

# Cellulose Acetate Reverse Osmosis Membranes: Optimization of Preparation Parameters

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**ABSTRACT:** Asymmetric cellulose acetate based membranes usually employed in reverse osmosis as well as in separations in aqueous systems can possibly be applied in the so-called salinity process of energy generation. For these applications, membranes with a relatively high water permeability (sometimes also called water flux) and low salt permeability (or high salt rejection) are required. In this study the authors present the optimization of such membranes, which concerns the preparation parameters. The membranes studied were prepared from a solution whose composition were

previously optimized.<sup>4</sup> The authors concluded that the optimum preparation parameters are as follows: thickness of the liquid film of 100  $\mu\text{m}$ ; 30 s allowed for evaporation of the solvent; and temperature of coagulation bath of 0–4°C and 80–85°C as annealing temperature. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 134–139, 2007

**Key words:** membranes; power production; selectivity; preparation parameters; annealing

## INTRODUCTION

Cellulose acetate asymmetric membranes have outstanding properties for desalination of seawater and potential use for power production by reverse osmosis.<sup>1,2</sup>

The integrally asymmetric membranes consist of a very thin dense skin layer practically pore-free, which is responsible for the selectivity of the membrane, over a porous support layer, which nearly represents the entire thickness of the membrane.

The procedure for the preparation of integrally asymmetric acetate membranes is as follows. In the first step, a solution of cellulose acetate in a suitable solvent or system of solvents is prepared and then a membrane is obtained by casting from the polymeric solution with a film-drawing device with a precise slit width on a smooth surface (e.g., glass surface). In subsequent steps, the volatile constituents of the solvent are partially evaporated at room temperature, and the liquid film is immersed in a water bath, giving rise to the beginning of the phase inversion, which leaves the membrane in the form of a water-swollen anisotropic gel of cellulose acetate.<sup>3</sup> Finally, and as an optional

step, the membrane can be annealed in a warm water bath, solidified in the previously established structure with a relatively small reduction in its water permeability.

Having in mind the permeability characteristics of the resulting membrane, we started by the preparation of membranes with a casting solution, whose optimization of composition is described elsewhere.<sup>4</sup>

The objective of this work was to prepare membranes, relating the influence of preparation parameters with the performance of the membranes. To do so, we have analyzed comparatively the performance (water and salt permeability values) of the membranes produced changing the following parameters:

- thickness of the liquid film;
- time allowed for evaporation of the solvent;
- temperature of coagulation bath; and
- annealing temperature.

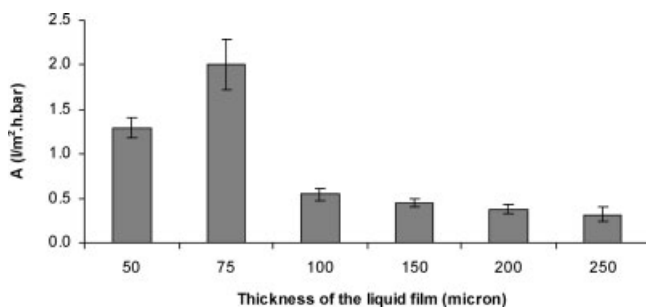
The water permeability was calculated using the following equation (assuming that specific gravity is very close to 1):

$$A = \frac{V}{A_{\text{memb}}tp} \quad (1)$$

where  $A$ , water permeability of the membrane ( $\text{L}/\text{m}^2 \text{ h bar}$ );  $V$ , volume of water through the membrane in a given time  $t$  ( $\text{L}$ );  $A_{\text{memb}}$ , membrane area ( $\text{m}^2$ );  $t$  time ( $\text{h}$ ); and  $p$ , pressure across the membrane ( $\text{bar}$ ).

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**Figure 1** Average water permeability data for the membranes produced with different thickness of the liquid film.

