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Y. Wang[a]; W. W. Y. Lau[a]; S. Sourirajan[a]
[a] DEPARTMENT OF CHEMICAL ENGINEERING, NATIONAL UNIVERSITY OF SINGAPORE, REPUBLIC OF SINGAPORE

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Effects of Membrane-Making Conditions and Shrinkage Treatment on Morphology and Performance of Cellulose Acetate Butyrate Membranes

Y. WANG, WAYNE W. Y. LAU, and S. SOURIRAJAN
DEPARTMENT OF CHEMICAL ENGINEERING
NATIONAL UNIVERSITY OF SINGAPORE
REPUBLIC OF SINGAPORE

ABSTRACT

The functions of additives in cellulose acetate butyrate (CAB) membrane casting solution, effect of thermal shrinkage treatment on porous CAB membranes, and the changes of CAB membrane surface morphology during the solvent evaporation step have been investigated. Additives (glycerol and lactic acid) in CAB membrane casting solution function only as pore number promoting agents when used at low concentration and function both as pore number and pore size promoting agents when used at higher concentrations. Triethyl phosphate in CAB membrane casting solution functions both as a pore number promoting agent and as a secondary solvent for CAB. Three distinct phases can be observed in the solvent evaporation step in making CAB membranes. With the increase in solvent evaporation time, the number of pores in the first pore size distribution increases in the initial small pore-forming phase and decreases in the large pore-forming phase, and the number of pores in the second pore size distribution always increases with solvent evaporation time. These changes in pore numbers, pore sizes, and pore number ratio in two pore size distributions as well as the membrane skin layer thickness together govern the ultimate membrane performance and result in a maximum solute separation which, in the case of CAB/acetone membranes, falls at 60 seconds of solvent evaporation time. Significant improvement of the performance of a porous CAB membrane can be achieved by thermal shrinkage treatment. Equally high CAB membrane performance can also be achieved by using a lower concentration of additives in the membrane casting solution.

INTRODUCTION

Cellulose acetate butyrate (CAB) membrane was first investigated for reverse osmosis (RO) separation by Sourirajan (1) in 1958 and was studied afterwards by Manjikian and others (2–9). These membranes offer high solute separation and acceptable membrane flux, and they do not need a thermal shrinkage pretreatment prior to use in RO processes.

Manjikian noted that additives in CAB membrane casting solution functioned as flux promoters (4), but the action of additives is not well understood. Kesting had described the general mechanism of pore formation and development in the processes of making RO membranes (10–18). He pointed out that swelling agents or additives in the casting solution were responsible for the formation of voids in the membrane structure, and that membrane porosity varied directly and membrane skin thickness varied inversely with increasing concentration of the swelling agents. Since membrane permeability increases with higher porosity and thinner membrane skin layer, the role played by swelling agents in the development of practical RO membranes is a crucial one.

Very few studies have been made on CAB membranes, and no systematic studies have been reported on the effects of membrane-making steps and shrinkage treatment on the morphology and performance of CAB membranes. This work will focus attention on a study on the effects of composition of membrane casting solution and the solvent evaporation step on membrane morphology and performance.

Following the gelation step a membrane is usually subjected to one or more pretreatments prior to using it in practical separation experiments. Film shrinkage by immersion in hot water is the most common among such pretreatments (10, 17, 18). By such thermal treatment the average pore size on the membrane surface is significantly reduced and the membrane shows quite different performance from that of an untreated membrane. Although CAB membranes may not need a thermal shrinkage pretreatment, the effect of such a pretreatment on the morphology and performance of porous CAB membranes was investigated in this work to see whether any valuable improvement on membrane performance can be achieved.

Membrane performance can be expressed in terms of permeated product rate PR (in g/h per given area of membrane) and solute separation f defined as

$$f = \frac{(\text{ppm solute in feed}) - (\text{ppm solute in permeate product})}{(\text{ppm solute in feed})} \qquad (1)$$

The solute chosen for this study was sodium chloride dissolved in deionized water.

Two effective methods can be used to characterize membrane morphology. One is that, at any given operating temperature and pressure, a RO membrane can be completely specified in terms of two parameters, namely, pure water permeability constant A and solute transport parameter $(D_{AM}/K\delta)$ for a suitable reference solute (10, 17, 19). A reflects the overall porosity of a membrane, and $(D_{AM}/K\delta)$ plays the role of a mass transfer coefficient with respect to solute transport through the membrane pores. In this study we use this method to characterize membrane morphology. Membrane morphology can also be expressed in terms of pure water permeation rate, PWP, and a set of parameters specifying the pore size and pore size distribution on the membrane surface on the basis of the surface force-pore flow (SFPF) model for RO transport. Details of the latter method of expressing membrane morphology are fully documented in the literature (10).

