

# Reverse Osmosis Characteristics of Cellulose Acetate Butyrate Membranes\*

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## Synopsis

Cellulose acetate butyrate membranes were cast from five different formulations. The pure water flux through the membrane increased with evaporation period. The separation of 4000 ppm NaCl aqueous solution remained unchanged until it reached a critical flux; at that point, separation decreased inversely proportional to the flux. Scanning electron microscope photography of the membranes corresponding to each evaporation period is reported.

## INTRODUCTION

Cellulose acetate butyrate film, which is more hydrophobic than cellulose acetate film, was investigated for the reverse osmosis separation of aqueous salt solutions by Sourirajan.<sup>1</sup> The permeability of the film was low and an operating pressure of 4000 psig was necessary to obtain a significant product rate. The film yielded essentially complete solute separation. Solute separation was above 99.9% in all cases. The average product rate was only 1.2 cm<sup>3</sup>/hr/ft<sup>2</sup> of film surface at 4000 psig. The problem was to develop a method for making membranes of appropriate porosity using cellulose acetate butyrate (CAB).

To purify spacecraft waste water by reverse osmosis, several attempts have been made to obtain a reverse osmosis membrane capable of separating both organic and inorganic solutes. Ohya and Sourirajan<sup>2</sup> studied an asymmetric cellulose acetate membrane; it was found effective for salt separation, but poor for urea separation. Manjikian and Foley<sup>3</sup> showed that the CAB membrane exhibits separation properties substantially better than cellulose acetate membrane for a variety of inorganic and organic solutes. The most significant data were obtained in treating urea. Wydeven and Leban<sup>4</sup> further investigated the effects of various parameters on the flux, salt separation, and urea separation of CAB membranes. Results indicated: the membrane is asymmetric and gives high salt and urea separation with water flux of about 3 gfd at 600 psig; CAB membrane cast from the formulation containing glyoxal showed a tendency towards increasing of water flux; urea and salt separation decreased with the evaporation period.

This paper reports the effect of evaporation period at casting stage on water flux, salt separation and membrane structure.

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## EXPERIMENTAL

### Casting Solution Materials and Preparation

Cellulose acetate butyrate was obtained from Eastman Chemical Products, Inc. (Eastman identification code No. EAB-171-15). Other starting materials were triethyl phosphate (TEP), glycerol, *n*-propyl alcohol, acetone, and 40% aqueous glyoxal solution, which was filtered before use. Other chemicals were used without further purification. The casting solution composition is shown in Table I.

### Casting Procedure

Film—15 cm wide and 30 cm long—was cast on a clean dry glass plate with multiple electric tapes 15 mm wide and 0.2 mm thick as guide and glass rod. The casting speed was about 20 cm/sec in ambient air. After casting, the membranes were dried. The cast films were gelled and floated free from the glass plate by quenching in ice water over one hour. Films were stored in 1 g/liter aqueous formalin solution.

### Reverse Osmosis Test Apparatus and Procedure

Membranes were tested for water flux and separation using the recirculating reverse osmosis system (Fig. 1). The test cell used was the same as reported by Sourirajan.<sup>5</sup> The effective membrane area of film used was 7.6 cm<sup>2</sup> in all cases. All membranes were subject to an initial pressure treatment of 24 bar with pure water for about 2 hr, prior to their subsequent use in reverse osmosis experiments. All experiments were carried out at the pressure of 20 bar and at 25°C. The average feed flow rate was about 200 cm<sup>3</sup>/min. The composition of feed was 3.5 g/liter sodium chloride.

### Analysis

Water flux was determined gravimetrically; concentration of sodium chloride was determined with a conductivity meter.

