Cellulose Acetate Ultrafiltration Membranes

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Synopsis

Twenty-three different casting solution compositions involving cellulose acetate (E-938-3 (polymer, P), acetone (solvent, S), and aqueous magnesium perchlorate $(Mg(ClO_4)_2:H_2O = 1:8.5)$ (nonsolvent, N) were studied for making ultrafiltration membranes. These compositions (expressed in weight units) involved N/P ratios of 0.817 to 1.3 and S/P ratios of 3.5 to 5.33. It was found that by adjusting the values of S/P and N/P ratios in the casting solution composition, temperature of the casting solution, temperature of the casting atmosphere, and solvent evaporation period during film formation, a wide variety of cellulose acetate membranes useful for both ultrafiltration and reverse osmosis applications could be obtained. The results of a continuous test run at 50 psig for a period of 250 hr with a typical set of membranes, and their separation characteristics for a group of solutes ranging in molecular weight from 58 to 160,000, are presented.

INTRODUCTION

An approach to the development of cellulose acetate ultrafiltration membranes was established in an earlier paper.[1] This approach was based on the solution structure–evaporation rate mechanism[2–5] governing the surface pore structure of Loeb-Sourirajan-type reverse osmosis membranes during film formation. This paper is an extension of the above work. As before, the film-casting solution (whose composition is given in weight units) consisted of a mixture of cellulose acetate (Eastman grade 398-3) (polymer, P), acetone (solvent, S), and aqueous magnesium perchlorate $(Mg(ClO_4)_2:H_2O = 1:8.5)$ (nonsolvent, N). It was pointed out that decrease in S/P, increase in N/S, and increase in N/P in the casting solution composition, decrease in temperature of the casting solution, and increase in solvent evaporation period during film formation tended to increase the size of pores on the surface of resulting membranes in the as-cast condition. Further, increase in S/P in the casting solution composition and increase in the temperature of the casting solution tended to increase the effective number of pores on the membrane surface. These criteria offer definite directions for creating cellulose acetate ultrafiltration membranes for practical purposes.

In this work, the effects of composition and temperature of the casting solution, and evaporation period during film formation, on subsequent membrane performance in reverse osmosis experiments were studied further. The results obtained confirm the criteria established earlier for creating relatively larger size and number of pores on the membrane surface and offer some definite casting solution compositions and film-casting conditions which can be used for making cellulose acetate ultrafiltration membranes for practical purposes.

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EXPERIMENTAL

Flat films were made using the casting solution compositions listed in Table I and indicated in the triangular polymer (P)–solvent (S)–nonsolvent (N) composition diagram, Figure 1. The film-casting conditions used were as follows: temperature (°C) of casting solution/temperature (°C) of casting atmosphere, 0/20, 10/30, or 20/40 as specified; relative humidity of the casting atmosphere, 60–65%; evaporation period during film formation, minimum (2 to 5 sec) to 120 sec as specified; gelation medium, ice-cold water; and gelation period, 1 hr. The temperature of the glass plate on which the film was cast was the same as the temperature of the casting solution in each case. The glass plate was protected against excessive moisture condensation prior to film casting. The membranes were tested in reverse osmosis experiments either with or without prior thermal shrinkage in hot water. The membranes were initially subjected to a pure water pressure of 150 or 70 psig for 1 hr in preparation for subsequent reverse osmosis experiments at 100 or 50 psig, respectively. Aqueous feed solutions containing 200 ppm NaCl or $MgSO_4$ were used in reverse osmosis experiments. All experiments were carried out at laboratory temperature (23° to 28°C). The effective area of the film surface was 13.2 cm² in all the cases. In each experiment, the pure-water permeation rate PWP and the membrane permeated product rate PR, in grams per hr per given area (13.2 cm²) of film surface, and fraction solute separation f obtained from the relation f = (solute ppm in feed − solute ppm in product) ÷ (solute ppm in feed) were determined. Since the osmotic pressure effects under the conditions of the experiments were negligible, the
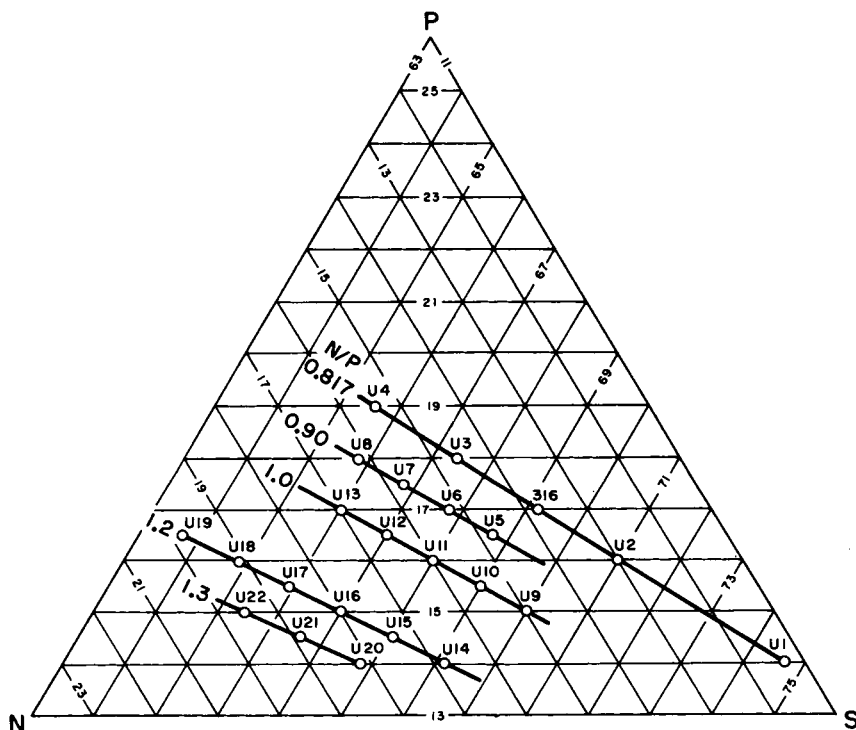

