Studies on the Development of Improved Reverse Osmosis Membranes from Cellulose Acetate–Acetone–Formamide Casting Solutions

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Synopsis

Improved membranes from cellulose acetate–acetone–formamide casting solutions have been prepared for low-pressure reverse osmosis applications. The film-casting details for one such type of membranes (Batch 400) are as follows. Casting solution composition: cellulose acetate (E-398-3), 17 wt-%, acetone, 56 wt-%, formamide, 27 wt-%; temperature of casting solution, 24°C; temperature of casting atmosphere, 24°C; casting atmosphere, ambient air in contact with 30 wt-% acetone in aqueous solution; solvent evaporation period, 30 sec; gelation medium, ice-cold water. Using aqueous feed solutions containing 3500 ppm of NaCl, the product rates obtained with the above membranes at 95, 90, and 60% levels of solute separation were 15.9, 22.1, and 58.7 gallons/(day ft²), respectively, at 250 psig under feed flow conditions corresponding to a mass transfer coefficient of 45×10^{-4} cm/sec on the high-pressure side of the membrane. The effects of casting solution composition, presence of acetone in the casting atmosphere, evaporation period, evaporation rate constant, and the remoteness of casting solution composition from the corresponding phase boundary composition on membrane performance and shrinkage temperature profile were found to be similar to those reported earlier for membranes obtained from cellulose acetate–acetone–aqueous magnesium perchlorate casting solutions. The results illustrate the practical utility of the approach based on the solution structure–evaporation rate concept for creating more productive reverse osmosis membranes.

INTRODUCTION

Porous cellulose acetate reverse osmosis membranes which are extensively being used in industry and research are generally obtained from one of two different types of casting solutions. One type involves a solution of cellulose acetate, acetone, and aqueous magnesium perchlorate, and the other type involves a solution of cellulose acetate, acetone, and formamide. The CA-NRC-18 (or simply, Batch 18) and the CA-NRC-47 (or simply, Batch 47) type membranes are examples of those obtained from the above two types of casting solutions, respectively.[1–4] The recent work of Kunst and

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Sourirajan[5−8] has led to a new approach to the general problem of developing more productive reverse osmosis membranes, i.e., membranes capable of giving higher permeation rates at any given level of solute separation under identical operating conditions. In this approach, the state or the structure of the casting solution (which is a function of its composition and temperature) and the rate of solvent evaporation during film formation (which is a function of solution structure, nature of the casting atmosphere, and the temperature of the casting atmosphere) together constitute an important interconnected variable governing the surface pore structure, and hence the performance of the resulting membrane. The distinguishing feature of this approach to reverse osmosis membrane development lies in the analysis of the usual film casting variables in terms of correlating membrane performance data with the casting solution structure, solvent evaporation rate during film formation, and the shrinkage temperature profile. Using this approach, more productive porous cellulose acetate membranes have been produced for low-pressure reverse osmosis applications using casting solutions of the first type mentioned above. Batch 301- and 316-type membranes are typical of such improved membranes.[6,8] This paper extends the new approach to the development of improved membranes for similar applications using casting solutions containing cellulose acetate, acetone, and formamide.

As in previous papers[5−8] the data are interpreted on the basis of surface pores, their number, size, and size distribution. It is recognized that flux changes could be caused by changes in the thickness of the surface layer also. But there is no simple way by which the thickness of the surface layer can be precisely fixed. Furthermore, one may consider that the microporous structure of the asymmetric membrane is a continuum made up of three mutually distinct regions, namely, a comparatively very thin, dense surface layer, a thicker transition layer, and a very much thicker spongy support layer, each region being successively more porous. There is, however, no precise boundary between adjacent regions. During film formation, any decrease in the thickness of the surface layer may also simultaneously result in the integration of a part of the transition layer into the surface region, thus affecting the number and size of pores on the membrane surface. Consequently, in a surface layer which is only a few molecular layers thick, one cannot isolate the effects of changes in the thickness of the surface layer from those due to changes in the number and size of pores in that layer. For practical purposes of membrane development, it has proved useful to discuss membrane performance on the basis of an effective number and size of pores on the membrane surface.

EXPERIMENTAL

Film Details

Eastman cellulose acetate (E-398-3) and technical-grade formamide were employed. The casting solution compositions and the film casting condi-

TABLE I
Film-Casting Details

Temperature of casting solution: 24°C
Temperature of casting atmosphere: 24°C
Casting atmosphere: ambient air, or ambient air in contact with aqueous solution of
  acetone as indicated
Solvent evaporation period: 30 sec unless otherwise specified
Gelation medium: ice-cold water
Duration of film setting in ice-cold water: >1 hr
Nominal film thickness: 0.005 in.
Casting solution composition, wt-%

Batch	47	403	400	401	402
cellulose acetate					
(acetyl content 39.8%), wt-%	25	17	17	17	17
acetone, wt-%	45	54	56	58	60
formamide, wt-%	30	29	27	25	23

tions used are given in Table I. The gelation medium was ice-cold water in all cases.