TABLE I  
Casting Solution Composition

Batch No. CAB-AN	A	F	I	J	W
Formulation parts					
EAB 171-15	22	22	19	25	20
glycerol	2	2	2	2	2
<i>n</i> -propyl alcohol	6	6	6	6	6
triethyl phosphate	25	25	25	25	25
acetone	55	55	55	55	55
40% glyoxal	10	15	10	10	—
water					5

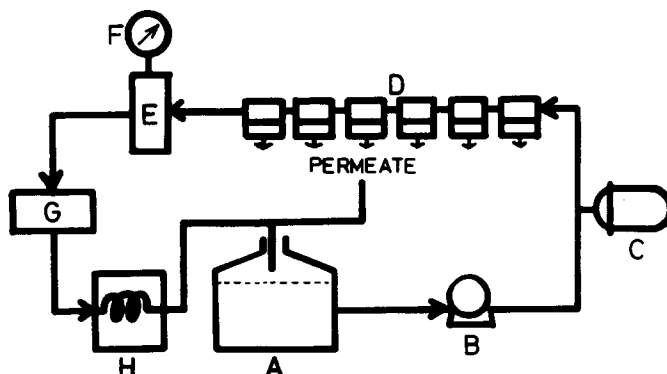


Fig. 1. Flow diagram of reverse osmosis test cells. (A) Storage tank; (B) pump; (C) surge tank; (D) cells; (E) pressure regulator; (F) pressure gauge; (G) filter; (H) cooler.

### Electron Microscopy

Extensive use was made of the scanning electron microscope in the central laboratory of Mitsui Toatsu Chemicals. Wet membrane samples were fractured in liquid nitrogen, freeze-dried overnight, shadowed with carbon, then gold, and examined with a JEOL electron scanning microscope at an angle of  $45^\circ$ .

## RESULTS AND DISCUSSIONS

### Solvent Evaporation Period

Figure 2 gives the relation between salt separation, water flux, and evaporation period for batch CAB-NA-A. With evaporation period, water flux steadily increases, and salt separation remains nearly constant until 100 sec, but thereafter, abruptly decreases to almost zero separation at 150–250 sec. This period of 100 to 150–250 sec is a transient period and longer evaporation period does not yield a reverse osmosis membrane for salt separation.

### Casting Thickness

Membranes of casting thickness 0.4 mm do not have the transient period; the evaporation period longer than 140 sec does not yield separation. It was impossible to obtain a membrane of medium separation 20%–70%. When the casting thickness was increased, a membrane of medium separation could be obtained at the transient period.

### Performance of CAB Membranes

Figures 3 and 4 show salt separation versus reciprocal of product rate for batch CAB-NA membranes at the operating pressure of 20 bar. Performance of the Batch CAB-NA membranes is expressed by two straight lines. Data move along the horizontal line from right to left with the evaporation time and then along the slant till zero separation. Further increase of the evaporation period does not cause higher flux and there might exist an intrinsic water flux for each casting thickness and each composition.

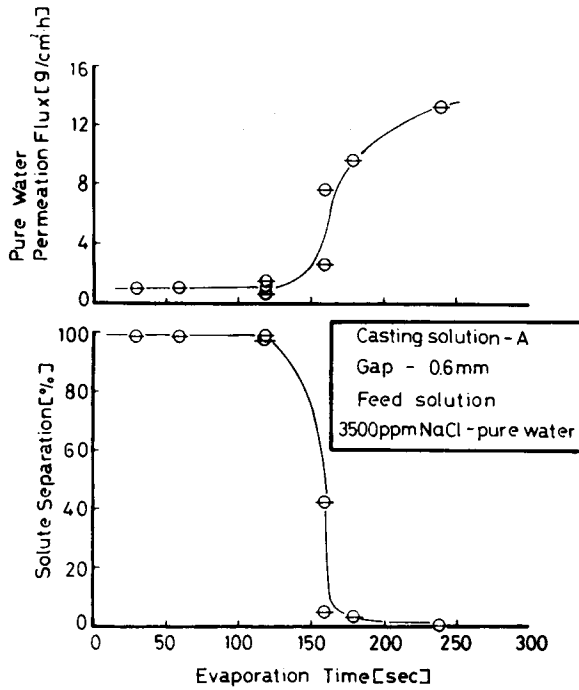


Fig. 2. Effect of evaporation period on membrane performance, solution system, NaCl-H<sub>2</sub>O, feed concentration 4000 ppm.