The salt rejection values ( $\langle R \rangle$ ) were calculated using the following equation:

$$R = \frac{C_0 - C_{\text{memb}}}{C_0} \times 100 \quad (2)$$

where  $R$ , salt rejection (%);  $C_0$ , conductivity of salty water at the pressure side in the beginning of the experiment (mS);  $C_{\text{memb}}$ , conductivity of water that went through the membrane (mS).

The eq. (2) assumes that conductivity has a linear relationship with the salt concentration, and this is approximately correct for the relevant range of concentrations.

## EXPERIMENTAL

### Materials and methods

Cellulose diacetate ( $(M_w) \sim 30,000 \text{ g mol}^{-1}$ , 39.8 wt % acetyl content) was received from Aldrich (180955, Madrid, Spain). The cellulose triacetate used was supplied by Sigma-Aldrich (181005, Madrid, Spain), with 46 wt % acetyl content (average). The cellulose fibers used were received from Sigma (S3504-Sigmacell R type 20) and are microcrystalline powder particle (size 20  $\mu\text{m}$ ), usually used in chromatography columns. 1, 4-Dioxane was supplied by Panreac Quimica S.A (Barcelona, Spain) and has a 99.5% of minimum purity. Methanol and acetone used were received from Lab solve (Lisbon, Portugal). The methanol has a minimum purity of 99.5% and acetone of 99%. Acetic acid with a minimum purity of 99.8% was supplied by BDH Anala R (England).

The water permeability ( $\langle A \rangle$ ) of the membrane was measured at 8 bar with a low pressure filtration cell mod. GN-10/400 from Berghof (Eningen, Germany).

The determination of the salt rejection was performed with a concentration of the salt (NaCl) in water of 5 g/L and the conductivity of water was measured with a Conductivity meter mod. HI 8733 of Hanna Instruments (Ronchi di Villafranca, Italy).

### PROCEDURE

The membranes were prepared using the formulation that was already optimized.<sup>4</sup> This formulation was prepared with the following raw materials:

- 45.77 wt % dioxane, 17.61 wt % acetone, and 8.45 wt % acetic acid as solvents;
- 14.09 wt % methanol as nonsolvent;
- 9.86 wt % cellulose diacetate and 4.22 wt % cellulose triacetate; and
- 0.5 wt % of cellulose fibers in relation of total content of polymer.

The membranes were obtained by spreading the solution (at room temperature  $T$  (25°C) on a glass plate with a calibrated ruler whose thickness was previously selected, at a constant speed of 23 mm/s using the Automatic Film Applicator from Braive Instruments. After a period of time for evaporation of the solvent, the polymeric film on the glass was immersed for 15 min in a water bath. After that, the film was placed in an ice cold water bath  $T$  (4°C) during 2 h. The last step of the process of preparation is the annealing posttreatment for 15 min.

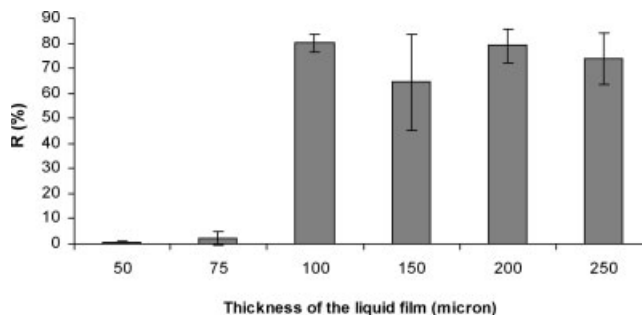
Since the main objective of this work was to relate the influence of preparation parameters with the performance of the membranes, we have analyzed comparatively the performance (water and salt permeability values) of the membranes produced, changing one parameter at a time.

To study the influence of the thickness of the liquid film in the performance of the membranes, we prepared membranes with 50, 75, 100, 150, 200, and 250  $\mu\text{m}$ .