Reverse Osmosis Experiments

The apparatus and experimental procedure employed were the same as those used by Kunst and Sourirajan.[5] Aqueous feed solutions containing 3500 ppm of sodium chloride (reagent grade) were used in conjunction with membranes preshrunk under water at different temperatures and initially subjected to a pure water pressure of 300 psig for 1 to 2 hr. 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], in grams per hour, and the pure water permeation rate [PWP], in grams per hour per given area of film surface, were determined at 250 psig using a feed flow rate of 350 cc/min. 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. The feed flow rate used gave a mass transfer coefficient k of 45×10^{-4} cm/sec on the high-pressure side of the membrane as calculated by the Kimura-Sourirajan analysis of experimental reverse osmosis data.[1,9] All performance data (i.e., data on solute separation and product rate) were compared at the above value of k, which was kept constant in all experiments.

Solvent Evaporation Rate Measurements

These were made by determining the change in weight of the polymer film cast on a small plate as a function of time, basically as described earlier by Kunst and Sourirajan.[7] Some improvements were made in the experimental technique. Small stainless steel plates (effective surface area 1.61 cm $\times$ 5.06 cm) grooved to different depths from 0.025 to 0.041 cm were used for film casting which was done by a hand-operated mechanical device attached to the side door of an analytical balance. In this arrangement, the plate entered the closed space of the balance case simultaneously as the film was being formed on it during casting. Since the atmosphere in the balance case could be maintained as desired, the nature of the casting atmosphere was held constant during the entire film-forming porcess. Further, when the film is cast on the plate, the latter could be easily slid on to the pan of the balance, if desired. Consequently, the time lag between casting and transfer of the plate to the pan of the balance was reduced to the minimum. To avoid end effects on film dimensions during casting, films were cast continuously on three plates placed in series, and only the middle plate was used for evaporation rate measurements. These improvements in technique resulted in more reproducible evaporation rate data.

The measurements were made at the laboratory temperature (23–24°C) with or without acetone vapor in the casting atmosphere. In the former case, the closed space of the balance case was kept in contact with the required concentration of aqueous acetone solution placed in a few shallow containers for at least 1 hr.

The weight of the casting plate plus film at any time t was designated as W_t. In the initial stages of solvent evaporation, weight changes were followed in 15-sec intervals, and, as the changes in weight became less, the weights were noted after longer time intervals until essentially a constant weight W_∞ was reached. Representing, as before,[7] the initial linear part of the log $(W_t - W_\infty)$ versus t plot by the equation

$$W_t - W_\infty = (W_0 - W_\infty)e^{-bt}$$

where W_0 is the extrapolated value of W_t at $t = 0$, the evaporation rate constant b (in min^{-1}) was determined for each film-casting condition. The value of b depends on the quantity $W_0 - W_\infty$ per unit area, which is a function of the thickness of the solution cast on the plate (i.e., groove depth), the viscosity of the casting solution, and the speed of film casting. Therefore, in order to obtain comparable values of b, a relative value of b, b_{rel}, was obtained for each casting condition, for a specified value of $W_0 - W_\infty$ per unit area, by interpolation from several experimentally determined evaporation rate constants.

Determination of Equilibrium Phase Separation Data

These data for the ternary system cellulose acetate (polymer)–acetone (solvent)–formamide (nonsolvent) were obtained following the same

method described earlier by Kunst and Sourirajan[7] for the ternary system cellulose acetate–acetone–aqueous magnesium perchlorate solution. The turbidity caused by phase separation was recognized by visual observation which was comparatively easier for the system studied because of the clarity of the solutions involved. All compositions stated are in weight per cent. Formamide has been designated as "nonsolvent" only for convenience of expression in the triangular composition diagram; in particular, such designation is not meant to imply that formamide has no solvent power for cellulose acetate.

RESULTS AND DISCUSSION

Effect of Casting Solution Composition

The preferred concentration of cellulose acetate was 25 wt-% in the cellulose acetate–acetone–formamide casting solution system developed by Manjikian, Loeb, and McCutchan[3]; this concentration was used in obtaining the Batch 47-type membranes (Table I). In comparison, in the original development of Loeb and Sourirajan,[10,11] the composition of the casting solution (Batch 25) was cellulose acetate 22.2 wt-%, acetone 66.7 wt-%, and magnesium perchlorate/water (1:9) 11.1 wt-%; in a latter development by Sourirajan and Govindan,[2] the composition of the casting solution (Batch 18)[11] was changed to cellulose acetate 17 wt-%, acetone 68 wt-%, and magnesium perchlorate/water (1:9) 15 wt-%. Under otherwise identical film-casting and operating conditions, the producitivity of Batch 18-type films is considerably higher than that of Batch 25-type films.[11] This result shows that a lower concentration of cellulose acetate in the casting solution tends to favor the formation of more productive reverse osmosis membranes. Further, a series of membranes with productivities much higher than those obtained with Batch 18-type membranes have been obtained by Kunst and Sourirajan[8] for low-pressure operation from cellulose acetate–acetone–aqueous magnesium perchlorate casting solution compositions containing 17 wt-% cellulose acetate. On the basis of the above results, the effect of decreasing the polymer concentration to 17 wt-% in the cellulose acetate–acetone–formamide casting solutions was investigated.

Table I gives the casting solution compositions and the other film casting details for the Batch 403-, 400-, 401-, and 402-type films used in this work. For comparison, the details for the Batch 47-type films are also included in the table. Batch 47-type films and the new films differ in the compositions of the film-casting solutions used and the specifications of the film-casting conditions. With respect to composition, the new casting solutions contained more solvent and less polymer and nonsolvent; compared within themselves, the new casting solutions had the same cellulose acetate content (17 wt-%) and progressively more acetone and correspondingly less formamide.