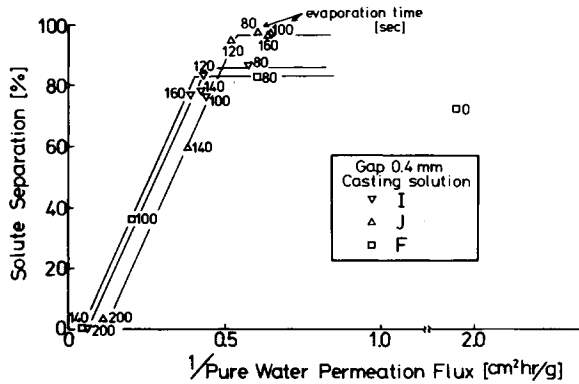


Fig. 3. Effect of evaporation period and casting thickness on membrane performance, numerals belonging to symbols designate evaporation period in sec, solution system, NaCl-H<sub>2</sub>O, feed concentration 4000 ppm.

Optimum membrane of higher separation and the highest water flux exists at the intersecting point of the two lines. This is the most significant result. The flux of the optimum membrane increases with decrease of casting thickness, increase of the content of glyoxal and the decrease of CAB concentration.

Membranes of higher separation were opaque and thicker, while membranes of separation less than 10% were transparent and one-third to one-half thinner. Membranes of medium separation had many small opaque spots of several tenths millimeter in transparent film. Hence, the membrane may consist of one part

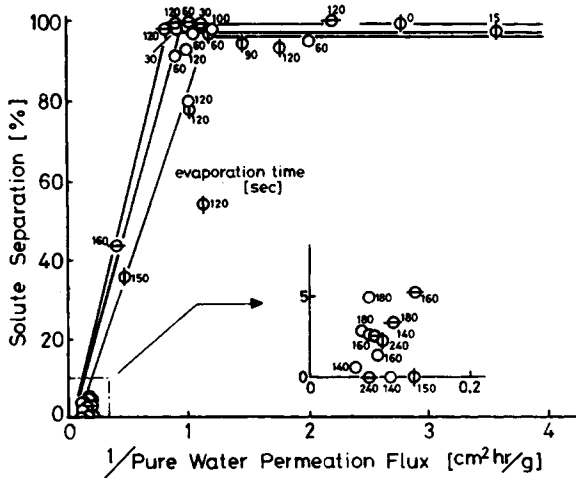


Fig. 4. Effect of evaporation period and casting solution composition on membrane performance, numerals belonging to symbols designate evaporation period in sec, solution system, NaCl-H<sub>2</sub>O, feed concentration 4000 ppm. Casting solution—A: ○, 0.4 mm gap; ⊖, 0.6 mm gap; ϕ, 0.8 mm gap.

of higher separation and rather lower flux and the other part of zero separation and higher flux.

**Membrane Model Consisted of Higher Separation and Zero Separation**

Let us assume that a membrane consisted of only two parts, i.e., one part of which water flux, salt separation, and fractional area are defined as  $J_1, R_1,$  and  $f_1,$  respectively; the other part  $J_2, R_2,$  and  $f_2,$  respectively.

The sum of two fractional areas should be 1.0:

$$f_1 + f_2 = 1.0 \tag{1}$$

From the water flux material balance over two parts the following equation may be obtained:

$$J_1 f_1 + J_2 f_2 = J_v \tag{2}$$

where  $J_v$  is total water flux through the membrane.