According to the solution structure-desolvation rate (SSDR) approach (10, 17), the structure of a film casting solution and the rate of solvent desolvation during film formation in the evaporation and gelation steps together govern the ultimate porous structure and hence the performance of the resulting membranes.

EXPERIMENTAL

Membrane Making

Cellulose acetate butyrate (CAB-17-15, butyryl content: 17%, viscosity (ASTM): 15 seconds) membranes of different surface morphology were made in the laboratory according to, unless otherwise specified, the following procedures (4): All the ingredients of a membrane casting solution were thoroughly mixed by a MDC-NR stirrer. The casting solution was cast onto a flat glass plate using a casting bar made of brass. The film on the glass plate was exposed to the atmosphere for 60 seconds and was then immersed in water, initially at 0 to 2°C, for at least an overnight period. The quench water temperature rose gradually from the initial temperature to room temperature during the immersion period. The film was washed with a large amount of water to thoroughly remove residual solvent and additives prior to using it in RO experiments. The composition of CAB membrane casting solution and details of membrane making in this work are summarized, unless otherwise specified, in Table 1. The CAB polymer was supplied by Eastman Kodak Company. The additives, lactic acid and glycerol, were supplied by Merck.

Membrane Shrinkage

After the membrane had been cut to size, it was placed in a water bath at room temperature. The water bath, with the membrane in it, was heated from room temperature to the desired temperature gradually in about 20 to 30 minutes, and the final temperature was kept constant for at least 10 minutes. Then the hot water bath together with the membrane was cooled rapidly to below 60°C by pouring cold water directly into the bath to freeze the membrane structure. The membrane was then transferred from the bath for storage in water at room temperature.

Membrane Cell

Thin channel ultrafiltration flow cells were used. They were of the same design as those used by Sourirajan (10) except that the effective area of a membrane in each cell was 18.06 cm^2. Cells were connected in series so that several membranes could be tested at the same time. Since the PR from each cell was usually much smaller than the feed flow rate, the difference in concentrations of the feed solution entering and leaving a cell on the high pressure side of the membrane was negligible. Feed concentrations in all cells were considered unchanged.

Experiments

All membranes after thermal shrinkage treatment were subjected to a pressurization treatment to stabilize their porous structures. All experiments were carried out using an aqueous sodium chloride solution at laboratory temperature (23.5–24.5°C). The operating pressure was in the range 250 to 1000 psig. The feed concentration was, unless otherwise stated, about 5000 ppm NaCl. The concentrations of NaCl in feed and product streams were determined by a Horiba Conductivity Meter ES-14. In each experiment the following data were collected: PWP, PR, and f. The PWP and PR data were corrected to 25°C using the viscosity data of pure water.

RESULTS AND DISCUSSION

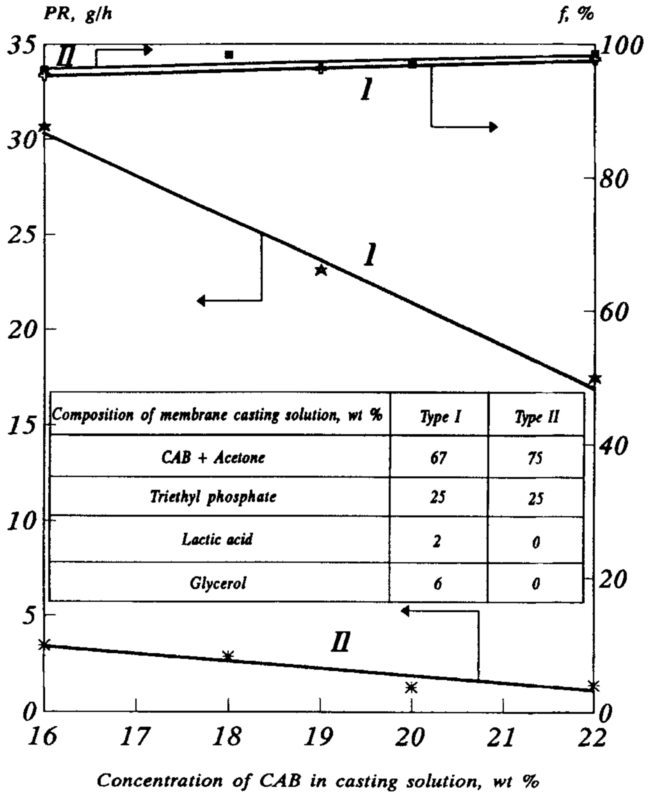
Membranes made under conditions given in Table 1 would possess an asymmetric porous structure (10, 17, 20). Membrane-making conditions and thermal shrinkage treatment will affect the structures of both the membrane skin layer and the supporting spongy layer. Such structural changes in the membrane morphology will be reflected in values of PR, f, A, and $(D_{AM}/K\delta)$.