Fig. 1. Polymer (P)–solvent (S)–nonsolvent (N) triangular composition diagram.

TABLE I
List of Casting Solution Compositions Studied

Group no.	Film no.	Casting solution compn., wt-%			S/P	N/P	N/S
		P	S	N			
I	U1	14.0	74.56	11.44	5.33	0.817	0.153
	U2	16.0	70.93	13.07	4.43	0.817	0.184
	316	17.0	69.20	13.80	4.07	0.817	0.201
	U3	18.0	67.29	14.71	3.74	0.817	0.218
	U4	19.0	65.48	15.52	3.50	0.817	0.233
II	U5	16.5	68.65	14.85	4.16	0.90	0.216
	U6	17.0	67.70	15.30	3.98	0.90	0.226
	U7	17.5	66.75	15.75	3.81	0.90	0.236
	U8	18.0	65.80	16.20	3.66	0.90	0.246
III	U9	15.0	70.00	15.00	4.67	1.00	0.214
	U10	15.5	69.00	15.50	4.45	1.00	0.225
	U11	16.0	68.00	16.00	4.25	1.00	0.235
	U12	16.5	67.00	16.50	4.06	1.00	0.246
	U13	17.0	66.00	17.00	3.80	1.00	0.258
IV	U14	14.0	69.20	16.80	4.94	1.20	0.243
	U15	14.5	68.10	17.40	4.70	1.20	0.255
	U16	15.0	67.00	18.00	4.47	1.20	0.268
	U17	15.5	65.90	18.60	4.25	1.20	0.282
	U18	16.0	64.80	19.20	4.05	1.20	0.296
	U19	16.5	63.70	19.80	3.86	1.20	0.310
V	U20	14.0	67.80	18.20	4.84	1.30	0.269
	U21	14.5	66.65	18.85	4.60	1.30	0.283
	U22	15.0	65.50	19.50	4.37	1.30	0.297

data on PWP and PR were essentially the same, and the data on solute separation and PWP were considered to give a measure of the size and number of pores, respectively, on the membrane surface. The reported PWP data are those corrected to 25°C using the viscosity and density data for water.

The NaCl or $MgSO_4$ concentrations in the feed and product solutions were determined by specific resistance measurements using conductivity bridge. Under the experimental conditions used, the correlation between the separation of NaCl and that of $MgSO_4$ for the films tested was as shown in Figure 2. A few ultrafiltration experiments were conducted using organic solutes. In the latter case, a Beckman total carbon analyzer was used for analysis of solutes. The accuracy of solute separation data was within 1%, and that of PWP data was within 3% in all cases.

