

## Effect of Secondary Additives in Casting Solution on the Performance of Porous Cellulose Acetate Reverse Osmosis Membranes

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### Synopsis

The solution structure and evaporation rate constant can be varied by changing the temperature of the casting solution and the temperature of the casting atmosphere for a given film-casting solution composition. The effects of the two temperature changes can be simulated (without changing the two temperatures) by replacing a small part of the solvent (acetone) by a secondary additive in the casting solution. The effect of 20 different secondary additives in the batch 316-type casting solution has been studied and is discussed. Porous cellulose acetate reverse osmosis membranes, capable of giving a 20% to 25% increase in productivity at a 90% level of solute separation for a 3500 ppm NaCl-H<sub>2</sub>O feed solution at 250 psig, have been produced using 5 wt-% ethyl ether as the secondary additive in the above casting solution. The use of secondary additives offers a new flexibility in the choice of film-casting conditions and in the general development of reverse osmosis membranes.

### INTRODUCTION

The basic concepts of Kesting on sol-gel transformation in the process of making porous cellulose acetate reverse osmosis membranes<sup>1-3</sup> led to the solution structure-evaporation rate criteria for the choice of casting conditions to bring about practical improvements in the performance of such membranes.<sup>4-10</sup> Of the several casting solution compositions tested, the following (batch 316)<sup>7</sup> gave the most promising results: cellulose acetate (acetyl content 39.8%), 17; acetone, 69.2; magnesium perchlorate, 1.45; and water, 12.35 wt-%. The most recent study<sup>10</sup> was concerned with the effects of casting conditions on the reverse osmosis performance of films obtained from the above casting solution using ice-cold water as the gelation medium. It was found<sup>10</sup> that the best membrane performance was obtained when the film-casting conditions were as follows: temperature of casting solution, 10°C; temperature of casting atmosphere, 30°C; relative humidity of casting atmosphere, 65%; and solvent evaporation period, 1 min. This work is a continuation of the above studies.

In the previous study,<sup>10</sup> both the state of supermolecular polymer aggregation in the casting solution (solution structure) and evaporation rate constant during film formation were changed by changing the temperature

of the casting solution and the temperature of the casting atmosphere. Even when the above temperatures are held constant, it should be possible to change the solution structure and evaporation rate constant by changing the composition of the casting solution. The latter change can be accomplished by a wide choice of variables. The object of this work was to investigate the effect of changes in solution structure brought about by incorporation of a relatively small amount of a "secondary additive" in the casting solution in partial replacement of the solvent acetone.

The term "secondary additive" used in this paper is meant to distinguish such additives from aqueous magnesium perchlorate used as the primary additive in the casting solution. In the rest of this paper, the term "additive" refers specifically to the secondary additive whether or not so specified.

For the purpose of this study, temperature of the casting solution, temperature of the casting atmosphere, relative humidity of the casting atmosphere, solvent evaporation period, and casting solution composition with respect to cellulose acetate, magnesium perchlorate, and water were held the same as those given above corresponding to the best performance of batch 316-type membranes. The change (unless otherwise specified) was only with respect to solvent in the casting solution which was modified to contain 5 wt-% secondary additive and 64.2 wt-% acetone. Thus, the change in casting solution structure was brought about by a change in solvent composition. The additive used in each case was one of 20 different organic compounds (excluding acetone) chosen for their differences in chemical nature, boiling point, and solubility parameter. By such modification of solvent composition, second-order changes in the casting solution structure could be expected. Since evaporation rate constant is sensitive to changes in solution structure,<sup>10</sup> it is reasonable to expect significant changes in the porous structure of the membrane surface resulting from solvent-modified casting solutions.

For purposes of comparison of relative membrane performance, data on shrinkage temperature and product rate are reported for a specified reference level of solute separation under otherwise identical experimental conditions. The reference level of solute separation was arbitrarily chosen for this study to be 90%. The shrinkage temperature and product rate data are then interpreted on the same basis as before.<sup>10</sup> At the level of solute separation specified above, an increase in shrinkage temperature is considered to represent a bigger average pore size on the membrane surface in the as-cast condition, and an increase in product rate is considered to represent a larger number of such pores on the membrane surface. The experimental data presented in this paper are consistent with the solution structure-evaporation rate concept governing pore formation and development, and the results indicate the possibility of creating more productive porous cellulose acetate reverse osmosis membranes by the appropriate choice of secondary additives for the casting solution and other film casting conditions.

