

Improvement of Porous Cellulose Acetate Reverse Osmosis Membranes by Change of Casting Conditions

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Synopsis

The effects of temperature of casting solution in the range -10° to 15°C , that of casting atmosphere in the range 10° to 30°C , relative humidity of casting atmosphere in the range 35% to 75%, and solvent evaporation period in the range 0.5 to 3 min were studied on shrinkage temperatures, solute separations, and product rates of Loeb-Sourirajan-type cellulose acetate membranes in reverse osmosis experiments. The composition of casting solution used was as follows: cellulose acetate, 17; acetone, 69.2; magnesium perchlorate, 1.45; and water, 12.35 wt-%. Best performance was obtained with membranes cast under the following conditions: temperature of casting solution, 10°C ; temperature of casting atmosphere, 30°C ; relative humidity of casting atmosphere, 65%; and solvent evaporation period, 1 min. For a 90% level of solute separation, the productivities of the above type of membranes were 22.9, 61.4, and 64.5 gallons/day-ft² at 250, 600, and 1500 psig using 3500 ppm NaCl-H₂O, 5000 ppm NaCl-H₂O, and 28395 ppm NaCl-H₂O feed solutions, respectively. In all cases, the feed flow rates corresponded to a mass transfer coefficient of 45×10^{-4} cm/sec on the high-pressure side of the membrane. The general specifications of the above type of membranes are given for the operating pressures of 250, 600, and 1500 psig. The effects of the above casting condition variables on the surface pore structure during film formation are discussed.

INTRODUCTION

The importance of casting conditions for improving the productivity and performance of Loeb-Sourirajan-type cellulose acetate membranes for reverse osmosis applications has been discussed and illustrated.¹⁻⁵ The above work led to a new approach to the problem of developing more productive membranes. In this approach, the state or the structure of the casting solution and the rate of solvent evaporation during film formation together constitute an important interconnected variable governing the ultimate porous structure and hence the performance of the resulting membranes. The term "solution structure" essentially refers to the state of supermolecular polymer aggregation in the casting solution, and it is a function of the composition and temperature of the casting solution. For a casting solution of given composition, supermolecular aggregation in the polymer solution is decreased by an increase in the temperature of the solution. Solvent evaporation rate during film formation refers to the rate of solvent removal from the surface which ultimately forms the dense

microporous layer in the resulting asymmetric porous membrane. The above rate is a function of solution structure, temperature of the casting atmosphere, and the ambient nature of the casting atmosphere, including humidity. The evaporation rate may be expressed quantitatively by a constant b , which is the initial slope of the log of solvent loss-versus-time (evaporation period) curve.² Both the solution structure and the evaporation rate constant are independent of solvent evaporation period. The latter is another variable in the specification of film-casting conditions because solvent evaporation period affects shrinkage temperature profile⁴ (solute separation-versus-shrinkage temperature correlation) which has been shown to be an important quality control parameter governing membrane development.²

The foregoing considerations point out that membranes of different surface pore structures can be obtained with a casting solution of given composition by changing the following casting condition variables: temperature of the casting solution and that of the casting atmosphere, humidity of the casting atmosphere, and solvent evaporation period. The object of this work is to explore the possibility of improving the productivity and performance of the Loeb-Sourirajan-type cellulose acetate membranes by appropriate choice of the above casting condition variables using a casting solution of the same composition.

As in previous papers,¹⁻⁵ the data are interpreted on the basis of surface pores and their number, size, and size distribution. There is no precise way of determining either the size of individual pores on the membrane surface or the thickness of the surface layer of the porous asymmetric membrane. Hence, for practical purposes, a smaller difference in shrinkage temperatures for a given range of solute separation is considered to represent a more uniform distribution of available pores and, for a given level of solute separation, a higher shrinkage temperature and a higher product rate are considered to represent a relatively bigger average size of the available pores and a larger number of such pores respectively on the membrane surface in the as-cast condition.

EXPERIMENTAL

The general experimental details are the same as those reported earlier.¹⁻⁵ The composition (wt-%) of the casting solution used in all cases was the same, as follows: cellulose acetate (Eastman 398-3), 17; acetone, 69.2; magnesium perchlorate, 1.45; and water, 12.35. This composition is the same as that used earlier for casting batch 316-type films.⁴ Consequently, all films used in this work are designated as batch 316-type films. Wherever necessary, the temperature (in °C) of the casting solution and that of the casting atmosphere are indicated in brackets. For example, the batch number 316 (10/30) represents films cast under conditions when the temperature of the casting solution and that of the casting atmosphere were 10° and 30°C, respectively. In all, 32 different sets of films were made

under different casting conditions involving temperatures of the casting solution in the range -10° to 15°C , temperatures of the casting atmosphere in the range 10° to 30°C , relative humidities of the casting atmosphere in the range 35% to 75%, and solvent evaporation periods in the range 0.5 to 3 min. Unless otherwise stated, the solvent evaporation period during film formation was 1 min. Ice-cold water was used for final gelation in all cases.

All the films were cast in a constant temperature-constant humidity room. The data on evaporation rate constants were obtained as before² by casting the films in small plates under the same casting conditions as those used for making films for use in reverse osmosis experiments. The temperatures on the membrane surface during film formation were also measured as before⁶ in separate experiments. Reverse osmosis data on membrane performance (solute separation and product rate) were obtained for conditions of feed concentration and feed flow rate (~ 400 cc/min) corresponding to a mass transfer coefficient $k = 45 \times 10^{-4}$ cm/sec on the high-pressure side of the membrane using aqueous sodium chloride feed solutions. Experiments at 250, 600, and 1500 psig were carried out with feed solutions containing sodium chloride in the amounts of 3500, 5000, and 28395 ppm (0.5M), respectively. All experiments were carried out at the laboratory temperature (23° - 25°C). Each film was subjected to a pure-water pressure treatment for 1 to 2 hr at 300, 700, or 1700 psig prior to subsequent reverse osmosis experiments at 250, 600, or 1500 psig, respectively. In all cases, the terms "product" and "product rate" refer to membrane-permeated solutions. Unless otherwise stated, all product rate data are for 7.6 cm² of effective membrane area, and the experiments were of the short-run type, each lasting for about 2 hr.

For salt concentrations of less than 5000 ppm, a conductivity bridge was used for analysis; for higher salt concentrations, a Bausch and Lomb refractometer was used for analysis. The fraction solute separation f was calculated from the relation

$$f = \frac{\text{solute concn. in feed (ppm)} - \text{solute concn. in product (ppm)}}{\text{solute concn. in feeds (ppm)}}$$

Data on product rates were obtained by direct weighing of samples. The reproducibilities of solute separation and product rate data were within 1% and 3%, respectively.

