Effect of Ethanol–Water Mixture as Gelation Medium During Formation of Cellulose Acetate Reverse Osmosis Membranes

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Synopsis

By using ethanol–water mixtures in a wide range of alcohol concentrations and temperatures, cellulose acetate membranes with a wide range of surface porosities can be obtained. Two different casting solution compositions were used, involving cellulose acetate, acetone, and aqueous magnesium perchlorate (composition I) or formamide (composition II). All reverse osmosis experiments were carried out at 250 psig using a 3500 ppm NaCl–H_2O feed solution at laboratory temperature. The effective area of film surface was 12 cm^2 in all cases. With composition I, with pure water gelation medium at 0°C, the resulting membrane gave a solute separation of 5% and product rate of 220 g/hr, whereas with 95% alcohol as gelation medium, the resulting membrane gave a solute separation of ~1% and product rate of 1240 g/hr under otherwise identical experimental conditions. With composition II membranes, the maximum product rate of 360 g/hr with the corresponding minimum solute separation of ~1% was obtained with 71.2% alcohol–water gelation medium at 0°C. Increase in the temperature of the gelation medium in the range 12°–25°C tends to increase the average size of pores on the membrane surface. These results offer a basis for the development of cellulose acetate ultrafiltration membranes.

INTRODUCTION

In the process of making asymmetric porous cellulose acetate reverse osmosis membranes, the effect of gelation medium on the porous structure of resulting membranes has been studied by several workers.[1–8] These studies show that membrane porosity is largely governed by the rates of exchange of solvent and nonsolvent during precipitation of the polymer in the gelation medium. The extensive discussions of Frommer et al.[3,4] and Strathmann et al.[5–7] are concerned explicitly with the porous structure of the membrane *underneath* the surface layer ("skin").

This paper is concerned with the porous structure of the surface layer which is primarily responsible for solute separation in reverse osmosis. On the basis that the rates of solvent–nonsolvent exchange in the nascent membrane during gelation govern the overall porous structure of the resulting membrane, it is reasonable to expect that the gelation environment and, more specifically, the composition and temperature of the gelation medium must have significant effects on the porous structure of the membrane surface. This is already evident from the experimental reverse osmosis data of Zisner and Loeb,[1] Frommer et al.,[2] and especially Carter et al.,[8] who showed that by using up to 8:7 molar ethanol–water mixture at 20°C as the gelation medium, cellulose acetate membranes capable of giving up to 85% solute separation for NaCl could be obtained without prior thermal shrinkage of the membranes. Extending the work of Carter et al.,[8] this work illustrates that by using ethanol–water mixtures in a wider range of

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alcohol concentrations and temperatures, cellulose acetate membranes with a wide range of surface porosities can be obtained.

EXPERIMENTAL

Two different casting solution compositions were used in this study for making the cellulose acetate membranes. These compositions and details of the film casting conditions used are given in Table I. Composition I is the same as that used for Batch-316 membranes about which detailed studies have been reported.[9] Composition II is the same as that used by Carter et al.[8] All membranes were hand cast as flat films on glass plates in a constant-temperature, constant-humidity room. Reverse osmosis experiments were carried out with both unshrunk and preshrunk (by immersion in hot water) membranes. All films were subjected to a pure water pressure of 300 psig for at least 1 hr prior to reverse osmosis experiments. All reverse osmosis experiments were carried out at 250 psig and laboratory temperature (23°–26°C) using 3500 ppm sodium chloride–water as the feed solution at a constant feed flow rate of 400 cm³/min. The apparatus used for reverse osmosis experiments is described in the literature.[10] The effective area of the film surface was 12 cm² in all experiments. All reverse osmosis experiments were of the short-run type, each lasting for about 2 hr. A conductivity bridge was used for determining solute concentrations in the feed and product solutions. The product rate in grams per hour for the specified area of film surface (12 cm² in this work) and fraction solute separation f were determined in each experiment using the relation

$$f = \frac{\text{solute ppm in feed} - \text{solute ppm in product}}{\text{solute ppm in feed}}$$

The terms "product" and "product rate" refer to membrane permeated solutions. All product rates reported are those corrected to 25°C using the viscosity and density data for pure water.