RESULTS AND DISCUSSION

Casting Solution Compositions

This work involves studies on 23 different casting solution compositions listed in Table I. This list includes the batch-316 composition chosen as the reference one in the earlier study.[1] The above compositions can be divided into five groups as shown in Figure 1. In each group, the N/P ratio is constant. Group I corresponds to an N/P ratio of 0.817, which is the same as that for the batch-316 composition. Groups II, III, IV, and V correspond to N/P ratios of 0.9, 1.0, 1.2, and 1.3, respectively. The composition changes in each group correspond to
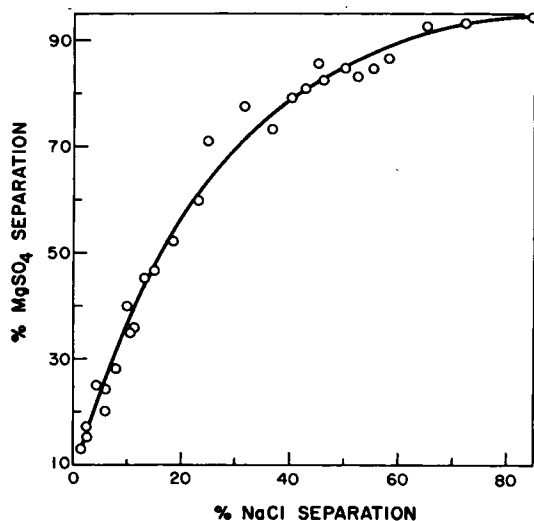
Fig. 2. Correlation of solute separation data for NaCl and MgSO₄ in the operating pressure range of 50 to 100 psig.

different values of S/P and N/S ratios.   From Figures 1 and 3, it is clear that the composition changes from right to left in each group correspond to decreasing values of S/P and increasing values of N/S.   The actual values of S/P and N/S ratios used in the compositions included in all the groups are in the range 3.5 to 5.33 and 0.153 to 0.310, respectively.   Values of S/P and N/P outside the ranges listed in Table I were not used in this work owing to practical difficulties in film making.

Membrane Porosity and Casting Solution Composition Variables

The data on solute separation for sodium chloride and pure water permeation rate at 100 psig obtained with films cast from the casting solution compositions listed in Table I are given in Figure 3.   In these experiments, the temperature of the casting solution was 0°C, the temperature of the casting atmosphere was 20°C, and the solvent evaporation period during film formation was kept at the minimum (2 to 5 sec).   The films were not subjected to any thermal (hot water) shrinkage treatment after gelation.   Because of the very short evaporation period used, the changes in the porous structure of the membrane surface could be considered as essentially due to the changes in the structure or the state of supermolecular polymer aggregation in the casting solution.   Further, since no film shrinkage was involved prior to reverse osmosis experiments, the data on solute separation and PWP given in Figure 3 could be considered respectively to give relative quantitative measures of the average pore size on membrane surface and overall porosity of the membrane in the as-cast condition.