TABLE 1
Film Casting Conditions

Composition of casting solution, wt%:	
CAB-17-15	15
Triethyl phosphate	23
Glycerol	2
Lactic acid	6
Acetone	54
Membrane casting time, s	3
Solvent evaporation time, s	60
Time of immersion in gelation bath, s	3
Temperature of casting solution, °C	23–24
Temperature of casting environment, °C	23–24
Gelation medium	Ice-cold water
Gelation bath temperature, °C	0–2
Period of leaching membrane in gelation bath	Overnight ($\geq$15 h)
Film casting tool	Polished brass casting bar

Effect of CAB Concentration and Functions of Additives

The effects of CAB concentration and additives (i.e., lactic acid and glycerol) in the membrane casting solution on membrane morphology and performance are shown in Figs. 1 and 2. Curves I and II represent data collected from membranes cast from solutions with and without additives respectively. Membranes cast from solutions without additives but with varied CAB contents (referred to as Membrane II) show only small changes in permeability (expressed by PR or A) and in solute transport parameters. The high solute separation indicated that both the pore size and number of pores on the membrane surface of these membranes were small and that the average pore sizes on the surface of these membranes were essentially the same in spite of variation in CAB concentration in the casting solution. On the other hand, membranes cast from solutions with additives (referred to as Membrane I) show much higher permeability than Membrane II with equally high solute separation, indicating that both Membranes I and II had same average pore size but Membrane I had a much higher surface pore density (number of pores per unit surface area) than Membrane II. One may conclude that the additives (glycerol and lactic acid) in CAB membrane casting solution function only as pore number promoting or pore-producing agents at the specified concentration. This conclusion is consistent with the finding of Manjikian (4).



Composition of membrane casting solution, wt %	Type I	Type II
CAB + Acetone	67	75
Triethyl phosphate	25	25
Lactic acid	2	0
Glycerol	6	0

FIG. 1 Effects of CAB concentration on PR and f. Operating pressure: 1000 psig. Feed rate: 1200 mL/min.

Table 2 further illustrates the function of the additives in CAB membrane casting. All these membranes from different batches had almost the same solution separation capability but quite different permeabilities (expressed in terms of PWP, PR, or A), indicating that all these membranes made under the specified experimental conditions had almost the same average pore sizes but quite different pore densities. Among the four batches of membranes, B3, whose casting solution contained all three additives, i.e., triethyl phosphate, glycerol, and lactic acid, showed the highest permeability; B5, whose casting solution contained no triethyl phosphate, and B2, without glycerol, showed the lowest and second lowest permeability, respectively, indicating that triethyl phosphate and glycerol functioned as the main pore-producing agents for CAB membrane. B4, whose casting solution contained no lactic acid, showed relatively

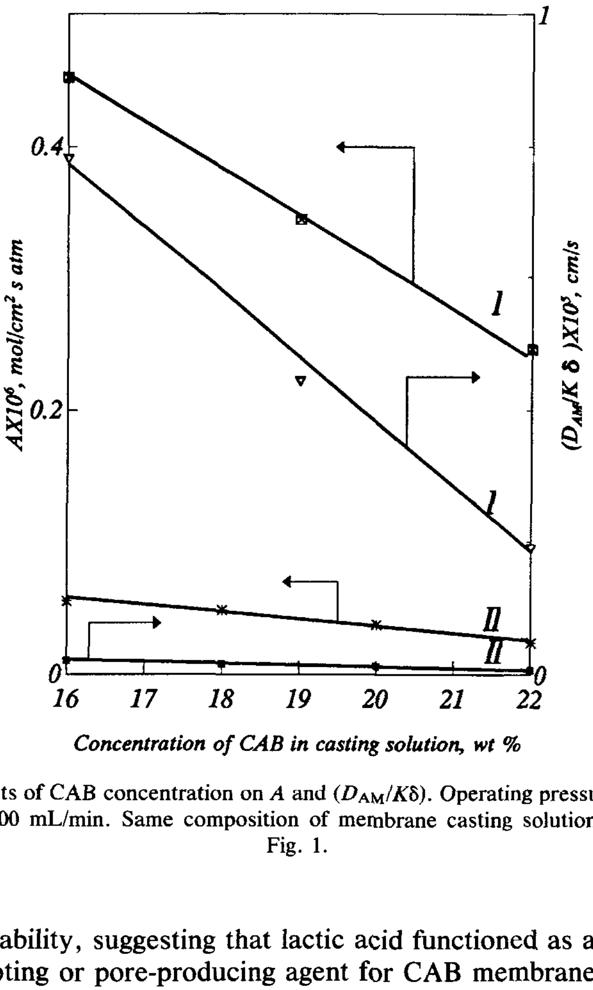


FIG. 2 Effects of CAB concentration on A and $(D_{AM}/K\delta)$. Operating pressure: 1000 psig. Feed rate: 1200 mL/min. Same composition of membrane casting solution as shown in Fig. 1.

high permeability, suggesting that lactic acid functioned as a secondary pore-promoting or pore-producing agent for CAB membranes. The fact that level of solute separation remained essentially unaffected for all batches of these membranes, but permeabilities were increased significantly when additives at the specified dosage were used, indicates again that these additives function only to increase the number of pores but not to increase pore size on the membrane surface.