RESULTS AND DISCUSSION

Data on Film-Casting Conditions and Membrane Performance

Using different combinations of temperature of casting solution (in the range -10° to 15°C) and temperature of casting atmosphere (in the range 10° to 30°C), 19 sets of films were made. The relative humidity of 55% and the solvent evaporation period of 1 min were held constant under the casting conditions in all cases. Figure 1 gives the solute separation-versus-

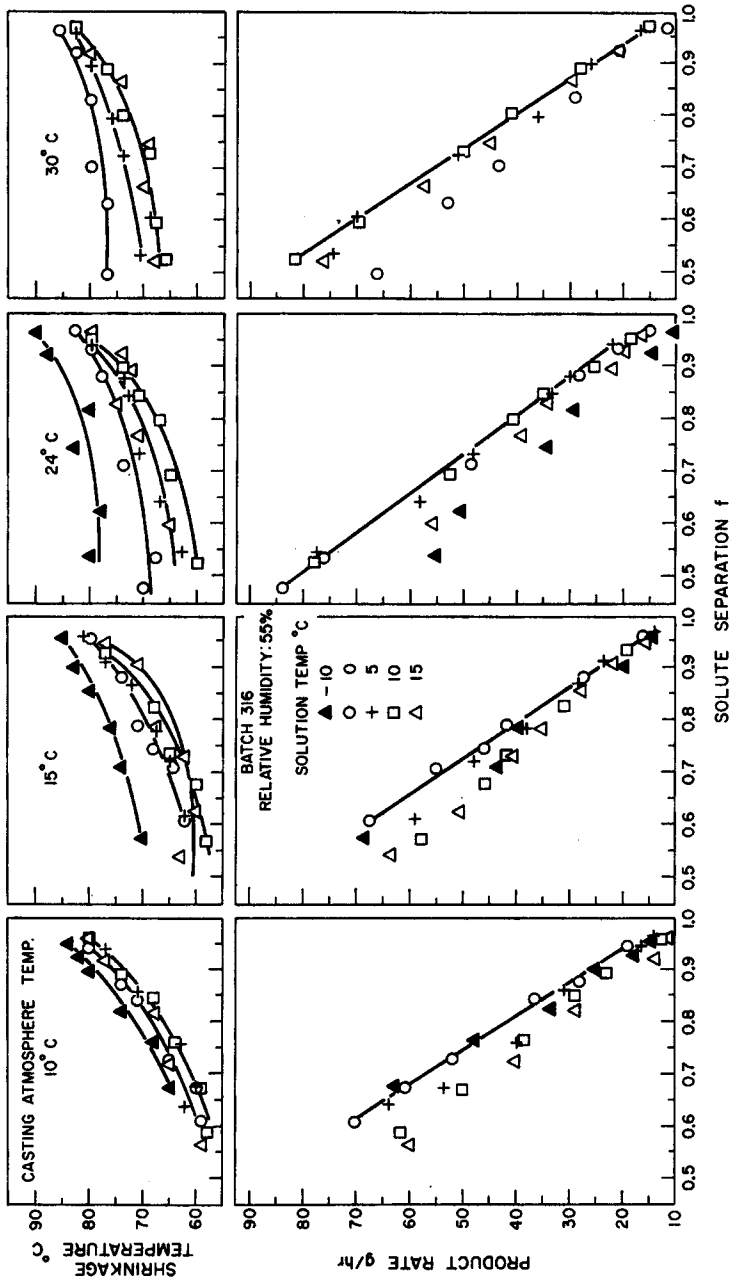


Fig. 1. Effects of temperature of casting solution and temperature of casting atmosphere on membrane performance and shrinkage temperature profile: evaporation period, 1 min; membrane area, 7.6 cm²; solution system, NaCl-H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig

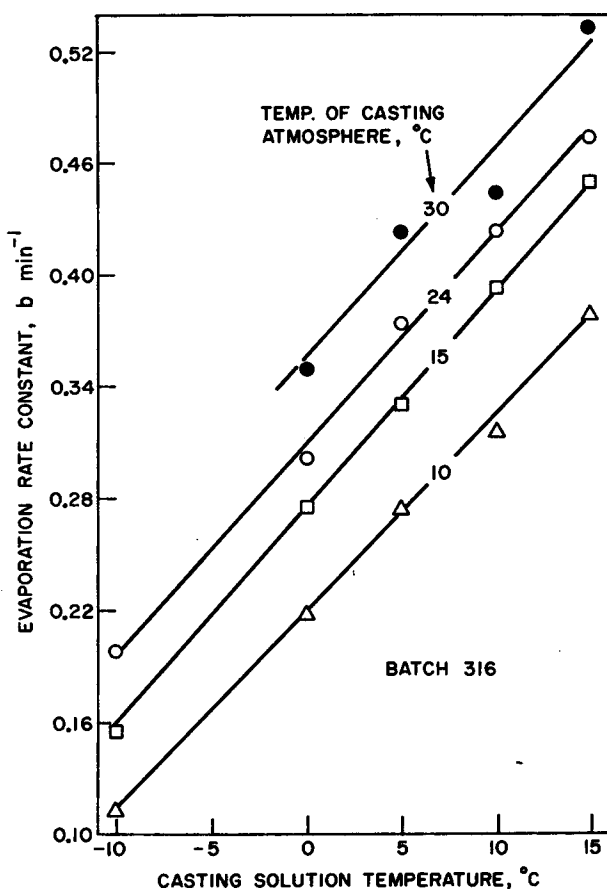


Fig. 2. Effect of temperature of casting solution and temperature of casting atmosphere on evaporation rate constant: Relative humidity, 55%.

product rate and shrinkage temperature correlations obtained with the above films in reverse osmosis experiments at 250 psig using 3500 ppm NaCl-H₂O feed solutions. Figure 2 gives data on the evaporation rate constant b (min⁻¹) corresponding to each casting condition employed. Figure 3 gives data on the temperature of the film surface during film formation at the 1-min solvent evaporation period, i.e., at the time just before gelation in ice-cold water.

Data on Shrinkage Temperature Profile and Membrane Productivity

Figure 1 shows that at any given temperature of the casting atmosphere, the relative location of the shrinkage temperature profile is lowered by an increase in the temperature of the casting solution in the range -10° to 10°C. These data confirm the observation made earlier^{1,4} that lower supermolecular polymer aggregation in the casting solution gives rise to smaller-size pores on the resulting membrane surface. Figure 1 also shows

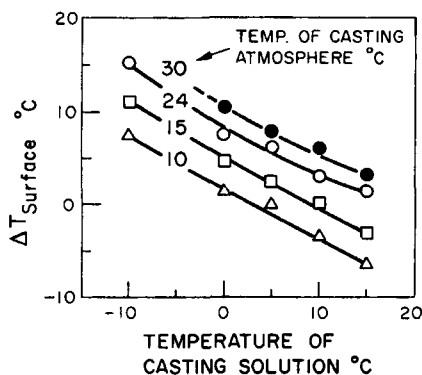


Fig. 3. Effects of temperature of casting solution and temperature of casting atmosphere on the temperature of the membrane surface during film formation: Film type, batch 316; evaporation period, 1 min; $\Delta T_{\text{surface}}$ is difference between temperature of film surface and the initial temperature of casting solution; relative humidity, 55%.

that for each temperature of the casting atmosphere there is a particular temperature of the casting solution which results in maximum product rate for any given level of solute separation, under otherwise identical experimental conditions of film casting and reverse osmosis operation. For example, when the temperature of the casting atmosphere was 10°, 15°, 24°, or 30°C, maximum membrane productivity for the widest range of solute separations was obtained when the temperature of the casting solution was 0°, 0° (or -10°), 5° (or 0°) and 10°C, respectively. At levels of solute separation greater than 80% (which are of more practical interest in reverse osmosis operations), the temperature of casting solution (°C)/temperature of casting atmosphere (°C) combinations corresponding to maximum productivity were 0/10, 0/15, 5/24, and 10/30. Further, the maximum productivity corresponding to each temperature of casting solution/temperature of casting atmosphere combination was different. These data support the basic contention of the solution structure- evaporation rate concept, namely that, from the point of view of membrane productivity, the temperature of the casting solution and that of the casting atmosphere together constitute a single interconnected variable governing the ultimate porous structure of the resulting membranes.