TABLE I

	Solution I	Solution II
Casting solution composition, wt-%		
Cellulose acetate (E-398-3)	17.0	25.0
Acetone	69.2	45.0
Magnesium perchlorate	1.45	—
Water	12.35	—
Formamide	—	30.0
Temperature of casting solution, °C	10	25
Temperature of casting atmosphere, °C	30	25
Humidity of casting atmosphere, %	50	50
Solvent evaporation period, sec	60	30
Gelation medium	0%–95% Ethanol–water mixture as specified	
Temperature of gelation medium, °C	−10 to 25, as specified	
Gelation period	15 min in ethanol-water and 1 hr in water	

RESULTS AND DISCUSSION

Effect of Alcohol Concentration in Gelation Medium on Membrane Performance

Figure 1 shows the effect of alcohol concentration in the gelation medium on the reverse osmosis performance of membranes resulting from casting solution compositions I and II. These membranes were not subjected to any shrinkage treatment prior to reverse osmosis experiments.

With reference to casting solution composition I, the data on membrane performance given in Figure 1 are for the gelation temperature of 0°C. These data fall in four distinct regions. In region 1, product rate decreases from 215 g/hr to 25 g/hr, and the corresponding solute separation increases from 5% to 58% with increase in alcohol concentration in the gelation medium up to ~30%. In region 2, product rate increases from 25 to 655 g/hr, and the corresponding solute separation decreases from 58% to 10% with increase in alcohol concentration from ~30% to ~47.5%. In region 3, product rate decreases from 655 to 500 g/hr, and the corresponding solute separation decreases from 10% to 3% with increase in alcohol concentration from 47.5% to 56.5%. And in region 4, the product rate increases from 500 to 1000 g/hr, and the corresponding solute separation decreases from 3% to practically zero with increase in alcohol concentration from 56.5% to 95%.
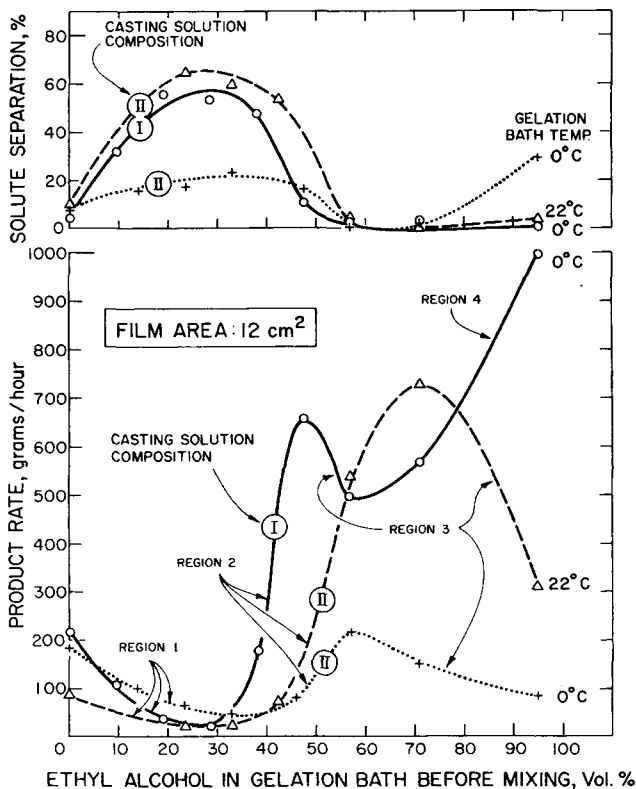

Fig. 1. Effect of ethyl alcohol concentration in gelation bath on reverse osmosis performance of unshrunk membranes. Feed solution, 3500 ppm NaCl–H₂O; feed flow rate, 400 cm³/min; operating pressure, 250 psig.

With reference to casting solution composition II, two sets of membrane performance data are given in Figure 1; one set of data corresponds to gelation temperature of 0°C, and the other corresponds to gelation temperature of 22°C. The data on membrane performance corresponding to both the above gelation temperatures fall into three distinct regions. At the gelation temperature of 0°C, in region 1, product rate decreases from 185 to 50 g/hr, and the corresponding solute separation increases from 8% to 23% with increase in alcohol concentration in the gelation medium up to ~33%. In region 2, product rate increases from 50 to 220 g/hr, and the corresponding solute separation decreases from 23% to 1% with increase in alcohol concentration from 33% to 57%. And in region 3, product rate decreases from 220 to 90 g/hr, and the corresponding solute separation increases from 1% to 25% with increase in alcohol concentration from 57% to 95%. At the gelation temperature of 22°C, in region 1, product rate decreases from 90 to 25 g/hr, and the corresponding solute separation increases from 10% to 65% with increase in alcohol concentration up to ~ 30%. In region 2, product rate increases from 25 to 730 g/hr, and the corresponding solute separation decreases from 65% to 1% with increase in alcohol concentration from ~30% to 71%. And in region 3, product rate decreases from 730 to 310 g/hr, and the corresponding solute separation increases from 1% to 4% with increase in alcohol concentration from 71% to 95%. Thus, the data on membrane performance in the above three regions are similar in effect and quite different in magnitude at the two gelation temperatures.