Figure 1a gives the performance data and the corresponding shrinkage temperature profiles for a set of films which were cast under identical condi-
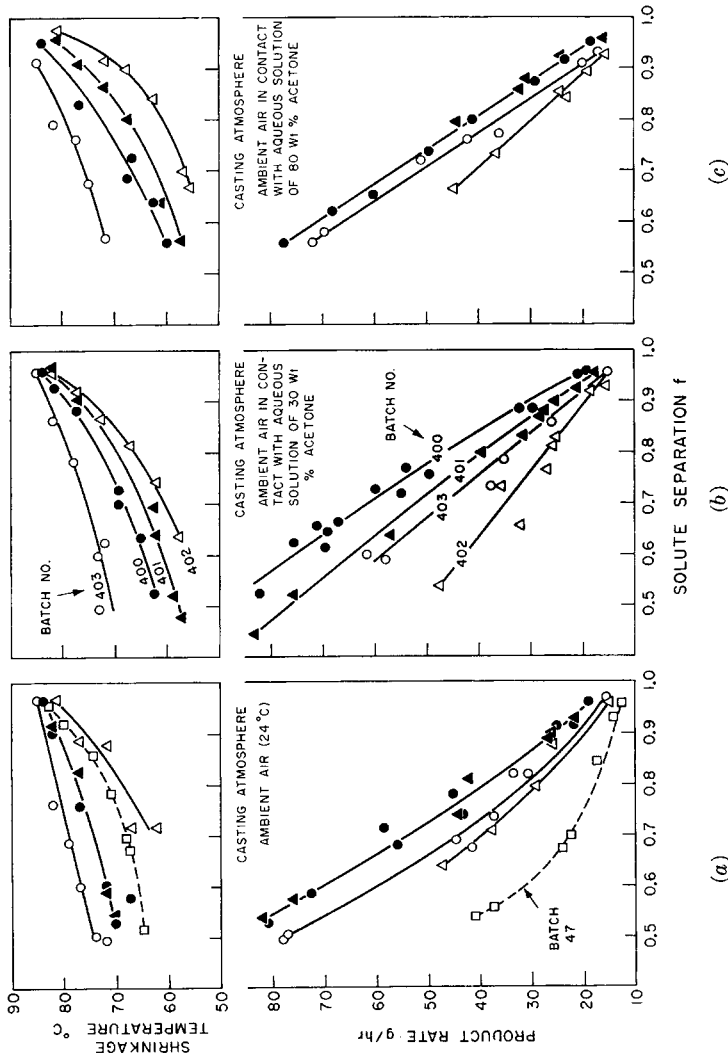
Fig. 1. Effect of casting solution composition and presence of acetone in the casting atmosphere on membrane performance and shrinkage temperature profile. Film type: (O) Batch 403; (●) Batch 400; (▲) Batch 401; (△) Batch 402; (□) Batch 47. Membrane area, 7.6 cm²; solution system, NaCl–H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

tions.   The results show that the productivities of the films obtained from the new casting solutions are far better than the productivity of the Batch 47-type membranes.   For example, at 95% level of solute separation, the product rate obtained with the Batch 47-type membrane was 13 g/hr, compared to 16.5, 18, 19, and 19 g/hr with the Batch 402-, 403-, 400-, and 401-type membranes, respectively.   At 60% level of solute separation, the product rate obtained with the Batch 47-type membrane was 32 g/hr, compared to 52, 56, 70, and 70 g/hr, respectively, with the new membranes specified above.   These data represent an increase in productivity by 25% to 118% for the new membranes.   Since all the membranes used were cast under identical conditions, the increase in productivity is attributed primarily to the changes in casting solution composition in general and the decrease in polymer concentration in particular.   These results not only confirm the practical validity of the general approach to membrane development established earlier by Kunst and Sourirajan,[5-8] but also give rise to a new class of more productive reverse osmosis membranes from cellulose acetate–acetone–formamide casting solutions.

The shrinkage temperature profile (i.e., shrinkage temperature-versus-solute separation correlation) for the Batch 403 films lies above all the other profiles and has the least slope; the corresponding profile for the Batch 402 films lies below all the others and has the highest slope.   These data indicate that the initial size of pores on the membrane surface in the Batch 403 films is relatively bigger and more uniform than that obtained in the other batches of new membranes studied.   Consequently, one may conclude that increase of acetone (with corresponding decrease in formamide) in the casting solution tends to create smaller and less uniform pores.

The shrinkage temperature profile for the Batch 47-type membranes is not too different from that obtained for the Batch 402-type membranes. Since the latter are more productive, and the other new membranes are even more so, it may be concluded that the new membranes have a larger effective number of pores compared to the Batch 47-type membranes.

The location and slope of the shrinkage temperature profile reflect the initial size and distribution of pores on the membrane surface.   Since the productivity of the membrane is a function of all the above factors, an optimum combination of such factors may be expected to exist for maximum productivity.   This is also indicated by the data given in Figure 1a which shows that, among the films tested, the highest productivity is shown by the Batch 400- and 401-type membranes which have essentially the same shrinkage temperature profile, lying between those obtained for the Batch 403- and 402-type membranes.

