

The Effect of Short Air Exposure Periods on the Performance of Cellulose Acetate Membranes from Casting Solutions with High Cellulose Acetate Content

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Synopsis

Highly productive cellulose acetate membranes were cast under conditions of very short air exposure periods from cellulose acetate-acetone-formamide casting solutions having a high cellulose acetate (CA) content and lying close to the phase boundary. Air exposure periods as short as 0.05 sec were used with CA content up to 32 wt-%. Membranes from a casting solution containing 30 wt-% cellulose acetate (E-398-3), 45 wt-% acetone, and 25 wt-% formamide perform as well as membranes from other compositions at all salt rejection levels for a 0.5 wt-% NaCl feed at 600 psig. Partial replacement of acetone by dioxane in the casting solution substantially increases the water flux from membranes cast with short air exposure periods at any given salt rejection level below 96% salt rejection. Addition of small amounts of ZnCl₂ to nondioxane casting solutions with 32 wt-% CA improves membrane performances remarkably for lower salt rejection levels, while the improvement in performance of membranes from 30 wt-% CA casting solutions with dioxane due to ZnCl₂ addition is marginal. Variation in air exposure from 0.05 to 2 sec results in minor performance variations in the membranes having any of these compositions. With air exposure periods beyond 2-3 sec, membrane fluxes drop drastically. The concept of a thinner skin satisfactorily explains the improvement in mixed solvent systems, whereas ZnCl₂ acts as a swelling salt. A Kimura-Sourirajan-type membrane performance plot indicates that for a 0.5 wt-% NaCl feed at 600 psig, membranes of the present work perform as well as the best performing membranes reported in the literature for conversion of brackish water.

INTRODUCTION

Asymmetric cellulose acetate (CA) membranes are nowadays extensively used by industry for purification or concentration of aqueous solutions by reverse osmosis. The requirement of more productive CA membranes for desalination and other applications has prompted numerous investigations about the composition of the casting solution and the nature of casting conditions necessary for obtaining membranes more productive than the original Loeb-Sourirajan¹ membrane. Other investigations have been directed toward elucidating the exact mechanism of formation of an asymmetric CA membrane. These investigations will not only enable manipulation of casting solutions and/or casting conditions for producing better CA membranes but also allow similar graded structures to be developed in permselective membranes made from polymers other than CA.

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Almost all casting solutions reported in the literature capable of forming asymmetric CA membranes are of two types: the first type, made of CA, acetone, and aqueous magnesium perchlorate, was originally used by Loeb and Sourirajan¹; the second type often used in industry contains CA, acetone, and formamide and was first developed by Manjikian et al.² for casting CA membranes at room temperature; the Loeb-Sourirajan¹ procedure involved casting at -5° – 10° C.

Modifications of the first type of casting solution include: partial or total replacement of acetone by other solvents,^{3,4} replacement of magnesium perchlorate by other additives,⁵ and addition of a second additive of various types.⁶ Sourirajan and Govindan⁷ have shown however that membranes cast from this type of solution with lower CA content, namely, 17% CA, 68% acetone, 1.5% magnesium perchlorate, and 13.5% water, yielded a higher solvent flux at a given salt rejection level than the original Loeb-Sourirajan¹ membrane (22.2% CA, 66.7% acetone, 1.1% magnesium perchlorate, 10.0% water).

The second type of casting solution, due to Manjikian et al.,² has been modified by Pilon, Kunst, and Sourirajan⁸ to contain 17% CA, 56% formamide, and 27% acetone for fabricating improved membranes instead of the original 25–30–45 formulation by Manjikian et al.² Recently some other modifications have also been made in the Manjikian formulation. These are discussed in the context of casting conditions below.

The compositional variables of the casting solution interact dynamically with the major variables in casting conditions, namely, air exposure period for the evaporation of the volatile solvent (acetone) before immersion in the gelation bath, composition of the casting atmosphere, temperature of surrounding as well as the casting solution, gelation temperature, etc. For example, both Kunst and Sourirajan⁹ and Pilon et al.,⁸ working respectively with modifications of the first type and the second type of casting solution, concluded that higher productivity in the membrane is a strong function of the rate of solvent evaporation from the cast film as well as the nature and conditions of the casting solution. The strong interaction between casting solution composition and casting conditions has prompted a number of investigators to optimize CA membrane performance by means of statistically designed experiments. In these experiments the interactions between the compositional variables of the casting solution, solvent evaporation time, water gelation bath temperature, annealing temperature, etc., are determined simultaneously to obtain an overall optimum. The works of Fahey and Grethlein¹⁰ and Chian and Fang¹¹ fall in this category. Fahey and Grethlein¹⁰ located the optimum coordinates around 27%–28% CA in a Manjikian—type-casting solution (e.g., 27.5% CA, 31.7% formamide, 40.8% acetone) with a short air evaporation period of around 1–2 sec. Chian and Fang¹¹ obtained an overall optimum where the evaporation period was 3.62 sec, the annealing temperature was 86° C, and the solution contained 35% formamide with CA and acetone in the ratio of 3:5 by weight.

None of the experimental investigations mentioned above was conducted at very short evaporation periods in the range of 0.00–0.20 sec. Only McCutchan and Johnson¹² carried out membrane fabrication at as short an evaporation period as 0.015 sec. Their casting solution, however, was the same as that of Manjikian et al.² They have concluded that tubular membranes formed with very short evaporation periods (\sim 0.015 sec) do develop a skin and perform approximately as well as standard membranes but only at higher annealing tem-

peratures (30 gfd, 86% rejection, cured at 80°C). In view of the strong interactions between the casting conditions and the casting solution composition, the beneficial effects of a short evaporation period (if any) are not going to be obtained with the casting solution of Manjikian et al.,² which requires quite a long evaporation time. Casting solutions with much higher CA concentration and with compositions close to phase boundary¹⁰ are necessary to compensate for the solvent loss that accompanies a long evaporation time. Moreover, according to Frommer and Lancet¹³ the possibility exists that only one dense precipitated layer on top of the CA membrane may be attained with short evaporation times, which may help eliminate the thick layer next to this dense layer thus improving membrane productivity. The photomicrographs of Frommer and Lancet¹³ further show a thickening of the topmost dense layer with increase in evaporation time, and these authors also state that the rate of thickening of this topmost layer is consistent with the rate of loss of acetone which is found to be very high initially. It may thus be postulated that a very short evaporation period is likely to produce a thinner skin with a much sharper transition into the porous backing in terms of pore diameters. On the other hand, the higher initial polymer concentration in the casting solution will produce a structure denser than that one would have obtained otherwise. Thus whether more productive membranes can be obtained at short evaporation times from the second type of casting solutions with high CA concentration and lying close to phase boundary is a subject worthy of investigation. Strathmann et al.¹⁴ have shown that high polymer concentration in the casting solution at the time of precipitation and slow rate of polymer precipitation in the gelation bath are required to produce uniform membranes without defects such as finger-like protrusions and cavities.

The object of this study is therefore to investigate the productivity of flat cellulose acetate membranes cast with very short evaporation periods from solutions containing formamide, acetone, and CA, the solution composition being close to the phase boundary in the CA–acetone–formamide phase diagram. Another object of the present work is to investigate the effect of partially replacing acetone in the above type of casting solutions by the higher-boiling dioxane. Such a mixed solvent system provides a way to control the rate of acetone loss from the cast film at short evaporation times which makes the control of the casting atmosphere difficult. Decrease in total amount of acetone lost, which is directly responsible for skin formation, will help in producing a thinner skin. It may be noted that King et al.¹⁵ have demonstrated the suitability of the acetone–dioxane solvent system for CA blend membranes in comparison to other mixed solvent systems containing acetone and a second solvent capable of dissolving cellulose triacetate. Kunst et al.²⁷ have shown, for the first type of solution, that if dioxane replaces acetone to the extent of 5%–15%, the relative acetone evaporation rate from the surface decreases with increase in dioxane concentration and the membrane performance is better with 10% dioxane. Furthermore, Frommer and Lancet's¹³ investigations show that membrane structure from the dioxane–CA system is somewhat closer to the membrane structure from the acetone–CA system in spite of their basic differences. We have in addition investigated the effect of adding small amounts of $ZnCl_2$ or ZnI_2 to the casting compositions stated earlier to explore the beneficial effects of swelling by inorganic salts. The object in these latter experiments with dioxane and/or $ZnCl_2$ has been to seek additional improvements in membrane perfor-

mances rather than an optimization in the manner of Fahey et al.¹⁰ and Chian et al.¹¹ The results of these investigations will demonstrate that CA membranes cast under short air exposure periods from high-CA casting solutions close to the phase boundary are highly productive for conversion of brackish water and other applications.

