

Effect of Casting Conditions on the Performance of Porous Cellulose Acetate Membranes in Reverse Osmosis

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Synopsis

Several sets of porous cellulose acetate membranes were made using the same casting solution composition and gelation conditions but varying the casting solution temperature and solvent evaporation conditions. The films were tested in reverse osmosis experiments at 250 psig using aqueous feed solutions containing 3500 ppm NaCl. The results show that the product rate obtained at a given level of solute separation is independent of evaporation time in the range tested and, for a given casting solution composition, the temperature of the casting solution and conditions of solvent evaporation during film formation together constitute an important interconnected variable governing the porous structure of the resulting membranes. These results offer a new approach to the problem of developing more productive reverse osmosis membranes and have led to a new class of porous cellulose acetate membranes capable of giving product rates 100% to 150% higher than those of the best membranes reported, at any given level of solute separation under the experimental conditions used. These results are of practical importance in low-pressure reverse osmosis applications.

INTRODUCTION

Since the announcement of the Loeb-Sourirajan technique for making asymmetric porous cellulose acetate membranes for water desalination in 1960,^{1,2} extensive investigations have been initiated in several laboratories in search for superior membranes for reverse osmosis applications. Two major accomplishments have since been reported with respect to porous cellulose acetate membranes, one by Sourirajan and Govindan³ and the other by Manjikian et al.⁴ The membranes prepared according to these two improvements are designated here as CA-NRC-18- and CA-NRC-47-type membranes, respectively. The rather slow advancement in the field of membrane development is obviously due to the fact that the mechanism of pore formation in the process of casting Loeb-Sourirajan-type membranes has not yet been fully understood. The membrane-making procedure involves generally the following steps: (i) casting the polymer solution as a thin film on a surface; (ii) evaporation of the solvent from the film surface; (iii) immersion of the film in an appropriate gelation medium such as cold water, and finally (iv) shrinking the membrane by contact with hot water

followed by a pressurization treatment.³ Maier and Scheuermann,⁵ Kesting and co-workers,^{6,7} and Banks and Sharples⁸ have done the most extensive work relating to the mechanism of the processes taking place in one or the other of the above steps. Their concepts show that film formation is the outcome of a phase separation process which occurs in the concentrated polymer solution containing the polymer (cellulose acetate), solvent (acetone), and the swelling agent (aqueous magnesium perchlorate solution or formamide). The object of this work is to make a further contribution to the subject from the point of view of developing methods for obtaining more productive porous cellulose acetate and similar membranes (i.e., membranes capable of giving higher product rates at any given level of solute separation) for reverse osmosis applications in general and brackish water conversion in particular.

EXPERIMENTAL

Reagent-grade sodium chloride and porous cellulose acetate membranes made in the laboratory were used. All the films used were obtained from casting solutions of the same following composition: acetone, 68.0 wt-%, cellulose acetate (acetyl content = 39.8%), 17.0 wt-%; water, 13.5 wt-%; and magnesium perchlorate, 1.5 wt-%. This composition is the same as that used for CA-NRC-18-type films.³ Different casting solution temperatures, evaporation periods, and evaporation conditions were used in film making. The gelation medium was ice-cold water in all cases, and all films had the same overall thickness (~ 0.004 in.). Membranes shrunk at different temperatures were obtained to give different surface pore structures and hence different levels of solute separations at preset operating conditions. All membranes were initially subjected to a pure water pressure of 300 psig for 1 hr before use in reverse osmosis experiments. The apparatus and experimental procedure have been reported.^{3,9} The reverse osmosis experiments were of the short-run type, each lasting for about 2 hr; they were carried out at the laboratory temperature, using aqueous feed solutions containing 3500 ppm of NaCl and a feed rate of 350 cc/min at the operating pressure of 250 psig. The reported product rates are those corrected to 25°C, using the relative viscosity and density data for pure water. In each experiment, the solute separation f , defined as

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

the product rate [PR], and the pure water permeability [PWP], in g/hr per 7.6 cm² of effective film area, were determined at the operating conditions. In all cases, the terms "product" and "product rate" refer to the membrane-permeated solutions. The solute concentrations in feed and product solutions were determined by specific resistance measurements using a conductivity cell. The accuracy of the separation data is within 1% and that of [PR] and [PWP] data is within 3% in all cases.