Data on Evaporation Rate Constants and Membrane Productivity

Figure 2 shows that the evaporation rate constant b increased both with increase in the temperature of the casting solution and with increase in the temperature of the casting atmosphere. Thus, both lower supermolecular polymer aggregation in the casting solution as well as a higher temperature of the casting atmosphere tend to increase b . At any given temperature of the casting solution, the average increase in b per degree rise in the temperature of the casting atmosphere was 0.0068; and, at any given temperature of the casting atmosphere, the average increase in b per

degree rise in the temperature of the casting solution was 0.0113. These data show that the evaporation rate constant is far more sensitive to changes in the temperature of the casting solution (and hence changes in the structure of the casting solution) than that of the casting atmosphere.

Figure 4 gives data on membrane productivity as a function of temperature of casting solution and the evaporation rate constant b . The figure shows that product rate either decreases, increases, remains the same, or passes through a maximum with increase in the value of b ; and all the data, taken together, do not lead to a generally valid deduction on the effect of b on product rate. These results are not surprising in view of the fact that while the product rate depends on evaporation time, b is independent of such time. The optimum evaporation period for maximum membrane productivity could be different for different combinations of temperature of casting solution and temperature of casting atmosphere, and b -versus-product rate correlation could be meaningful only for data on membrane productivity at optimum evaporation period. All the product rate data plotted in Figure 4 are for a constant evaporation period of 1 min which was found to be optimum for the casting solution temperature of 5°C in the particular range of b values studied. Considering the latter data only, Figure 4 shows that product rate passes through a maximum with increase in the value of b , confirming the deduction made earlier^{1,2,4} that there exists an optimum value of b for maximum membrane productivity. The data also indicate that the above optimum value of b is not necessarily the same for different levels of solute separation even for the same casting solution structure.

All data presented in Figure 4 illustrate that several unique combinations of the temperature of casting solution and temperature of casting atmosphere yield the same product rate at any given level of solute separation. These results indicate the existence of competing effects on pore formation, development, and depletion during the processes of film formation and film shrinkage.

Data on Temperature of Casting Solution on Film Surface

The temperature on the film surface during film formation immediately after casting depends on the initial temperature of the casting solution, the temperature and humidity of the casting atmosphere, and the time elapsed after casting.⁶ Consequently, at any given time after casting, the temperature on the film surface may be greater than, equal to, or less than the initial temperature of the casting solution, depending on casting conditions. This is illustrated by the data in Figure 3, which shows the difference between the temperature of the film surface and the initial temperature of the casting solutions ($\Delta T_{\text{surface}}$) 1 min after casting under the conditions used for making films whose performance data are given in Figure 1.

Since supermolecular polymer aggregation in solution is sensitive to changes in the temperature of the solution, it is only reasonable to expect

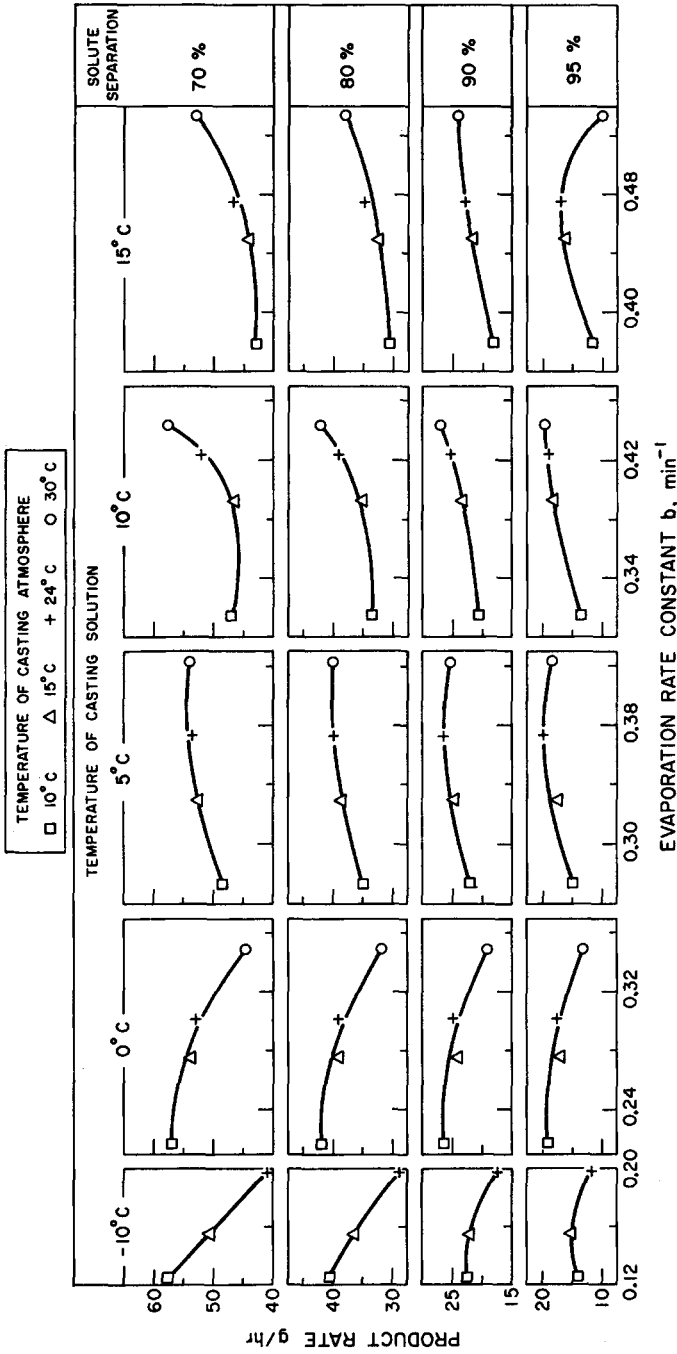


Fig. 4. Effect of evaporation rate constant on membrane performance: film type, batch 316; relative humidity, 55%; evaporation period, 1 min; membrane area, 7.6 cm²; solution system, NaCl-H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

that the temperature on the film surface will have an effect on the local disposition of polymer aggregation on the film surface. For example, when the temperature of the casting solution on the film surface is higher than the initial temperature of the casting solution, a break in polymer aggregation may be expected to occur on the film surface, which may give rise to a larger number of nuclei for droplet formation and development in the interdispersed phase. It was pointed out earlier that when the temperature of the casting atmosphere was 10°, 15°, 24°, or 30°C, maximum membrane productivity was obtained when the temperature of the casting solution was 0°, 0°, 5°, and 10°C, respectively. Figure 3 shows that, under the above film-casting conditions, the difference between the temperature of film surface and the initial temperature of the casting solution was positive in all cases. These results seem to point out that, during film formation, a temperature of the film surface higher than the initial temperature of the casting solution is a necessary (but not a sufficient) condition for maximum membrane productivity.