EXPERIMENTAL

Materials

Eastman cellulose acetate (E-398-3), analytical reagent-grade acetone, dioxane, formamide, and zinc chloride were used in preparing casting solutions in flasks which were rotated while partially immersed in a thermostat maintained at 45°C. The purity of zinc iodide used was 98%. Cellulose acetate powder was used in the as-received state from the same lot (No. AC-2109) in all experiments unless otherwise mentioned, since McCutchan and Johnson¹² have shown that drying CA had no effect on membrane performance. The water content of the CA powder was found to be 4 wt-% as observed by McCutchan and Johnson.¹² Laboratory-grade sodium chloride and distilled water were used for preparing 5000 ppm brackish water feed. Analytical-grade sodium chloride was used for standardization of AgNO₃ solutions used for salt analysis of the feed and permeate.

Membrane Fabrication

Two simple manual flat membrane casting apparatuses using a doctor's knife were used for membrane casting. The details of the equipment are available in the thesis by Agarwal.¹⁶ The horizontal casting apparatus was used when the air evaporation period was more than 2 sec. The vertical/casting apparatus (inclined at 4° with respect to the vertical) was used when the air evaporation period was less than or equal to 2 sec. Figure 1 gives a schematic of the vertical casting arrangement in which the speed of the glass plate going down could be varied from 3 ft/min to 12 ft/min. The acetone evaporation time in air could be varied from 2 to 0.05 sec in this apparatus by simultaneously varying the height of the gap between the doctor knife and the gelation bath level. Since the casting was done by hand driving of glass plates in a guided channel into the ice-cold gelation bath, the speed of casting was somewhat nonuniform. It was estimated that the evaporation periods reported later may have a maximum error of about 10%. The gelation bath was maintained at 1°C. Casting of films was done at room temperature and humidity. Since the air exposure region of the vertical membrane casting arrangement had a small volume (some of the smaller values of the airgaps being ¼ in. or even lower), its conditions were controlled more by the ice-cold water bath rather than by the ambient temperature and humidity variations. As shown by Rangaiah,¹⁷ membranes cast from similar casting solutions on two different days with ambient temperatures being 37° and 25°C, respectively, exhibited negligible differences in performances. Most of the membranes were cast in a room temperature range of 20°–27°C. A few were cast with the room temperature of 30°–35°C. All membranes were cast to a thickness of 0.008 in. (8 mils) unless otherwise specified. The membranes were kept in

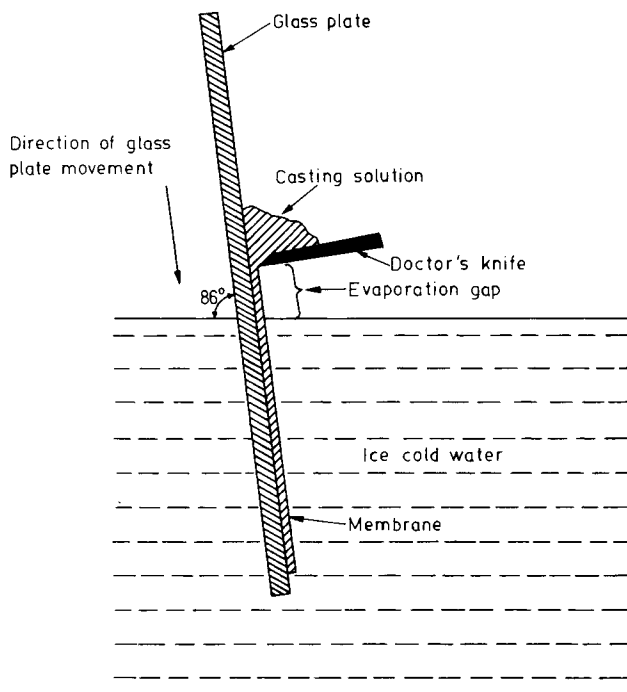


Fig. 1. Schematic diagram of vertical membrane casting setup.

the ice-cold gelation bath for 1 hr. Some membranes were tested without heat treatment. Most others were cured in the hot water of a thermostat for 5 min which was followed by immediate immersion in water at room temperature. The thermostat bath temperature was the annealing temperature.

Testing of Membranes

Circular pieces of membrane were mounted and tested in stainless-steel test cells having a design quite similar to that of Manjikian.¹⁸ The effective membrane area for desalination was 1.225 in.² (~7.88 cm²) corresponding to a 1.25-in. diameter. The feed solution flowed radially along the membrane surface at a rate of 600 cc/min for all the experiments reported here. Rangaiah¹⁷ has shown that regardless of whether a particular membrane is more porous (80% salt rejection, 66 gfd) or less porous (96.1% salt rejection, 35.5 gfd), the membrane performances steadily improve as the feed flow rate is increased from 100 cc/min to attain a constant level around 590 cc/min and beyond. This was the basis for selecting the feed flow rate at 600 cc/min. At the outer diameter of the active membrane section, the Reynolds number based on the channel gap was 112, and the mass transfer coefficient k was determined from Kimura-Sourirajan²⁰ analysis to be 40×10^{-4} cm/sec. Two identical test cells were used in series for a large number of runs, before which only one cell was used for membrane testing. All membranes were pressure treated with distilled water at 700 psig for 1 hr, and the pure water permeability (PWP) was determined from the permeate volume collected in 1 hr. After releasing the pressure, all membranes were tested with a 0.5 wt-% aqueous solution of sodium chloride at room temperature under a pressure of 600 psig and a feed flow rate of 600 cc/min through the test cells.

The performances measured and reported correspond to the data taken in the first 1½ hr. The water fluxes reported are those corrected to 25°C using the relative viscosity and density data for pure water as suggested by Sourirajan.¹⁹ The permeate salt content was determined by titrating against standard AgNO₃ solution as well as by measuring the solution conductivity with the help of a Direct-Reading Conductivity Meter Type 303 of Systronics Inc. The room temperature was noted to determine the concentration from standard plots of conductivity versus concentration at different temperatures available in the literature.²⁶

RESULTS AND DISCUSSION

The desalination performances of cellulose acetate membranes prepared from various casting solutions under conditions of very short air exposure periods are presented and discussed under the following headings: (1) concentration of CA in casting solutions close to the phase boundary; (2) effect of partial replacement of the solvent acetone by dioxane; (3) effect of adding ZnCl₂ to casting compositions; and (4) effect of variation in air exposure period. All the casting compositions reported are in weight percent.

Effect of CA Concentration in Casting Solutions

The phase diagram of the ternary system of CA, formamide, and acetone at temperatures¹⁰ between 0° and 50°C is shown in Figure 2. The compositions of six different casting solutions containing CA over a range of 17%–32% have been plotted in this figure along with those of Manjikian² and Fahey et al.¹⁰ for comparison. It may be noted that all of these six casting solutions used to develop membranes for this study have compositions quite close to the phase

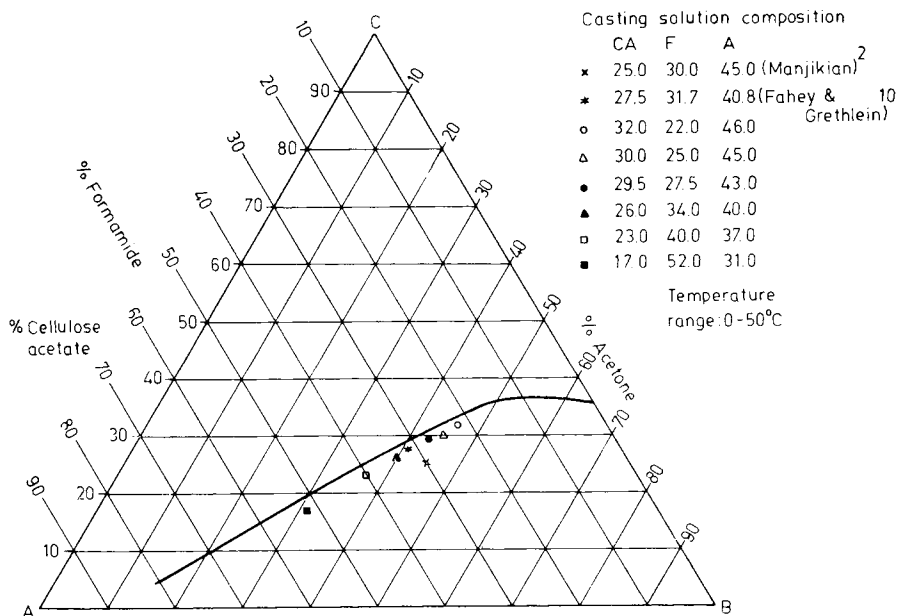


Fig. 2. Phase diagram of the system CA-formamide-acetone.

boundary. The performances of some of the films from each of these six casting compositions are given in Table I for short air exposure periods. The performances of some of these films with an evaporation time range of 0.05–0.60 sec are plotted in Figure 3, where the heat treatment temperature of each membrane is noted beside the point representing its performance. It is clear from this figure that membranes cast from solutions close to the phase boundary and containing CA between 26% and 32% have excellent desalination performance and are almost as good as the optimized membranes of Fahey and Grethlein¹⁰ whose optimum composition contained 27.5% CA (a formal comparison will be carried out later).