All the three experimentally determined quantities [PWP], [PR], and f are needed to calculate the mass transfer coefficient k on the high pressure side of the membrane.¹⁰ The significance of k on membrane performance has been discussed in the literature.¹¹ Since the relative variations of [PR] and f are the pertinent data of interest for the purpose of this paper, they are reported here at an arbitrarily chosen constant value of $k = 45 \times 10^{-4}$ cm/sec which corresponds to a feed flow rate of 350 cc per min under the conditions of the experiments.

RESULTS AND DISCUSSION

Keeping the temperature of the casting solution and that of the casting atmosphere (air) constant at -10°C , four different sets of films were made with evaporation periods of 1, 2, 4, and 6 min, respectively. The gelation medium was ice-cold water in all cases. By shrinking the films at different temperatures, membranes capable of giving different levels of solute separation were obtained for each set.

Figures 1 and 2 represent the performance of the above sets of films in reverse osmosis experiments. Figure 1 shows that the product rate obtained at a given level of solute separation is independent of evaporation time in the range tested. This indicates that a change in evaporation time results in no significant change in the effective number of pores on the membrane surface. However, the shrinkage temperature versus solute separation correlation (shrinkage temperature profile) is a function of the evaporation time. This is illustrated in Figure 2. The relative position and shape of the shrinkage temperature profile lead to possible conclusions on the effective pore size and pore size distribution in the surface layer of the membrane. A higher shrinkage temperature to give a given level of solute separation would indicate a larger initial size of pores; a steeper shrinkage temperature profile would indicate a more uniform pore size distribution. Consequently, Figure 2 shows that a longer evaporation time results in bigger and more uniform pores, and a shorter evaporation time results in smaller and less uniform pores on the surface layer of the membrane.

Seven different sets of films were made using the same casting solution composition, evaporation time (2 min) and the gelation medium (ice-cold water). The temperature of the casting solution and the conditions of evaporation were the variables studied. The casting solution was conditioned at different temperatures and the evaporation rate was varied by varying the temperature of the casting atmosphere and the equilibration of acetone vapor in the casting atmosphere in the manner of Knapp and Ward.¹² This latter variation was accomplished by casting the films in a closed atmosphere in equilibrium with different concentrations of aqueous acetone solutions. As before, films shrunk at different temperatures were used to give different levels of solute separation in reverse osmosis experiments. Figure 3 gives the separation-versus-product rate data for the