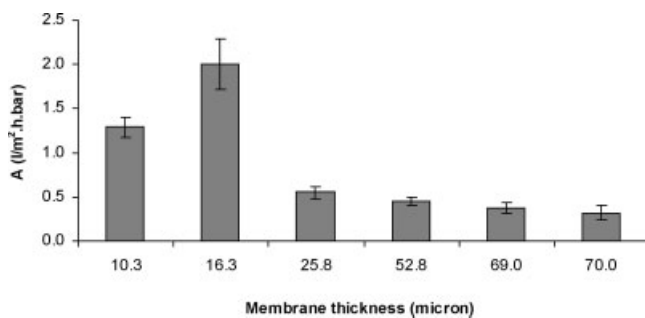
Note that the indicated thickness is the thickness of the calibrated ruler, not the final membrane thickness, since this is the control parameter; however, we will present the results for water permeability and salt rejection for both thickness of the liquid film and final thickness of the membrane.

Considering the time allowed for evaporation of the solvent, we studied the following five situations: (1)  $t_{\text{ev}} = 15 \text{ s}$ , (2)  $t_{\text{ev}} = 30 \text{ s}$ , (3)  $t_{\text{ev}} = 45 \text{ s}$ , (4)  $t_{\text{ev}} = 60 \text{ s}$ , and (5)  $t_{\text{ev}} = 90 \text{ s}$ .

In what concerns the temperature of the coagulation bath, the influence of the following range of temperatures have been studied: (1)  $T = 0\text{--}4^\circ\text{C}$ , (2)  $T = 4\text{--}8^\circ\text{C}$ , (3)  $T = 8\text{--}12^\circ\text{C}$ , (4)  $T = 12\text{--}16^\circ\text{C}$ , (5)  $T = 16\text{--}20^\circ\text{C}$ , and (6)  $T = 20\text{--}24^\circ\text{C}$ .



**Figure 2** Average salt rejection data for the membranes produced with different thickness of the liquid film.



**Figure 3** Average water permeability data for the membranes with different final thickness.

To study the influence of the temperature of the annealing posttreatment the membranes were annealed for 15 min at the following temperatures: (1)  $T = 20\text{--}25^\circ\text{C}$ , (2)  $T = 40\text{--}45^\circ\text{C}$ , (3)  $T = 60\text{--}65^\circ\text{C}$ , (4)  $T = 70\text{--}75^\circ\text{C}$ , (5)  $T = 80\text{--}85^\circ\text{C}$ , and (6)  $T = 90\text{--}95^\circ\text{C}$ .

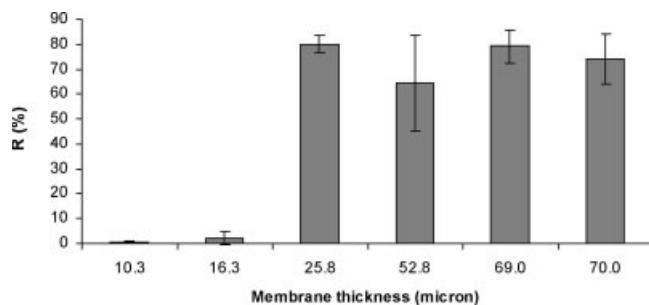
## RESULTS AND DISCUSSION

The membranes were produced using the same solution and under the effect of similar external conditions (mainly temperature and humidity), the only changes being the ruler (for obtaining different thickness of the liquid film) and the consequent preparation parameters. The average value of the water permeability,  $\langle A \rangle$ , and salt rejection,  $\langle R \rangle$ , for five membranes obtained for each treatment, along with the error bars, will be presented in the following figures, each of one corresponding to the variation of one parameter at a time, while the others remain fixed, thus retaining only the influence of the parameter under study.

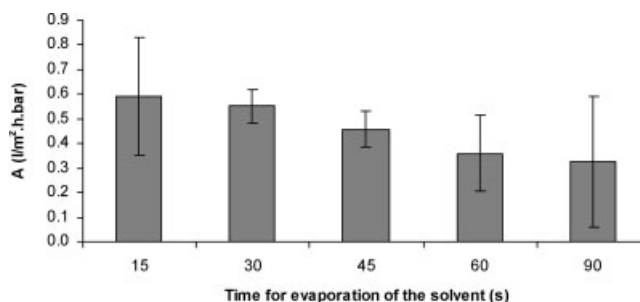
Figures 1 and 2 present the results of water permeability and salt rejection for the membranes produced with different thickness of the initial liquid film.