Effect of Temperature of Casting Solution and That of Casting Atmosphere on Pore Structure on Membrane Surface

The data on shrinkage temperature profile and membrane performance given in Figure 1 offer a basis for an understanding of the relative effects of temperature of casting solution and temperature of casting atmosphere

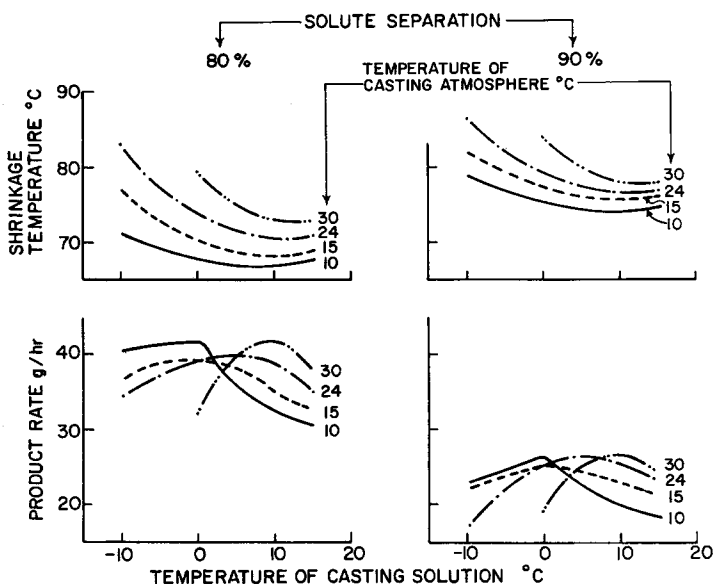


Fig. 5. Effects of temperature of casting solution and temperature of casting atmosphere on product rate and shrinkage temperature for 80% and 90% levels of solute separation: film type, batch 316; relative humidity, 55%; evaporation period, 1 min; membrane area, 7.6 cm²; solution system, NaCl-H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

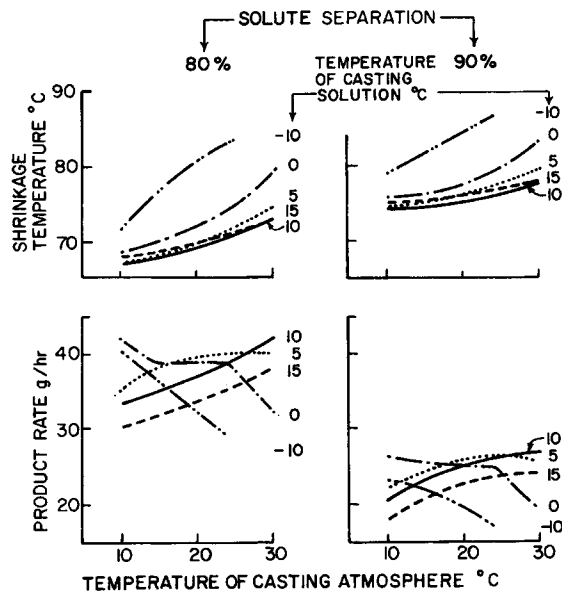


Fig. 6. Effects of temperature of casting atmosphere and temperature of casting solution on product rate and shrinkage temperature for 80% and 90% levels of solute separation: film type, batch 316; relative humidity, 55%; evaporation period, 1 min; membrane area, 7.6 cm²; solution system, NaCl-H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

on the average size and number of pores on the surface of resulting membranes. For such an understanding, it is helpful to consider the variations in shrinkage temperature and product rate brought about by changes in the temperature of the casting solution and that of the casting atmosphere to yield a given level of solute separation under otherwise identical experimental conditions of film casting and reverse osmosis operation. For purposes of illustration and discussion, such data relating to 80% and 90% levels of solute separation were obtained from Figure 1 and replotted in Figures 5 and 6.

The changes in the shrinkage temperature and product rate brought about by changing the temperature of the casting solution when the temperature of the casting atmosphere was held constant are shown in Figure 5 and those brought about by changing the temperature of the casting atmosphere when the temperature of the casting solution was held constant are shown in Figure 6. Figures 5 and 6 express the same data in different forms.

At any given temperature of the casting solution, the shrinkage temperature increased with increase in the temperature of the casting atmosphere. Therefore, a higher temperature of the casting atmosphere tends to increase the average size of pores on the membrane surface in the as-cast condition. A higher average size of pores on the membrane surface may be due to a higher rate of droplet formation and growth and/or droplet

coalescence in the interdispersed phase during film formation; the former should result in a larger number of pores and hence higher productivity, and the latter should result in a smaller number of pores and hence lower productivity. Both the above effects on productivity were observed under different film-casting conditions. For example, when the temperature of the casting solution was 0°C, an increase in the temperature of the casting atmosphere from 10° to 30°C decreased the product rate from 42.0 to 32.0 g/hr (for the 7.6 cm² area of the film used) at the 80% level of solute separation, and from 26.5 to 19.5 g/hr at the 90% level of solute separation. On the other hand, when the temperature of the casting solution was 10°C, the corresponding product rates increased from 32.5 to 42.0 g/hr at the 80% level of solute separation and from 20 to 27 g/hr at the 90% level of solute separation. These data show that a higher temperature of the casting atmosphere, and hence a higher evaporation rate constant, favors both droplet formation and growth and droplet coalescence in the interdispersed phase during film formation.

At any given temperature of the casting atmosphere in the range 10° to 30°C, the shrinkage temperature passed through a minimum and the corresponding product rate passed through a maximum with increase in the temperature of the casting solution. These data illustrate the opposing effects of pore generation by droplet formation and growth and pore depletion by droplet coalescence resulting from lower supermolecular polymer aggregation in the casting solution. The above minima in shrinkage temperature and maxima in product rate did not necessarily coincide, and the absolute values for the maxima in product rates were not necessarily the same for all casting conditions studied. These data show that the processes of pore generation and pore depletion are mutually independent.

Referring to data corresponding to the casting atmosphere temperature of 10°C, an increase in the temperature of the casting solution from -10° to 0°C decreased the shrinkage temperature from 71.5° to 68°C and increased the product rate from 40.5 to 42 g/hr at the 80% level of solute separation; at the 90% level of solute separation, the shrinkage temperature decreased from 79° to 75.5°C, and the product rate increased from 23 to 26.5 g/hr under the above conditions. These data show that a lower supermolecular polymer aggregation in the casting solution tends to generate a larger number of smaller-size pores on the membrane surface in the as-cast condition, and when the temperature of the casting solution increased from -10° to 0°C, the process of pore depletion was more than compensated by the process of pore generation so that a net increase in the number of pores on the film surface occurred during film formation. Under the above film-casting conditions, the difference between the temperature of the casting solution on the film surface and the initial temperature of the casting solution ($\Delta T_{\text{surface}}$) decreased from 7.5 to 0.6°C (Fig. 3). These data show that high positive values of $\Delta T_{\text{surface}}$ may tend to favor droplet coalescence and pore depletion on membrane surface during film formation.