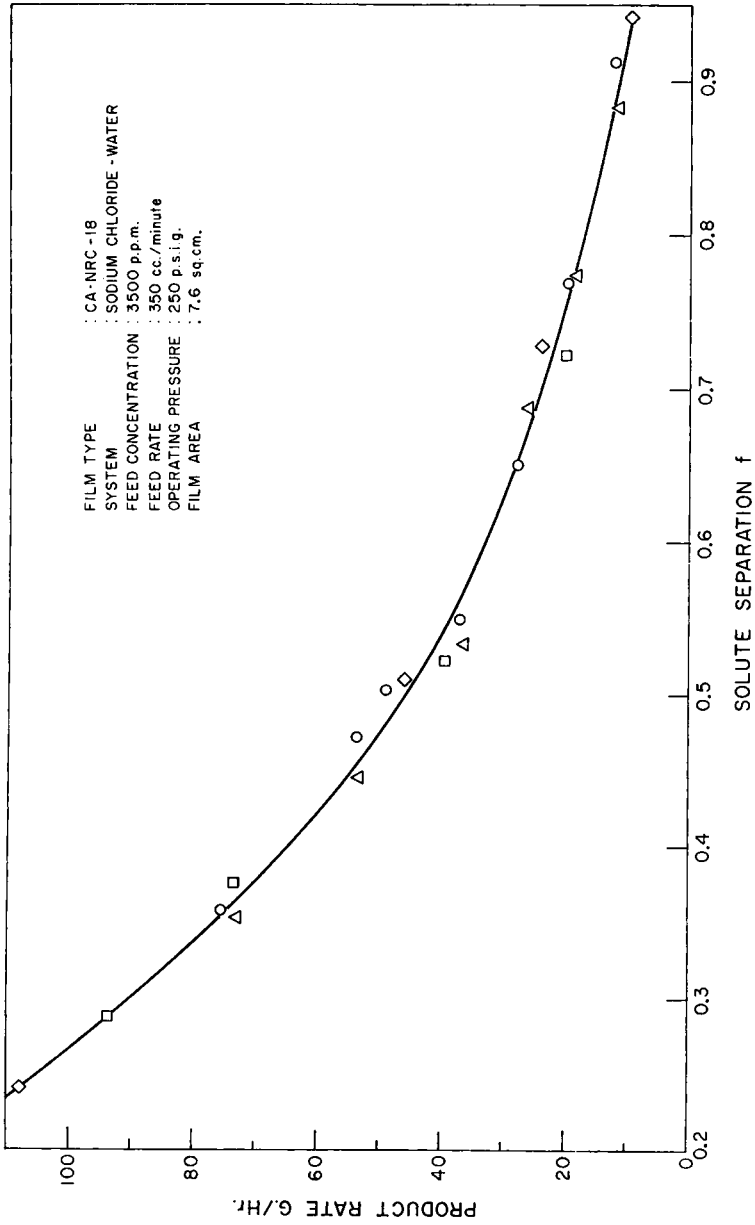


Fig. 1. Effect of solvent evaporation time on membrane performance. Evaporation period: (Δ) 1 min; (\circ) 2 min; (\square) 4 min; (\diamond) 6 min.

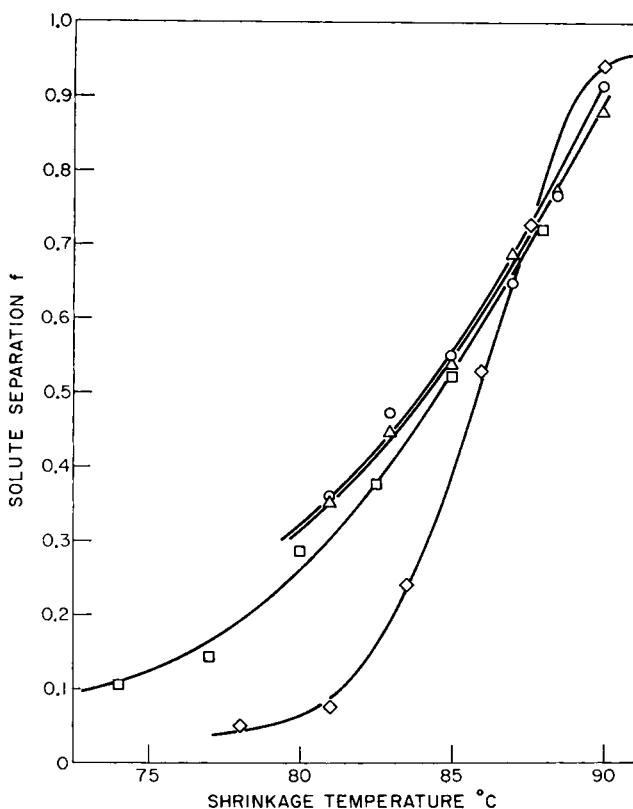


Fig. 2. Effect of solvent evaporation time on film shrinkage temperature profile. (Symbols same as those used in Fig. 1.)

above sets of films along with their corresponding casting conditions; Figure 4 gives their respective shrinkage temperature profiles.

The films whose performance data are given in Figures 3 and 4 may be broadly divided into two groups, I and II. Curves 1, 2, and 3 belong to films of group I, and curves 4, 5, 6, and 7 belong to films of group II. The casting solution temperature for group I films was -10°C and that for group II films was 0°C . It is immediately obvious that the productivity of group II films is higher than that of group I films at any given level of solute separation, showing thereby that a higher casting solution temperature favors the creation of a higher effective number of pores.

