Ionically Crosslinked Poly(acrylic Acid) Membranes. III. Reverse Osmosis Results for Dry Cast Membranes

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Synopsis

The reverse osmosis properties of ionically crosslinked polyacrylic acid membranes were investigated in terms of the salt separation of a 0.1% NaCl solution and water flux. The membranes were synthesized and crosslinked with the metal ion Al^{3+} via the dry casting technique described in a previous paper. The effect of such variables as the polymer concentration in the casting solution, the ratios of solvents used (DMF/H_2O), the ratio of monomer to the crosslinking agent (AA/Al), the evaporation time and temperature, and the nonsolvent nature and treatment times were studied in some detail. The most important variable was found to be the length and nature of the treatment in the nonsolvents acetone and methanol. In the best series of the membranes that were synthesized, fluxes of more than 3.0 gfd, with salt separations at the 80%–85% level, were obtained.

INTRODUCTION

The favorable results obtained when ionically crosslinked poly(acrylic acid) membranes, prepared via the "dry" casting technique, were tested for reverse osmosis applications[1] prompted further investigations in this vein. The experiments reported here were designed to examine a number of variables capable of influencing the separation characteristics of polyacrylic acid (PAA) membranes ionically crosslinked with the metal ion Al^{3+} via the "dry" casting technique.[1] A list of such variables includes: (1) the structure of polymer casting solution, (2) evaporation of solvents in the oven, (3) rate and degree of crosslinking, and (4) the nature of the nonsolvent treatment.

The structure of the polymer casting solution is a description of the size and number of polymer molecules and aggregates. These factors are important in determining the final structure of the membrane. The structure of the solution is dependent on temperature, concentration, and solvent/polymer interactions. In this work, all of the membranes were cast at room temperature and the conditions of solvent/polymer system had been fixed by previous experiments.[1] Therefore, the structure of the casting solution was adjusted by varying its evaporation temperature and concentration. This is similar to the model proposed by Kesting[2] and utilized subsequently by Sourirajan and Kunst.[3]

The evaporation of the solvent from the membrane in the oven will also be an important variable in determining the membrane surface pore characteristics and thus affect its transport properties. The evaporation rate is determined

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by the temperature and concentration of the casting solution. In the experiments reported here, no attempt was made to measure the rate of evaporation, but it was expected that the concentration, temperature, and evaporation time would be important in determining the membrane structure.

The third factor affecting the membrane fabrication is ionic crosslinking. The rate and extent of crosslinking are dependent primarily on the concentration of the crosslinking agent and the time and temperature in the oven. The concentration of the crosslinking agent can be represented by the molar ratio of acrylic acid units to the number of Al^{3+} species (AA/Al) in the casting solution. Since aluminum has a valency of 3, the stoichiometric ratio is 3/1. Thus, the ratio and extent of crosslinking are also dependent on the same variables: casting temperature, solution concentration, and evaporation time.

The final factor is the nonsolvent treatment. Based on previous experimental findings, acetone was selected as the nonsolvent followed by a methanol treatment in some experiments. A large improvement in the uniformity of the membranes was obtained by including a methanol treatment after the acetone. The acetone treatment resulted in changes in both the porosities of the membrane and its mechanical properties. Since the acetone must diffuse from the top, the extent to which acetone affects the structure will depend on the time in the acetone treatment bath.