Figure 3 illustrates the effects of S/P, N/P, and N/S ratios on solute separation and PWP.   These data can be analyzed on the same basis as before.[1]   A decrease in solute separation represents an increase in the average pore size on the membrane surface.   For practical purposes, an increase in PWP at a given level of solute separation is considered to represent an effective increase in the number of pores on the membrane surface.
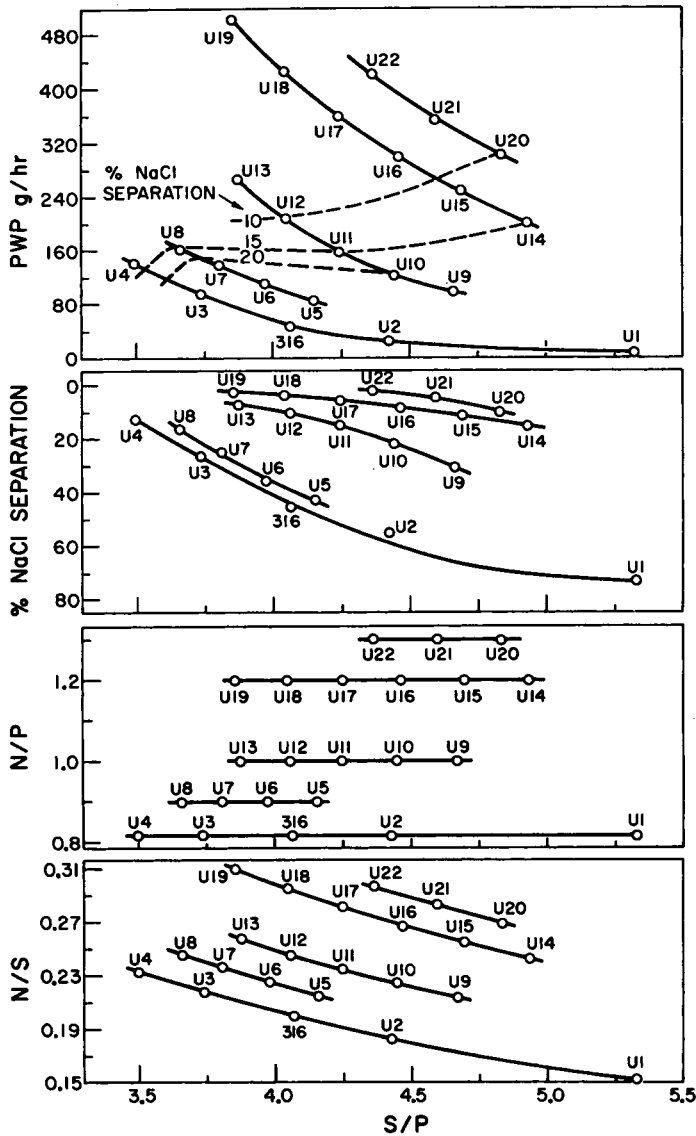
Fig. 3. Effects of S/P, N/P, and N/S ratios in casting solution composition on performance of resulting membranes: temperature of casting solution, 0°C; temperature of casting atmosphere, 20°C; solvent evaporation period, minimum (2 to 5 sec); solute concentration in feed, 200 ppm; operating pressure, 100 psig; effective film area, 13.2 cm².

Figure 3 shows a wide range of solute separations for NaCl (2 to 72%) and PWP data (8 to 500 g/hr). Further, at 10% level of solute separation for NaCl, the corresponding PWP data are in the range 200 to 300 g/hr. These results show that changes in the casting solution structure result in significant changes both in the size and number of pores on the surface of the resulting membranes.

At any given value of N/P, an increase in S/P and decrease in N/S in the casting solution composition tend to increase solute separation and decrease PWP; this means that the above changes tend to decrease the average size of pores on

the membrane surface. These changes are understandable on the basis that increase in S/P and decrease in N/S tend to decrease the size of supermolecular polymer aggregates in the casting solution, which results in the formation of smaller size pores on the membrane surface.[5]

At any given value of S/P, an increase in N/S and an increase in N/P in the casting solution composition tend to decrease solute separation and increase *PWP;* this means that the above changes tend to increase the average size of pores on the membrane surface. These changes are again understandable on the basis that increases in N/S and N/P tend to increase the size of supermolecular polymer aggregates in the casting solution which results in the formation of bigger size pores on the membrane surface.[5-8]

Referring to Figure 3, it can be seen that for the casting solution compositions studied, when S/P is increased keeping N/S constant, solute separation passes through a maximum and the corresponding *PWP* passes through a minimum indicating the effect of two opposing tendencies. This is only to be expected because, at constant N/S, an increase in S/P is also accompanied by an increase in N/P; while the former increase tends to favor the formation of smaller supermolecular polymer aggregates in the casting solution, the latter increase tends to do the opposite.

In making ultrafiltration membranes, one is generally interested in NaCl separations of the order of 10% or less. Figure 3 shows that at 10% level of NaCl separation, *PWP* increases by over 50% by increasing simultaneously the S/P ratio from 4.05 to 4.85, and N/P ratio from 1.0 to 1.3. At 20% and 30% levels of NaCl separations (i.e., with smaller average pore sizes on the membrane surface), similar increases in S/P and N/P result in much less increase in *PWP*. These results are consistant with the concept that increase in S/P tends to increase the number of pores, and increase in N/P tends to increase the size of pores on the surface of the resulting membranes. A smaller size of pores on the membrane surface in the as-cast condition is the result of an increase in the number of supermolecular polymer aggregates for a given polymer concentration in the casting solution.[4-6] An increase in the number of such aggregates also tends to increase the probability of permanent collision of polymer particles[9] in the interdispersed phase during film formation, which in turn tends to reduce the number of pores on the surface of the resulting membranes. This probably explains why the increases in *PWP* at 20% and 30% levels of solute separation are much less than at 10% level of solute separation for similar simultaneous increases in S/P and N/P ratios in the casting solutions.