## EXPERIMENTAL

The general experimental details are the same as those reported for the earlier study.<sup>10</sup> The composition (weight-%) of the casting solution used in all cases was as follows: cellulose acetate (Eastman 398-3), 17; acetone + secondary additive, 69.2; magnesium perchlorate, 1.45; and water, 12.35. The secondary additives used are listed in Table I. Unless otherwise stated, the amount of secondary additive in the casting solution was 5 wt-%, temperature of the casting solution was 10°C, temperature of casting atmosphere was 30°C, solvent evaporation time was 1 min, and relative humidity of the casting atmosphere was 65%. The gelation medium was ice-cold water in all cases. All the films were cast in a constant temperature-constant humidity room. The data on evaporation

TABLE I  
List of Secondary Additives Used and Their Properties

No.	Name	Boiling point, °C	Solubility parameter
Alcohols			
1	Methanol	65	14.5
2	Ethanol	78.5	12.7
3	<i>n</i> -Butanol	117.7	11.4
4	3-Methyl-2-pentanol	134	10
Ethers			
5	Ethyl ether	34.6	7.4
6	1,4-Dioxane	101.3	10
7	<i>n</i> -Butyl ether	142	7.1
Ketones			
8	Acetone	56.5	10
9	Methyl ethyl ketone	79.5	9.3
10	Cyclohexanone	155.7	9.8
11	Isobutyl ketone	168	7.8
Esters			
12	Methyl formate	31.5	10.2
13	Ethyl formate	54.3	9.4
14	Methyl acetate	57.1	9.6
15	Ethyl acetate	77.2	9.1
Nitro Compounds			
16	Acetonitrile	82	11.9
17	Nitromethane	101	12.7
18	Nitroethane	115	11.1
Hydrocarbons			
19	Isopentane	27.9	6.9
20	<i>n</i> -Hexane	68	7.3
21	<i>n</i> -Heptane	98	7.4

rate constants were obtained as before<sup>5</sup> 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 before<sup>9</sup> 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 ( $\sim 400$  cc/min) corresponding to a mass transfer coefficient  $k = 25 \times 10^{-4}$  cm/sec on the high-pressure side of the membrane using aqueous sodium chloride feed solutions. Most of the experiments were carried out at 250 psig with an aqueous feed solution containing 3500 ppm of NaCl. A few experiments were also performed at 600 and 1500 psig using aqueous feed solutions containing 5000 ppm and 28395 ppm (0.5M) of NaCl, 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 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. All product rate data are for 13.2 cm<sup>2</sup> of effective membrane area. Unless otherwise stated, all 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 employed for analysis. The fraction solute separation  $f$  was calculated from the relation

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

Data on product rates were obtained by direct weighing of samples and expressed as grams per hour for the given film area (13.2 cm<sup>2</sup>).

Membranes preshrunk in hot water at different temperatures were used to obtain different levels of solute separation. From the plot of solute separation versus product rate and shrinkage temperature, the latter values corresponding to any specified level of solute separation were obtained. Unless otherwise stated, all product rate and shrinkage temperature data given in this paper correspond to a 90% level of solute separation.

## RESULTS AND DISCUSSION

### Effect of Secondary Additive in Casting Solution

**Data on Properties of Additives and Membrane Performance.** Figure 1 shows the effect of boiling point of additives on shrinkage temperature and product rate of resulting membranes at 90% level of solute separation at 250 psig. Data on solubility parameters of additives are also included in Figure 1. The additive numbers in Figure 1 are the same as those given in Table I. Several aspects of Figure 1 are interesting.

The replacement of a small amount of the solvent by an additive in the casting solution brought about wide changes in the shrinkage temperature and product rate. With the additives tested, the shrinkage temperature varied from 67° to 84°C, and the product rate varied from 3.5 to 30.5 g per hour (for the given film area) under the specified operating conditions. These results show that even small variations in the casting solution composition cause significant changes in solution structure and in the porous structure of the resulting membrane surface.