A large quantity (25% of total) of triethyl phosphate was used in B2, B3, and B4. At this high concentration triethyl phosphate can function as a pore-promoting agent as well as a secondary solvent. This is also consistent with the finding of Manjikian (4).

It should be noted that the above experimental results were obtained from membranes made from solutions with low concentrations of glycerol

TABLE 2
Functions of Additives in Membrane Casting Solutions[a]

Membrane batch number	B3	B5	B2	B4
Composition of membrane casting solution, wt%:				
CAB-17-15	16	16	16	16
Triethyl phosphate	25	0	25	25
Glycerol	3	3	0	3
Lactic acid	9	9	9	0
Acetone	47	72	50	56
PWP, g/h	66.97	1.976	10.47	35.65
PR, g/h	54.29	1.890	7.527	31.64
f, %	86.56	89.96	86.28	87.12
$A \times 10^6$, mol/cm^2·s·atm	0.8400	0.0248	0.1313	0.4472
$(D_{AM}/K\delta) \times 10^5$, cm/s	3.443	0.3846	0.3270	4.114

[a] Experimental conditions: Operating pressure, 1000 psig; feed rate, 1200 mL/min; feed concentration, 5000 ppm NaCl; effective membrane area, 18.06 cm^2.

and lactic acid. At higher concentrations of these additives the pores on the membrane surface become larger to give higher flux and lower solute separation, as shown in Figs. 3 and 4. In this case larger droplets of the additives (which are "nonsolvent swelling agents") can form at the surface layer, which ultimately resulted in the formation of larger pores on the membrane surface.

Shrinkage Treatment

The effects of membrane shrinkage pretreatment on membrane morphology and performance are shown in Figs. 5 and 6. For the purpose of comparison, the unshrunk membrane may be considered as if it were shrunk in water at laboratory temperature (about 24°C) so that its experimental data could be plotted together with those shrunk at higher temperatures. Shrinkage treatment had a significant effect on CAB membrane morphology and performance in the temperature range 60 to 95°C. When the shrinkage temperature was below 60°C, the heat treatment had little effect on membrane morphology, indicating no membrane shrinkage occurred at temperatures below 60°C (represented by dotted lines in Figs. 5 and 6). When the temperature was higher than 60°C, an increase in shrinkage temperature led to a significant increase in solute separation and steep decreases in permeated product rate, pure water permeation constant, and solute transport parameter, indicating that higher shrinkage temperature resulted in the formation of pores of much smaller average

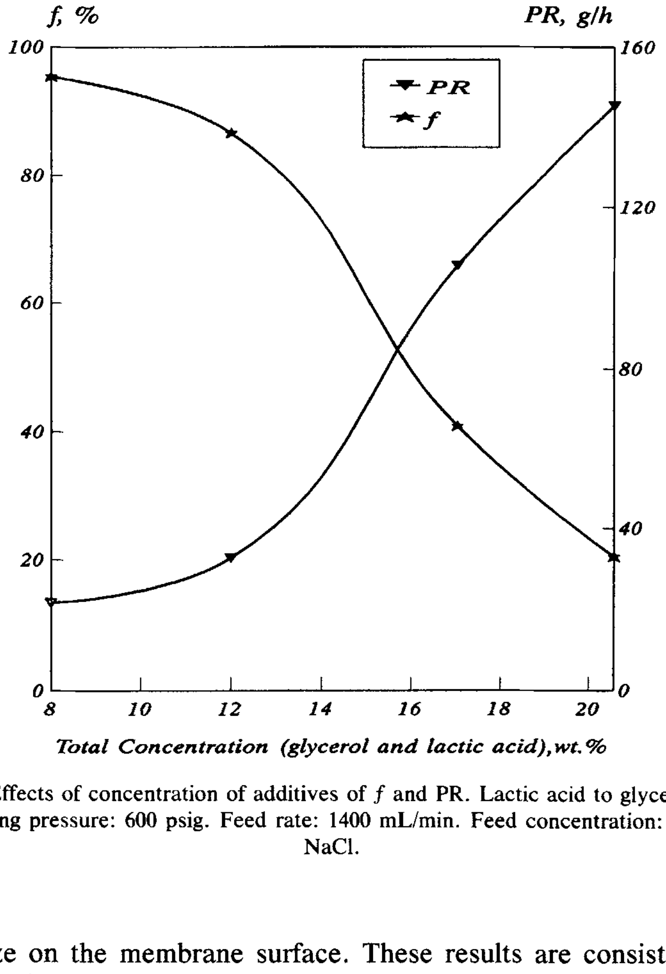


FIG. 3 Effects of concentration of additives of f and PR. Lactic acid to glycerol (w/w): 3. Operating pressure: 600 psig. Feed rate: 1400 mL/min. Feed concentration: 4900 ppm NaCl.