Comparing data on membrane performance at the gelation temperature of 0°C, those for composition I and II membranes in regions 1, 2, and 3 are again similar in effect but quite different in magnitude, and data similar to those in region 4 for composition I membranes are absent for composition II membranes.

Carter et al.[8] used the casting solution composition II and alcohol concentrations up to 8.7 molar (which is less than 50% alcohol by volume) in the gelation medium at 20°C. Under the conditions of their experiments, product rate decreased and the corresponding solute separation increased with increase in alcohol concentration. These results are qualitatively similar to those obtained in region 1 for both casting solution composition I and composition II membranes given in Figure 1. In addition, the present work shows that by using higher alcohol concentrations in the gelation medium, membrane performance data similar to those given for regions 2, 3, and 4 in Figure 1 can be obtained for different casting solution compositions.

The decrease in product rate with corresponding increase in solute separation obtained with both composition I and composition II membranes with the initial increase in alcohol concentration in the gelation medium (region 1) is also qualitatively similar to the changes observed by both Zisner and Loeb[1] and Frommer et al.[3] Since water is the predominant nonsolvent precipitating agent in region 1, following Fromer et al.[3] the above changes may be attributed to the decrease in water activity with increase in alcohol concentration in the gelation medium, and the consequent decrease in the rate of water penetration in the membrane resulting in finer precipitation of polymer material constituting the membrane surface. Thus, in region 1, an increase in alcohol concentration in the gelation medium results in a decrease in average pore size on the membrane surface.

As the alcohol concentration in the gelation medium increases further into regions 2, 3, and 4 in Figure 1, the polymer precipitating power of alcohol and its interactions with the polymer (cellulose acetate), solvent (acetone), and nonsolvent swelling agent (aqueous magnesium perchlorate or formamide) in the membrane matrix become progressively more important. These factors could affect both the precise instant of phase inversion and also the size, number, and distribution of nonsolvent droplets (incipient voids) in the interdispersed phase during gelation, which ultimately determine the surface pore structure of the resulting membrane. The general increase in product rate with increase in alcohol concentration in the gelation medium in regions 2, 3, and 4 in Figure 1 and the existence of maxima and minima in product rate and solute separation data in the above regions indicate that the above factors include those having opposing tendencies in the direction of change of size, number, and distribution of pores on the membrane surface and the effective thickness of the membrane.

The foregoing conclusion is consistent with that of earlier studies. According to Kesting,[2] as the alcohol concentration in the gelation medium increases, its effect on the porous structure of the membrane changes continuously from that of a swelling agent to that of a nonsolvent. As a swelling agent, alcohol tends to promote an increasing number of smaller-size droplets in the interdispersed phase resulting in finer precipitation of the polymer with smaller-size pores on the membrane surface, whereas alcohol as a nonsolvent tends to produce the opposite result in the final membrane. In a gelation medium containing a mixture of alcohol and water, both the above effects can be expected; the experimental data are consistent with such expectation. Further, the results show that the nonsolvent effect is generally predominant with increase in alcohol concentration in the gelation medium in regions 2, 3, and 4 in Figure 1.