Effect of Presence of Acetone in the Casting Atmosphere

Figures 1b and 1c, along with Figure 1a, illustrate the effect of the presence of acetone in the casting atmosphere on the shrinkage temperature profile and performance of Batch 403-, 400-, 401-, and 402-type membranes. The results show that, with respect to each batch of membranes, the initial

size of pores on the membrane surface decreased progressively with increase in the amount of acetone in the casting atmosphere. This effect is most noticeable with the Batch 402 membranes, which were obtained from casting solution containing the highest amount of acetone.

An increase in the amount of acetone in the casting solution would increase the solvent evaporation rate, and the presence of acetone in the casting atmosphere would decrease the solvent evaporation rate during film formation. Since both these effects lead to the generation of relatively smaller-size pores on the membrane surface, it is clear that solvent evaporation rate is not the only factor affecting the ultimate size of the surface pores and that a decrease in pore size on the membrane surface can be accomplished either by increasing the acetone content in the casting solution or by decreasing the evaporation rate or by a combination of both.

From the point of view of membrane productivity, the formation of the required size of pores on the membrane surface must also be simultaneously accompanied by the generation of the largest number of such pores. Hence, as pointed out already by Kunst and Sourirajan,[5] the solvent evaporation rate should be appropriately adjusted to the state of the casting solution for best practical results. Too slow an evaporation rate could result in too slow a rate of droplet formation and development, which determines the ultimate size and number of surface pores. The solvent evaporation rate should be high enough to generate the largest number of dispersed droplets and low enough to prevent excessive rupture of the polyhedra walls prior to gelation.[5,12] Thus, an optimum evaporation rate would be expected for each casting solution structure for highest membrane productivity. This is indicated by the performance data given in Figure 1, which shows that Batch 400-type membranes, when cast in an atmosphere in contact with 30 wt-% acetone in aqueous solution, give the highest productivity among the membranes made under the other conditions of casting specified in Table I. For example, using aqueous feed solutions containing 3500 ppm of sodium chloride, the product rates obtained with the above Batch 400-type membranes at 95, 90, and 60% levels of solute separation were 15.9, 22.1, and 58.7 gallons/day/ft^2, respectively, at 250 psig under the feed flow condition corresponding to $k = 45 \times 10^{-4}$ cm/sec; these productivities are essentially the same as those obtained with the Batch 316-type membranes reported earlier by Kunst and Sourirajan.[8]

Effect of Evaporation Time

Figure 2 gives the shrinkage temperature profiles and the performance data for Batch 400-type membranes cast in an acetone atmosphere with evaporation periods of 30 sec, 1 min, and 2 min. The results show that a change in evaporation time affects both the shrinkage temperature profile and membrane performance. A longer evaporation time results in relatively bigger and more uniform pores, and a shorter evaporation time results in smaller and less uniform pores on the membrane surface. The performance is adversely affected by longer evaporation time, which indicates
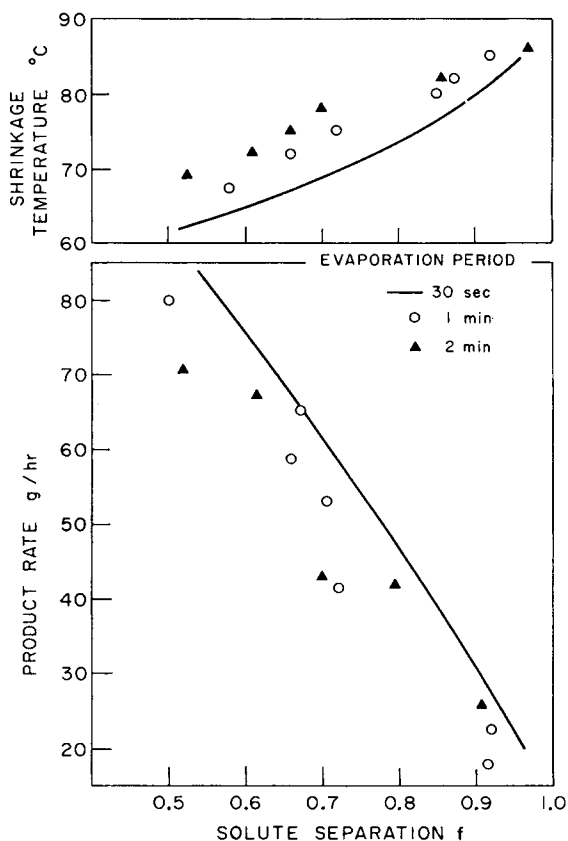
Fig. 2. Effect of evaporation period on membrane performance and shrinkage temperature profile. Film type, Batch 400; casting atmosphere, 24°C ambient air in contact with 30 wt-% acetone in aqueous solution; membrane area, 7.6 cm²; solution system, NaCl–H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec; operating pressure, 250 psig.

partial depletion and/or coalescence of the smaller, especially less than critical size,[1] pores on prolonged evaporation. An evaporation time of 30 sec seems to be best for the type of membranes used from the point of view of membrane productivity.