The results reported here represent our findings with regard to the influence of these variables on the reverse osmosis properties of ionically crosslinked polyacrylic acid membranes.
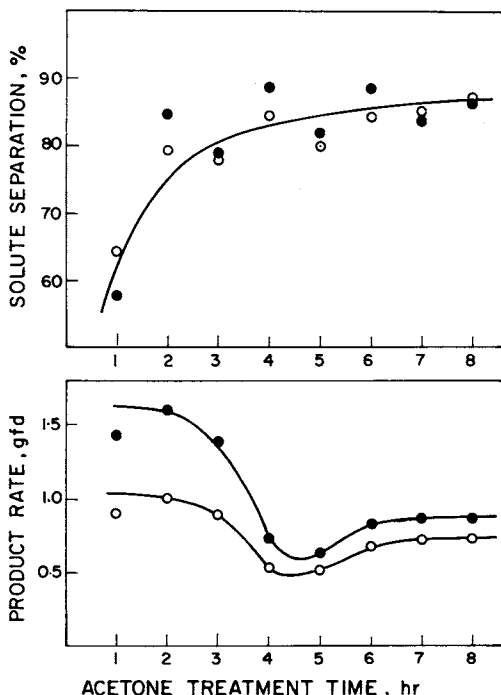

Fig. 1. Effect of acetone treatment time on product rate and separation. C_p = 0.13; DMF/H$_2$O = 0.90; AA/Al = 7/1; evaporation time = 90 min; evaporation temperature = 80°C; 600 psig; 0.1% NaCl feed solution; (O) run; (●) repeat.
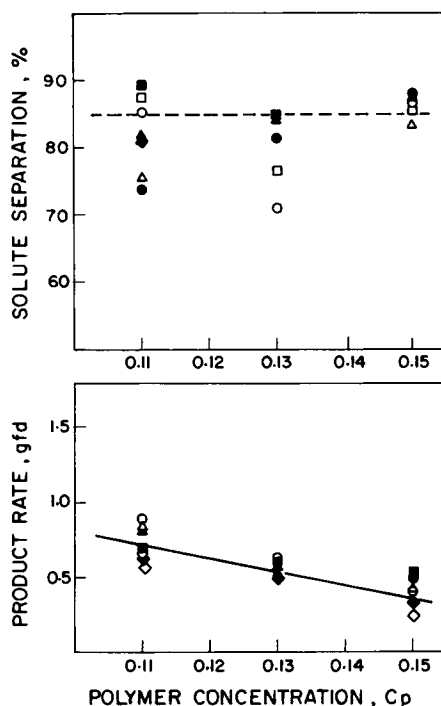
Fig. 2. Effect of polymer concentration on product rate and separation. DMF/H$_2$O = 0.900; AA/Al = 7/1; evaporation temperature = 80°C; acetone treatment >8 hr; 600 psig; 0.1% NaCl feed solution:

Evaporation time	Run	Repeat
30 min	(O)	(●)
60 min	(□)	(■)
90 min	(△)	(▲)
120 min	(◇)	(◆)

EXPERIMENTAL

The polyacrylic acid employed was purchased from the Monomer-Polymer laboratories, Borden Chemical Co., Philadelphia, Pa., in the form of an aqueous solution of 25% by weight PAA (molecular weight > 150,000). The actual concentration was determined by titration. The Al(NO$_3$)$_3$·9H$_2$O and dimethylformamide (DMF) were reagent grade supplied by the J. T. Baker Chemical Co., Phillipsburg, N.J., and were used without any further purification. The method of preparing the casting solutions and the fabrication of the membranes have been described previously.[1]

The reverse osmosis experiments were carried out in stirred bath cells similar to the ones described previously.[1] The experiments were conducted at 600 psig, at room temperature of approximately 24°C, with a sodium chloride feed solution of 0.1% by weight. Upon placement in the cell the membrane was subjected to a pressurization treatment at 750 psig for 1 hr. The membrane was then allowed

TABLE I
Casting Solution Composition

Batch No.	C_p[a]	AA/Al[b]	DMF/H_2O[c]
15	0.100	4.50	0.500
16	0.100	5.00	0.500
17	0.0833	4.50	0.500
18	0.0833	4.50	1.00
19	0.120	4.50	0.500
20	0.170	4.50	0.500
21	0.120	5.00	0.500
22	0.120	4.50	1.00
23	0.120	4.50	0.400
24	0.150	4.50	0.500