Let  $c_3^1, c_3^2,$  and  $c_3$  be defined as the concentration of permeate through the part of higher separation, of zero separation and of the total permeate. Then from the solute material balance over two parts, the following equation is obtained:

$$c_3^1 J_1 f_1 + c_3^2 J_2 f_2 = c_3 J_v \tag{3}$$

Total separation and separation on each part are defined as follows:

$$R = (c_1 - c_3)/c_1, \quad i = 1, 2 \tag{4}$$

$$R_i = (c_1 - c_3^i)/c_1$$

Using eqs. (1) to (4), the following equation may be obtained:

$$(R_2 - R_1) J_1 J_2 (1/J_v) = (R_2 J_2 - R_1 J_1) + R (J_1 - J_2) \tag{5}$$

When membranes consist of two parts, there may exist a linear relationship between the reciprocal of water flux ( $1/J_v$ ) and total salt separation  $R,$  which corresponds to the slanted line (Figs. 3 and 4).

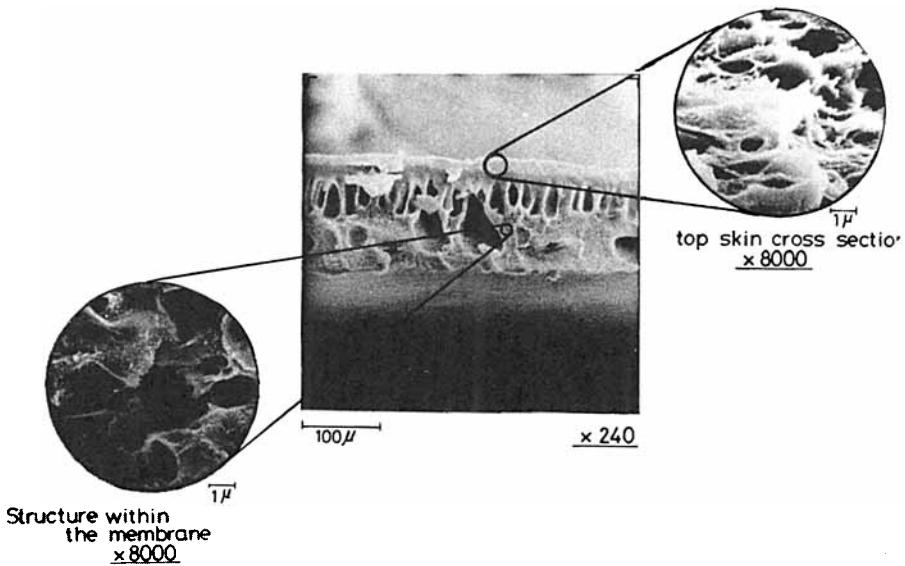


Fig. 5. Scanning electron micrograph of a membrane with finger structure; prepared from casting solution batch CAB-NA-A, casting thickness 0.4 mm, evaporation period 80 sec.

### Membrane Structure

By electron microscopy, two general classes of membrane have been observed, depending on the evaporation period during film casting. If the evaporation period is short, membranes with large fingerlike cavities are formed. This type of membrane is shown (Fig. 5).

There are rather small cavities of several  $\mu\text{m}$  and large tapering fingerlike cavities of about 10  $\mu\text{m}$  which reach to the dense skin layer, but there are no holes on the upper most surface.