Equilibrium Phase Separation Data

Figure 3 represents a triangular composition diagram for the polymer (P)–solvent (S)–nonsolvent (N) systems under study. The compositions at which phase separation occurs (phase boundary curve) with respect to the cellulose acetate–acetone–formamide system in the temperature range 0° to 30°C are plotted in Figure 3 along with the corresponding curve for the cellulose acetate–acetone–aqueous magnesium perchlorate system at 24°C reported earlier.[7] The figure also indicates the location of the compositions
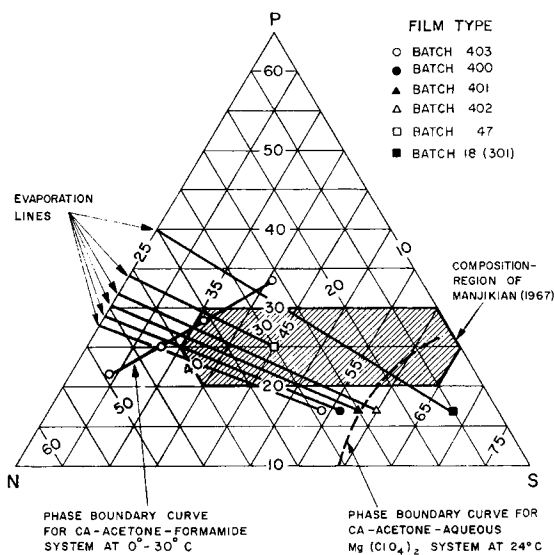
Fig. 3. Equilibrium phase separation compositions (wt-%) at different solution temperatures for the polymer (P)–solvent (S)–nonsolvent (N)–systems.

of the film-casting solutions used in making the Batch 403-, 400-, 401-, 402-, 47-, and 18-type membranes. (The casting solution compositions are identical for Batch 18- and 301-type membranes.) The shaded area is that given by Manjikian[4] representing the compositions from which successful membranes were prepared by him; his optimum composition (Batch 47-type) lies well within this area.

Several aspects of the data given in Figure 3 are significant. The compositions of the casting solutions used for *all* the improved membranes (Batch 403-, 400-, 401-, 402-, and 301-types) lie outside the composition region given by Manjikian. This means that fabrication of successful membranes is neither limited to casting solution compositions represented by the shaded area nor does the composition used for the Batch 47-type membranes represent an optimum from the point of view of membrane productivity. Casting solution composition is not the only factor governing membrane productivity.

The phase boundary curve for the cellulose acetate–acetone–formamide system is much farther away from the point S (Figure 3) than is the corresponding curve for the cellulose acetate–acetone–aqueous magnesium perchlorate system. In addition, the location of the phase boundary curve for the former system is unaffected by changes in solution temperature in the range 0° to 30°C, in contrast to the corresponding curve for the latter system.[7] These data support the conclusions of Kesting and Menefee[12] that formamide serves to increase the solvent power of acetone and that the polymer molecules within the supermolecular aggregates tend to dissociate and exist as individual molecules. These conclusions mean that the state of

supermolecular polymer aggregation (solution structure) in the cellulose acetate–acetone–formamide casting solution system does not change significantly by changes in solution temperature in the range 0° to 30°C.

The points representing the compositions used for the new casting solutions are more remote from the phase boundary line than the point representing the Batch 47 composition; such greater remoteness indicates lesser supermolecular polymer aggregation in the new casting solutions used. Comparing the new casting solutions within themselves, the point representing the Batch 403 composition is least remote, and that representing the Batch 402 composition is most remote from the phase boundary curve. In conjunction with the shrinkage temperature profiles and performance data given in Figure 1, Figure 3 indicates that, when cellulose acetate concentration in the casting solution and the evaporation period during film formation remain constant, the greater the remoteness of the point representing the composition of the casting solution from the phase boundary curve (i.e., the lesser the supermolecular polymer aggregation in the casting solution), the smaller are the pores produced on the membrane surface.

Data on Evaporation Rate Constants

Table II and Figures 4 and 5 give relative quantitative data on the evaporation rate constant b for an arbitrarily chosen quantity of solvent
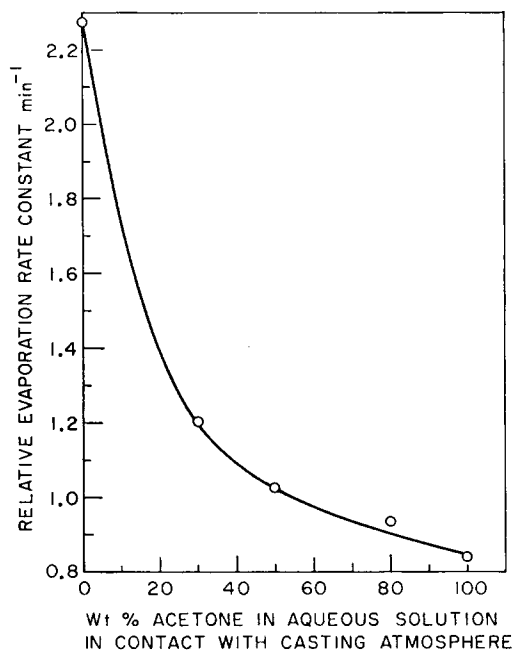
Fig. 4. Effect of presence of acetone in casting atmosphere on relative evaporation rate constant. Film type, Batch 400; temperature of casting solution, 24°C; temperature of casting atmosphere, 24°C; $W_0 - W_\infty = 0.065$ g.