When the temperature of the casting solution was increased from 0° to 10°C, the shrinkage temperature decreased from 68° to 67°C, and the product rate also decreased from 42 to 32.5 g/hr at the 80% level of solute separation; at the 90% level of solute separation, the shrinkage temperature decreased from 75.5°C to 74°C and the product rate decreased from 26.5 to 20 g/hr under the same conditions. These data indicate a reduction in both the number and the average size of pores on the membrane surface in the as-cast condition. Under the above film-casting conditions, $\Delta T_{\text{surface}}$ decreased from 0.6° to -3.5°C (Fig. 3), indicating that the reduction in the number of pores formed was probably due to polymer reaggregation, and the consequent reduction in the nuclei for droplet formation, on the membrane surface due to low surface temperatures.

When the temperature of the casting solution was increased from 10° to 15°C, the shrinkage temperature increased from 67° to 68°C, and the product rate further decreased from 32.5 to 30.5 g/hr at the 80% level of solute separation; at the 90% level of solute separation, the shrinkage temperature increased from 74° to 75°C, and the product rate decreased from 20 to 18 g/hr. These data indicate the formation of a still smaller number of slightly larger-size pores on the membrane surface in the as-cast condition. Under the above film-casting conditions, $\Delta T_{\text{surface}}$ decreased further from -3.5° to -6.5°C, which supports the concept that negative values of $\Delta T_{\text{surface}}$ decrease the number of pores on the film surface due to polymer reaggregation caused by lower surface temperatures.

Referring to data corresponding to the casting atmosphere temperatures of 15°, 24°, and 30°C, the shrinkage temperature was minimum when the temperature of the casting solution was 10°C, indicating that the latter temperature was critical for the particular casting solution composition and the range of the temperature of the casting atmosphere studied.

Any increase in the temperature of the casting solution above 10°C decreased membrane productivity at the temperature of the casting atmosphere in the range 10° to 30°C. These data show that at temperatures higher than 10°C, the supermolecular polymer aggregation in the casting solution used was so low that the consequent high initial density of droplets in the interdispersed phase during film formation was also simultaneously accompanied by too high a rate of droplet coalescence, resulting finally in a smaller number of pores on the membrane surface. Therefore, one may conclude that while a lower supermolecular polymer aggregation in the casting solution is desirable to obtain a larger number of smaller-size pores, too low a supermolecular aggregation may promote excessive droplet coalescence and result ultimately in a smaller number of pores and hence is not desirable from the point of view of maximum membrane productivity.

The combinations of data on temperature (°C) of casting solution/temperature (°C) of casting atmosphere for maximum membrane productivity, namely 0/10, 0/15, 5/24, and 10/30, show a discernible tendency that when the temperature of the casting atmosphere is increased, the re-

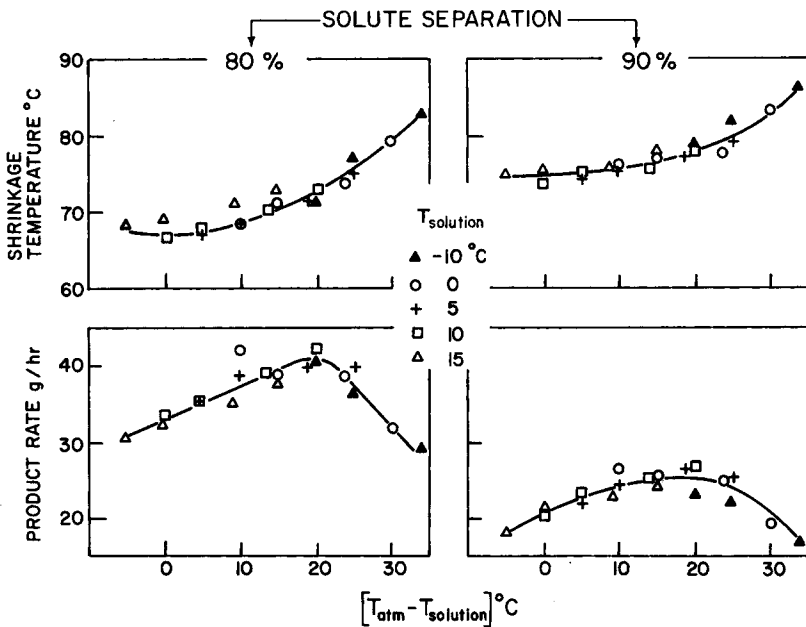


Fig. 7. Effect of difference between temperature of casting atmosphere (T_{atm}) and that of casting solution ($T_{solution}$) or product rate and shrinkage temperature for 80% and 90% levels of solute separation: film type, batch 316; relative humidity, 55%; evaporation period, 1 min; membrane area, 7.6 cm²; solution system, NaCl-H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

quired temperature of the casting solution is also increased. This tendency would indicate that, from the point of view of maximum membrane productivity, the difference between the temperature of the casting atmosphere and that of the casting solution has an even greater practical significance than the above individual temperatures. This is clearly illustrated in Figure 7, which gives the correlations of the difference between the temperature of the casting atmosphere and that of the casting solution versus product rate and shrinkage temperature for 80% and 90% levels of solute separation. These correlations point out that for all temperatures of the casting solution in the range -10° to 15°C , the temperature of the casting atmosphere must be 10° to 25°C (or roughly about 20°C) higher than that of the casting solution for maximum membrane productivity. The latter corresponded neither to the lowest nor the highest shrinkage temperature, indicating thereby that an optimum initial size of droplets in the interdispersed phase during film formation was necessary to yield ultimately (after the required shrinkage) the largest number of pores. The productivities of the batch 316 (0/10) and 316 (10/30) films were essentially identical for the 80% and 90% levels of solute separation. These data indicate that an initial formation of a relatively smaller number of larger-size droplets under one set of conditions and a larger number of smaller-

size droplets under another set of conditions may ultimately result in the same effective number of pores on the membrane surface.

The importance of the difference between the temperature of the casting atmosphere and that of the casting solution to the productivity of resulting membranes confirms that the above two temperatures together constitute a single interconnected variable in the membrane-making procedure, which is the basis of the solution structure–evaporation rate concept in the material science of reverse osmosis membranes. This basis is further confirmed by the fact that for all the film-casting conditions tested, maximum membrane productivity corresponded to a narrow range (0.6° to 6°C) of $\Delta T_{\text{surface}}$ (Fig. 3) which is a function of both the temperature of the casting atmosphere and that of the casting solution.

Using the same casting solution composition, depending on the temperature of the casting solution and the temperature of the casting atmosphere, a wide range of product rates and applicable shrinkage temperatures were found for a given level of solute separation. For example, under the casting conditions discussed above, product rates ranged from 42.5 to 30.5 g/hr for 80% level of solute separation, and the applicable shrinkage temperatures were in the range 83° to 67°C; and, for the 90% level of solute separation, product rates ranged from 26.5 to 17 g/hr, and the applicable shrinkage temperatures ranged from 86.5° to 74°C. These data point out that, even for a given casting solution composition, specification of shrinkage temperatures alone can say nothing about the obtainable solute separation and product rate.