The data given in Figures 3 and 4 show that there are differences among membranes within each group. They are evidently caused by the change in the rate of solvent evaporation as a result of variation of two factors: the increase of temperature of the casting atmosphere and the introduction of acetone vapor in the casting atmosphere. It can be expected that the first factor increases the solvent evaporation rate and the second factor decreases it. The influence of the evaporation rate on membrane performance is more evident within group II films, although it can also be seen

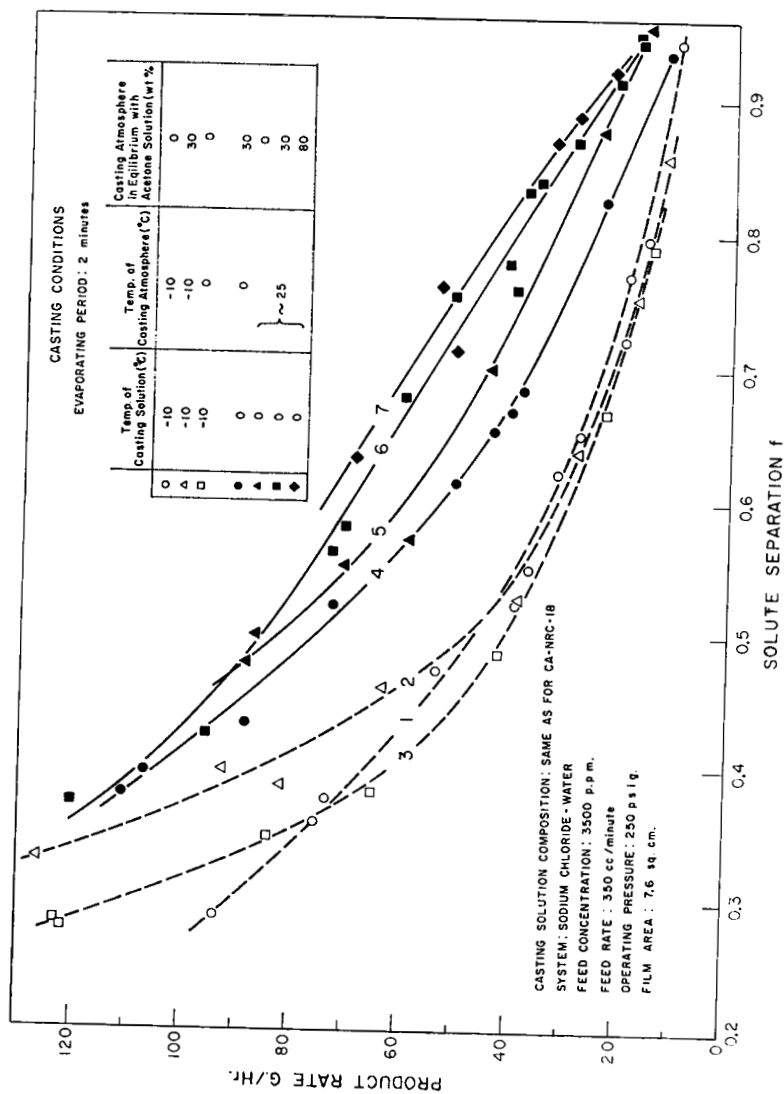


Fig. 3. Effect of casting solution temperature and solvent evaporation rate on membrane performance.

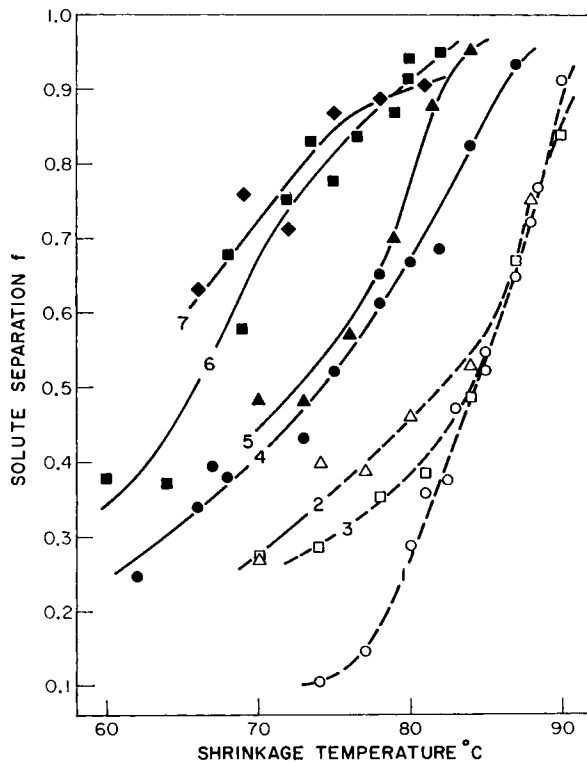


Fig. 4. Effect of casting solution temperature and solvent evaporation rate on film shrinkage temperature profile. Evaporation period 2 min. (Symbols same as those used in Fig. 3.)

within group I films, particularly at lower levels ($< \sim 50\%$) of solute separation.