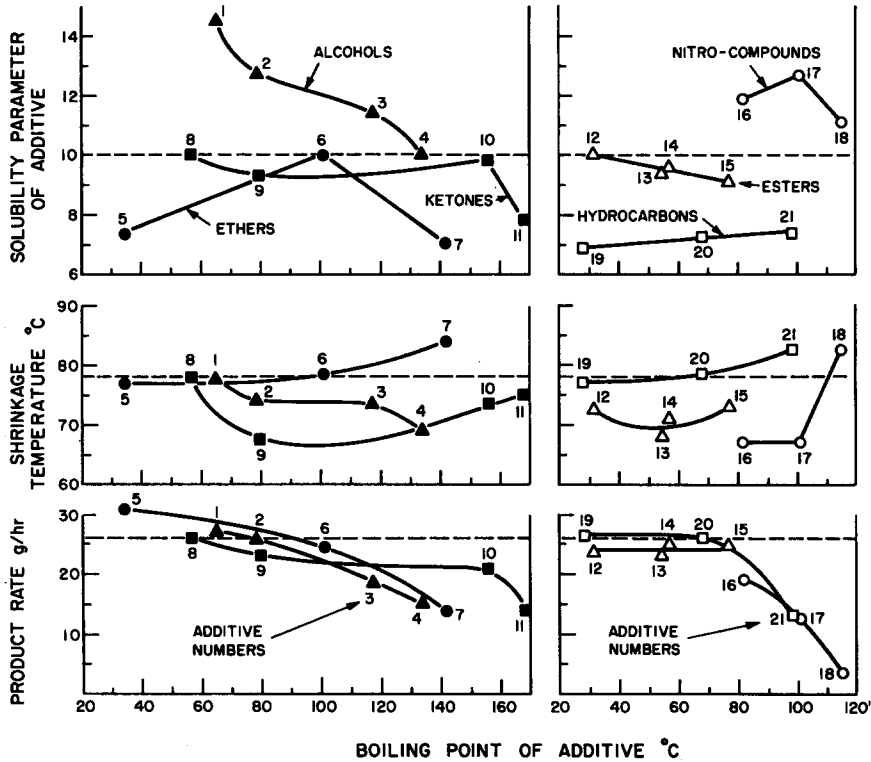


Fig. 1. Effect of boiling point and solubility parameter of additives on shrinkage temperature and product rate of membranes at 90% level of solute separation. Additive numbers same as in Table I; membrane area, 13.2 cm<sup>2</sup>; solution system, NaCl-H<sub>2</sub>O; feed concentration, 3500 ppm NaCl;  $k = 25 \times 10^{-4}$  cm/sec; operating pressure, 250 psig.

The effect of the additive depends not only on its physical properties such as boiling point and solubility parameter, but also on its specific chemical nature as represented by the functional group in the organic molecule. The 21 different additives (including acetone) used in making membranes are hence grouped under alcohols, ethers, ketones, esters, nitrocompounds, and hydrocarbons, and the effect of each additive is best viewed with respect to the other compounds in the same group.

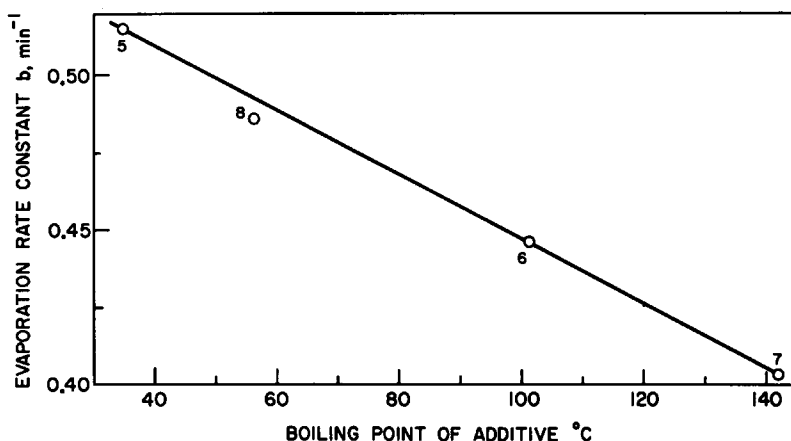


Fig. 2. Effect of boiling point of additives on evaporation rate constant during film formation. Additive numbers same as in Table I.

Within each group of additives studied, two observations are evident. The product rate generally decreased with an increase in the boiling point of the additive; the shrinkage temperature either decreased, increased, or remained unchanged depending on the additives used. These results obviously reflect the effect of the additive on the state of supermolecular polymer aggregation in the casting solution and the evaporation rate condition during film formation.

Some correlation exists between the solubility parameter of the additive and its effect on shrinkage temperature and product rate of resulting membranes. The range of solubility parameters to obtain dissolution of cellulose acetate in different classes of solvents is listed by Tanner et al.<sup>11</sup> Since the solubility parameter of acetone is 10, it is reasonable to assume that those additives whose solubility parameters are close to 10 will affect the solvent power of acetone much less than those additives whose solubility parameters are far above or below 10. The latter additives may be expected to decrease significantly the solvent power of acetone for the polymer and hence increase the extent of supermolecular polymer aggregation in the casting solution.