Membrane Performance at Higher Operating Pressures

The results discussed above have shown that batch 316 (0/10)-, 316 (0/15)-, 316 (5/24)-, and 316 (10/30)-type membranes showed maximum productivities at 250 psig. The performances of the above membranes were tested at the operating pressures of 600 and 1500 psig using aqueous feed solutions containing 5000 and 28,395 ppm of NaCl, respectively. The results obtained are shown in Figure 8, which also gives for comparison the corresponding results obtained with batch 18- and 301-type membranes reported earlier.³

It was pointed out that, compared with the performance of batch 18-type membranes, the productivities of the batch 301-type membranes were about 25% higher at 600 psig and were no different at 1500 psig under the conditions of reverse osmosis operation used in this work. Figure 8 shows that the productivities of all the batch 316-type membranes tested were better than those of batch 301-type membranes at both 600 and 1500 psig; in particular, the productivities of batch 316 (10/30) were significantly better. For example, at a 90% level of solute separation, the product rates obtained with batch 18-, 301-, and 316 (10/30)-type membranes at 250 psig were 10.1, 18.7, and 21.0 gallons/day-ft², respectively using 3500 ppm NaCl–H₂O feed solutions. At 600 psig, the corresponding product rate data were 36.9, 47.4, and 61.4 gallons/day-ft² using 5000 ppm NaCl–H₂O feed solutions; and at 1500 psig, the product rates were, respectively,

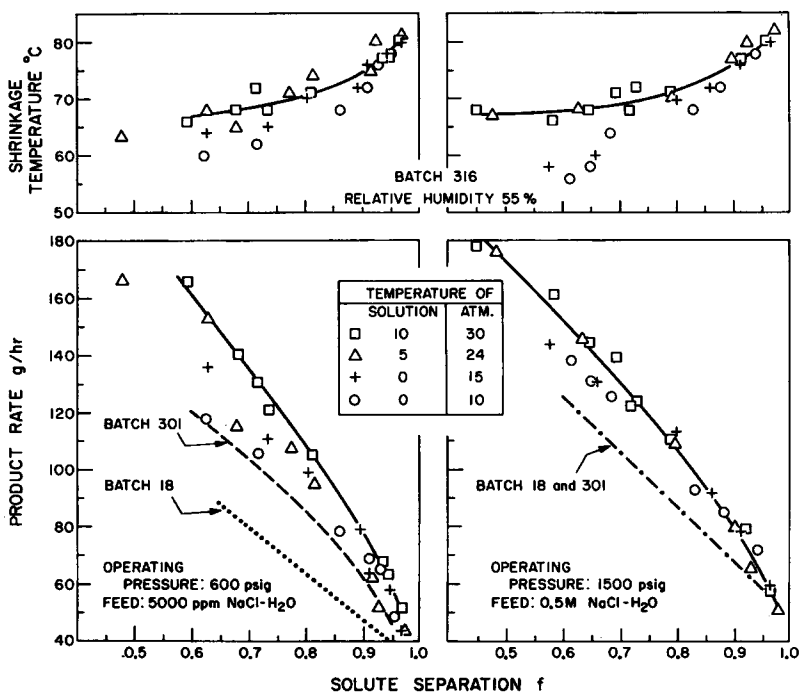


Fig. 8. Membrane performance at operating pressures of 600 and 1500 psig; membrane area, 7.6 cm².

52.1, 52.1, and 61.4 gallons/day-ft² using 28,395 ppm NaCl-H₂O feed solutions. These results show that membrane productivity can be significantly increased by appropriate changes in the composition of the casting solution and choice of film-casting conditions.

As pointed out already,⁵ the microporous structure of the asymmetric membrane may be considered as a continuum made up of three mutually distinct regions, namely, a dense surface layer of only a few molecular layers of thickness, a comparatively thicker transition layer underneath the surface layer, and a very much thicker spongy support layer (constituting the bulk of the membrane material) underneath the transition layer, each region being successively less dense and more porous. The polymer morphology in the transition layer may be expected to play a dominant role on the pressure stability of the porous structure of the asymmetric membrane. The performances of batch 18-, 301-, 316 (0/10)-, 316 (0/15)-, 316 (5/24)-, and 316 (10/30)-type membranes at different operating pressures indicate the possibility that both casting solution composition and film-casting conditions affect significantly the morphology of the transition layer. The data presented in Figures 1 and 8 show that of all the films tested, the batch 316 (10/30)-type membranes have the highest number of surface pores retained on the membrane surface (as represented by the initial membrane productivity data) for a wide range of solute separations in the operating pressure range 250 to 1500 psig, and hence the above type of membranes is of practical interest for reverse osmosis applications.

Effect of Humidity of Casting Atmosphere

All the results discussed above were obtained from films which were cast in an atmosphere whose relative humidity was 55%. In order to study the effect of humidity of casting atmosphere on the surface pore structure and performance of resulting membranes, three further sets of batch 316 (10/30)-type films were cast under atmospheric relative humidities of 35%, 65%, and 75%, respectively. These films were used subsequently in reverse osmosis experiments at 250 psig using aqueous feed solutions containing 3500 ppm of NaCl. The results obtained are given in Figure 9, which also includes the similar data obtained with the above type of films cast in an atmosphere of 55% relative humidity. The results showed that the shrinkage temperature profiles and membrane productivities were essentially the same for the 55% and 65% relative humidity films; the latter

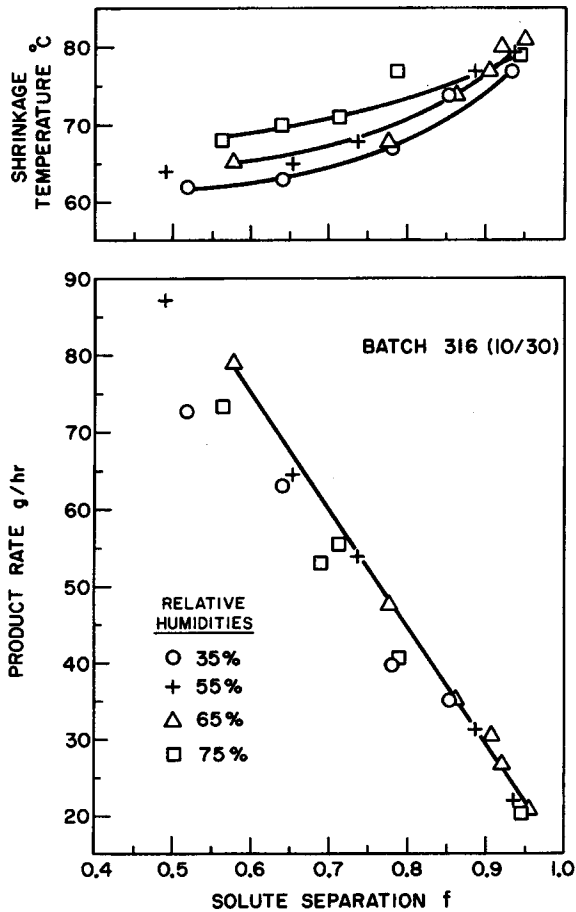


Fig. 9. Effect of relative humidity of casting atmosphere on membrane performance and shrinkage temperature profile: evaporation period, 1 min; membrane area, 7.6 cm²; solution system, NaCl-H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

films also gave the maximum product rates for any given level of solute separation. The shrinkage temperatures for the 75% humidity films were higher, and those for the 35% humidity films were lower, than those for the 55% and 65% humidity films. The productivities of the 35% and 75% humidity films were lower than those of the 55% and 65% humidity films.