[a] Weight fraction of polymer.
[b] Molar ratio of acrylic acid units (AA) to aluminum ions (Al).
[c] Weight ratio of DMF to H_2O.

to rest at atmospheric pressure for at least 2 hr prior to evaluating the membrane performance. The pure water permeability was determined by measuring the flux of water under a pressure of 600 psig. The product rate and solute separation were determined by collecting, weighing, and analyzing a sample of the permeate. This sample was small relative to the volume of the cell. Sodium chloride separation f was determined by the following equation:

$$f = (m_1 - m_3)/m_1$$

where m_1 and m_3 are the feed and product molal concentrations, respectively. The value of the feed concentration was approximated by the average concentration measured before and after the NaCl runs. Sodium chloride concentrations were determined using a Waters Associates differential refractometer Model R 403.

TABLE II
Batch 19 Reverse Osmosis Results[a]

Film No.	Evaporation Time, min	Temp., °C	Acetone time, hr	Methanol time, min	PWP, gfd	PR, gfd	Separation, %
19-2	20	80	4	N/A	1.14	0.967	69.11
19-3	20	80	2	N/A	0.895	0.806	85.49
19-4	20	80	1	N/A	1.12	0.978	83.20
19-10	15	90	2	N/A	2.61	2.48	80.38
19-13	15	80	2	N/A	1.52	1.48	83.80
19-11	15	90	2	N/A	1.23	1.24	80.82
19-14	15	70	2	N/A	2.35	2.16	82.75
19-18	15	80	2	10	1.96	1.95	82.08
19-19	15	80	2	10	2.02	1.89	67.03
19-19	15	80	2	10	1.75	1.81	84.75

[a] Tested at 600 psig and 0.1% NaCl solution in static cells. PWP = Pure water permeability; PR = product rate; N/A = not applicable.

RESULTS AND DISCUSSION

The following variables were studied with regard to their influence on both product rate and separation: polymer concentration C_p, the ratios DMF/H$_2$O and AA/Al, evaporation time and temperature, and the nonsolvent nature and treatment time.

The last variables studied, the length and the nature of the nonsolvent treatment, had the most significant influence on the membrane performance and therefore will be discussed first.

The effect of the length of time in acetone at room temperature is shown in Figure 1. The salt separation was strongly influenced by the treatment time in the range of 1 to 2 hr of treatment, the separation increasing in this range. The product rate shows a large decrease with treatment times in the range of 1 to 4 hr, a slight increase between 5 and 6 hr of treatment, and little or no influence of further acetone treatment. The trends illustrated in Figure 1 were readily explained in terms of membrane surface modification caused by the acetone. Such a treatment might result in smaller pores in the membrane surface layer thereby decreasing production rate and increasing separation. The longer the membrane remains in acetone, the greater this region grows to encompass the entire membrane. From Figure 1, this limit is reached in approximately 6 hr. It appears that an optimal treatment time which combines both good separation and production rate can be determined from Figure 1. This appears to be in the range of 2 to 3 hr.

A large improvement in the uniformity of the membranes was obtained by including a methanol nonsolvent treatment after the acetone. The quality of these membranes was markedly better. They were more pliable and smoother. A qualitative description of this is as follows. When the membrane is removed from the acetone, it is quite smooth and is easily removed from the glass plate. It is immediately immersed in water where it swells and then shrinks back again to its original size. Apparently this swelling occurs while the acetone is being leached out of the membrane. By adding an intermediate, methanol is leached

TABLE III
Batch 22 and 23 Reverse Osmosis Results[a]