**Data on Evaporation Rate Constants.** Figure 2 gives a set of data on evaporation rate constant  $b$  ( $\text{min}^{-1}$ ) for casting solutions containing ethyl ether, 1,4-dioxane, or *n*-butyl ether as additive. The value of  $b$  for the casting solution where the solvent (acetone) contained no additive is also given in Figure 2. The results show that evaporation rate constant is essentially a linear function of the boiling point of the additive and the magnitude of  $b$  increases with decrease in the boiling point of the additive.

**Data on Change of Surface Temperature During Film Formation.** The temperature of the film surface immediately after casting was measured<sup>9</sup> as a function of time for each of the casting solutions containing one of the ether additives; the corresponding data were also obtained for the casting

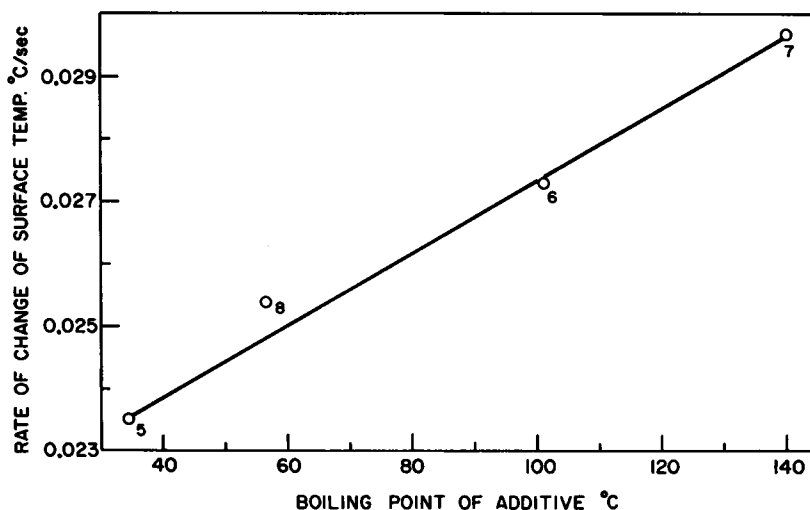


Fig. 3. Effect of boiling point of additive on rate of change of surface temperature during film formation. Additive numbers same as in Table I.

solution with the solvent acetone containing no additive. In the solvent evaporation period of 10 to 100 sec, the increase in temperature on the film surface was linear with time, and the rate of change of temperature per unit time increased linearly with increase in the boiling point of the additive, as shown in Figure 3. The latter data are consistent with the decrease in the value of the evaporation rate constant obtained (Fig. 2) with increase in the boiling point of the additive.

**Some Previous Data on Shrinkage Temperature and Membrane Performance.** Referring to previous data on batch 316-type casting solution composition and 1-min evaporation period given in Figure 5 in reference 10 (these data are hereafter referred to as "ref. 10-5"), it was observed that for the 90% level of solute separation, shrinkage temperature increased with increase in the temperature of the casting atmosphere for a given temperature of the casting solution. At a given temperature of the casting atmosphere, the shrinkage temperature showed a tendency to pass through a minimum with increase in the temperature of the casting solution. These results indicate that both higher and lower values for the evaporation rate constant, and bigger- and smaller-size polymer aggregates in the initial casting solution, ultimately result in an increase in the average size of initial pores on the membrane surface. The above work<sup>10</sup> also showed that, for the same (90%) level of solute separation, product rate increased with increase in the temperature of the casting atmosphere when the temperature of the casting solution was in the vicinity of 10°C, but decreased with increase in the temperature of the casting atmosphere when the temperature of the casting solution was -10°C. These results indicate that at a given level of solute separation, a relative increase in product rate (i.e., a relative increase in the number of pores on the membrane

surface) results from an increase in the temperature of the casting atmosphere when the size of the polymer aggregates in the initial casting solution is sufficiently small, and also from a decrease in the temperature of the casting atmosphere when the size of the polymer aggregates in the initial casting solution is sufficiently large.<sup>12,13</sup> An earlier work<sup>7</sup> has also shown that a small decrease in acetone content in the casting solution tends to increase the size of supermolecular polymer aggregates in the casting solution and hence increase shrinkage temperature for a given level of solute separation.

The foregoing results indicate that bigger initial pores on the membrane surface are the result of larger supermolecular polymer aggregates in the initial casting solution and/or a higher rate of droplet coalescence in the interdispersed phase during film formation. For a given evaporation period, there is an optimum both with respect to size of polymer aggregate in the initial casting solution and evaporation rate constant during film formation for maximum product rate. The data presented in Figure 1 are understandable on the above basis.