pore size on the membrane surface. These results are consistent with those obtained in other works (10, 21–24). One may note that two methods could be used to obtain high solute separation for CAB membranes. One is to use unshrunk membranes made from casting solution with a low concentration of additives. The other is to thermally shrink porous membranes made from solutions with a high additive concentration. The former method could be economically and technologically more attractive as it requires only a low concentration of additive.

Phases in Solvent Evaporation Step

Although the effect of solvent evaporation time on cellulose acetate membrane performance has been extensively studied (10, 25–27), the

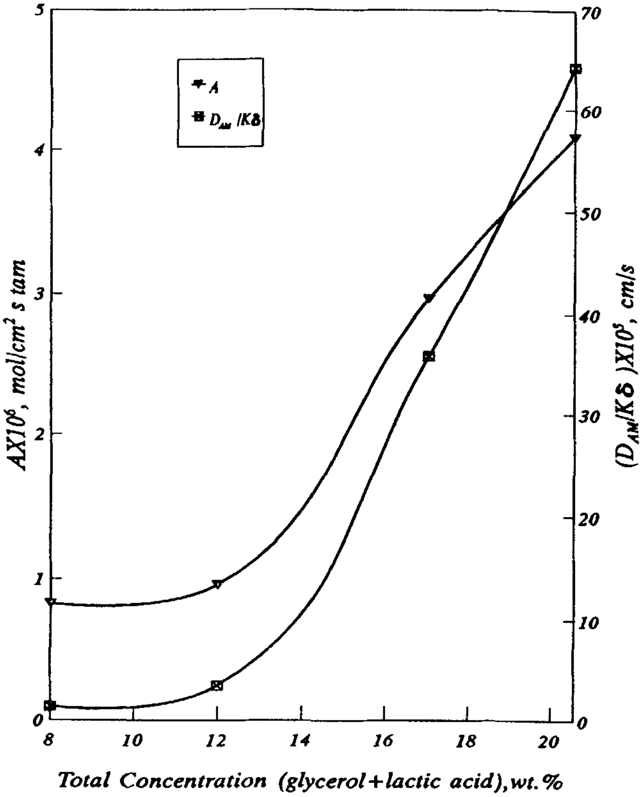


FIG. 4 Effects of concentration of additives on A and $(D_{AM}/K\delta)$. Lactic acid to glycerol (w/w): 3. Operating pressure: 600 psig. Feed rate: 1200 mL/min. Feed concentration: 4900 ppm NaCl.

change in morphology on the membrane surface with an increase of solvent evaporation time is not well understood. Figures 7 and 8 show the effects of solvent evaporation time on the morphology and performance of CAB membranes. Three regions can be noted in these figures. In Region II, solute separation passed through a maximum for which the membrane was made at a solvent evaporation time of 60 seconds. Permeated product rate increased with an increase in solvent evaporation time in the whole range tested. In Fig. 8, pure water permeability constant A increased with an increase in solvent evaporation time in the whole range of 0 to 150 seconds. The solute transport parameter appeared to be small for membranes made at solvent evaporation times of 0 to 90 seconds, after which

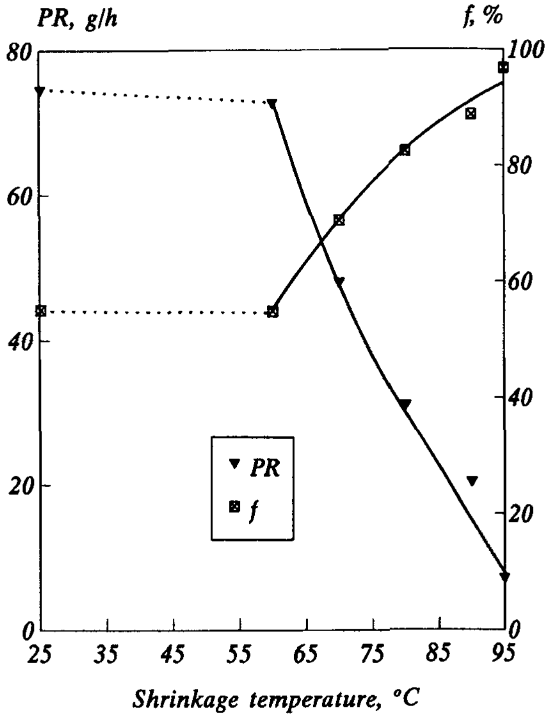


FIG. 5 Effects of shrinkage temperature on PR and *f*. Operating pressure: 1000 psig. Feed rate: 1200 mL/min. Feed concentration: 4900 ppm NaCl.

it increased rapidly in the 90 to 150 seconds range. The above observations may be qualitatively analyzed as follows.