Further, as Table I indicates, many of these membranes have been cast with a very short evaporation period of 0.05–0.07 sec. Thus highly productive CA membranes can be obtained by casting with very short air exposure periods as long as the casting compositions are close to the phase boundary. In addition, the polymer concentration in the casting solution being used under short evaporation periods should also be high, since it is obvious from Figure 3 that membranes cast from casting solutions with 17% CA and 23% CA (both being close to the phase boundary) yield salt rejections of only 37.6% and 61% at the high curing temperature levels of 90° and 85°C, respectively. These results are indicative of the dynamic interaction between the air evaporation period and the casting solution composition, since McCutchan and Johnson¹² obtained standard performance membranes only (30 gfd, 86% rejection, 80°C cure) with Manjikian² composition away from the phase boundary for air evaporation periods in the range of 0.015–0.10 sec and higher. Similarly, Manjikian et al.² found the performance of membranes prepared from a 30% CA, 14.3% formamide, and 55.7% acetone solution with a 60-sec evaporation period to be only 8 gfd and 92% rejection. Thus it is obvious that CA membranes prepared with very short air exposure periods can be highly productive only if the CA content in the solution is high and the casting composition is close to the phase boundary.

A few more observations can be made from Figure 3 which has a dotted line representing the area of best membrane performances over all possible ranges of salt rejections. This area includes the performances of cured membranes from 17% and 23% CA solutions as well as the performances of uncured membranes from solutions with high CA, namely, 30%, at similar levels of salt rejection. The same uncured membrane from a 30% CA solution has an excellent desalination performances when cured. It may be concluded tentatively that, for a particular range of low evaporation times and for casting compositions close to the phase boundary, the reduced pore statistics of the skins of membranes cast from solutions having a wide range of CA content are approximately similar even though the absolute values of the pore sizes at any given curing temperature are strongly controlled by the CA concentration in the casting solution. Here, reduced pore statistics of a membrane skin implies the statistics of pores in the membrane skin normalized with respect to the average pore size of the same membrane. A closer examination of the data in Figure 3 will also indicate that the membranes from a 32% CA solution are somewhat inferior to those from other compositions at almost all salt rejection levels. The much higher initial polymer concentration has, in this case, produced a denser skin structure resulting in a reduction of flux. On the other hand, membranes from a 30% CA solution perform as well as the best membrane from any of the other compositions at all levels of salt rejection.

TABLE I
Performance of Cellulose Acetate Membranes from Casting Solutions Close to the Phase Boundary for Very Short Air Evaporation Periods^a

Sample no.	Solution composition CA-F-A, wt-%	Evap. period, sec	Curing temp., °C	PWP, gfd	Flux, gfd	Salt rejection, %
1	17-52-31	0.05	90	110	102.3	33.6
2	17-52-31	0.10	90	100	91.5	37.6
3	17-52-31	0.05	88	148.5	128.0	18.8
4	17-52-31	0.20	88	158.5	134.5	22.0
5	23-40-37	0.15	76	214.0	167.0	13.0
6	23-40-37	0.15	81	105.0	93.2	42.2
7	23-40-37	0.15	85	81.2	63.7	61.0
8	26-34-40	0.12	81.5	47.7	38.4	93.9
9	26-34-40	0.12	81.5	49.5	36.0	95.7
10	29.5-27.5-43	0.07	82.0	30.7	24.3	96.9
11	29.5-27.5-43	0.33	82.0	22.8	17.2	96.8
12	29.5-27.5-43	0.07	82.0	30.4	22.5	97.0
13	30-25-45	0.06	70.5	61.8	46.7	89.5
14	30-25-45	0.17	70.5	62.0	46.0	90.5
15	30-25-45	0.06	80.5	39.0	30.3	96.5
16	30-25-45	0.17	80.5	42.0	31.0	96.3
17	30-25-45	0.06	uncured	205.0	114.0	26.4
18	32-22-46	0.1	60.0	65.3	49.1	73.8
19	32-22-46	0.6	71.5	43.2	33.4	95.0
20	32-22-46	0.6	80.0	27.5	20.8	96.8
21	32-22-46	0.1	uncured	126.0	84.0	28.0

^a Feed 5000 ppm NaCl. All fluxes normalized to 25°C. Test conditions as in Figure 3.

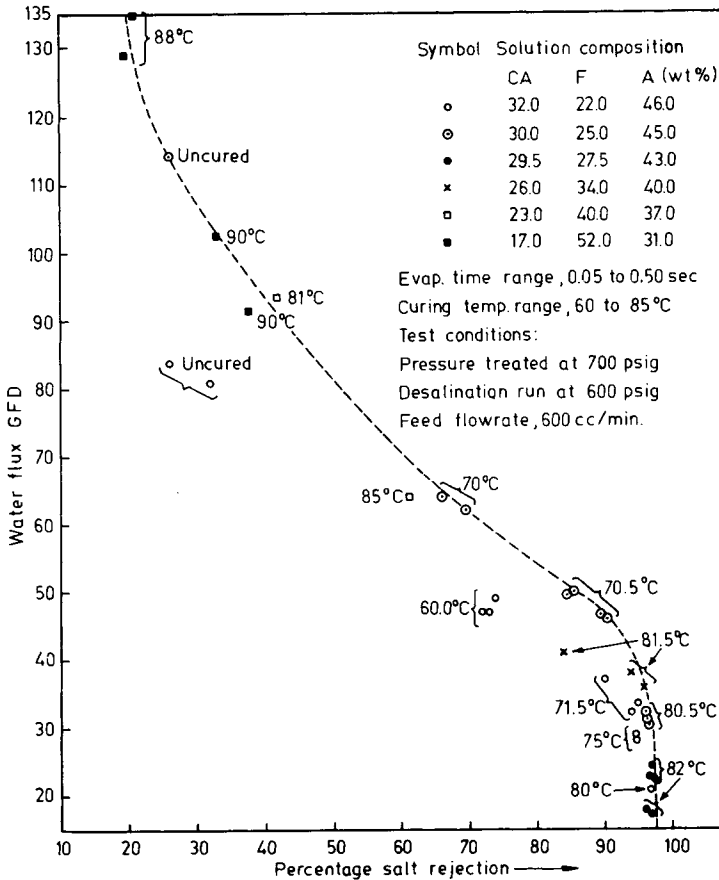


Fig. 3. Effect of CA concentration. Evaporation time range 0.05–0.50 sec. Curing temperature range 60°–85°C. Test conditions: pressure treated at 700 psig; desalination run at 600 psig; feed flowrate 600 cc/min. Solution composition (wt-%): (○) CA 32.0, F 22.0, A 46.0; (◉) CA 30.0, F 25.0, A 45.0; (●) CA 29.5, F 27.5, A 43.0; (×) CA 26.0, F 34.0, A 40.0; (◻) CA 23.0, F 40.0, A 37.0; (■) CA 17.0, F 52.0, A 31.0.

In addition, the heat treatment temperature required to achieve any particular salt rejection level seems to go down drastically with increase in CA concentration in the casting solution. For example, Table I indicates that a membrane from a 32% CA solution needs curing only at 71.5°C for achieving 95% salt rejection and a flux of 33.4 gfd. This conclusion is however valid for membranes from solutions with high CA content and away from the phase boundary as well² and is intimately connected also with the formamide content of the casting solution.

Conclusions arrived at by Kesting²⁷ from SEM photomicrographs of the membrane formation processes observed when dry RO membranes and wet membranes are being formed are of considerable help in interpreting some of the above results. In the preparation of wet membranes, the casting solution undergoes desolvation in air prior to gelation in an ice-cold water bath. The appearance of two interdispersed liquid phases with spherical droplets has been related by Kesting²⁷ and other workers to the paracrystalline nodules which have been found in the skins of both wet as well as dry RO membranes. In the wet membranes, annealing at temperatures close to the glass transition temperature

will cause these nodules to move closer and form larger aggregates identifiable by their diffraction patterns. In unannealed dry RO membranes, Kesting²⁷ points out that differential scanning calorimetry indicates the presence of some crystalline structure presumably because the small nodules have been able, as a result of complete evaporation of solvent, to form larger crystalline aggregates. In wet membranes, the quenching action of precipitating water freezes the microcrystallites in place before the skin has achieved its maximum density. Since the space between microcrystallites in the skin of wet membranes in the primary gel condition is relatively large due to the dilute polymer solution used normally with inadequate evaporation time, salt rejection by the wet unannealed membrane is very low. As the polymer concentration in the solution is increased due to rapid initial evaporation and an initial high CA content of the casting solution, the space between microcrystallites in the wet membrane skin will decrease. The resulting densified skin layer requires lower annealing temperatures of 71.5°C for achieving 95% salt rejection. One may conjecture, therefore, that the skins of the wet membranes of this study prepared from high-CA casting solutions are of an intermediate nature between normal wet CA membranes and dense CA membranes.