The rate of precipitation of the polymer during gelation (which determines the overall porosity of the membrane including its surface structure) is controlled not only by the diffusive exchange of the solvent and nonsolvent but also by the similar exchange of the swelling agent and the gelation medium. All these rates are functions of the chemical nature and physical properties of the components involved. So et al.[6] pointed out the importance of solubility parameter of the components on rates of such exchange. The solubility parameters for cellulose acetate, acetone, ethyl alcohol, formamide, and water are 10.9, 9.6, 12.8, 17.9, and 23.5, respectively. On the basis of these data, compared to water ethyl alcohol has greater affinity for acetone which probably explains the observation of Carter et al.[8] that alcohol penetrates into the film matrix faster than water. While the available experimental data do not warrant any unequivocal statement on the effect of solubility parameter on competing rates of exchange in a multicomponent system, it is reasonable to expect that the exchange rates of individual components in such a system are controlled by the total environment in the system. Consequently, increase in alcohol concentration in the gelation medium may be expected to have varying effects on the rates of exchange of the individual components and the resulting rate of precipitation of the polymer during gelation. The experimental data presented in Figure 1 show that control of gelation environment is a potential means of creating a wide range of porosities on the membrane surface in the as-cast condition.

Alcohol Concentration in the Gelation Medium and Shrinkage
Temperature Profile of Resulting Membranes

Figure 2 shows the correlation of solute separation versus product rate and the corresponding shrinkage temperature required for such performance for the membranes made from casting solution compositions I and II, as a function of alcohol concentration in the gelation medium at 0°C. The shrinkage temperature profiles offer a means of interpreting data on the basis of size, number, and distribution of pores on the membrane surface. As pointed out already,[9] there is no precise way of determining either the size of individual pores on the membrane surface or the thickness of the surface layer of the porous asymmetric membrane. Hence, for practical purposes, a smaller difference in shrinkage temperatures for a given range of solute separation may be considered to represent a more uniform distribution of available pores; and, for a given level of solute separation, a higher shrinkage temperature and a higher product rate may be considered to represent a relatively bigger average size of available pores and a larger number of such pores, respectively, on the membrane surface in the as-cast condition.
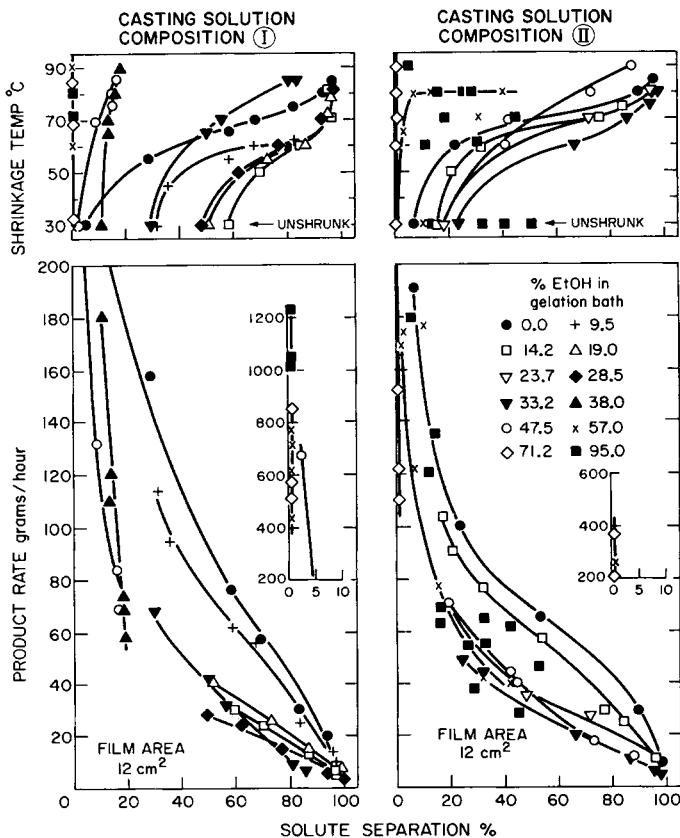

Fig. 2. Effect of ethyl alcohol concentration in gelation bath on shrinkage temperature profile and reverse osmosis performance of preshrunk membranes. Feed solution, 3500 NaCl–H_2O; feed flow rate, 400 cm^3/min; operating pressure, 250 psig.

With reference to both the casting solution compositions tested, Figure 2 shows a continuous change in the location of the shrinkage temperature profile and product rate data correlations as the concentration of alcohol in the gelation medium increases. The correlating lines given for pure-water (i.e., 0% alcohol) gelation medium may be taken as references for purposes of comparison of other data in Figure 2.