**Effect of Alcohols as Additives.** Figure 1 shows that the effect of methanol, ethanol, *n*-butanol, or 3-methyl-2-pentanol as additive is to decrease both shrinkage temperature and product rate with increase in the boiling point of the alcohol. Since the latter change also corresponds to a decrease in the value of the respective solubility parameters from 14.5 to 10, the increase in the boiling point of the alcohol additive used corresponds to a simultaneous decrease both in the relative evaporation rate constant and the size of supermolecular polymer aggregates in the casting solution. Referring to the previous data (ref. 10-5) for batch 316(10/30)-type film, one notes correspondingly that the effect of simultaneous decrease in temperature of casting atmosphere (i.e., decrease in evaporation rate constant) and increase in temperature of casting solution (i.e., decrease in the size of supermolecular polymer aggregates in the casting solution<sup>12,13</sup>) tend to decrease both shrinkage temperature and product rate. Thus, at the film-casting conditions used in this work, the effect of the above alcohol additives on the porous structure of the resulting membrane surface is similar to that produced by the simultaneous decrease in both the evaporation rate constant and size of supermolecular polymer aggregates in the casting solution brought about by appropriate changes in the temperature of the casting atmosphere and that of the casting solution without solvent modification by additive.

**Effect of Ethers as Additives.** The effect of ethyl ether, 1,4-dioxane, or *n*-butyl ether as additive (Fig. 1) is to increase shrinkage temperature and decrease product rate with increase in the boiling point of the additive. The low solubility parameters for ethyl ether and *n*-butyl ether indicate that the latter additives are poor solvent substances for cellulose acetate compared to acetone. The solvent power of 1,4-dioxane (in spite of its solubility parameter of 10) for cellulose acetate is much less than that of acetone as indicated by the data on relative values of solution viscosities<sup>14</sup>



and Mark-Houwink constants.<sup>15</sup> Consequently, it may be stated that the effect of all the above ether additives in the casting solution is to decrease the solvent power of acetone for cellulose acetate and hence increase the size of supermolecular polymer aggregates in the casting solution. Both increase in the boiling point of the additive and increase in the extent of supermolecular polymer aggregation in the casting solution decrease the evaporation rate constant. Since the latter is particularly more sensitive to casting solution structure, increase in the extent of supermolecular polymer aggregation in the casting solution may be expected to be the predominant effect of the additive on the porous structure of the resulting membrane surface. Referring to previous data (ref. 10-5) for batch 316-(10/30)-type films, one notes correspondingly that the effect of decrease in the temperature of the casting solution (i.e., simultaneous decrease in evaporation rate constant and increase in the size of supermolecular polymer aggregates in the casting solution) is to increase shrinkage temperature and decrease product rate. Thus, at the film-casting conditions used in this work, the effect of the above ether additives on the porous structure of the resulting membrane is similar to that produced by increase in the size of supermolecular polymer aggregates in the casting solution brought about by the appropriate change in the temperature of the casting solution without solvent modification by additive.

Previous data (ref. 10-5) on batch 316-type membranes also showed that product rate increased and shrinkage temperature decreased with decrease in the temperature of the casting atmosphere (i.e., decrease in evaporation rate constant) at the casting solution temperature of 0°C. On the basis of the foregoing discussion, the effect of the above decrease in the temperature of the casting atmosphere can be simulated by using an additive of high boiling point in the casting solution. This possibility was confirmed by a set of experiments with membranes obtained from a casting solution containing 5 wt.-% *n*-butyl ether (boiling point 142°C) as the additive. The temperature of the casting solution and the temperature of the casting atmosphere were kept at 0° and 30°C, respectively, during film casting. The latter membrane yielded a product rate of 28.6 g/hr at 90% level of solute separation, and the corresponding shrinkage temperature was 79°C, compared to a product rate of 14 g/hr and shrinkage temperature of 84°C for the membrane obtained from the same casting solution under the film casting conditions specified for the data in Figure 1.

**Effect of Ketones as Additives.** Figure 1 shows that shrinkage temperature passes through a minimum and product rate decreases with increase in the boiling point of the ketones used (acetone, methyl ethyl ketone, cyclohexanone, and isobutyl ketone) as additives. The existence of a minimum in shrinkage temperature indicates that the inclusion of the additive in the casting solution generates competing effects on the porous structure of the resulting membranes.