Figures 3 and 4 present similar results but corresponding to the final thickness of the membrane.

Previous studies<sup>5-7</sup> showed that water permeability of membranes is indirectly proportional to their thickness. On the contrary, the salt rejection increases slightly



**Figure 4** Average salt rejection data for the membranes with different final thickness.



**Figure 5** Average water permeability values for the membranes produced with different time allowed for evaporation of the solvent.

with membrane thickness,<sup>8</sup> depending mostly on the coherence of the dense film.

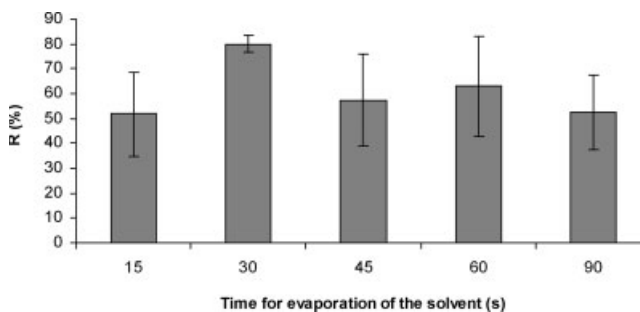
Considering the results, and as expected,  $\langle A \rangle$  values decrease with the thickness of the initial liquid film, but only after 75  $\mu\text{m}$ . After 200  $\mu\text{m}$  the differences are rather small. The reason for this lies, probably, in the fact that increasing thickness results in an increase of the overall pressure drop across the membrane microporosity (selective layer).

Concerning the  $\langle R \rangle$  values it was proved that it increases with the thickness of the initial liquid film, for the lower thicknesses, attaining a similar value for the higher thicknesses evaluated. The selective layer is formed in a smooth way when the thickness is higher and this is probably the cause for the observed behavior.

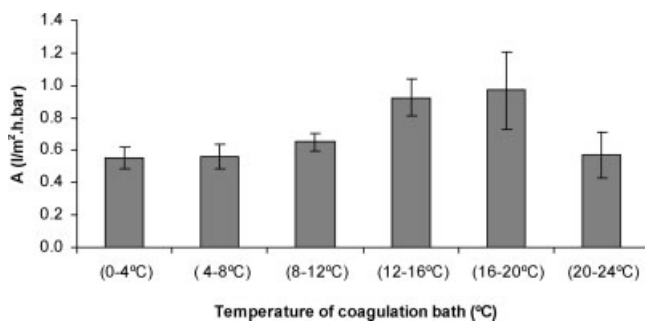
Even though the  $\langle R \rangle$  values are very similar for the membranes made with thickness higher than 100  $\mu\text{m}$ , the average water permeability decreases with the increase of the film thickness for thicknesses higher than 75  $\mu\text{m}$ , which means that the optimum value of the thickness is therefore 100  $\mu\text{m}$ , which corresponds to a final thickness of the membrane of 25.8  $\mu\text{m}$ .

In Figures 5 and 6, the effect of the time allowed for evaporation of the solvent on the performance of the membranes is studied.

During the evaporation step, usually done at room temperature, the solvent is removed from the space



**Figure 6** Average salt rejection values for the membranes produced with different time allowed for evaporation of the solvent.



**Figure 7** Average water permeability values for the membranes placed on water coagulation bath at different temperatures.