The solution structure–rate of evaporation concept developed by Sourirajan and coworkers in a number of papers and applied by Pageau and Sourirajan²⁸ and Kunst and Sourirajan²⁹ for understanding membrane performances may provide additional insights into the performances of membranes of the present study. The casting solution compositions of this work are such that as CA concentration increases from 17% to 32%, the formamide content decreases from 52% to 22% and the acetone content increases from 31% to 46%. Therefore, as the CA concentration increases, the rate of acetone evaporation is likely to go up so that the rate of formation and growth of droplets will increase. This in turn will cause a greater rate of droplet coalescence to produce a smaller number of larger pores. In addition, the reduction in formamide content with increase in CA concentration will generate a lesser number of smaller droplets of non-solvent in the interdispersed phase leading to a lower annealing temperature for a given rejection level. The mutually opposing effects in the formation of droplets due to simultaneous increase of acetone and CA and decrease of formamide as well as in the formation, growth, and coalescence of droplets may provide an optimum evaporation rate. One notices from Figures 2 and 3 and Table I that among casting solution compositions close to the phase boundary, 32% CA solution is inferior due to the lower number of smaller pores that developed in the film. On the other hand, the 23% casting solution is not useful since it develops a smaller number of larger pores due to the lower acetone content resulting in lower evaporation rate and a very high formamide content generating large pores since the polymer concentration is low.

Attempts to cast films from solutions close to the phase boundary and with CA contents higher than 32% (e.g., 33% or 34%) were unsuccessful since the solutions behaved more as viscoelastic solids rather than viscoelastic liquids. It should be recognized that on a dry polymer basis and 4% moisture, a 32% CA casting solution has 30.72 wt-% CA. In fact, when a casting solution containing 32 wt-% dried CA was prepared with 1.33 g ZnCl₂ per 100 g solution, the casting solution was too viscous for film making since the viscosity increases very rapidly with concentration in this range. It may be noted, however, that in the reverse

osmosis membrane literature reporting of composition of the polymer in the solution is almost always done on the as-received basis, and not dry basis.

The present set of experiments with casting solutions containing CA-formamide-acetone were not intended for determining an overall optimum in casting composition and casting conditions for short air exposure periods by employing statistically designed experiments in the manner of Fahey et al.¹⁰ and Chian et al.¹¹ The performances of CA membranes cast with short air exposure periods from casting solutions close to the phase boundary are themselves considered to be of sufficient interest. In the same vein, experiments were conducted with the solvent dioxane partially replacing acetone in the 30% CA casting composition (30 CA-25 formamide-45 acetone). These results are discussed next.

Effect of Partially Replacing Acetone by Dioxane

The performances of membranes cast with short air exposure periods from a 30% CA casting solution with acetone being partially replaced by dioxane are shown in Figures 4 and 5. Five casting solutions were tested with the dioxane-acetone ratio varying in the following manner: 20-80, 40-60, 50-50, 60-40, or 80-20 (e.g., a 20-80 solution implies 20% dioxane and 80% acetone by weight used as solvent, the total weight of the solvent in the casting solution being 45%). Figure 4 shows the performance data of these membranes over a wide range of salt rejections (i.e., 50%-96%) whereas Figure 5 concentrates on the data above 92% salt rejection. The performances of membranes cast from a 30% CA solution with acetone as the only solvent are included in both of these figures for the sake

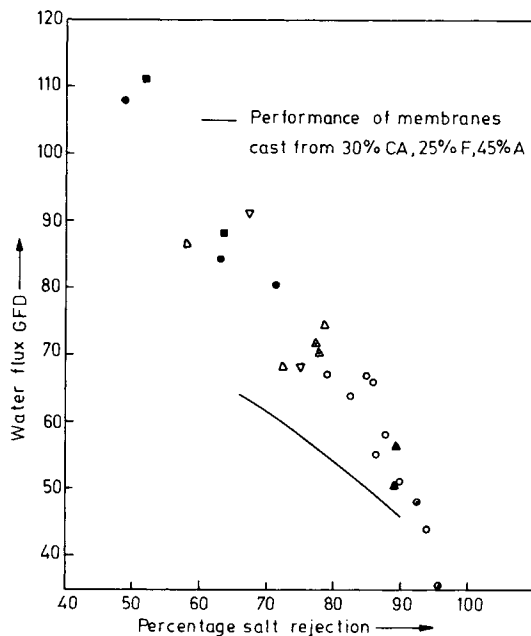


Fig. 4. Performance of dioxane membranes: (—) performance of membranes cast from 30% CA, 25% F, 45% (A + D). Sol. evaporation period 0.05-1.0 sec. Test conditions: pressure treated at 700 psig; desalination run at 600 psig; feed flow rate 600 cc/min; (○) 20-80, curing temp. 71.5°C; (◊) 20-80, 75.5°C; (△) 40-60, 71.5°C; (▲) 40-60, 75.5°C; (▲) 40-60, 76.0°C; (▽) 50-50, 72.0°C; (●) 60-40, 71.5; (■) 80-20, 71.5.

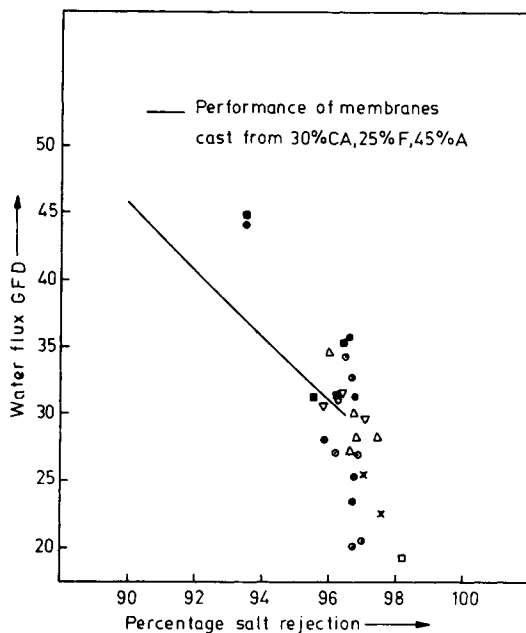


Fig. 5. Performance of dioxane membranes: (—) performance of membranes cast from 30% CA, 25% F, 45% (A + D). Solution composition, evaporation period, and test conditions same as in Fig. 4; (○) 20–80, curing temp. 78.0°C; (◐) 20–80, 82.0°C; (×) 20–80, 83.0°C; (△) 40–60, 81.5°C; (▽) 50–50, 82.0°C; (□) 50–50, 85.0°C; (●) 60–40, 82.0°C; (■) 80–20, 82.0°C.

of comparison. It is evident from these figures that for salt rejections less than 96%, all dioxane membranes perform better than the nondioxane 30% CA membranes. Further, the lower the salt rejection level, the more productive dioxane membranes become in comparison with the 30% CA nondioxane membranes. Around and beyond 96% salt rejection, Figure 5 shows that water flux is decreasing sharply with very minor increases in salt rejection level. As shown in Figure 3, nondioxane membranes also display the same behavior around 96% salt rejection. Since a higher curing temperature of 78°–85°C is needed for the higher salt rejections, it may be postulated that the smaller pores in such membranes become closed at higher curing temperatures. The net effect may be somewhat similar to the closing of many small pores (initially generated) at a higher operating pressure as observed by Pilon et al.⁸ so that their Batch 316 and 400 membranes were only as productive as the Batch 18 and 47 membranes at high pressure.