The above results illustrate that even though humidity has only a second-order effect on membrane productivity, there exists an optimum humidity or humidity range of the casting atmosphere for best membrane performance, and this humidity range is between 55% and 65% for the batch 316 (10/30)-type films. A higher humidity in the casting atmosphere tends to give rise to bigger-size pores on the membrane surface in the as-cast condition. At the 1-min evaporation period after film casting, the temperature of the casting solution on the membrane surface was found to be 15°, 16.4°, 16.8°, and 18.2°C, respectively, for the 35%, 55%, 65%, and 75% humidity films. These results offer firm experimental confirmation for Kesting's conclusion⁷ that the effect of atmospheric moisture is to hasten gelation and retard solvent loss which in turn increase average pore size on the membrane surface. The effect of the tendency for gelation due to atmospheric moisture is to increase supermolecular polymer aggregation on the membrane surface, and the effect of the tendency for lower solvent evaporation rate is to increase the surface temperature which tends to break such surface supermolecular aggregation. Thus, there are two opposing tendencies affecting solution structure on the

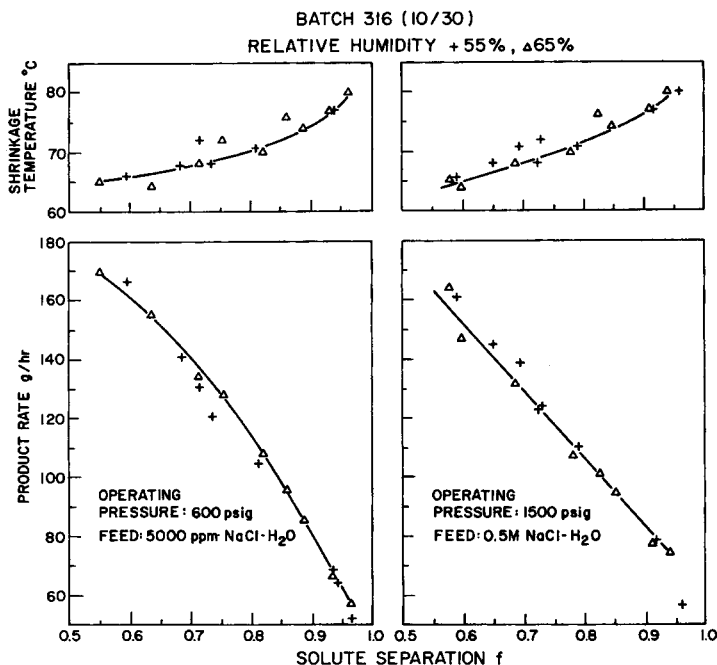


Fig. 10. Membrane performance at operating pressures of 600 and 1500 psig; membrane area, 7.6 cm².

TABLE I
Typical Performance of Porous Cellulose Acetate Membranes^a

Film type (batch no.)	Membrane productivity, gal/day-ft ²			
	70% ^b	80% ^b	90% ^b	95% ^b
Operating pressure, 250 psig; feed concn., 3500 ppm NaCl				
18	17.9	13.2	10.1	8.6
301	44.3	31.9	18.7	12.4
316 (10/30) ^c	46.6	35.0	22.9	17.1
Operating pressure, 600 psig; feed concn., 5000 ppm NaCl				
18	61.4	49.0	36.9	31.1
301	80.8	65.3	47.4	35.8
316 (10/30) ^c	108.8	87.8	61.4	45.1
Operating pressure, 1500 psig; feed concn., 0.5M NaCl ^d				
18	82.4	67.6	52.1	44.7
301	82.4	67.6	52.1	44.7
316 (10/30) ^c	101.0	82.4	64.5	54.4

^a Solution system: sodium chloride-water; feed flow rate corresponds to a mass transfer coefficient k of 45×10^{-4} cm/sec on the high-pressure side of membrane; operating temperature, 23°–25°C.

^b Solute separation.

^c Relative humidity of casting atmosphere, 65%.

^d 28,395 ppm NaCl.

membrane surface, which account for the existence of an optimum in relative humidity for highest membrane productivity.

The 65% humidity films were also subjected to reverse osmosis operating pressures of 600 and 1500 psig using aqueous feed solutions containing 5000 and 28,395 ppm NaCl, respectively. The results obtained are plotted in Figure 10, which also includes similar data obtained with the 55% humidity films for comparison. Figures 9 and 10 show that the shrinkage temperature profiles and membrane productivities were essentially the same for both the 55% and 65% humidity films at all operating pressures in the range 250 to 1500 psig. Table I gives some typical data on the comparative performance of batch 18-, 301-, and 316-type films at the operating pressures of 250, 600, and 1500 psig for aqueous feed solutions of different NaCl concentrations. These data illustrate that the batch 316 (10/30)-type films cast in an atmosphere of relative humidity 55% to 65% have the highest productivity of all the cellulose acetate membranes reported thus far in the literature.

Effect of Solvent Evaporation Period

Kesting⁷ has pointed out that the evaporation time prior to immersion in the nonsolvent medium (in the present case, ice-cold water) should be of critical importance with respect to surface pore structure and hence the performance of the resulting membrane. In order to study the effect of this casting variable, six different sets of batch 316 (10/30)-type films were made with evaporation periods of 0.5, 0.75, 1.0, 1.5, 2, and 3 min, respectively; for these sets of films the humidity of the casting atmosphere was

52%. Using the above membranes, reverse osmosis experiments were carried out at 250 psig with aqueous feed solutions containing 3500 ppm of NaCl. From the experimental shrinkage temperature and product rate data obtained from such experiments, the corresponding data for 70%, 80%, 90%, and 95% levels of solute separation were obtained by interpolation. These latter data are plotted in Figure 11, which shows the effect of evaporation period on shrinkage temperature and product rate for the specified levels of solute separation. The results illustrate the existence of an optimum evaporation period for maximum membrane productivity, and this period is 1 min for the particular casting solution composition and the film-casting conditions tested.

As the evaporation period was increased, both the shrinkage temperature and product rate passed through a maximum value for each. The product rates were maximum for the 1-min evaporation period, and the shrinkage temperatures were maximum for the 2-min evaporation period. The max-