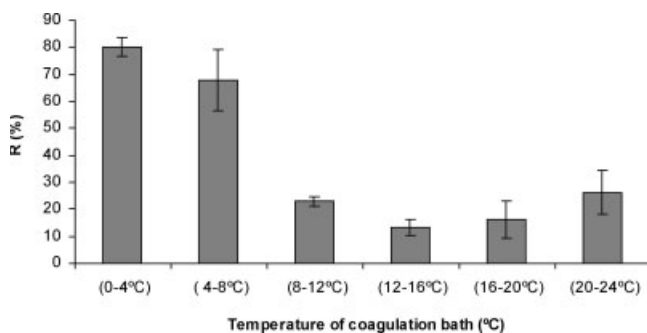
devoid of the polymer aggregate and the sizes of such spaces are expected to reduce. As a result, a sharp decrease in both the size and the number of aggregate pores is expected. Besides, the solvent may evaporate from within the polymer aggregate itself. Thus, the density of polymer segments in a polymer aggregate may also become high, leading to the decrease in the size of the space surrounded by the polymer segments. This results in a reduction in the size of the network pore. All these phenomena take place at the top layer of the cast polymer solution, since the solvent evaporates from its surface. Thus, the increase of thickness of the surface layer, which is decisive to the membranes separation properties, becomes slower as the evaporation process proceeds.<sup>2</sup>

The results indicate that, as expected, the  $\langle A \rangle$  values decrease with the time of evaporation of the solvent because of the increase of the thickness of the membrane superficial skin (selective layer).

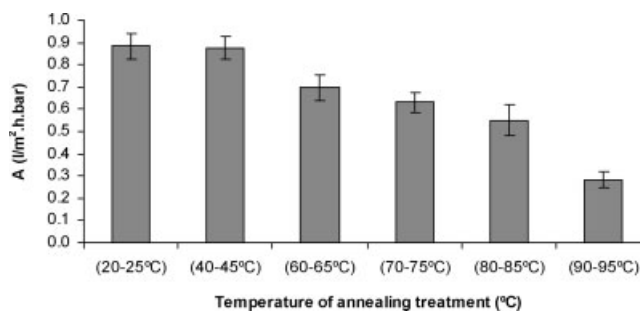
For this same reason  $\langle R \rangle$  values start to increase with time, reaching a maximum at about 30 s.

Taking into account the results for water permeability and salt rejection, 30 s for evaporation of the solvent seems to be the correct choice.

Figures 7 and 8 show the effect of the temperature of coagulation bath in the performance of the membranes. These results were obtained with the membranes placed for 15 min on water coagulation bath.



**Figure 8** Average salt rejection values for the membranes placed on water coagulation bath at different temperatures.



**Figure 9** Average water permeability values for the membranes annealed at different temperatures.

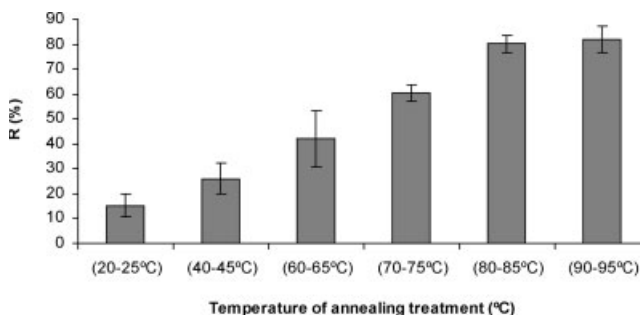
The results indicate that membranes formed on water coagulation bath at a temperature between 12 and 20°C present higher  $\langle A \rangle$  values, while membranes submitted to lower coagulation bath temperatures have relatively low average water permeability. This most probably happens because the effect of water as nonsolvent decreases with the temperature and consequently the film precipitation is retarded, increasing the absorption of water as well as the permeability of the membrane.

Concerning  $\langle R \rangle$  values, the membranes with the best performance are formed on the water coagulation bath at  $T = 0-4^\circ\text{C}$ . As expected, all the membranes produced with a temperature of the coagulation bath higher than  $8^\circ\text{C}$  present a very low salt rejection.

This happens because, as explained above, the non-solvent effect decreases with the temperature of the coagulation bath and consequently the precipitation of the skin layer as well as the rest of the film membrane is retarded, increasing the permeability and decreasing the selectivity of the membrane.