Representative performances of dioxane membranes 1, 3, 6, 9, 10, 13, and 15 shown in Table II indicate that the salt rejection level goes down with increase in dioxane concentration at any particular shrinkage temperature for salt rejection levels lower than 96%. One may conclude that increase in dioxane content of the casting solution produces initial pores of larger sizes. Further, the performances of all membranes in Table II show that the shrinkage temperature profile becomes steeper as the dioxane concentration increases. This would suggest that the pore size distribution is becoming more and more uniform as the dioxane concentration increases. For a given air exposure period, the extent of loss of acetone from the top of the cast film should decrease with increase in dioxane concentration²⁷ since the volatility of dioxane is negligible under casting

TABLE II
Performance of Some Membranes from 30% Cellulose Acetate Solution with Dioxane^a

Sample no.	Casting solution composition CA-F-S, ^b wt-%	Evaporation period, sec	Curing temp., °C	PWP, gfd	Flux, gfd	Salt rejection, %
1	30-25-45 (0-100) ^c	0.17	70.5	62	46	90.5
2	30-25-45 (0-100)	0.17	80.5	42	31	96.3
3	30-25-45 (20-80)	0.12	71.5	84	66	85.8
4	30-25-45 (20-80)	2.0	71.5	91	64	82.8
5	30-25-45 (20-80)	0.12	82.0	44	34.2	96.5
6	30-25-45 (40-60)	0.09	71.5	102.5	74.6	78.5
7	30-25-45 (40-60)	0.09	81.5	38	28.3	97.5
8	30-25-45 (40-60)	0.09	81.5	40.5	30.0	96.8
9	30-25-45 (50-50)	0.11	72.0	105.5	68.0	75.0
10	30-25-45 (50-50)	0.14	72.0	124.0	91.5	66.8
11	30-25-45 (50-50)	0.11	82.0	39.5	31.7	96.4
12	30-25-45 (50-50)	0.06	85.0	28.0	19.6	98.2
13	30-25-45 (60-40)	0.07	71.5	115.0	80.5	70.8
14	30-25-45 (60-40)	0.07	82.0	42.4	31.4	96.8
15	30-25-45 (80-20)	0.40	71.5	121	88	63.6
16	30-25-45 (80-20)	0.10	82.0	48.2	35.4	96.5

^a Feed 5000 ppm NaCl; all fluxes normalized to 25°C. Test conditions as in Figure 4.

^b S represents total solvent content in wt-% (i.e., S = %D + %A).

^c Membrane from solution without dioxane.

conditions. The rate of acetone evaporation will also be lower with increase in dioxane concentration. Following Pageau and Sourirajan,²⁸ we may postulate that as the acetone evaporation rate decreases with increasing dioxane concentration, the rate of droplet formation and growth will decrease. This in turn will reduce the rate of coalescence of droplets. While the former condition leads to reduced membrane productivity, the latter situation leads to higher productivity since a larger number of smaller pores remains at the surface. Thus an optimum is likely with regard to dioxane concentration leading to an optimum evaporation rate. As will be pointed out soon, such an optimum is somewhat discernible around 40% dioxane due to the generation of a larger number of ultimate pores even though the pore sizes increase as the dioxane concentration increases with a highly reduced evaporation rate.

A more definite conclusion about the optimum evaporation rate would require

data on solvent evaporation rate during film formation for short evaporation times. This, however, was not attempted in this work. Further investigation is also necessary to determine the nature of the supermolecular polymer aggregation in the casting solution containing dioxane. Since for cellulose acetate of 39.8% acetyl content, Johnston and Sourirajan³⁰ have shown that the Mark-Houwink constant α is 0.83 for acetone and 0.63 for dioxane, it is likely that the supermolecular polymer aggregation will increase with increasing dioxane concentration. However Kunst et al.²⁷ have expressed doubt regarding this conclusion, and work on solvent power of mixed solvents is necessary for CA membranes.

In terms of a phenomenological approach of a thicker skin or thinner skin, King et al.¹⁵ had concluded that their CA blend membrane productivity with a mixed solvent system of acetone and dioxane was higher since the membrane skin was thinner. No morphological explanations have been offered by King et al.¹⁵ We have observed in this work that as the dioxane content increases, the color of the membrane turns whitish and the membrane becomes quite opaque as compared to the bluish transparency ever present in the nondioxane CA membranes. Frommer et al.¹³ have demonstrated that the system CA-dioxane when precipitated by water produced white and opaque membranes. Further, there exists a large number of fingerlike cavities and protrusions in dioxane membranes, and these are responsible for their opacity. These fingerlike cavities and protrusions extended almost right up to the top of the skin, which appears more like a fractured polymer layer with channels (see also Figs. 12 and 13 in Strathmann et al.¹⁴). These cavities and protrusions will certainly decrease the skin resistance to water transport. The skin, looking like a fractured polymer layer, will have big pores which will prevent the achievement of a very high level of salt rejection except at high curing levels with its concomitant flux decrease. In fact, investigative experiments with some of these dioxane-acetone mixed solvent membranes by changing the pressure of operation from 600 to 800 psig (pressure treatment at 900 psig) indicated no increase in salt rejection even though the flux increased substantially as shown in Table III. Further the salt rejection values of 97.1% and 96.5% in Table III are lower than the asymptotic salt rejections attainable with E-398-3 CA membranes. This prompts us to hypothesize that the membranes cast from an acetone-dioxane mixture have a thinner skin and have defects, although whether these defects are artifacts of the casting procedure (e.g., wavemarks of King et al.¹⁵) or due to the nature of the solvent-precipitant interaction is not totally clear. It should be recognized, however, that the present casting solutions have high initial polymer concentration. Therefore at the moment of precipitation of the solution in the film, a still higher polymer concentration present will increase the strength of the surface layer and prevent the initiation of fingers to a large extent as observed by Strathmann et al.¹⁴

It may be pertinent here to conjecture upon the presence of a thinner skin in our high-CA membranes cast with very short air exposure periods. A thinner skin merely means a faster change in polymer concentration from high values at the membrane top to low values in the porous backing, the latter having a uniform concentration. This is especially likely under low evaporation times since only the topmost layer becomes densified. The lengths of the pores in the skin are reduced and the increase in "pore diameters" from the skin top to the porous backing is much quicker. Such an explanation will have some validity

TABLE III
Performance of Some Dioxane Membranes at 600 psig and 800 psig^a

Sample no.	Casting solution composition CA-F-A, wt-%	Membrane identification	Evap. period, sec	Curing temp., °C	Pressure Tr.		Desalination		
					Pressure, psig	PWP, gfd	Pressure, psig	Flux, gfd	Salt rejection, %
1	30-27-43 (40% acetone replaced by dioxane)	M-30-1	0.06	82	700	39.8	600	29.9	97.1
2	(40% acetone replaced by dioxane)	M-30-1	0.06	82	900	48.1	800	37.8	97.1
3	(40% acetone replaced by dioxane)	M-30-3	0.11	82	700	39.5	600	31.7	96.4
4	(40% acetone replaced by dioxane)	M-30-3	0.11	82	900	48.8	800	37.8	96.5

^a Feed composition 5000 ppm NaCl; feed flow rate 600 cc/min. Order of testing: pressure treatment at 700 psig for 1 hr; desalination run at 600 psig; pressure treatment at 900 psig for 1 hr; desalination run at 800 psig. All fluxes normalized to 25°C.

for both dioxane and nondioxane membranes since Frommer et al.¹³ have shown that only an "upper" active layer is responsible for salt rejection whereas there are also a "lower sublayer" and a porous layer.

It appears from Figures 4 and 5 that membranes from 20% and 40% dioxane solutions perform somewhat better than the membranes from 50%, 60%, and 80% dioxane solutions. King et al.¹⁵ had arrived at a similar conclusion. They had observed that a decrease in the acetone-dioxane ratio in their CA blend membrane formulations increases the frequency with which voids appear, voids being potential regions for salt leaks. No comparison of performances of dioxane-acetone blend membranes of King et al.¹⁵ is being made with the membranes of this work since the data of King et al.¹⁵ are not treated in the manner of Kimura and Sourirajan²⁰ whose analysis has been used by us. Some of the best membranes of King et al.¹⁵ have the following performances: (a) 50 gfd flux and 91% salt rejection for 1% NaCl feed at 800 psig and 25°C; (b) 37 gfd flux and 93.6% salt rejection for 0.5% NaCl feed at 600 psig and 25°C. It may be noted that the membranes of the present work are better than those quoted above. We would like to close this section by pointing out that partial replacement of acetone by dioxane has been carried out in casting solutions of other compositions as well with CA concentrations on both sides of 30%, and the performances are good.