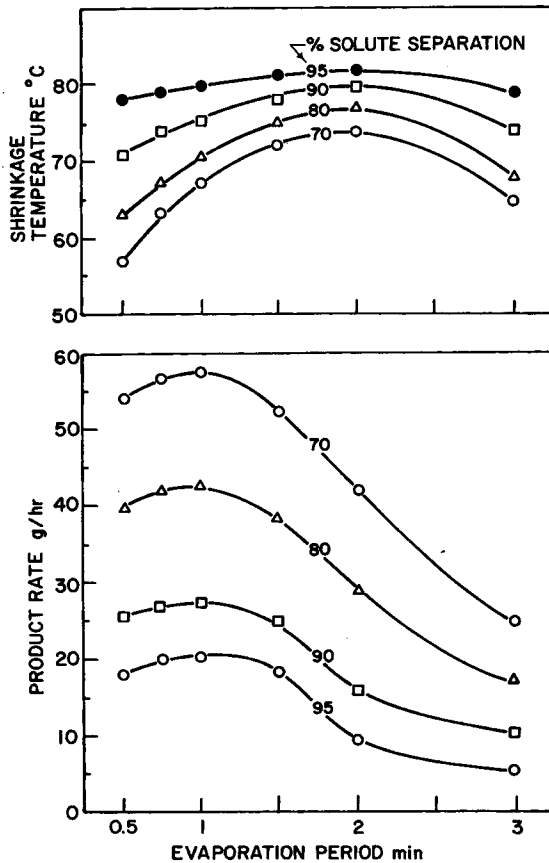


Fig. 11. Effect of evaporation period on membrane performance and shrinkage temperatures: film type, batch 316 (10/30); relative humidity, 52%; membrane area, 7.6 cm²; solution system, NaCl-H₂O, feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

imum product rates did not correspond to either the highest or the lowest shrinkage temperature. Within the range of evaporation periods tested, the values of the ratios of maximum to minimum product rate were 2.3, 2.4, 2.6, and 3.6 for the 70%, 80%, 90%, and 95% levels of solute separation, respectively. All the above results illustrate the critical importance of evaporation period to the changes in pore structure occurring on the membrane surface and the consequent productivities of the resulting membranes.

The increase in both the shrinkage temperature and product rate during the first minute of the evaporation period indicates that, during this period, there is a growth both in the number and size of droplets in the interdispersed phase. During the second minute of the evaporation period, the droplet growth and droplet coalescence become predominant. As a result, the number of droplets decreases and the average size of droplets increases, which account for a further increase in the shrinkage temperature and a sharp decrease in product rate. A decrease in shrinkage temperature during the third minute of the evaporation period indicates that, during the latter period, partial surface shrinkage occurs decreasing the average size of pores on the membrane surface, possibly as a result of the microcrystallites on the membrane surface moving closer together and decreasing the diameter of the interlamellar channels.⁷ The latter effect apparently also results in a partial depletion of pores and hence a decrease in their effective number in addition to that caused by further droplet coalescence, which accounts for a further sharp decrease in product rates. These decreases in product rates should only be expected to be progressively more significant as the required size of effective pores becomes smaller.

Specifications of Batch 316 (10/30)-Type Cellulose Acetate Membranes

In view of the high productivities of these membranes (Table I), numerical data on their specifications are of practical interest in reverse osmosis process design. From experimental pure-water permeation rate, product rate, and solute separation data using the above membranes and aqueous sodium chloride feed solutions at the operating pressures of 250, 600, and 1500 psig, the membrane-specifying parameters of pure-water permeability constant A and the solute transport parameters $D_{AM}/K\delta$ for NaCl were calculated by the Kimura-Sourirajan analysis.⁸ From the correlations of A and $D_{AM}/K\delta$ for NaCl, the values of A corresponding to specified values of $D_{AM}/K\delta$ for NaCl were obtained by interpolation. The latter data are given in Table II, and they constitute the general specifications of the batch 316 (10/30)-type cellulose acetate membranes cast in an atmosphere of relative humidity of 65%, with a solvent evaporation period of 1 min. These data refer to short-time tests.

In order to find out the general compaction characteristics of the above type of membrane, three-day-long continuous test runs were also conducted with the above membranes using aqueous sodium chloride feed solutions at operating pressures of 250, 600, and 1500 psig. At the end of 72 hr of continuous operation, the product rates were 90–98%, 80–87%,

TABLE II
General Specifications of Batch 316 (10/30)-Type Cellulose Acetate Membranes^a

$(D_{AM}/K\delta) \times 10^5$, for NaCl at operating pressure, cm/sec	$A \times 10^6$, g-mole H ₂ O/cm ² -sec-atm		
	1500 psig ^b	600 psig ^b	250 psig ^b
1	1.45	1.9	2.4
2	1.70	2.35	2.95
3	1.85	2.65	3.35
4	2.0	2.90	3.65
5	2.1	3.10	3.9
6	2.2	3.30	4.2
7	2.3	3.45	4.35
8	2.35	3.60	4.55
9	2.4	3.70	4.7
10	2.5	3.85	4.9
20	2.95	4.75	6.0
30	3.25	5.40	6.75
40	3.50	5.90	7.5
50	3.65	6.3	8.0
60	3.8	6.6	8.5
70	3.95	7.0	8.9
80	4.1	7.2	9.3
90	4.2	7.5	9.6
100	4.3	7.8	10.0

^a Relative humidity of casting atmosphere, 65%; evaporation period, 1 min.

^b Operating pressure.

and 68–75% of the initial product rates at the operating pressures of 250, 600, and 1500 psig. These data showed that the compaction characteristics of the batch 316 (10/30)-type membranes were no different from those of batch 18- and 301-type membranes reported earlier.^{3,8} Hence, it seems worthwhile and necessary to undertake more extensive long-time tests with the batch 316 (10/30)-type membranes for practical assessment of their compaction characteristics under different conditions of continuous operation.

CONCLUSIONS

Even with a given composition of the casting solution, the productivity of the Loeb-Sourirajan-type cellulose acetate membranes can be improved significantly by simply changing the casting conditions.

Referring to a cellulose acetate-acetone-magnesium perchlorate-water casting solution of given composition, a higher solution temperature lessens supermolecular polymer aggregation and tends to generate a larger number of smaller-size droplets of the nonsolvent swelling agent in the interdispersed phase during film formation. Since these droplets are incipient voids, a higher solution temperature has the potential for creating a larger number of pores on the membrane surface. A higher temperature of the casting atmosphere promotes a more rapid rate of growth of such droplets and increases the temperature of the casting solution on the membrane

surface. The latter increase tends to bring about local deaggregation of the polymer, and the consequent effects on droplet formation, at the membrane surface.

Increase in the number of droplets and the increase in the rate of growth of such droplets both favor droplet coalescence, which results ultimately in a smaller number of bigger-size pores on the membrane surface. Thus, droplet formation and droplet coalescence have opposing effects on the ultimate number of pores on the surface of the resulting membrane. This ultimate number is controlled more by the difference between the temperature of the casting atmosphere and the temperature of the casting solution than by the above individual temperatures.

A higher humidity of the casting atmosphere hastens surface gelation and increases surface temperature. While the former effect promotes local polymer aggregation at the surface during film formation, the latter effect does the opposite.

An increase in solvent evaporation period gives an opportunity for more droplets to form, smaller ones to grow, and the bigger ones to coalesce. A further increase in evaporation time favors partial surface shrinkage and possible further depletion of pores.

From the point of view of highest membrane productivity, the largest possible number of pores should be generated and maintained on the membrane surface just up to the moment of quenching the process (gelation in ice-cold water), which means that more numerous droplet formation and controlled growth of such droplets should be promoted, and droplet depletion by coalescence or surface shrinkage should be decreased under the casting conditions. These requirements account for the existence of an optimum for each one of the casting condition variables mentioned above, namely, the temperature of the casting solution/temperature of the casting atmosphere combination, the humidity of the casting atmosphere, and the solvent evaporation time. By the appropriate choice of the above variables, the productivity of the batch 316-type membranes has been significantly improved.

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