According to the surface force-pore flow (SFPF) model and the solution structure-desolvation rate (SSDR) approach (10, 17), pores on the membrane surface generally fall into two pore size distributions, one having a smaller average pore size (usually referred to as the first pore size distribution) and the other having a larger average pore size (usually referred to as the second pore size distribution). Membrane flux or permeability (expressed by PWP, PR, or *A*) depends on three factors: 1) the average pore sizes in the two pore size distributions, 2) the number of pores per unit area of membrane surface (surface pore density) in the two distributions and their ratio, and 3) the effective thickness of the surface skin layer. Solute separation by membrane depends on both the pore sizes and the pore number ratio of the two distributions on the membrane surface.

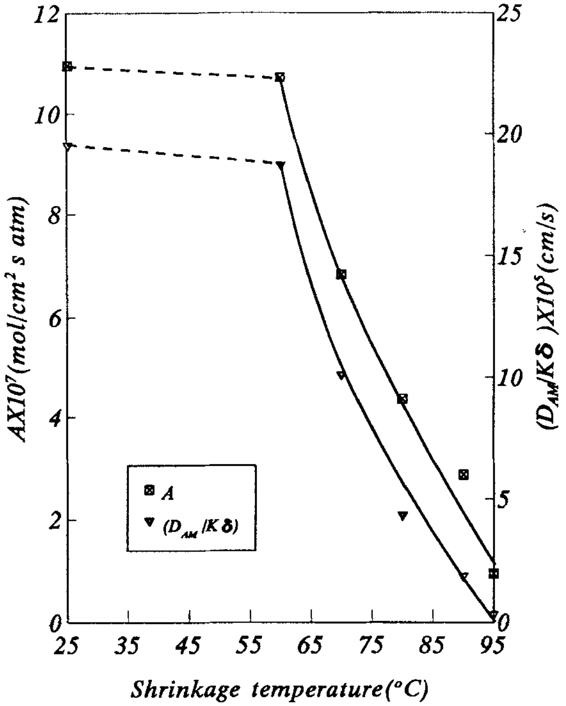


FIG. 6 Effects of shrinkage temperature on A and $(D_{AM}/K\delta)$. Operating pressure: 1000 psig. Feed rate: 1200 mL/min. Concentration of feed: 4900 ppm NaCl. Membrane type: CAB.

During a membrane-making process, three distinct phases with respect to pore formation can be visualized.

1. Intrinsic pore-determining phase (Phase I, little or no solvent evaporation occurs). In this phase a cast film is immediately immersed into a gelation bath after casting. The so-made membrane would have no or only a very thin "skin" layer with few pores on it, and these pores are big because they just start to form from the "intrinsic pores" in the casting solution (10, 17). So one may visualize that this membrane would yield low flux and low solute separation, as shown in Region I of Figs. 7 and 8.
2. Small pore-forming phase (Phase II). With longer solvent evaporation time, the air-surface skin layer gets thicker because of desolvation, and more small droplets of nonsolvents (additives) are formed in the air-surface layer by diffusion of nonsolvent molecules from the bulk