In the development of ultrafiltration membranes, one is interested in creating not only bigger size of pores on the membrane surface, but also a larger number of such pores for increasing the productivity (i.e., membrane flux at a given level of solute separation) of such membranes. From this point of view, the casting solution compositions included in group IV (N/P = 1.2) and group V (N/P = 1.3) are particularly useful for making ultrafiltration membranes. The membranes made from the above casting solution compositions gave NaCl separations of 2% to 15% and *PWP* values of 200 to 500 g/hr (which correspond to 90 to 224 gal/day-ft² at 100 psig). Since more highly permeable membranes are inevitably more prone to compaction effects,[6] group IV compositions (N/P = 1.2) were considered more suitable for further studies in this work. Further, the available results indicated that the initial rate of compaction passed through a minimum

with increase in S/P ratio in the casting solution composition; among the group IV membranes studied, U17 seemed to exhibit the least initial compaction. Hence U17-composition was chosen for some further studies in this work.

In the rest of this work, reverse osmosis experiments were conducted at 50 psig using 200 ppm $MgSO_4-H_2O$ as the feed solution for the following reasons. At 50 psig, membrane compaction effects were much less; with $MgSO_4-H_2O$ feed solutions, solute separations obtained were sufficiently high so that changes in experimental solute separation data could be determined more accurately.

Effect of Film Shrinkage in Hot Water on
Porous Structure of the Membrane

Figure 4 shows data on solute separation and the corresponding PWP, and temperature of hot water during film shrinkage (shrinkage temperature) for the films U22, U17, U12, U8, and U6 cast under conditions specified in the previous section. The data show that with increase in shrinkage temperature, solute separation increased and PWP decreased with respect to films U22, U17, and U12. With respect to the other two films (U8 and U6), however, PWP decreased
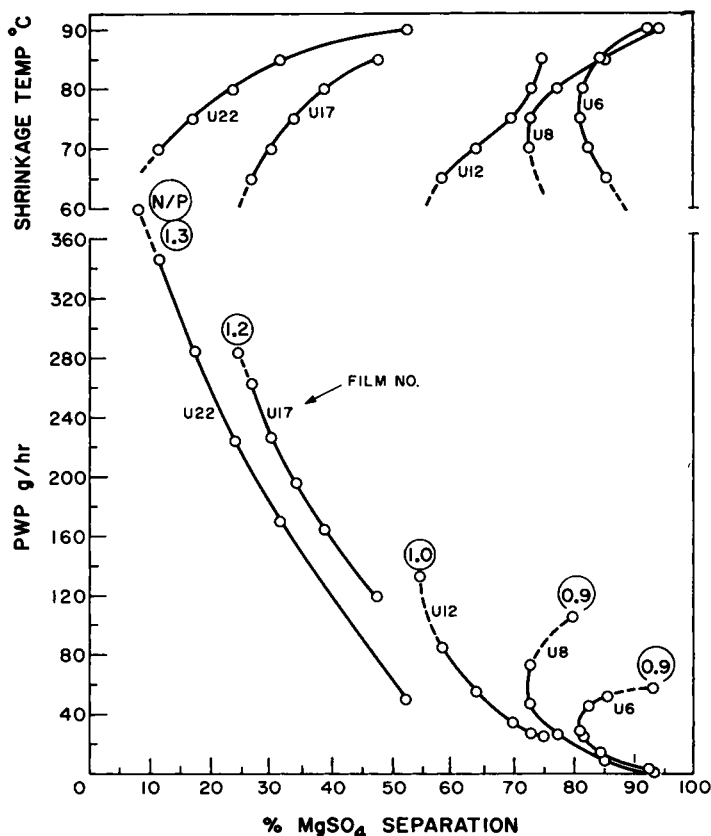