TABLE II
Effect of Casting Solution Composition on Relative
Evaporation Rate Constants[a]

Acetone in aqueous solution in contact with casting atmosphere, wt-%	b_{rel}, min^{-1}			
	Batch 403	Batch 400	Batch 401	Batch 402
0	1.428	2.275	2.936	3.017
30	1.142	1.204	1.842	2.086
80	0.951	0.944	1.128	1.175

[a] Temperature of casting solution, 24°C; temperature of casting atmosphere, 24°C; $W_0 - W_\infty = 0.065$ g; area of evaporating surface, 1.61 cm $\times$ 5.06 cm.

evaporated ($W_0 - W_\infty = 0.065$ g) from the casting solution spread on an area of 8.15 cm^2 as stated earlier.

Table II shows that b increases with increase in acetone content in the casting solution and decreases with increase in acetone content in the casting atmosphere. Since both changes (i.e., increase in acetone content in the casting solution and increase in acetone content in the casting atmosphere) lead to the generation of smaller and more numerous pores, the data in Table II and Figure 1 indicate the existence of an optimum value of b for maximum membrane productivity, and that the casting solution structure
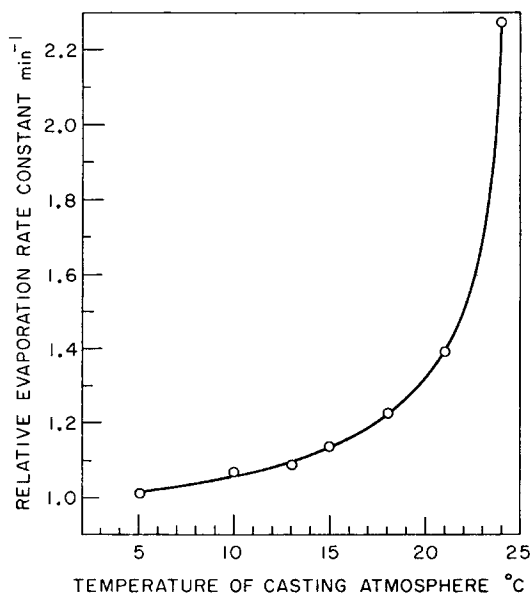

Fig. 5. Effect of temperature of casting atmosphere on relative evaporation rate constant. Film type, Batch 400; temperature of casting solution, 24°C; casting atmosphere, ambient air; $W_0 - W_\infty = 0.065$ g.
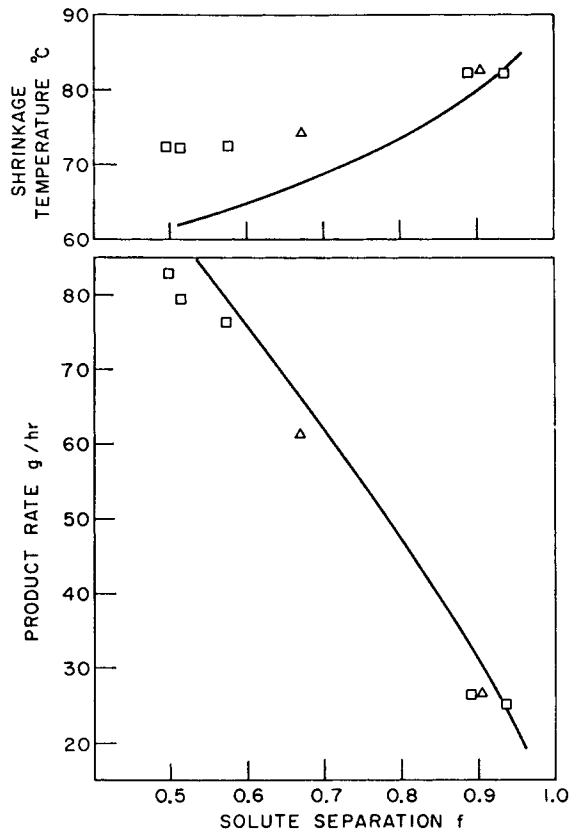
Fig. 6. Effect of different casting conditions on membrane performance and shrinkage temperature profile. Film type, Batch 400; temperature of casting solution, 24°C. Casting conditions: (—) 24°C ambient air atmosphere in contact with 30 wt-% acetone in aqueous solution; (△) ambient air at 18°C; (□) ambient air at 5°C. 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.

and solvent evaporation rate together constitute an interconnected variable governing the surface pore structure obtained during film formation.

The changes in the value of b caused by the presence of acetone in the casting atmosphere whose temperature was held constant at 24°C are shown in Figure 4, and those caused by changes in the temperature of the acetone-free casting atmosphere are shown in Figure 5. In the acetone-free casting atmosphere at 24°C, the value of b was 2.275 min⁻¹. At the above temperature, when the casting atmosphere was in contact with 30 wt-% acetone in aqueous solution, the value of b steeply dropped to 1.204 min⁻¹ (Fig. 4); the latter value of b is the same as that obtained in an acetone-free casting atmosphere held at 17.6°C (Fig. 5).

