple, *Can. J. Chem.,* **35,** 795 (1957).

10. R. W. Baker, *J. Appl. Polym. Sci.,* **13,** 369 (1969).

11. R. W. Baker and M. Strathmann, *J. Appl. Polym. Sci.,* **14,** 1197 (1970).

12. S. C. Edberg, P. M. Bronson, and D. J. van Oss, *Prep. Biochem.,* **1,** 249 (1971).

13. W. F. Blatt, B. G. Hudson, S. M. Robinson, and E. M. Zipilivan, *Nature,* **216,** 511 (1967).

14. R. G. Booth and A. R. Cooper, *Am. Chem. Soc., Div. Polym. Chem., Prepr.,* **17,** 476, (1976).

15. D. J. Dawson, R. D. Gless, and R. E. Wingard, Jr., *Chem. Tech.,* **6,** 724 (1976).

16. D. J. Dawson, R. D. Gless, and R. E. Wingard, Jr., *J. Am. Chem. Soc.,* **98,** 5996 (1976).

17. N. Bellanca and W. J. Leonard, Jr., presented at the Am. Chem. Soc. Food Color Symposium, New Orleans, March 21, 1977, in *Current Aspects of Food Colorants,* T. E. Furia, Ed., CRC Press, Cleveland, Ohio, 1977.