The performance curves 4, 5, 6, and 7 in Figure 3 are progressively one above the other, and the corresponding shrinkage temperature profiles in Figure 4 are progressively shifted to the left, indicating the creation of a progressively larger number of smaller-size pores on the membrane surface under the conditions of casting, resulting ultimately in more productive reverse osmosis membranes. Compared to films represented by curve 3, those represented by curve 4 (Fig. 3) were made using a higher solution temperature and conditions which favor a lower evaporation rate. The results show better membrane performance and a shrinkage temperature profile shifted significantly to the left. These data indicate that a combination of higher solution temperature and a lower evaporation rate tends to produce more productive reverse osmosis membranes.

The performance data represented by curves 4 and 5 (Fig. 3) show that the solution temperature- evaporation rate combination represented by curve 4 is not the optimum, and a better combination of such factors can be found as illustrated by the data given by curve 5. The films represented

by curve 5 were cast at the laboratory temperature (23°–25°C) where a higher evaporation rate is probably achieved than that at the casting conditions represented by curve 4.

The performance data represented by curves 6 and 7 (Fig. 3) show that the evaporation rate obtained under the conditions of casting represented by curve 5 is too high, and better results could be obtained under conditions which favor a decrease in evaporation rate to some extent. This was done by equilibrating the casting atmosphere at the laboratory temperature with 30% (curve 6) or 80% (curve 7) solution of acetone in water. Presumably similar results can be obtained by lowering the temperature of the casting atmosphere. Curve 7 (Figs. 3 and 4) represents the best results obtained in these studies. No attempt was made to optimize the casting conditions to give the best performance.

The differences among the membranes represented by curves within Group I are not so well delineated as those within Group II, although the general trends are the same. The solvent evaporation rates for the films represented by the curves 2 and 3 (Fig. 3) are probably lower and higher, respectively, than the evaporation rate for the films represented by curve 1. If so, the corresponding performance data would indicate, as before, that a lower evaporation rate tends to increase productivity of films at a given level of solute separation. Referring to the corresponding shrinkage temperature profiles in Figure 4, it is seen that the profiles are essentially identical at solute separation levels $> \sim 50\%$; below this level, the films represented by curve 1 have bigger and more uniform pores and the films represented by curve 2 have smaller and less uniform pores, whereas the films represented by curve 3 have a surface pore size and pore size distribution intermediate between the above two cases. These data indicate that a lower evaporation rate tends to produce a larger number of smaller-size pores on the membrane surface. Also, the fact that the shrinkage temperature profile 3 is located between 1 and 2 in Figure 4 and the corresponding performance data are also similarly situated at lower levels of solute separation, even though the evaporation rates are not in the same order, indicates that evaporation rate is only one of the factors that determine the number, size, and distribution of pores on the membrane surface.

The experimental results presented above are understandable on the basis of the general concepts of phase separation proposed by Kesting and others.^{6,7}

Immediately after casting, i.e., spreading the polymer solution in the form of a film on a surface, evaporation of solvent starts at the air-solution interface. As the result of solvent loss, a cloud point in the surface region is reached when droplets of the swelling agent separate from the solution as a second interdispersed phase, with the polymer molecules concentrated at the exterior surfaces of the droplets. On continued desolvation, the droplets (micelles) in the surface region contact one another forming polyhedra whose number, size, and wall thickness depend on the composition and polymer structure in the casting solution and on the desolvation conditions.