Effect of ZnCl₂ in Casting Solutions

Loeb and McCutchan⁵ were the earliest to incorporate inorganic salts such as ZnCl₂, ZnBr₂, ZnI₂, etc., in type 1 casting solutions instead of magnesium perchlorate and found that the membrane performances were not substantially affected even though the effectiveness of the additive followed the order ZnI₂ > ZnBr₂ > ZnCl₂. In the present work, ZnCl₂ was added in small amounts to two different casting solutions: the first one had 32% CA, 22% formamide, and 46% acetone; the performances of membranes from this type of casting solution with varying amounts of ZnCl₂ are shown in Figure 6. The second casting solution contained 30% CA (one solution had 29.6% CA) with 20 wt-% acetone being replaced by dioxane and varying amounts of ZnCl₂. The membrane performances for this composition are shown in Figure 7. Figure 6 demonstrates that small amounts of ZnCl₂, especially 1.33 g salt per 100 g solution, improve the membrane performances from 32% CA solutions substantially for salt rejection levels lower than 96%. On the other hand, any improvement due to ZnCl₂ is marginal in membranes cast from 30% CA solution (with 20% dioxane) as is evident from Figure 7. However the performances of the better membranes of Figure 7 are the best among all reported in this work. Of these, the membranes from the composition containing 2.2% ZnCl₂ appear somewhat better. Some of these performance data are reported in Table IV. Any explanation for the improvement of membrane performance due to the addition of ZnCl₂ should take into account the experiments of Kesting et al.²¹ and Vinit et al.²² Kesting et al.²¹ have demonstrated that with type 1 casting solutions, the presence of a swelling agent such as ZnCl₂ modifies the action of any water present in the casting solution. Instead of forming microgels, water molecules aggregate around the electrophilic cations and act more as a swelling agent rather than as a nonsolvent, and the membrane performance improves drastically. Further, with increase in water-ZnCl₂ ratio from 1:1 to 2:1 and 3:1 in the membranes of Kesting et al.,²¹

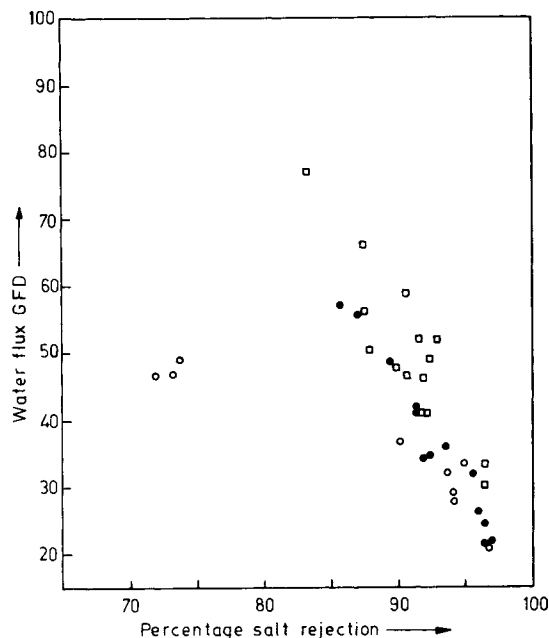


Fig. 6. Effect of zinc chloride. Solution composition: CA = 32%, F = 22%, A = 46%; evap. time range 0.05–1.0 sec; curing temp. range 60°–85°C. Test conditions: pressure treated at 700 psig; desalination run at 600 psig; feed flow rate 600 cc/min. (○) 0.00 g ZnCl₂/100 g solution; (□) 1.33 g; (●) 2.25 g.

the membrane performances improve. Vinit et al.²² have also demonstrated that with type 1 casting solutions, membranes perform much better in the presence of swelling salts such as Mg(ClO₄)₂, etc., rather than gelling salts such as NaCl, etc. But casting solutions of type 1 have water whereas the type 2 casting solutions of the present work were not prepared with any water. It is known, however, that the cellulose acetate polymer used in the present study without drying had 4% water from absorption. Therefore it may be presumed that the presence of swelling salts will lead to the formation of flexible, better organized swollen polymer structure in the top dense layer where formation of intermolecular hydrogen bonds between free hydroxyl groups in the polymer chains and water molecules are more probable. The performance variation in the membranes of the present study from solutions with the varying ZnCl₂ as shown in Figure 6 is to be attributed to the varying water–ZnCl₂ ratio since the water content of the casting solution is almost constant due to moisture absorption. The present data are insufficient for deciding what would be an optimum ratio of water to swelling salt for ZnCl₂. In addition, the extent of improvement due to a salt such as ZnCl₂ in casting solutions of type 2 without any water at all remains unknown.

The performance of membranes from casting solutions with ZnI₂ are shown in Table IV and are somewhat lower than those prepared from solutions with ZnCl₂. This would reverse the order observed by Loeb and McCutchan,⁵ but Vinit et al.²² also found out that ZnI₂ membranes were not as good as others; in fact, they had classified ZnI₂ as a gelling salt.

At salt rejection levels around 95%–96% and higher, Figures 6 and 7 indicate no improvement due to the addition of ZnCl₂. The reasons for this are to be

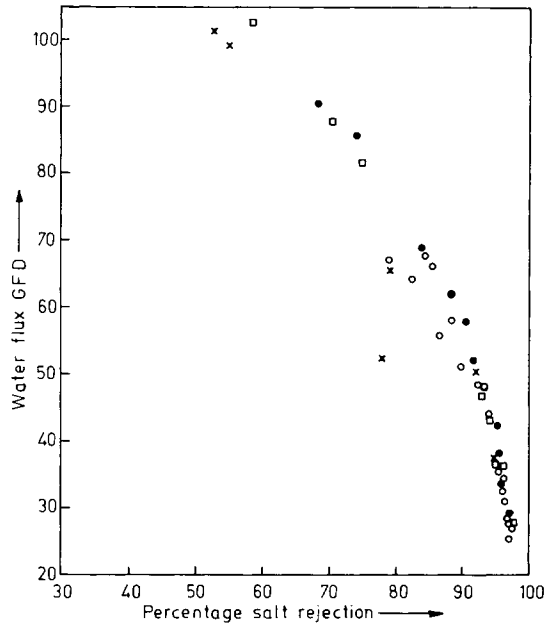


Fig. 7. Effect of zinc chloride. Evap. time range 0.05–1.0 sec; curing temp. range 70–85°C. Test conditions: Pressure treated at 700 psig; desalination run at 600 psig; feed flow rate 600 cc/min. Solution composition: (○) 30.0% CA, 25.0% F, 36.0% A, 9.0% D 0.0 ZnCl₂; (□) 29.6, 24.7, 35.5, 8.9, 1.3; (●) 30.0, 25.0, 33.8, 9.0, 2.2; (×) 30.0, 23.7, 33.8, 9.0, 3.5.

traced to a gradual disappearance of the initially swollen polymer structure in the skin with increase in the annealing temperatures which facilitates intermolecular hydrogen bonds between polymer molecules, thus reducing the free volume and forcing some of the bound water out. The possible presence of membrane defects will accentuate this trend at higher salt rejections.

Effect of Air Evaporation Time

The effect of air evaporation period on membrane performances are shown in Figures 8, 9, 10, and 11. Of these, Figures 8, 9, and 10 indicate performances of membranes cast with low evaporation times in the range of 0.06–2.0 sec from three different but representative casting compositions. The range of evaporation time is at least over an order of magnitude in Figures 8 and 10 and somewhat less in Figure 9. The membrane performances in these three figures appears to be almost independent of air evaporation time. The shrinkage profiles shown in Figure 9 also show little effect of the variation in evaporation time. Kunst and Sourirajan⁹ have also concluded that the effect of variation in air evaporation time over a range of 1–6 min is negligible for membranes cast from a type 1 solution with 17% CA. One notices similarly in Table I of Fahey and Grethlein¹⁰ that variation in evaporation time from 1 to 7 sec produces minor changes in the performances of membranes from type 2 casting solution with 27.5% CA. Chian et al.¹¹ have noted similarly that their membrane performances are insensitive to variations in the evaporation period from 2 to 6 sec. On the other hand, Figure 11 of this work shows that if air evaporation time for membranes cast from solutions close to the phase boundary and containing high

TABLE IV
Performance of CA Membranes from Casting Solution with $ZnCl_2$ or ZnI_2 ^a

Sample no.	Casting solution composition CA-F-A-D-Salt (wt %)	Evaporation period, sec.	Curing temp., °C	PWP gfd	Flux gfd	Salt rejection, %
1	29.6-24.7-35.5-8.9-1.3	0.08	71.5	142	102.5	58.8
2	29.6-24.7-35.5-8.9-1.3	0.06	71.5	109.5	81.6	75.0
3	29.6-24.7-35.5-8.9-1.3	0.15	78.0	64	48.3	93.1
4	29.6-24.7-35.5-8.9-1.3	0.06	82.0	36.2	27.0	97.3
5	30-25-33.8-9-2.2	0.05	71.5	116	85.8	74.0
6	30-25-33.8-9-2.2	0.20	80.0	72	58.0	90.9
7	30-25-33.8-9-2.2	0.06	80.0	55.5	42.5	95.3
8	30-25-33.8-9-2.2	0.05	82.0	38.3	28.6	97.0
9	30-23.7-33.8-9-3.5	0.05	78.0	89.9	65.3	79.2
10	30-23.7-33.8-9-3.5	0.05	80.0	71.8	50.3	91.9
11	30-23.7-33.8-9-3.5	0.05	82.0	47.8	36.6	95.4
12	32-22-46	0.23	70.0	76.7	58.7	90.7
13	32-22-46	0.12	70.0	66.0	51.7	93.1
14	32-22-46	0.09	80.0	41.5	31.5	96.5
15	32-22-46	0.06	78.0	48.8	34.8	92.5
16	32-22-46	0.05	71.5	78.2	57.1	85.7
17	32-22-46	0.70	82	28.6	22.0	97.1
18	32-22-46	0.60	70	46.3	34.2	88.9
19	32-22-46	0.40	75	32	24.7	96.4

^a Feed-5000 ppm NaCl. All fluxes normalized to 25°C. Test conditions as in Figures 3 and 4.