Film No.	Evaporation time, min	Temperature, °C	Acetone time, hr	Methanol time, min	PWP, gfd	PR, gfd	Separation, %
22-1	10	70	2	N/A	3.16	2.61	74.82
22-2	15	70	2	N/A	1.60	1.55	52.4
22-3	20	70	2	N/A	1.97	1.90	72.08
22-4	25	70	2	N/A	1.90	1.83	80.35
22-5	15	70	2	10	2.97	3.14	76.62
22-6	15	70	2	15	3.06	3.14	79.11
22-7	15	70	2	20	3.78	3.91	61.72
23-1	25	70	2	N/A	2.29	2.20	84.19
23-2	15	70	2	N/A	1.30	1.22	85.12
23-5	15	70	2	N/A	2.58	2.61	69.83
23-6	10	70	2	N/A	1.63	1.55	78.62
23-7	20	70	2	N/A	0.985	1.12	82.89

[a] Batch 22 was tested at 600 psig and 0.12 NaCl solution in static cells, with methanol after treatment. Batch 23 was tested at 600 psig and 0.1% NaCl solution in static cells, no methanol after treatment.
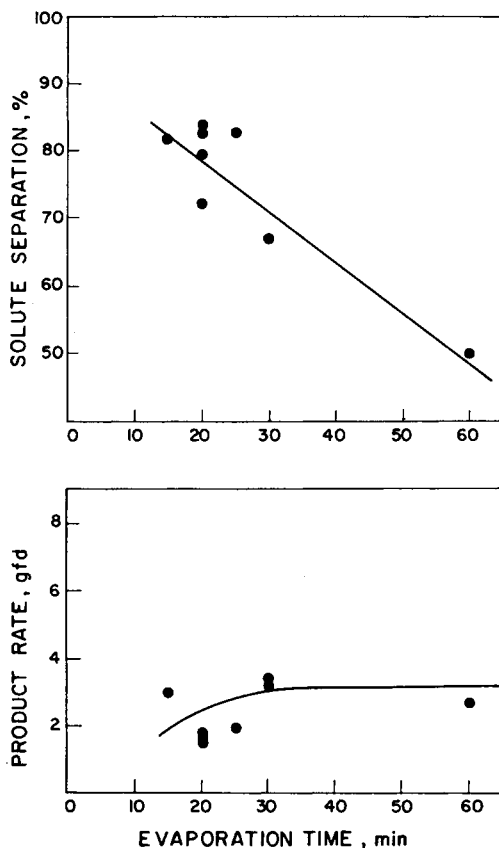
Fig. 3. Effect of evaporation time, Batch 24 membranes. Evaporation temperature = 70°C; acetone treatment 2 hrs; 600 psig; 0.1% NaCl solution; static cells: (□) oven circulation, no methanol treatment; (O) oven circulation, 10 min methanol treatment; (●) no oven circulation, 10 min methanol treatment.

out first in the water. This allows a smoother transition from the nonsolvent acetone to the water. As a result, the surface is much more uniform and smooth.

The reverse osmosis results for some of these membranes made with an additional methanol treatment are given in Table II. Comparison with the other data in the same table shows that these membranes give about the same flux and separation as the nonmethanol-treated membranes. With the addition of a methanol treatment, the batch 22 membranes also showed improved qualities. Table III illustrates that the flux is improved to more than 3.0 gfd for these batch 22 membranes.

Other variables studied, prior to determining the influence of treatment time, will now be discussed. Although these variables were expected to play some role in influencing the membrane performance, it will be seen that these influences are minor in comparison to the effect of acetone and the methanol treatment times.

