

Effect of Different Alcohol-Water Mixtures as Gelation Mediums during Formation of Cellulose Acetate Reverse Osmosis Membranes*

INTRODUCTION

Using ethanol-water mixtures (in a wide range of alcohol concentrations) as gelation mediums, cellulose acetate reverse osmosis membranes with a wide range of surface porosities have been obtained.^{1,2} In the above studies it was observed that the experimental data on membrane performance in reverse osmosis fell in four or five distinct regions with progressive increase in ethanol concentration in the gelation medium. Starting with pure water as the gelation medium, in the initial region (region 1), the rate of membrane permeated product decreased and the corresponding solute separation (for a reference inorganic solute such as NaCl or MgSO₄) increased with increase in ethanol concentration in the gelation medium; in the next region (region 2), the product rate increased and solute separation decreased with further increase in ethanol concentration in the gelation medium; in the subsequent regions 3 to 5, with still further increase in ethanol concentration in the gelation medium, the product rates obtained were relatively high, and they passed through successive maxima and minima while the corresponding solute separations were relatively low or practically zero. The magnitude of the above changes also depended on the composition of the film casting solution, solvent evaporation period prior to gelation, and the temperature of the gelation medium. This paper extends the above work, and reports some experimental data on the effect of nature of alcohol in the gelation medium on performance of resulting membranes in reverse osmosis.

EXPERIMENTAL

Laboratory made cellulose acetate membranes were used in this work.³ The composition of the film casting solution, and the details of the film casting conditions used were as follows: casting solution composition (wt. %): cellulose acetate (E-398-3), 17.0; acetone, 69.2; magnesium perchlorate, 1.45; water, 12.35; temperature of casting solution: 10°C; temperature of casting atmosphere: 30°C; humidity of casting atmosphere: (50–55)%; solvent evaporation period: <5 sec in most cases; gelation medium: alcohol-water mixture as specified; temperature of gelation medium: ~1°C; and gelation period: 15 min. Following gelation, the membrane was transferred to an ice-water bath where it was kept immersed overnight allowing the water soluble components in the membrane to be leached out. The alcohol component in the gelation medium was either methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, or ethylene glycol. The apparatus and the general experimental procedure used for reverse osmosis experiments were the same as before.^{1,4} All membranes were initially subjected to a pure water pressure of 300 psig for a few hours prior to subsequent reverse osmosis experiments. The latter experiments were carried out at lab temperature (23–25°C) and at 250 psig using 300 ppm NaCl–H₂O feed solutions at a feed flow rate of 400 cm³/min. Solute concentrations in the feed and membrane permeated product solutions were determined by conductivity measurements. All reverse osmosis experiments were of the short-run type, and in each experiment the product rate (in g/hr) for the effective area of film surface used (12.5 cm² in this work), and the fraction solute separation f defined as

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

were obtained. In view of the very dilute feed solutions used, the osmotic pressure effects in reverse osmosis could be considered negligible. The data on product rates reported in the paper are those corrected to 25°C using the data on viscosity and density for pure water.

* Issued as NRC No. 17333.

RESULTS AND DISCUSSION

Effect of Alcohol Concentration in the Gelation Medium

Figure 1 shows the effect of concentration of different alcohols in the gelation medium on data on membrane performance in reverse osmosis. The results show that the general trends in the correlations of mole fraction of alcohol in the gelation medium versus product rate and solute separation (for the reference NaCl solute) are similar for all the alcohols studied, in that the experimental data fell broadly in several distinct regions.^{1,2} There were however some significant differences in the variations of the above experimental data depending on the nature of the alcohol in the gelation medium.