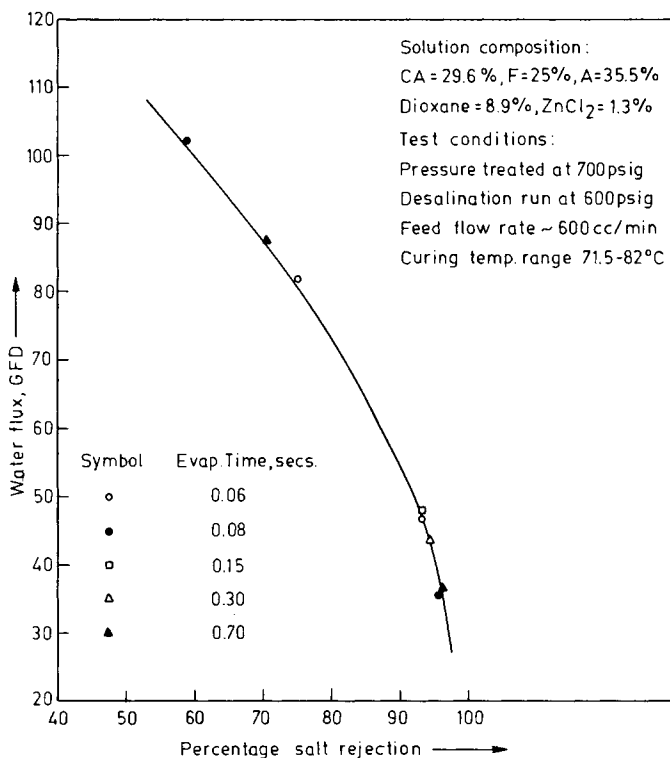


Fig. 8. Effect of evaporation time. Solution composition: CA = 29.6%, F = 25%, A = 35.5%, dioxane = 8.9%, ZnCl₂ = 1.3%. Test conditions: pressure treated at 700 psig, desalination run at 600 psig, feed flow rate 600 cc/min. Curing temperature range 71.5°-82°C. Evaporation time, sec: (○) 0.06; (●) 0.08; (□) 0.15; (△) 0.30; (▲) 0.70.

percentage of CA is extended up to 12 sec, the membrane water flux deteriorates strongly without any substantial improvement in salt rejection. The membranes of Figure 11 with evaporation periods between 0.5 and 0.8 sec perform as well as the membranes of Figure 9, but the membrane performances in Figure 11 for air evaporation times between 3 and 12 sec indicate greatly reduced flux without much change in salt rejection. The evaporation time range of 3-12 sec is therefore outside the optimum range for this nondioxane high CA-containing casting composition. As Pageau and Sourirajan²⁸ have pointed out in their studies on the effect of solvent evaporation period, with a large increase in the solvent evaporation period, the number of droplets will decrease while their average size will increase due to droplet growth and coalescence. McCutchan and Johnson¹² have obtained similar performances from tubular CA membranes cast from the Manjikian² composition. The water flux in their membranes dropped suddenly beyond 30 sec of air evaporation time with only a minor increase in salt rejection. Further work is necessary on the optimum range of evaporation times for dioxane-containing solutions.

One may now arrive at several generalizations. The variation in air evaporation time in a given small range will have a minor influence on performances of membranes prepared from a given casting solution. In order to fabricate productive membranes from casting solutions of particular compositions, a particular order of magnitude of evaporation period is necessary. Secondly, to

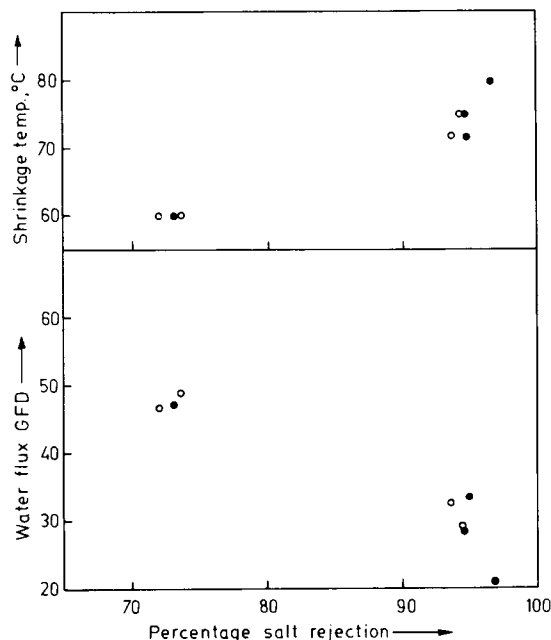


Fig. 9. Effect of evaporation time. Solution composition: CA = 32%, F = 22%, A = 46%. Test conditions: pressure treated at 700 psig; desalination run at 600 psig; feed flow rate 600 cc/min. Evap. time, sec: (O) 0.1 ± 0.01 ; (●) 0.6 ± 0.06 .

achieve an effective skin layer, a very small air evaporation period (≤ 0.05 sec) is sufficient as long the CA concentration in the casting solution is high and the casting solution is close to the phase boundary. A very low concentration of CA in the casting solution (say, 17%) will not produce an efficient skin capable of high salt rejection (as shown in Table I and Fig. 3). Our experiments therefore reinforce McCutchan and Johnson's¹² conclusion that membrane skins are formed at very low evaporation times (~ 0.015 sec). Thirdly, fabrication of membranes need not be restricted to the inconveniently low evaporation time of 0.05 sec.

Comparison of Membrane Performance

It will be quite useful to compare the performances of membranes of this study cast with a short air exposure period with those of membranes reported in the literature. The comparison is usually carried out in any of the following two ways. The permeate flux-versus-percent solute rejection relationships are compared for various membranes under apparently identical test conditions. This method of comparison does not account for the effects of concentration polarization. Such a comparison is shown in Table V of some of the best membranes of this work with the membranes of references 24, 8, 10, and 11. The second way of comparing is based on Kimura-Sourirajan analysis²⁰ which is an unambiguous method of comparing membrane performances through the plot of pure water permeability coefficient A versus solute transport parameter ($D_{AM}/K\delta$) for a given operating pressure. This plot is to be accompanied by the value of k , the mass transfer coefficient at the high pressure side of the membrane characterizing the feed flow conditions.

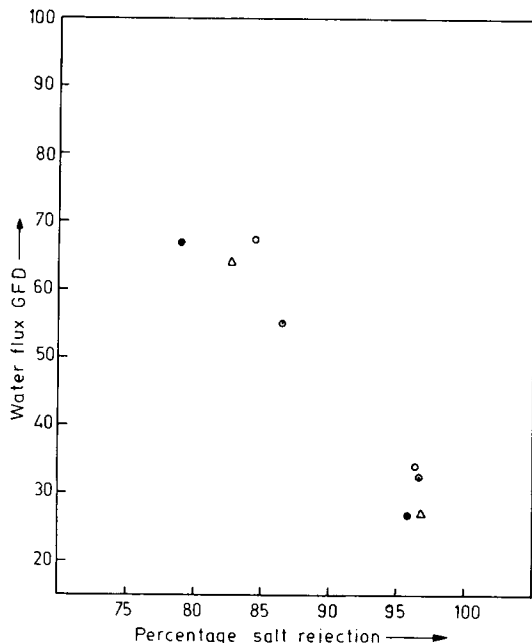


Fig. 10. Effect of evaporation time. Solution composition: CA = 30%, F = 25%, (A + D) = 45%, D in (A + D) = 20%, curing temp. 70°–83°C. Test conditions: pressure treated at 700 psig; desalination run at 600 psig; feed flow rate 600 cc/min. Evap. time, sec: (○) 0.10 ± 0.01; (△) 0.40 ± 0.04; (●) 0.80 ± 0.08; (▲) 2.00 ± 0.20.