The shrinkage temperature (75°C) corresponding to the additive (isobutyl ketone) whose boiling point is highest is less than the shrinkage tem-

perature (78°C) corresponding to the additive (acetone) whose boiling point is the lowest used. This result is analogous to the effect on shrinkage temperature brought about by a decrease in evaporation rate constant caused by a decrease in the temperature of the casting atmosphere only, at any temperature of the casting solution for the batch 316-type films as shown in ref. 10-5.

On the basis of the data on solution viscosity,<sup>14</sup> Mark-Houwink constants,<sup>15</sup> and solubility parameter (Table I), one can conclude that the solvent powers of the additive substances for cellulose acetate are in the order acetone > methyl ethyl ketone > cyclohexanone > isobutyl ketone. This means that the effect of the above additives in the casting solution is to progressively decrease the solvent power of the additive-modified acetone solvent for cellulose acetate and hence increase the size of supermolecular polymer aggregates in the casting solution. This effect on casting solution structure also tends to decrease evaporation rate constant during film formation. While a decrease in evaporation rate constant caused by a decrease in the temperature of the casting atmosphere tends to decrease shrinkage temperature, a similar decrease in evaporation rate constant caused by an increase in the size of supermolecular polymer aggregates in the casting solution tends to increase the shrinkage temperature for resulting membranes as shown by data in ref. 10-5. These two opposing tendencies account for the existence of a minimum in shrinkage temperature as the overall effect of the ketone additives used.

Referring to product rate data in ref. 10-5 for the batch 316-type membranes, it may be noted that at each temperature of the casting atmosphere, the product rate passes through a maximum by changing the temperature of the casting solution. When the temperature of the casting atmosphere is reduced, the temperature of the casting solution corresponding to maximum product rate is also reduced. The disposition of the locus of the maxima in product rates indicates that a simultaneous decrease in the temperature of the casting atmosphere and the temperature of the casting solution within certain ranges of the above temperatures may result in very little change in product rates. This possibility is reflected in the product rate data in Figure 1, which shows that the product rates obtained with methyl ethyl ketone and cyclohexanone as additive are not too different in spite of a significant difference in their boiling points.

It may hence be concluded that under the film-casting conditions used in this work, the effect of the above ketone additives on the porous structure of the resulting membrane is similar to that produced by a simultaneous decrease in the temperature of the casting atmosphere and the temperature of the casting solution without solvent modification by additive.

#### **Effect of Esters, Nitro Compounds, and Hydrocarbons as Additives.**

Figure 1 shows that shrinkage temperature passed through a minimum and product rate remained essentially unchanged with increase in the boiling point of the esters used (methyl formate, ethyl formate, methyl acetate, and ethyl acetate) as additives. These results are similar to those

obtained with the ketone additives discussed earlier. Figure 1 also shows that shrinkage temperature increased and product rate decreased with increase in the boiling point of the nitrocompounds (acetonitrile, nitromethane, and nitroethane) and hydrocarbons (isopentane, *n*-hexane, and *n*-heptane) used as additives. These results are similar to those obtained with the ether additives discussed earlier.

**Secondary Additives and Membrane Productivity.** Under the experimental conditions specified in Figure 1, the use of ethyl ether as the secondary additive in the casting solution improved the productivity of the resulting membranes from 26 to 30.5 g/hr. The use of methanol, ethanol, isopentane, or *n*-hexane as the secondary additive under similar conditions did not change the productivity of the resulting membranes, and the use of each of the other additives tested decreased the productivity of the resulting membranes significantly. These results show that the use of secondary additives in the casting solution has important consequences on the surface pore structure of resulting membranes and indicate the possibility of improving the product rate of cellulose acetate membranes by appropriate choice of secondary additives. In view of the encouraging results obtained with ethyl ether as the additive, some further experiments were carried out with ethyl ether.

#### Casting Solutions Containing Ethyl Ether as Secondary Additive

**Effect of Ether Content in Casting Solution.** Figure 4 illustrates the effect of ether content in the casting solution on shrinkage temperature and product rate obtained for the resulting membranes. The results showed that shrinkage temperature passed through a minimum and product rate passed through a maximum with increase in ether content in the casting solution. An increase in ether content in the casting solution increases both the size of supermolecular polymer aggregates in the casting solution and evaporation rate constant during film formation. The former effect tends to generate a smaller number of bigger-size pores, and the latter effect tends to generate a larger number of smaller-size pores on the membrane surface during film formation. These two opposing tendencies are reflected in the shrinkage temperature and product rate correlations shown in Figure 4.