The subsequent immersion of the spreaded polymer solution in the gelation medium (cold water) accelerates and completes the desolvation process both in the surface layer and the bulk region underneath. During the desolvation process, the walls of the polyhedra rupture and closed cells give way to more numerous open cells which, together with the voids between cells, give rise to a microporous surface structure. On the other hand, in the interior bulk region of the film, the polymer molecules aggregate and precipitate rapidly, giving rise to a spongy porous mass underneath the surface layer. The final result is the formation of a completely open-celled asymmetric porous structure for the entire membrane.

This model of the phase separation process points out the importance of the initial polymer solution structure as well as the evaporation conditions during film formation, which together affect the nature of the resulting membrane. The structure of the concentrated polymer solution prior to evaporation is determined by its composition and temperature. Since the composition of the casting solution is constant in this work, its temperature is the factor responsible for any change in its structure. Higher temperature of the casting solution diminishes the possibility of supermolecular aggregation within the concentrated polymer solution and makes possible the formation of more numerous smaller-size droplets of the dispersed phase in the surface region during solvent evaporation. On immersion of the film in the gelation medium, the thin walls of the polyhedra formed from the droplets rupture, giving rise to numerous micropores in the surface layer of the membrane. This might explain why the membranes cast from solutions at 0°C (curves 4 to 7 in Fig. 3) show higher productivity at any given level of solute separation than those cast from solutions at -10°C.

However, the higher temperature of casting solution is not sufficient condition for obtaining more productive membranes. For the best results, the solvent evaporation rate should be appropriately adjusted to the state of the casting solution. Too rapid an evaporation rate could cause excessive rupture of polyhedra walls prior to gelation resulting in big size pores; the size of pores thus formed would be further increased during the subsequent gelation process. On the other hand, too slow an evaporation rate could result in the coalescence of the small droplets to form bigger ones with consequent decrease in the number of pores and increase in the size of pores on rupture of polyhedra walls during gelation. Consequently, the solvent evaporation rate should be high enough to prevent coalescence of the dispersed droplets and low enough to prevent excessive rupture of the polyhedra walls prior to gelation. These conclusions are consistent with the experimental results illustrated by the curves 5, 6, and 7 in Figure 3. Prolongation of evaporation time can be expected to lead to the formation of larger dispersed phase droplets in the surface region and hence larger pores as a result of rupture of the polyhedra during the desolvation process, as seen from Figure 2.

The experimental results and the considerations presented above illus-

trate the practical importance of the combined influence of the state (composition and temperature) of the casting solution and the conditions which control evaporation rate in making more productive reverse osmosis membranes. In particular, the results illustrate the need for the quantitative determination of both phase separation parameters for different casting solutions and their evaporation rates under the conditions of film casting.

The effect of variations of temperature and composition of the gelation medium has not been studied in this work. Since ice-cold water is a convenient gelation medium, it was held constant in these experiments. It is however obvious that the above variations may have significant consequences on the rate of desolvation during gelation, and hence on the final porous structure of the resulting membranes.

CONCLUSIONS

The foregoing experimental results and discussions lead to a new approach to the problem of development of more productive membranes for reverse osmosis applications. In this approach, the temperature of the casting solution and the temperature of the casting atmosphere together constitute an important interconnected variable governing the ultimate porous structure of the resulting reverse osmosis membranes. The optimum specification of these two temperatures for producing more productive reverse osmosis membranes depends on the casting solution composition and the evaporation and gelation conditions. The effectiveness of this approach is illustrated by the performance data given in Figure 3, which show that the productivities of the membranes represented by curve 7 is 100% to 150% higher than those of the membranes represented by curve 1 in the 60% to 90% level of solute separations. Another illustration is provided by the following results obtained with a set of CA-NRC-18- and CA-NRC-47-type membranes¹³ and a membrane prepared under conditions represented by curve 6 in Figure 3. Using aqueous feed solutions containing 1500 ppm NaCl, at an operating pressure of 250 psig, solute separations obtained with the above three membranes were 85.4%, 86.2%, and 87.2%, respectively, and the corresponding product rates were 15.1, 13.1, and 33.6 gallons per day per sq. ft. These data represent an order-of-magnitude improvement in productivity obtained with the membranes made on the basis of the new approach presented in this paper compared with the best earlier membranes. The above performance data obtained with the new membranes are also of practical interest for low-pressure reverse osmosis applications in general and brackish water conversion in particular.

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