Such a comparison is shown in Figure 12. The variables, pure water permeability constant A (in g-mole/cm²-sec-atm) and the solute transport parameter $D_{AM}/K\delta$ (in cm/sec), were calculated from the experimental data following the scheme developed by Kimura and Sourirajan.²⁰ The same plot contains the parameters of Agarwal and Sourirajan's membranes²³ as well as those of Fahey et al.¹⁰ The membranes of Chian et al.¹¹ are not shown in this figure since they fall essentially on Agarwal and Sourirajan's²³ line. It is quite clear from Figure 12 that the CA membranes of the present study obtained from different casting solutions under very short air exposure periods are much more productive than those of Chian et al.¹¹ and Agarwal and Sourirajan.²³ Figure 12 and Table V also demonstrate that the present membranes are as productive as those of Fahey et al.¹⁰

CONCLUSIONS

Very short air exposure periods lead to the development of highly productive cellulose acetate (CA) membranes from CA-acetone-formamide type casting solutions if the CA content is high in the casting solution, which in addition should be close to the phase boundary. For a particular range of short air exposure periods, the reduced pore statistics of the salt rejecting skins of membranes cast from solutions close to the phase boundary and having a wide range of CA content (17–32 wt-%) are approximately similar even though the absolute values of the pore sizes in a membrane at any given curing temperature are strongly controlled by the CA concentration in the casting solution. A membrane

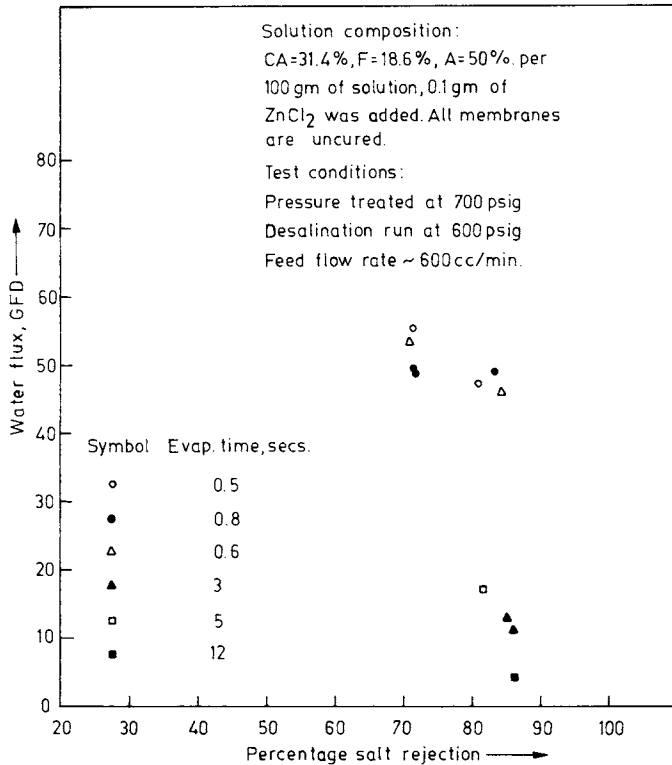


Fig. 11. Effect of evaporation time. Solution composition: CA = 31.4%, F = 18.6%, A = 50%. Per 100 g Solution, 0.1 g ZnCl₂ was added. All membranes are uncured. Test conditions: pressure treated at 700 psig, desalination run at 600 psig, feed flow rate 600 cc/min. Evaporation time, secs: (○) 0.5; (●) 0.8; (△) 0.6; (▲) 3; (□) 5; (■) 12.

from a 32% CA casting solution, for example, needs curing only at 71.5°C for achieving a 95% salt rejection and a flux of 33.4 gfd with a 0.5 wt-% NaCl feed at 600 psig. For identical feed conditions of 5000 ppm at 600 psig, membranes from a casting solution containing 30 wt-% CA, 45 wt-% acetone, and 25 wt-% formamide show the best performance—a water flux of 28.3 gfd and a salt rejection of 97.5%.

Partial replacement of the solvent acetone by dioxane in the high-CA casting compositions of the above type leads to the development of improved membranes with substantially higher water fluxes at given salt rejection levels. This is most likely due to a thinner skin resulting from a reduced rate and extent of acetone evaporation under low air exposure conditions. The fingerlike protrusions in the layer immediately below the top of the skin layer also contribute toward a thinner skin. Increase in dioxane content produces a larger initial size of pores and a more uniform pore size distribution. The solution structure–evaporation rate concept is capable of explaining most of the observed membrane performances. The addition of small amounts of the salt ZnCl₂ to the nondioxane casting composition with 32 wt-% CA yields membranes much better than those cast from a similar casting composition without ZnCl₂. Any improvement due to dioxane and/or ZnCl₂ is restricted to a salt rejection level less than 96%. Further, membrane performances are unaffected if the air evaporation period is varied from 0.05 sec to 1–2 sec, beyond which flux drops drastically due to

TABLE V
Comparison of Membrane Performance

Membrane	Feed concentration, ppm	Pressure of operation, psig	Flux, gfd	Rejection, %	Reference
(i) RO-97	5000	600	16-22	96-98	Eastman membranes ²⁴
(ii) RO-94	5000	600	22-28	92-96	
(iii) RO-89	5000	600	28-35	86-92	
(iv) HT-00	5000	600	200-275	0-20	
Batch-316 and -400	5000	600	42.0	95.0	Pilon et al. ⁸
Batch-316 and -400	5000	600	53.0	90.0	
Batch-316 and -400	5000	600	70.0	80.0	
Batch-316 and -400	5000	600	110.0	60.0	
Solution composition: 27.5% CA, 31.7% formamide, and 40.8% acetone	5000	600	30.0	97.7	Fahey et al. ¹⁰
Solution composition: 27.5% CA, 31.7% formamide, and 40.8% acetone	5000	600	48.3	91.0	
Solution composition: 27.5% CA, 31.7% formamide, and 40.8% acetone	5000	600	71.0	70.1	
CA-acetone ratio 3-5, 35% formamide	5000	600	14.52	97.0	Chian et al. ¹¹ this work
CA-F-A, 30-25-45 (40D-60A) Table II serial no. 7	5000	600	28.3	97.5	
30-25-33.8-9.0(D)-2.2 ZnCl ₂ Table IV serial no. 6	5000	600	58.0	90.9	
30-25-33.8-9.0(D)-2.2 ZnCl ₂ Table IV serial no. 5	5000	600	85.8	74.0	

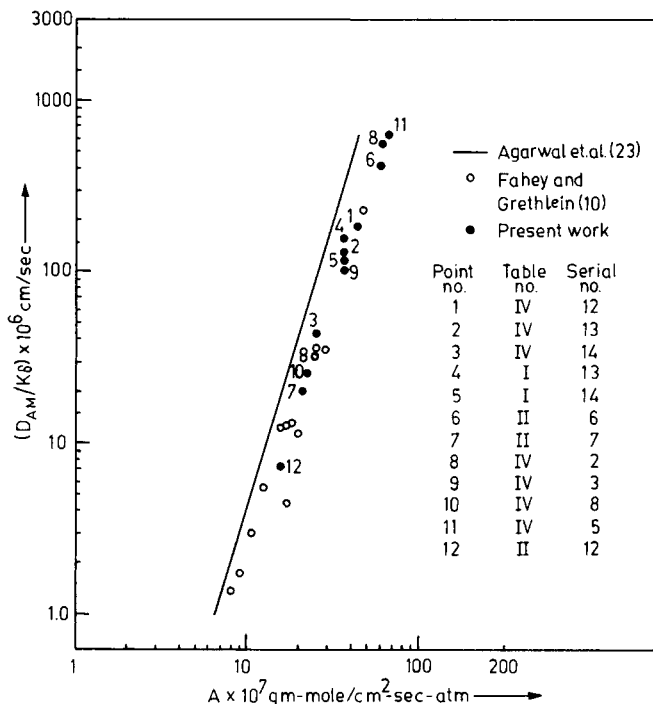


Fig. 12. Salt transport parameter ($D_{AM}/K\delta$) vs pure water permeability constant (A): (—) Agarwal et al.²³; (O) Fahey and Grethlein¹⁰ (●) present work. (1) Table IV, sample 12; (2) Table IV, sample 13; (3) Table IV, sample 14; (4) Table I, sample 13; (5) Table I, sample 14; (6) Table II, sample 6; (7) Table II, sample 7; (8) Table IV, sample 2; (9) Table IV, sample 3; (10) Table IV, sample 8; (11) Table IV, sample 5; (12) Table II, sample 12.

thickening of the top skin layer. Kimura-Sourirajan analysis of the performances of all of these membranes indicates that membranes cast under conditions of short air exposure periods from suitable casting solutions perform as well as the best CA membranes reported in the literature.

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