The casting solution was produced by mixing an aqueous solution of PAA with a solution of $Al(NO_3)_3 \cdot 9H_2O$ in DMF. The composition of the solution may therefore be represented by three variables quantities: the polymer weight
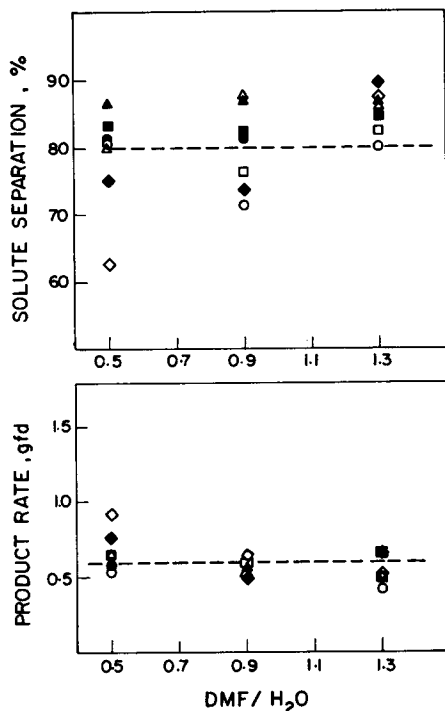
Fig. 4. Effect of methanol treatment with Batch 24 membranes; evaporation temperature = 70°C; evaporation time = 15 min; acetone time = 2 hr; no oven circulation; 600 psig, 0.1% NaCl; static cells: (O) 1 samples; (●) different samples from the same films; (□) new sample from new film.

fraction C_p, the solvent weight ratio DMF/H$_2$O, and the mole ratio AA/Al. This is shown in Table I.

The effect of C_p on the membrane performance is shown in Figure 2, where product rates and separation are plotted as a function of C_p for four different evaporation times. No discernible trend can be found in the separation data, with most of the results occurring in the narrow region of 85% ± 4%. However, there is a noticeable decrease in the product rate with increasing polymer concentration. This increase may be explained by considering that the increased polymer concentration results in an increase in the density of the membrane and therefore a decrease in product rate without any significant influence on the separation, at least in this range of C_p. No discernible trend was reflected in the different evaporation times, as is discussed below.

Since one of the most significant improvements in membrane quality was obtained by raising C_p values, it was decided to try to increase C_p even more. This gave batch 24 casting solution with a C_p value of 0.15. These results are illustrated in Figure 3. The membranes were made without a methanol treatment and were relatively impermeable, approximately 1.0 gfd. By adding the methanol treatment, the membranes were again softer and more uniform. Their flux doubled to about 2.2 gfd and the solute separation remained at the 80%–85% level. Once again the results indicated that increasing the evaporation time acted to decrease the solution separation. The final data are for membranes made with no oven circulation. The rejection was decreased to the 70%–75% level. This clearly shows the increase in the flux effected by the addition of the methanol step and the turning off of the oven circulation.
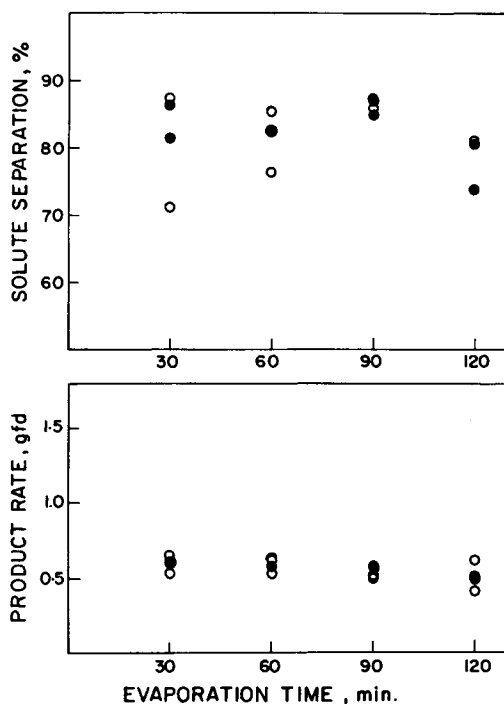
Fig. 5. Acetone treatment time with Batch 24 membranes; evaporation temperature = 70°C; evaporation time = 1 min; methanol time = 3 min; no oven circulation; 600 psig; 0.1% NaCl; static cells.