Fig. 4. Effect of film shrinkage in hot water on porous structure of membrane surface: temperature of casting solution, 0°C; temperature of casting atmosphere, 20°C; solvent evaporation period, minimum (2 to 5 sec); solute concentration in feed, 200 ppm; operating pressure, 50 psig; effective film area, 13.2 cm².

but solute separation passed through a minimum with increase in shrinkage temperature. The former data (those for films U22, U17, and U12) are readily understood since the introduction of thermal energy tends to bring the polymer segments closer together and thus reduce the average size of pores on the membrane surface. The latter data (those for films U8 and U6) indicate the simultaneous effect of two changes. As Kesting points out,[6] these changes could arise from the growth of crystallite size from paracrystalline nodules to microcrystallites. The above growth disrupts the uniformity of crystallite spacing and also reduces the effective diameter of interlamellar channels.

A decrease in solute separation during hot water treatment has been attributed to the disruption of the uniformity of crystallite spacings.[6] Consequently, one may conclude that while both the effects occur simultaneously for all the membranes during hot water treatment, the effect of disruption in the uniformity of crystallite spacings seems more evident with membranes obtained from casting solutions containing relatively smaller size of supermolecular polymer aggregates. Also, the initial decrease in solute separation and PWP on thermal shrinkage could be simply due to closing of the very small pores present on the membrane surface in the as-cast condition.

Effect of Casting Conditions on the Performance of U17 Membranes

Using U17-casting solution composition (Table I), three sets of films were cast under the casting conditions given by the temperature of casting solution (°C)/temperature of casting atmosphere (°C) combinations of 0/20, 10/30, and 20/40. Under each one of the above set of conditions, the effect of variation of solvent evaporation period (in the range of minimum (2 to 5 sec) to 120 sec) on membrane performance (i.e., solute separation and PWP) in the as-cast condition was investigated. The results obtained are given in Figure 5.

Figure 5 shows that under each one of the above three sets (0/20, 10/30, and 20/40) of casting conditions, PWP increased and solute separation decreased with increase in evaporation period up to a time after which PWP decreased and solute separation showed a tendency to increase with further increase in evaporation period. For all the three sets of casting conditions, solute separation was minimum and PWP was maximum at the solvent evaporation period of $\sim$50 sec. These results are consistent with the effect of solvent evaporation period on pore formation and development on membrane surface discussed earlier.[5] The data show that the effect of droplet growth in the interdispersed phase during film formation is predominent in the first 50 sec, after which the simultaneous effect of pore depletion by droplet coalescence and partial surface shrinkage begin to control membrane performance.

Figure 5 also shows that for a given evaporation period, solute separation is more and PWP is less for a membrane obtained under the casting conditions given by higher values for temperature of casting solution and temperature of casting atmosphere. Such higher values tend to decrease the size of supermolecular polymer aggregates in the casting solution and at the same time increase the solvent evaporation rate during film formation. The increase in solute separation referred above could be attributed to the formation of smaller size pores as a result of lesser supermolecular polymer aggregation in the casting solution. The decrease in productivity (i.e., decrease in PWP at a given level of solute separation) could be attributed to the effect of increased droplet
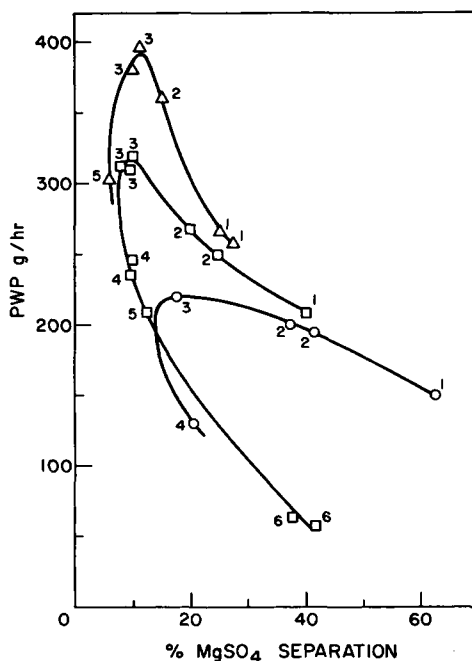
Fig. 5. Effects of casting conditions on performance of U17 membranes. Temperature (°C) of casting solution/temperature (°C) of casting atmosphere: (△) 0/20; (□) 10/30; (○) 20/40. Solvent evaporation period: (1) 5 sec; (2) 30 sec; (3) 50 sec; (4) 80 sec; (5) 90 sec; (6) 120 sec. Solute concentration in feed, 200 ppm; operating pressure, 50 psig; effective film area, 13.2 cm².

coalescence in the interdispersed phase during film formation caused by the casting solution structure at higher temperature and to the higher solvent evaporation rate under the film-casting conditions used.[5] Further, the available PWP data also showed that compaction effect was less severe with membranes obtained with longer evaporation period than with those obtained with minimum evaporation period.