With reference to casting solution composition I, Figure 2 shows that the productivity of the membrane (i.e., product rate for any given level of solute (NaCl) separation) is highest with the pure-water gelation medium for which case, however, there is an upper limit to the size of pores on the membrane surface obtainable under the casting conditions used. With sufficiently high (>~35%) concentrations of alcohol in the gelation medium, corresponding to part of region 2 and the regions 3 and 4 in Figure 1, the above upper limit for the size of pores on the membrane surface can be increased as illustrated by the following data. With pure-water gelation medium, the resulting membrane (without any preshrinking) gave a solute separation of 5% and product rate of 220 g/hr, whereas with 95% alcohol as gelation medium the resulting membrane gave a solute separation of ~1% and a product rate of 1240 g/hr under otherwise identical reverse osmosis experimental conditions.

The relative locations of the shrinkage temperature profiles together with those of the product rate correlations given in Figure 2 reflect the changes in the surface pore structure which took place during membrane formation. It is useful to compare the shrinkage temperature and product rate data at any specific level of solute separation. For example, with reference to casting solution composition I, at 60% level of solute separation, the shrinkage temperature and product rate were 68°C and 74 g/hr, respectively, for pure-water gelation medium. As the alcohol concentration in the gelation medium increased from 0% to ~30% (region 1 in Fig. 1), the shrinkage temperature first decreased (up to ~15% alcohol) and then increased but still less than 68°C. The corresponding product rate also decreased to 30 g/hr at about 15% alcohol concentration and then oscillated in the range of 25–35 g/hr with further increase in alcohol concentration. These results show that, compared with membranes obtained with pure-water gelation, the effect of alcohol in the gelation medium in region 1 is to decrease both the average size and number of pores on the membrane surface, and the changes in such size and number are mutually independent. Figure 2 also shows that at shrinkage temperatures above 60°C, the shrinkage temperature profiles and hence pore size distributions are unaffected by alcohol concentration in the gelation medium in region 1.

The shrinkage temperature profile crosses that for pure-water gelation for the alcohol concentration of ~35% in the gelation medium (region 2 in Fig. 1), at which point the product rate obtained for the latter case is less than half of that obtained for the case of pure-water gelation medium. With further increase in alcohol in the gelation medium (regions 3 and 4 in Fig. 1), the shrinkage temperature profiles move more and more steeply toward lower levels of solute separation with corresponding steep increase in product rates. These results confirm that in regions 2, 3, and 4 in Figure 1, increase of alcohol concentration in the gelation medium results in a decreasing number of larger-size pores on the membrane surface.

With reference to casting solution composition II, Figure 2 shows results

generally similar to those discussed above for composition I, with two important exceptions. Referring to the performance of membranes obtained from composition II, the maximum product rate with minimum solute separation was obtained with 71.2% alcohol–water gelation medium, for which case the product rate was 360 g/hr and solute separation was 1%; the corresponding performance data for membranes obtained with pure-water gelation medium were 191 g/hr and 7%, respectively. Thus, compared with the product rate obtained for the as-cast membrane with pure-water gelation medium, the maximum increase in product rate obtained for the as-cast membrane with alcohol–water gelation medium was relatively less for composition II than for composition I. Further, the membrane performance data for 95% alcohol–water gelation medium were significantly different for composition II membranes, which were very sensitive to changes in shrinkage temperature and possibly also to small changes in alcohol concentration in the gelation medium; the data obtained were too much scattered with no definite trends. Results similar to those shown in Figure 2 for 95% alcohol–water gelation medium have been reported before[11] and explained on the basis of changes arising from the growth of crystallite size from paracrystalline nodules from microcrystallites in the structure of the membrane surface during membrane formation and subsequent shrinkage in hot water. The above growth disrupts the uniformity of crystallite spacing and also affects the size of the interlamillar channels.[2] The same explanation may be valid in the present case also.
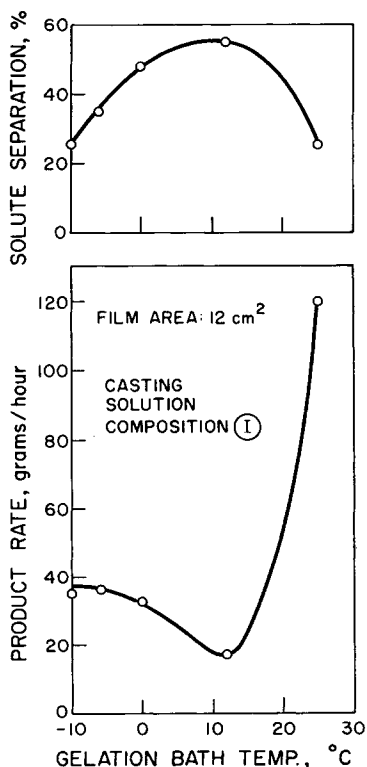