The length of time in the methanol bath also affected the results. When a membrane is placed in methanol, it swells. Too long an immersion time produced very weak films which could not be handled. Thus, very short times were examined in the 0 to 10 min range. These results are given in Figure 4. Although there is some scatter, the results tend to indicate an increase in separation with longer times of immersion in methanol. With increasing time of immersion in methanol, the flux initially increases to a relatively high value of 3.5 gfd and then decreases. This indicates that optimum flux will be obtained at about 3 to 6 min. The solute separation is 75%–80%.

The acetone immersion times have been kept constant at 2 hr for most of the data shown. However, since many other variables have been changed, this was investigated again. Figure 5 illustrates the increase in flux observed with shorter acetone immersion times. At 1 hr and less the flux appears constant at about 4.5 gfd. This is the highest flux obtained so far. The solute separation increases from about 65% at 30 min and levels out at about 75% after 1 hr. The nonsolvent acetone may act to draw the polymer molecules closer together. With increasing immersion time this may increase the surface skin thickness which decreases the membrane flux. Times of 30 min or less are not long enough to impart sufficient strength to the film, and low separation is the result.

The effect of the mole ratio AA/Al on the product rate and separation is illustrated in Figure 6. The alteration of this ratio, and thus the crosslink density, plays a more significant role than either of the other concentration variables. As the ratio increases, the crosslink density plays a more significant role than
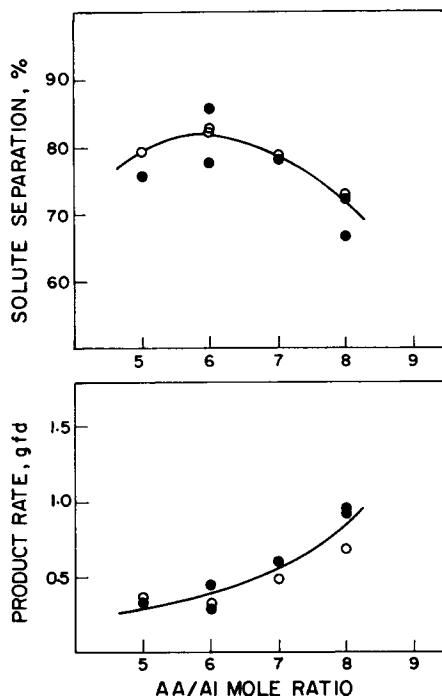
Fig. 6. Effect of AA/Al on product rate and separation. $C_p = 0.13$; DMF/H$_2$O = 0.900; evaporation time = 90 min; evaporation temperature = 80°C; acetone treatment > 8 hr; 600 psig; 0.1% NaCl feed solution; (O) run; (●) repeat.

either of the other concentration variables. As the ratio increases and the crosslink density decreases, the membrane structure becomes less dense, thereby allowing the passage of more bulk solution and a decrease in selectivity. The separation, therefore, shows a maximum at AA/Al of approximately 6. Below this value the separation appears to establish no trends. The product rate shows a steady increase as the ratio AA/Al increases and the crosslinking decreases. In order to obtain a high product rate while maintaining a high solute separation and good mechanical strength, a value of 7 for AA/Al was used for most of the remaining experiments.

From the results presented in Figure 5, along with those shown in Figures 2 and 3, it can be concluded that in the range of times studied, the evaporation time has little or no effect on either the separation or product rate. It may be thus concluded that this influence is experienced in time periods shorter than those studied here at the temperature employed.

Similarly, the results shown in Figure 7 indicate that the casting temperature has little effect on the membrane in the range of temperature studied, provided that the temperature is sufficient to initiate the crosslinking and evaporate some solvent when the membrane is formed. Any such critical temperature is obviously below 60°C.