A Continuous Test Run

The productivities of all the three sets (0/20, 10/30, and 20/40) of membranes obtained from the U17 casting-solution composition with ~50-sec solvent evaporation period, shown in Figure 5, are probably sufficiently good for many ultrafiltration applications. Among the above three sets of films tested, the productivities are in the order film U17(0/20)>film U17(10/30)>film U17-(20/40); their susceptibilities for compaction under conditions of continuous operation may also be expected to be in the same order. For practical purposes, one may like to choose a membrane which has a higher productivity and at the same time less susceptibility for compaction. From this point of view, the film U17(10/30), with ~50-sec evaporation period, may be considered to be an appropriate one for practical use. A set of these latter films (including an unshrunk film and a set of films preshrunk at 65°, 75°, 80°, and 85°C) were subjected to a continuous test run at 50 psig for a period of 250 hr using pure water as the feed fluid. Data on PWP obtained as a function of time are shown in Figure
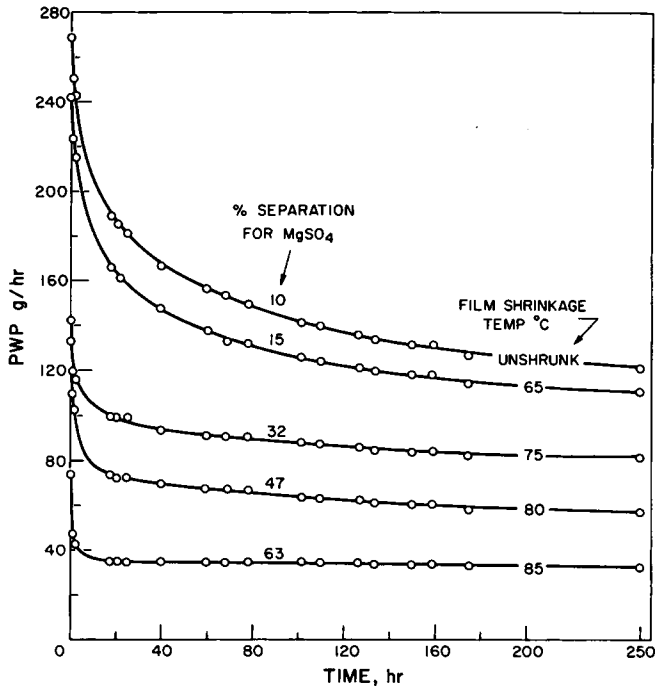
Fig. 6. Results of continuous test run with U17 membranes: temperature of casting solution, 10°C; temperature of casting atmosphere, 30°C; solvent evaporation period, 50 sec; solute concentration in feed, 200 ppm; operating pressure, 50 psig; effective film area, 13.2 cm².

6. These data show that all the membranes tested were subject to significant compaction even at an operating pressure of 50 psig. The as-cast (not heat treated) membrane was more slow in its tendency to reach steady state flux than the other heat treated membranes. At the end of 250 hr of continuous operation at 50 psig, the membrane flux was about 40% or more of the initial flux for all the membranes tested; solute separations for $MgSO_4$ at 50 psig were 10%, 15%, 32%, 47%, and 63%, respectively, for the unshrunk membrane and other membranes preshurnk at 65°, 75°, 80°, and 85°C. The corresponding pure water fluxes were 54.6, 49.2, 37.2, 25.5, and 14.3 gallons/day-ft² at 50 psig. The foregoing data on solute separation for $MgSO_4$ and pure water flux indicate that the above membranes could be useful for many ultrafiltration applications.