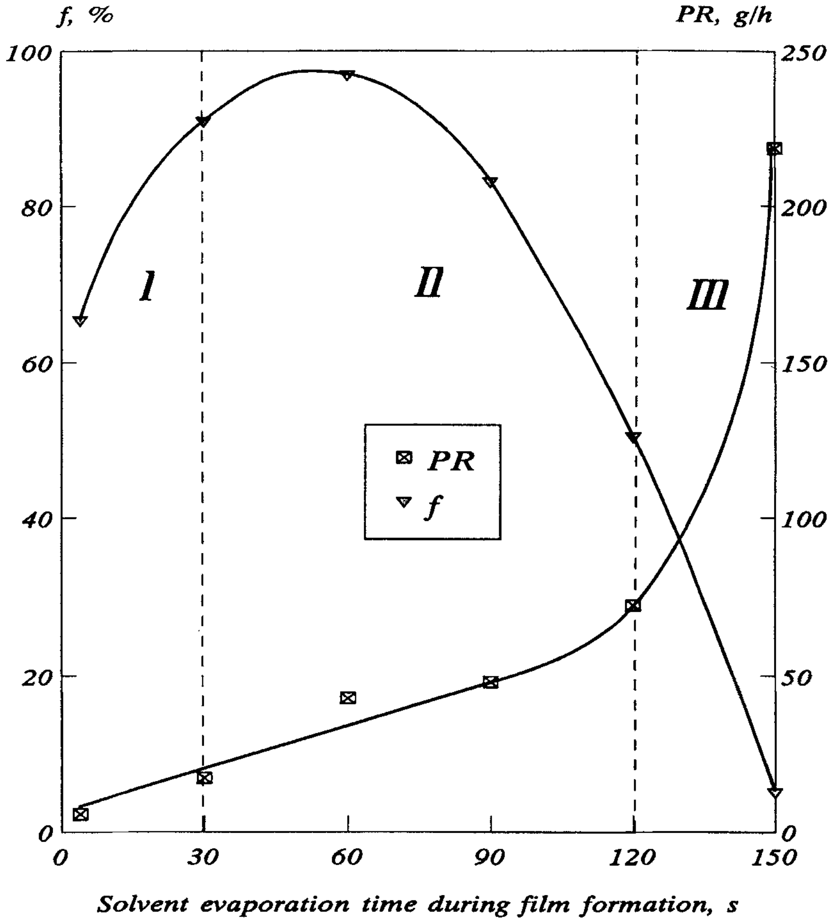


FIG. 7 Effects of solvent evaporation time on PR and *f*. Operating pressure: 1000 psig. Feed rate: 1200 mL/min. Feed concentration: 4850 ppm NaCl.

casting solution underneath the surface layer. These small droplets of nonsolvents in the surface layer lead to the formation of a large number of small pores (which, of course, belong to the first pore size distribution) upon gelation. They play a dominant role in determining membrane performance. One, therefore, may expect that a membrane made in this phase would yield both higher solute separation and flux, as shown in Region II of Figs. 7 and 8.

3. Large pore-forming phase (Phase III). In this phase, small droplets of nonsolvents in the surface layer coalesce to form larger nonsolvent

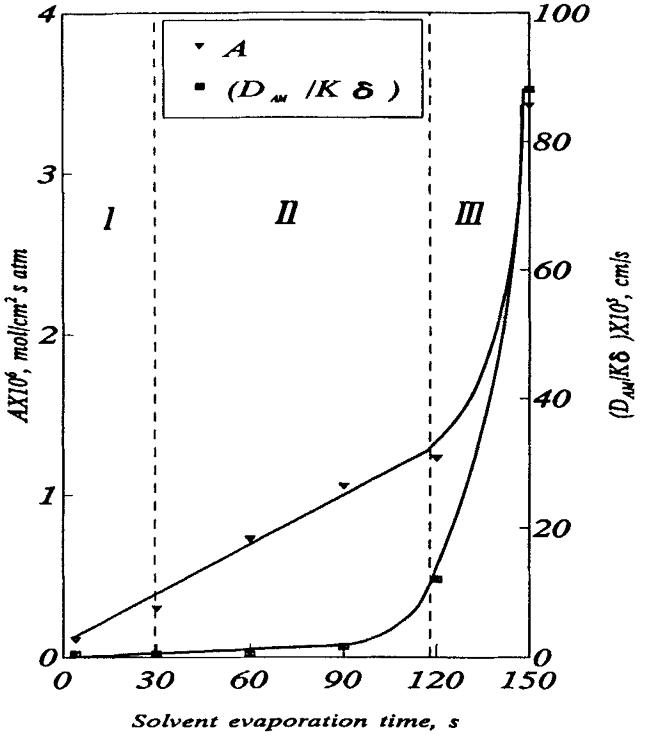


FIG. 8 Effects of solvent evaporation period during film formation on A and $(D_{AM}/K\delta)$. Operating pressure: 1000 psig. Feed rate: 1200 mL/min. Feed concentration: 4850 ppm NaCl.

droplets, which ultimately form larger pores (which belong to the second pore size distribution) in the skin layer upon gelation. These larger pores play a dominant role in determining performance of membranes made in this phase. One therefore may expect that a membrane made in this phase would yield low solute separation but high flux, as shown in Region III of Figs. 7 and 8.

It should be noted that the number of pores in the second (larger pore size) distribution always keep increasing with an increase in solvent evaporation time, and the number of pores in the first (smaller pore size) distribution increases with an increase in solvent evaporation time in Phases I and II but decreases with an increase in solvent evaporation time in Phase III. Since there are far more pores in the first distribution than in the second (10, 28), the pores in the first distribution thus play the dominant role in determining the magnitude of solute separation. On the other hand, permeability of membranes made in Phases I and II is determined mainly by the pore size and number of pores in the first distribution and that of membranes made in Phase III by pore sizes and number of pores in both distributions. According to the above analyses, one may expect that a maximum in solute separation would exist in Phase II, which in the case of CAB/acetone casting solution falls in the vicinity of 60 seconds of solvent evaporation time, and that the membrane flux would always keep increasing with an increase in solvent evaporation time, as shown in Figs. 7 and 8. A quantitative analysis (in terms of average pore sizes, pore numbers, and their ratio in two pore size distributions as well as the membrane surface skin layer thickness) for the above behavior will be given in a later communication.