The overall process of pore generation and development includes also the simultaneous process of pore depletion by droplet coalescence in the interdispersed phase during film formation. In the ether concentration range up to 5%, the shrinkage temperature decreased and product rate increased with increase in ether content. These results indicate that in the above range, the predominant effect of the additive is the increase in evaporation rate constant during film formation, as a result of change in solution structure. This is confirmed by the similarity of the above data with those obtained for the batch 316-type casting solution in the casting solution temperature range of 0° to 10°C at the casting atmosphere tem-

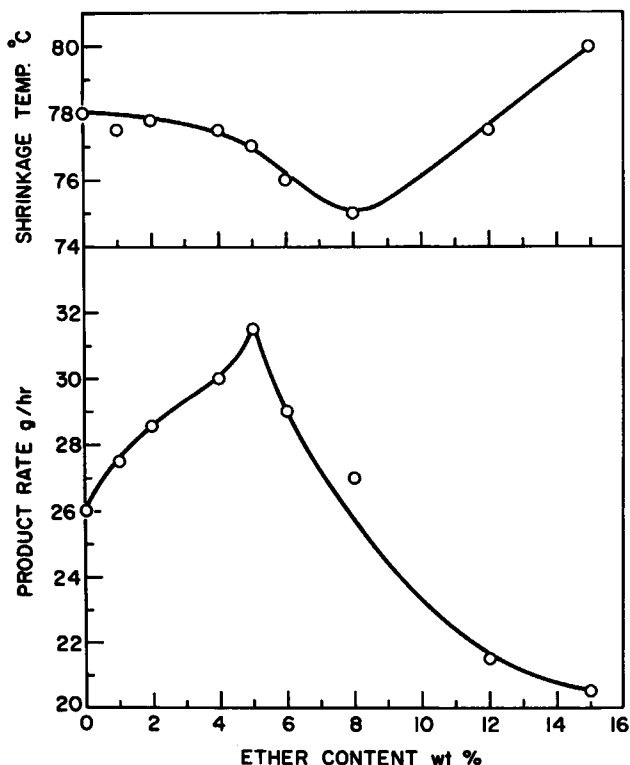


Fig. 4. Effect of ether content in casting solution on shrinkage temperature and product rate of membranes at 90% level of solute separation. Membrane area, 13.2 cm<sup>2</sup>; solution system, NaCl-H<sub>2</sub>O; feed concentration, 3500 ppm NaCl;  $k = 25 \times 10^{-4}$  cm/sec; operating pressure, 250 psig.

perature of 30°C (ref. 10-5). In the ether concentration range of 5% to 8%, the shrinkage temperature decreased still further, but the product rate also decreased with increase in ether content. These results show that in the above range, the predominant effect of the additive is the simultaneous decrease in evaporation rate constant and increase in droplet coalescence in the interdispersed phase during film formation. In the ether concentration range of 8% to 15%, the shrinkage temperature increased and the product rate decreased still further with increase in ether content. These results indicate that in the above range of ether concentration in the casting solution, the nonsolvent effect of the additive is predominant.

Figure 4 shows that the shrinkage temperature was lowest with ether content of 8%, whereas the product rate was highest with the ether content of only 5% in the casting solution. These results again suggest<sup>10</sup> that the simultaneous processes of pore generation by droplet formation and growth and pore depletion by droplet coalescence in the interdispersed phase during film formation are mutually independent.

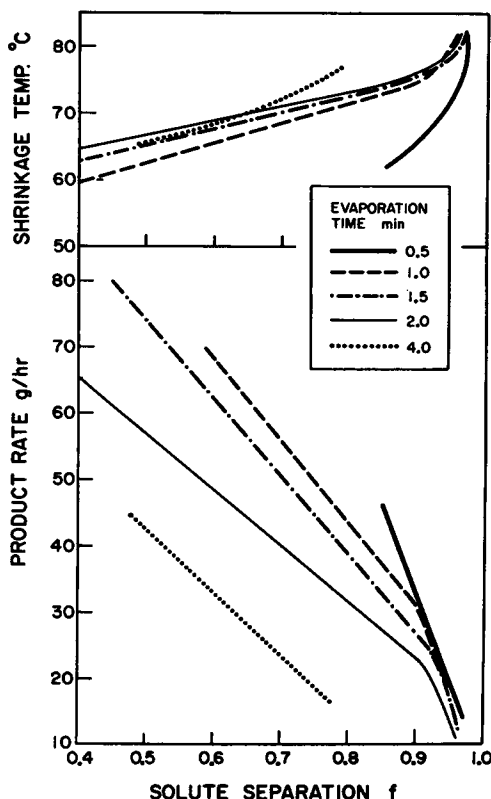


Fig. 5. Effect of evaporation time on shrinkage temperature and product at different levels of solute separation. Membrane area, 13.2 cm<sup>2</sup>; solution system, NaCl-H<sub>2</sub>O; feed concentration, 3500 ppm NaCl;  $k = 25 \times 10^{-4}$  cm/sec; operating pressure, 250 psig.