Some Ultrafiltration Experiments

Using the U17(10/30) membranes with about 50-sec solvent evaporation period during film formation, separation data were obtained at 50 psig for a set of membranes including one unshrunk and four preshrunk membranes. The aqueous feed solution contained 50 to 1000 ppm of one of the following solutes: sodium chloride, magnesium sulfate, sucrose, raffinose, dextran, bacitracin, cytochrome C, pepsin, insulin, pectin, and γ-globulin. These solutes involve a molecular weight range of 58 to 160,000. Table II gives the data obtained on solute separation. The results show that cytochrome C and γ-globulin are essentially completely separated by the unshrunk membrane; a membrane preshrunk in hot water at 75°C separates essentially completely dextran and pectin in addition to

TABLE II
Data on Solute Separation at 50 psig Given by Ultrafiltration
Membranes Obtained from U17 Casting-Solution Composition[a]

Solute			Solute separation, %				
Name	Molecular weight	Concn. in feed, ppm	85°C[b]	80°C[b]	75°C[b]	65°C[b]	Un-shrunk
NaCl	58.5	200	23	13	7	6	5
MgSO₄	264.5	200	59	44	23	23	17
Sucrose	342.3	1000	28	14	9	8	8
Raffinose	594.5	1000	32	18	8	6	6
Dextran	1370	1000	100	100	100	99	99
Bacitracin	1400	1000	63	27	16	9	8
Cytochrome C	12384	50[c]	100	100	100	100	100
Pepsin	35000	1000	61	40	34	33	31
Insulin	36000	800[d]	99	35	21	18	17
Pectin		1000	100	100	100	98	97
γ-Globulin	160000	50	100	100	100	100	100

[a] Film-casting conditions: temperature of casting solution, 10°C; temperature of casting atmosphere, 30°C; solvent evaporation period during film formation, 50 sec.

[b] Film shrinkage temperature.

[c] A visible film was formed on the membrane surface; the film could be removed easily.

[d] International units per liter.

cytochrome C and γ-globulin. The other solutes listed above are separated to different extents by the membranes used. The results illustrate that solute separation depends both on the chemical nature and molecular weight of the solute for a given membrane; further, there is no necessary correlation between molecular weight of solute and its separation in the ultrafiltration experiments. It has already been established[10] that with a given average pore size on the membrane surface, solute separation in reverse osmosis is a function of the chemical nature (polar, nonpolar, and steric character) of both the solute and membrane material. It is hence best to consider ultrafiltration membranes simply as reverse osmosis membranes with relatively bigger average size of pores on the membrane surface, the dividing line between the range of pores sizes involved being entirely arbitrary.

CONCLUSIONS

This work confirms the conclusions stated earlier on the validity and utility of the solution structure—evaporation rate approach to the development of cellulose acetate ultrafiltration membranes. By adjusting the values of S/P and N/P ratios in the casting solution composition, temperature of the casting solution and that of the casting atmosphere, and solvent evaporation period during film formation, a wide variety of cellulose acetate membranes useful for both ultra-filtration and reverse osmosis applications can be obtained. The actual choice of film-casting conditions for any specific application would depend upon the pore size requirement and compaction tolerance during operation. The principles developed for the creation of cellulose acetate membranes for ultrafiltration and reverse osmosis applications in this and the earlier studies[1–5] offer a reasonable basis for the creation of other cellulosic membranes for similar applications.

References

1. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **18**, 3423 (1974).
2. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 723 (1970).
3. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 1983 (1970).
4. B. Kunst and S. Sourirajan, *J. Appl. Polym. Sci.*, **14**, 2559 (1970).
5. L. Pageau and S. Sourirajan, *J. Appl. Polym. Sci.*, **16**, 3185 (1972).
6. R. E. Kesting, *Synthetic Polymeric Membranes*, McGraw Hill, New York, 1971, Chap. 5.
7. R. E. Kesting, *J. Appl. Polym. Sci.*, **17**, 1771 (1973).
8. A. S. Michaels, Proc. Conference on Reverse Osmosis and Ultrafiltration, Chemical Center, Lund University, Alnarp, Sweden, May 17, 1971.
9. H. K. Johnston and S. Sourirajan, *J. Appl. Polym. Sci.*, **17**, 3717 (1973).
10. S. Sourirajan and T. Matsuura, Proc. Symp. on Membranes in Separation Processes, Case Western Reverse University, Cleveland, Ohio, May 8–10, 1973, pp. 24–36.