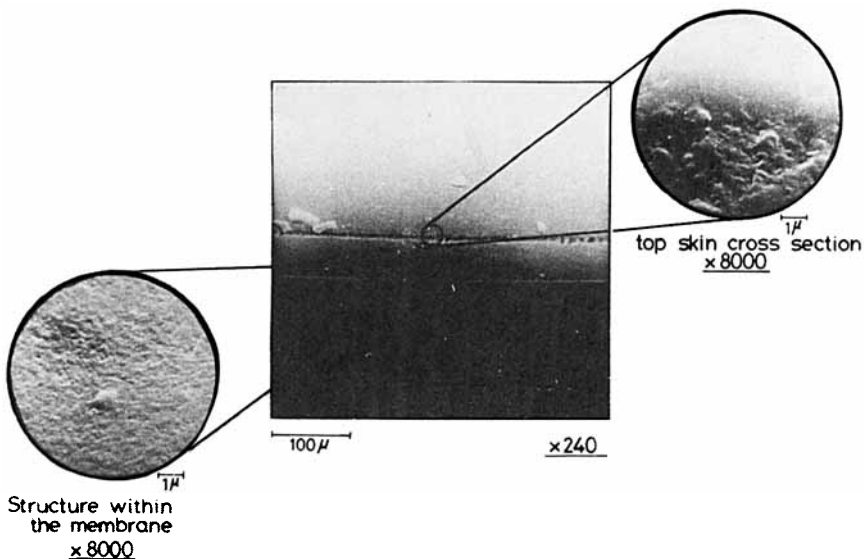


Fig. 6. Scanning electron micrograph of a membrane with solid structure; prepared from casting solution batch CAB-NA-A, casting thickness 0.4 mm, evaporation period 140 sec.

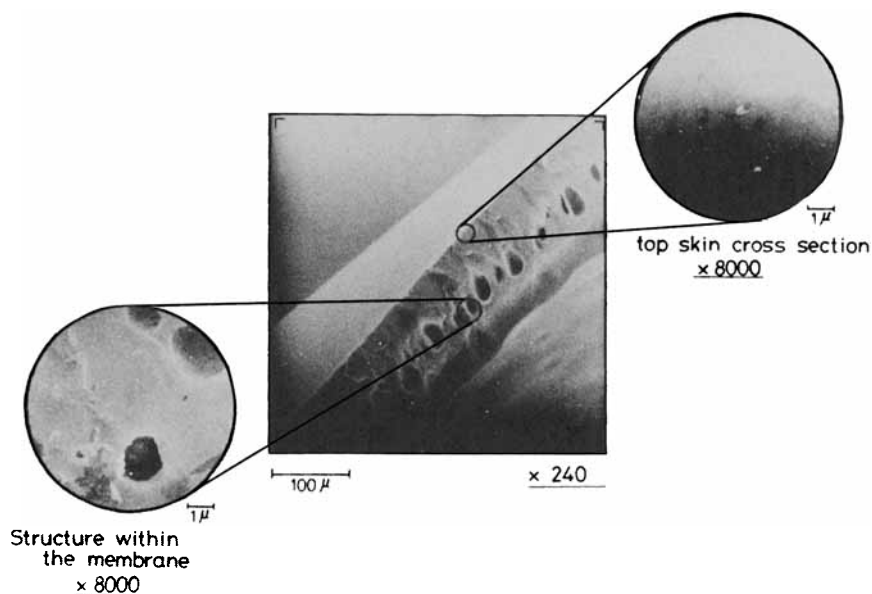


Fig. 7. Scanning electron micrograph of a membrane with the transient from finger structure to solid structure; prepared from casting solution batch CAB-NA-A, casting thickness 0.4 mm, evaporation period 100 sec.

The membrane (Fig. 5) is opaque, porous, and has a fingerlike structure and a dense surface layer. Yet, it has a high salt separation and low water flux.

The second type of membrane is of the solid structure (Fig. 6). It is formed when the evaporation period is long. Membranes of this type usually have a high flux and low separation; they do not have cavities and appear transparent.

This phenomenon is quite different from that observed with the cellulose acetate membrane.

Figure 7 shows a medium separation membrane which has independent fingerlike cavities of 1–2  $\mu\text{m}$  and a solid structure on both top and bottom surfaces. We can not offer a reasonable explanation for the relationship between membrane structure and its characteristics.

## CONCLUSIONS

Cellulose acetate butyrate membranes differ from cellulose acetate membranes, particularly in the membrane structure and reverse osmosis. Membranes show a significant increase in flux and decrease in salt separation with drying time as stated by Wydeven and Leban.<sup>4</sup> The structure of the membrane was porous at zero drying time and became tighter with increasing drying time.

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