Although it was expected that the evaporation time and temperature would alter the membrane structure significantly enough to be reflected in the separation and product rate, the lack of any such trend does not discredit the theory that the surface structure is altered by nonsolvent treatment but rather lends considerable support to the theory.
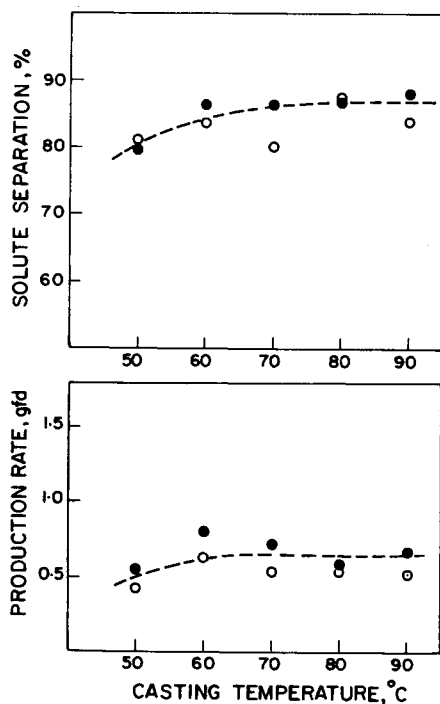
Fig. 7. Effect of casting temperature on product rate and separation. C_p = 0.13; DMF/H_2O = 0.90; AA/Al = 7/1; evaporation time = 90 min; acetone treatment > 8 hr; 600 psig; 0.1% NaCl feed solution; (O) run; (●) repeat.
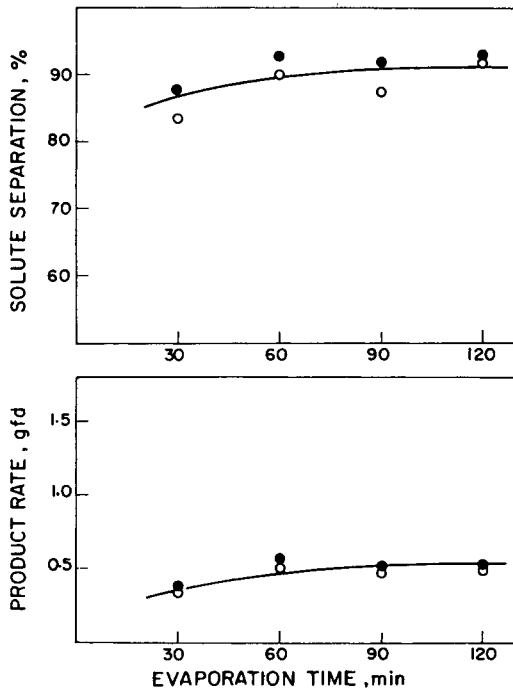

Fig. 8. Effect of evaporation time on product rate and separation with a shorter acetone treatment. C_p = 0.13; DMF/H_2O = 0.90; AA/Al = 6/1; evaporation temp. = 80°C; acetone treatment = 2 hr; 600 psig; 0.1% NaCl feed solution; (O) run; (●) repeat.

The results shown for changes in evaporation time and temperature merely illustrate that in the ranges studied any effects are minimal in comparison with the effect of the nonsolvent treatment.

In order to test the effect of shorter treatment times, one set of membranes was fabricated with 2 hr of acetone immersion time. These results are illustrated in Figure 8. The AA/Al ratio was decreased in this case to 6 in order to improve the mechanical strength of the film by increasing the crosslinking. Although these membranes did not retain the higher product rate observed in Figure 1, they did show relatively high separation, > 90%. Also a small increase in product rate with increasing evaporation time was observed. This supports the suggestion made earlier that it may be possible to improve the membrane performance and study the effect of other casting variables by using shorter nonsolvent treatment times.

CONCLUSIONS

It may be concluded that in the preparation of ionically crosslinked poly(acrylic acid) membranes via the "dry" technique, the performance of the membrane may be most significantly altered via a postcasting nonsolvent treatment with acetone followed by methanol. The second most significant variable is of course the crosslink density reflected in the mole ratio AA/Al. The effects of other concentration variables are of lesser importance. Performance of the membranes may be improved by investigating the use of shorter nonsolvent treatment times as well as the nature of the nonsolvent.

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