Figure 6 gives the performance data for a few membranes cast in acetone-free ambient air at 18°C using the Batch 400-type casting solution at 24°C

and 30-sec evaporation period.   These data differed very little from those
obtained with the membranes made from the same casting solution but cast
in a 24°C ambient air atmosphere in contact with 30 wt-% acetone in
aqueous solution.   The small difference between performances is under-
standable on the basis of the difference in their respective shrinkage tem-
perature profiles.   The results hence confirm the observation made earlier[7]
that with casting solutions of identical structure, evaporation conditions
during film formation corresponding to the same value of b result in the
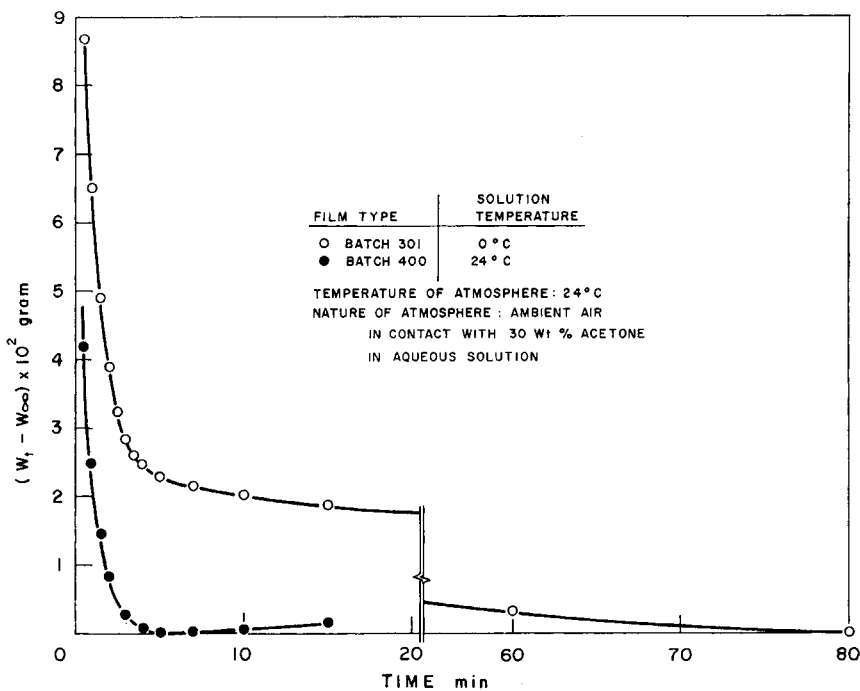
Fig. 7. Comparative solvent evaporation rates for the cellulose acetate–acetone–
aqueous magnesium perchlorate (Batch 301) and cellulose acetate–acetone–formamide
(Batch 400) casting solution systems.

same membrane performance provided the shrinkage temperature profiles
are not too far different.

Figure 6 also gives the performance data for a few membranes obtained
from the same casting solution (Batch 400-type at 24°C) and cast in an
acetone-free ambient air atmosphere at 5°C (corresponding to $b = 1.013$
min^{-1}) using the same evaporation period (30 sec).   The performance data
and the shrinkage temperature profile obtained were identical with those
given above for membranes cast at 18°C (corresponding to $b = 1.232$
min^{-1}).   These results give an indication of the degree of sensitivity of
membrane productivity to changes in the value of b for the cellulose acetate–
acetone–formamide casting solution systems.

Figure 7 gives two typical plots of experimental data on $W_t - W_\infty$ versus t (which also express solvent loss as a function of time) for the cellulose acetate–acetone–aqueous magnesium perchlorate (Batch 301) and cellulose acetate–acetone–formamide (Batch 400) casting solution systems. An analysis of these data indicates that, under the specified conditions of evaporation, the evaporation rate constant for the Batch 400-type casting solution is about twice that for the Batch 301-type casting solution and
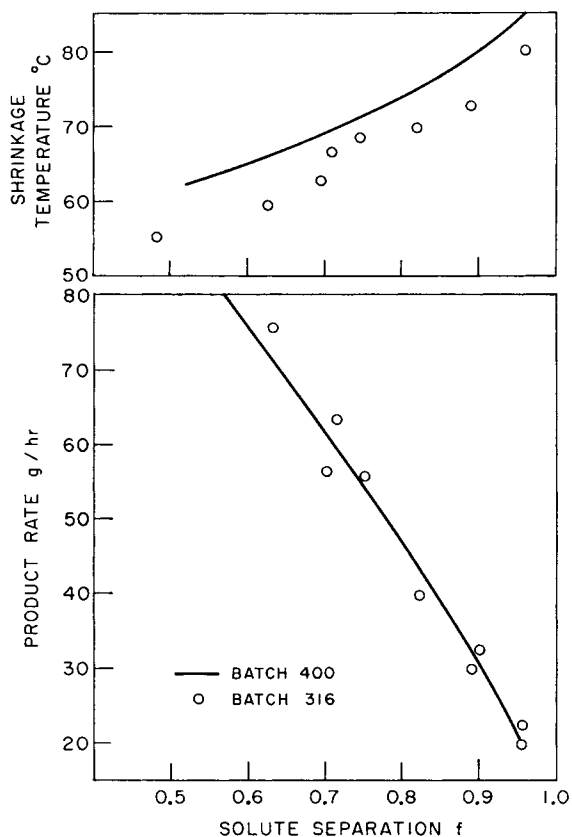
Fig. 8. Comparative performance of membranes at 250 psig. Casting solution temperature, 24°C; casting atmosphere, 24°C ambient air in contact with 30 wt-% acetone in aqueous solution; membrane area, 7.6 cm²; solution system, NaCl–H₂O; feed concentration, 3500 ppm NaCl; $k = 45 \times 10^{-4}$ cm/sec.

that, while acetone is the only significant evaporating component from the Batch 400-type casting solution, both acetone and water are significant evaporating components in the other casting solution. The above interrelated factors seem to explain the necessity for short evaporation periods needed for the Batch 400-type casting solution system (under the conditions used in this work) for best membrane productivity.