CONCLUSIONS

Glycerol and lactic acid as additives in CAB membrane casting solution function only as pore number promoting agents when used at low concentrations. They function both as pore number and pore size promoting agents when used at higher concentrations. Triethyl phosphate in CAB membrane casting solution functions both as a pore number promoting agent and as a secondary solvent for the polymer.

During the solvent evaporation step, an increase in solvent evaporation time increases the number of smaller pores in the initial phase but the number of small pores decreases in a later phase, which favors the formation of larger pores. The number of pores in the larger pore size distribution always increases with solvent evaporation time. It is these changes in the number of pores, pore sizes, and pore number ratio in the two distributions as well as the membrane skin layer thickness that together govern ultimate membrane morphology/performance which, in the case of the CAB/acetone system, shows a maximum solute separation by CAB membranes made at 60 seconds of solvent evaporation time.

Improvement of the performance of a porous CAB membrane can be achieved by thermal shrinkage treatment. Equally high membrane performance can also be obtained by using a lower concentration of additives in the casting solution.

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REFERENCES

1. S. T. Yuster and S. Sourirajan, *Department of Engineering, UCLA, Report 58-26*, 1958.
2. S. Manjikian, S. Liu, M. I. Foley, C. Allen, and B. Fabrick, *Office of Saline Water R & D Progress Report 534*, US Department of the Interior, Washington, D.C., 1970.
3. S. Manjikian and M. I. Foley, *Office of Saline Water R & D Progress Report 612*, US Department of the Interior, Washington, D.C., 1970.
4. S. Manjikian, US Patent 3,607,329 (1971).
5. T. Wydeven and M. Leban, *J. Appl. Polym. Sci.*, *17*, 2277 (1973).
6. J. Anderson, S. Hoffman, and C. Peters, *J. Phys. Chem.*, *76*, 4006 (1972).
7. H. Ohya, *J. Appl. Polym. Sci.*, *23*, 663 (1979).
8. H. Ohya, N. Akimoto, and Y. Negishi, *Membrane*, *5*(3), 179 (1980).
9. X. Lu, Y. Liu, P. Zhou, and X. Sun, *Water Treat.*, *2*(1), 15 (1987).
10. S. Sourirajan and T. Matsuura, *Reverse Osmosis/Ultrafiltration Process Principles*, National Research Council Canada, Ottawa, 1985.
11. R. E. Kesting, *Materials Science of Synthetic Membranes*, American Chemical Society, Washington, D.C., 1985, p. 131.
12. R. E. Kesting, in *Reverse Osmosis and Synthetic Membranes* (S. Sourirajan, Ed.), National Research Council Canada, Ottawa, 1977, Chap. 5.
13. R. E. Kesting, *Synthetic Polymeric Membranes*, McGraw-Hill, New York, 1971, Chap. 5.
14. R. E. Kesting and A. Menefee, *Kolloid-Z. Z. Polym.*, *230*, 341 (1969).
15. R. E. Kesting, *J. Appl. Polym. Sci.*, *9*, 663 (1965).
16. R. E. Kesting, *Ibid.*, *17*, 1771 (1973).
17. S. Sourirajan, *Lectures on Membrane Separations*, Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Canada, 1991.
18. S. Sourirajan, *Reverse Osmosis and Synthetic Membrane, Theory—Technology—Engineering*, National Research Council of Canada, Ottawa, 1977.
19. S. Sourirajan, "Cellulose and Cellulosic Membranes for RO/UF and Related Separations," Plenery lecture presented at Cellulose '91, ACS Meeting, New Orleans, Louisiana, December 2–6, 1991.
20. H. Strathmann, *Materials Science of Synthetic Membranes*, American Chemical Society, Washington, D.C., 1985, p. 165.
21. Y. Wang, W. W. Y. Lau, and S. Sourirajan, "Effects of Pretreatments on Morphology and Performance of Cellulose Acetate (Formamide Type) Membranes," *Desalination*, 1994, In Press.
22. J. Kopecek and S. Sourirajan, *J. Appl. Polym. Sci.*, *13*, 637 (1969).
23. B. Kunst and S. Sourirajan, *Ibid.*, *14*, 1983 (1970).
24. O. Kutowy and S. Sourirajan, *Ibid.*, *19*, 1449 (1975).
25. B. Kunst and S. Sourirajan, *Ibid.*, *14*, 2559 (1970).
26. L. Pageau and S. Sourirajan, *Ibid.*, *15*, 705 (1971).
27. T. A. Tweddle and S. Sourirajan, *Ibid.*, *22*, 2265 (1978).
28. T. Matsuura and S. Sourirajan, *Ind. Eng. Chem., Process Des. Dev.*, *20*, 273 (1981).

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