Fig. 3. Effect of temperature of gelation bath on reverse osmosis performance of unshrunk membranes. EtOH concentration in gelation bath, 28.5%; feed solution, 3500 ppm NaCl–H_2O; feed flow rate, 400 cm^3/min; operating pressure, 250 psig.
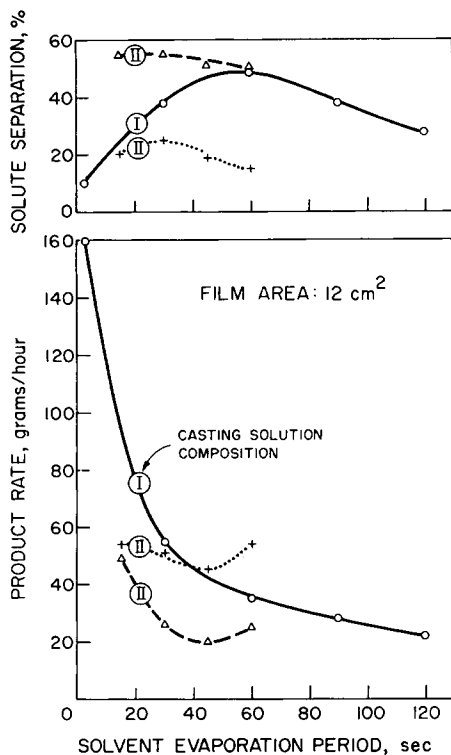
Fig. 4. Effect of solvent evaporation period on reverse osmosis performance of unshrunk membranes. EtOH concentration in gelatin bath: (I) 28.5%; (II) 33.2%: Temperature of gelation bath: (O), (Δ) 0°C; (+) 22°C. Feed solution, 3500 ppm NaCl–H_2O; feed flow rate, 400 cm^3/min; operating pressure, 250 psig.

Effect of Temperature of Gelation Bath

Figure 3 illustrates the effect of increasing the temperature of 28.5% alcohol–water gelation medium in the range of −10°–25°C on the performance of unshrunk membranes made from casting solution composition I. The results show that at 12°C, solute separation passes through a maximum (55%) and product rate passes through a corresponding minimum (17 g/hr), and the product rate increases steeply in the gelation temperature range of 12°–25°C. At the gelation temperature of −10°C, the solute separation and product rates were 25% and 35 g/hr, respectively; at the gelation temperature of 25°C, solute separation was again 25%, but the product rate increased to 120 g/hr. These results show that in the temperature range of −10°–12°C, increase in gelation temperature tends to promote the formation of smaller-size pores on the membrane surface, whereas in the temperature range of 12°–25°C, increase in temperature tends to increase both the size and number of pores on the membrane surface. These results are understandable on the basis that increasing the temperature of gelation tends to increase both the swelling and the rates of diffusive exchange of components in the nascent membrane system affecting the rate of precipitation of the polymer.

Effect of Solvent Evaporation Period

Kesting[2] has pointed out that solvent evaporation time prior to immersion in the gelation medium is of critical importance with respect to surface pore structure and hence the performance of resulting membranes. Figure 4 illustrates the effect of solvent evaporation period prior to gelation on the performance of unshrunk membranes made from casting solution compositions I and II using 28% alcohol–water and 33% alcohol–water gelation mediums, respectively. With respect to composition I membranes, the results show that solute separation passes through a maximum and product rate decreases with increase in solvent evaporation period. With respect to composition II membranes, solute separations pass through a maximum, and product rates independently pass through a minimum with increase in solvent evaporation period. These data again indicate that the porous structure of the membrane surface is governed by simultaneous processes tending to change the size and number of surface pores and that both the solvent evaporation period and the following gelation process together determine the final porous structure of the membrane surface.

CONCLUSIONS

The porous structure of the membrane surface depends on the casting solution composition, solvent evaporation period, and the total gelation environment. By changing the latter alone, a wide range of surface porosities can be obtained for the resulting membranes. The data presented in this paper are particularly significant in the development of big-pore membranes useful for many ultrafiltration applications. This paper is issued as N.R.C. No. 16726.

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