Data on Continuous Test Runs

A one-week continuous test run was conducted at 250 psig with two different samples of Batch 400-type membranes.　One of them gave 91% and the other gave 81% solute separation with aqueous feed solutions containing 3500 ppm NaCl.　In both cases, solute separation remained the
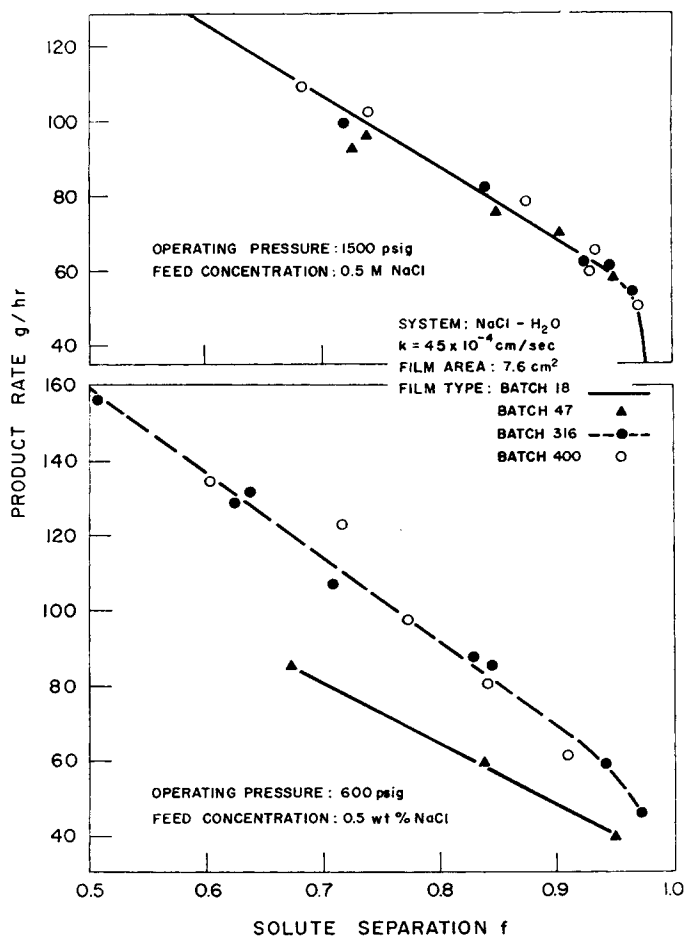

Fig. 9. Comparative performance of membranes at 600 and 1500 psig.　Casting solution temperature, $-10°C$ for Batch 18 and $24°C$ for other batches;　temperature of casting atmosphere, $-10°C$ for Batch 18 and $24°C$ for other batches;　casting atmosphere, ambient air for Batch 18- and 47-type membranes and ambient air in contact with 30 wt-% acetone in aqueous solution for Batch 316- and 400-type membranes; evaporation time, 4 min for Batch 18-, 30 sec for Batch 47- and Batch 400-, and 6 min for Batch 316-type membranes.

same during the entire test period.　After 24 hr of continuous reverse osmosis operation, the membrane fluxes were 91.2% and 88.8%, respectively, of those obtained initially for the above two membranes;　after seven days of continuous operation, the corresponding data were 91.2% and 88.0% of

initial fluxes.   Thus there is practically no change in membrane flux after the first 24 hr of continuous operation.   These limited data show that the compaction characteristics of Batch 400-type membranes are not too different from those observed for Batch 316-type membranes studied earlier.[8,13] However, more extensive data are needed for a critical evaluation of the new membranes for practical applications.

Comparative Performance of Membranes

Figure 8 gives the performance data and the shrinkage temperature profiles for the Batch 400- and 316-type membranes.   The latter type of membranes is one of the best obtained from cellulose acetate–acetone–aqueous magnesium perchlorate casting solution systems.[8]   The results show that both the above types of membranes have the same productivity at the operating pressure of 250 psig and that the Batch 316-type membranes have initially smaller pores.   Figure 9 gives the performance data for Batch 18-, 47-, 316-, and 400-type membranes[6] at 600 and 1500 psig.   The results again show that the Batch 400- and 316-type membranes have the same productivity at the above higher operating pressures also.   Further, while their performances are considerably better than those of Batch 18- and 47-type membranes at 600 psig, all the four types of membranes tested have essentially the same productivity at 1500 psig, which indicates that high operating pressures tend to close the small-size pores initially generated during film formation in the Batch 316- and Barch 400-type membranes.

CONCLUSIONS

The effects of film-casting variables (casting solution composition, presence of acetone in the casting atmosphere, evaporation period, evaporation rate constant, and the remoteness of the casting solution composition from the corresponding phase boundary composition) on membrane performance and shrinkage temperature profile observed for membranes obtained from cellulose acetate–acetone–formamide casting solutions are exactly similar to those observed for membranes obtained from cellulose acetate–acetone–aqueous magnesium perchlorate casting solutions reported earlier.[5–8]   The results illustrate the general validity, and the practical utility, of the approach based on the solution structure–evaporation rate concept for creating more productive reverse osmosis membranes.   Batch 400-type membranes represent a new class of highly productive membranes obtained from cellulose acetate–acetone–formamide casting solution system for low-pressure reverse osmosis applications.

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