The best temperature gap for the water coagulation bath is therefore  $T = 0-4^\circ\text{C}$  because the membranes produced in this conditions present relatively good  $\langle A \rangle$  and  $\langle R \rangle$  values ( $\langle A \rangle = 0.55 \text{ L/m}^2 \text{ h bar}$  and  $\langle R \rangle = 80\%$ ).

Figures 9 and 10 show the influence of the annealing posttreatment temperature on the performance of the membranes.



**Figure 10** Average salt rejection values for the membranes annealed at different temperatures.

TABLE I  
Statistical Treatment of Water Permeability and Salt Rejection Values

Modified parameters		Water permeability (A) ( $L/m^2 h bar$ )		Salt rejection (R) (%)	
		$\langle A \rangle$	$\sigma^* (A)$	$\langle R \rangle$	$\sigma^* (R)$
Thickness of the liquid film ( $\mu m$ )	50	1.29	0.11	1	0
	75	2.00	0.28	2	3
	100	0.55	0.07	80	3
	150	0.45	0.05	64	19
	200	0.38	0.06	79	7
	250	0.32	0.09	74	10
Time allowed for evaporation of the solvent (s)	15	0.59	0.24	52	17
	30	0.55	0.07	80	3
	45	0.46	0.07	57	18
	60	0.36	0.15	63	20
	90	0.33	0.27	52	15
Temperature of coagulation bath ( $^{\circ}C$ )	(0–4)	0.55	0.07	80	3
	(4–8)	0.56	0.08	68	11
	(8–12)	0.65	0.05	23	2
	(12–16)	0.93	0.11	13	3
	(16–20)	0.97	0.24	16	7
	(20–24)	0.57	0.14	26	8
Annealing temperature ( $^{\circ}C$ )	(20–25)	0.88	0.06	15	5
	(40–45)	0.88	0.05	26	6
	(60–65)	0.70	0.06	42	11
	(70–75)	0.63	0.04	60	3
	(80–85)	0.55	0.07	80	3
	(90–95)	0.28	0.04	82	5

\* Standard deviations.

Considering the annealing posttreatment, it was found<sup>3</sup> that the annealing of the cellulose acetate membranes in hot water led to irreversible changes in properties concerning water permeability and salt rejection values. The annealing posttreatment provide thermal energy to the polymeric matrix of the membranes, which gives rise to translational movements of the macromolecules of cellulose acetate, resulting in the approaching of the polar groups, allowing for the formation of hydrogen bonds. These links reduces the content and the mobility of water inside the polymeric matrix and, as a consequence, decrease the water and salt permeability of the membrane.<sup>3</sup> The degree of shrinkage of the membrane progressively increases with increasing temperature of annealing, simultaneously, the water permeability decreases and the salt rejection increases.<sup>1</sup>

Experiments made with the membranes annealed in water at different temperatures during 15 min, show that the water permeability values decrease with the temperature, while salt rejection values strongly increase, as expected.

Having in mind the results of both water permeability and salt rejection, we conclude that the optimum value of the annealing posttreatment temperature is between 80 and 85 $^{\circ}C$ .

Table I presents the statistical treatment of all the results presented above. The average and the standard deviation were determined by the well-

known equations that can be found in any book on Statistics.

## CONCLUSIONS

After the study of the preparation parameters of the membranes produced starting from an optimized solution,<sup>4</sup> we can conclude that the optimum values of the studied preparation parameters are close to the following:

- thickness of the liquid film of 100  $\mu m$  (which corresponds to a final thickness of the membrane of 25.8  $\mu m$ );
- time allowed for evaporation of the solvent of 30 s (for the used external conditions);
- temperature of coagulation bath of 0–4 $^{\circ}C$ ; and
- annealing temperature of 80–85 $^{\circ}C$ .

It should be observed that variables of the optimization are not independent and that the saturation of the solution that induces the formation of the selective layer depends on a number of parameters. Therefore, the present values should be considered a coherent assembly of parameters.

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