**Effect of Evaporation Time on Membrane Performance.** An evaporation time of 1 min was used in all the experiments discussed above. The effect of variation of evaporation time in the range of 0.5 to 4 min on membrane performance (shrinkage temperature and product rate versus solute separation) was studied at an operating pressure of 250 psig. Membranes obtained from casting solutions containing 5 wt-% ethyl ether as the secondary additive were used in these studies. The other details of casting solution composition and film-casting conditions used were the same as before. The results obtained are given in Figure 5, in which experimental points are omitted for clarity of presentation.

Figure 5 shows that generally shrinkage temperature increased and product rate decreased with increase in evaporation period. At levels of solute separation <95%, the shrinkage temperature was considerably less, the shrinkage temperature profile was more steep, and the corresponding product rates were a little more for a 0.5-min evaporation period than for longer evaporation periods. With a 4-min evaporation period, the shrink-

age temperature profile tended to become steeper compared to that obtained for a 1- to 2-min evaporation period, and the corresponding product rates were far less than those obtained for the shorter evaporation periods. These results show that a 0.5-min evaporation period resulted in an initial larger number of smaller size pores on the membrane surface, and longer evaporation periods promoted droplet growth and coalescence in the interdispersed phase during film formation resulting ultimately in a smaller number of bigger pores on the membrane surface in the as-cast condition. Similar results have been reported and discussed before.<sup>7,8</sup>

**Effect of Operating Pressure and Continuous Operation on Membrane Performance.** The data given in Figures 1 and 5 show that the productivity of membranes obtained from the casting solution containing 5 wt-% ethyl ether as the secondary additive was 20% to 25% more than the productivity of membranes obtained from the corresponding casting solution (batch 316(10/30)-type) without solvent modification by additives. A few experiments were also carried out with the former membranes at the operating pressures of 600 and 1500 psig using 5000 ppm NaCl-H<sub>2</sub>O and 0.5M NaCl-H<sub>2</sub>O as feed solutions. Continuous test runs were also carried out for 72-hr periods at operating pressures of 250, 600, and 1500 psig. The data obtained were compared with those obtained with the batch 316(10/30)-type membranes reported earlier.<sup>10</sup> The results showed no pronounced improvement in productivity at 600 and 1500 psig experiments, and no change in compaction characteristics at all the three pressures tested. Therefore, one may conclude that while the membranes obtained from the ether-modified casting solutions are significantly better for low-pressure reverse osmosis operations, they are not significantly better than the batch 316(10/30)-type membranes at higher operating pressures.

As pointed out earlier,<sup>8</sup> flux changes could be caused by changes in the effective thickness of the transition layer as well as the number and size of pores in the surface layer. There is no simple way by which the effects of the above two variables can be isolated. Consequently, for practical purposes, the results obtained in this work were discussed above as though the number and size of pores on the membrane surface were the only variable. The results of the reverse osmosis experiments at different operating pressures indicate that the importance of possible changes in the effective thickness of the transition layer as a factor governing membrane flux cannot be overemphasized. The most efficient ether-containing casting solution was characterized by a shorter evaporation time to produce the most efficient low-pressure membranes. A slightly faster compaction rate (over batch 316(10/30)-type) at 600 and 1500 psig implied that the transition layer in the membrane might not have had the same structural integrity as the batch 316(10/30)-type membranes. Thus, one may surmise that the effective thickness of the transition layer of the membrane tends to increase with an increase in operating pressure and/or continued reverse osmosis operation for an extended period of time at the same operating pressure.

## CONCLUSIONS

The results presented in this paper are consistent with the concept that 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 of the membrane surface and hence the performance of the membrane in reverse osmosis. In the previous paper,<sup>10</sup> it was shown how solution structure and evaporation rate could be varied by changing the temperature of the casting solution and the temperature of the casting atmosphere for a given casting solution composition. This paper illustrates how the effects of the above two temperature changes can be simulated (without changing the above two temperatures) by replacing a small part of the solvent by a secondary additive in the casting solution. Thus the use of secondary additives in the casting solution gives a new flexibility to the choice of film casting conditions and offers the possibility of generating new techniques for optimization, quality control, and the general development of reverse osmosis membranes.

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