With respect to all the alcohols studied, in region 1, the product rates decreased and the corresponding solute separations increased with increase in alcohol concentration in the gelation medium. This result is generally attributed to the decrease in water activity with increase in alcohol concentration in the gelation medium.⁵

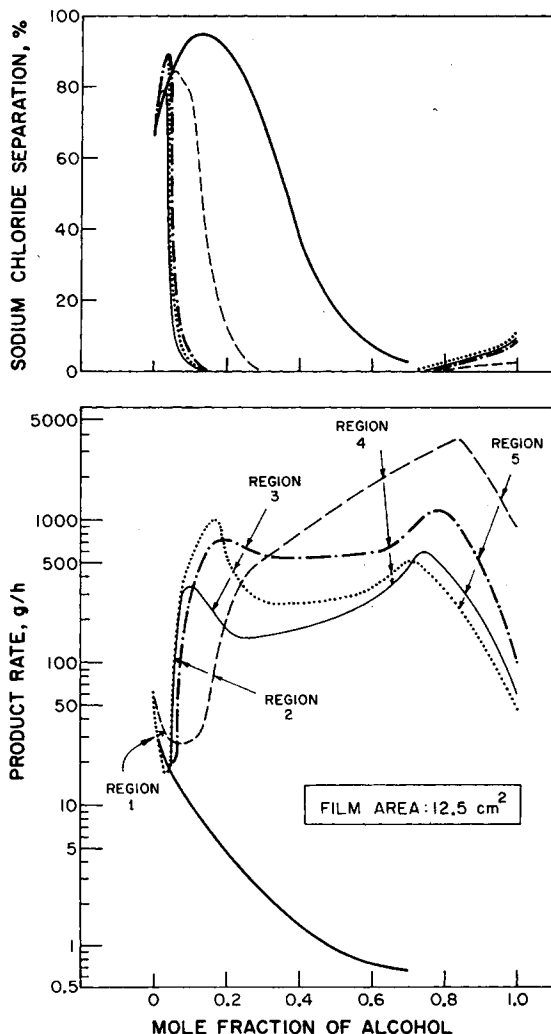


Fig. 1. Effect of alcohol concentration in gelation medium on membrane performance. Operating pressure, 250 psig; NaCl concentration in feed solution, 300 ppm; feed flow rate, 400 cm³/min; solvent evaporation period during film formation, <5 sec. ---, Methyl alcohol; - · - · -, ethyl alcohol; —, propyl alcohol; - - - -, isopropyl alcohol; ———, ethylene glycol.

Except with respect to ethylene glycol, for the other four alcohols studied, in each case, the product rate passed through an initial minimum with progressive increase in alcohol concentration in the gelation medium starting with pure water. The mole fractions of alcohol in the gelation medium corresponding to the above initial minimum in product rate were 0.059, 0.042, 0.032, and 0.032 for MeOH, EtOH, PrOH, and *iso*-PrOH, respectively. Reference to earlier work^{1,2} shows that the corresponding mole fractions were different for EtOH when the other factors involved in the gelation environment, such as composition of the film casting solution and temperature of the gelation medium, were different. One may hence conclude that the above initial minimum in product rate data is a characteristic feature common to all of the above alcohol-water gelation mediums, and the concentration of alcohol in the gelation medium corresponding to the above initial minimum in product rate is a definite one, different for different alcohols and the other factors involved in the gelation environment.

Considering that in region 1 (Fig. 1), it is the water-acetone exchange that primarily governs the porous structure on the surface layer of the resulting membrane, the kinetics of such exchange may be expected to be a function of the rate of water penetration into the incipient membrane phase during gelation. This rate in turn may be expected to be governed both by the activity of water in the gelation medium *and* the diffusivity of water in the membrane phase. That the diffusivity of a chemical species in the membrane phase is proportional to that in the aqueous phase, has already been shown to be a reasonable assumption in the analysis of experimental membrane performance data.⁶⁻⁸ Using the available physicochemical data⁹⁻¹² for calculating the numerical values for the activity (a_w) and diffusivity (D_w in cm^2/sec) of water in the alcohol-water gelation medium at the composition corresponding to the initial minimum in product rate, and considering the above data in conjunction with those on membrane performance given in Figure 1 for two extreme cases, one notes the following:

Gelation medium	Mole fraction of alcohol	a_w	$a_w D_w \times 10^5$ (cm^2/sec)	Product rate (g/hr)	Solute separation, %
MeOH-H ₂ O	0.059	0.964	0.784	26.8	85
<i>iso</i> -PrOH-H ₂ O	0.032	0.956	0.440	16.8	90

The above results show that in region 1 of Figure 1, variations in the values of a_w are less significant than those in the values of $a_w D_w$ in terms of their effect on membrane performance; further, as the value of $a_w D_w$ decreases, there is a corresponding relative decrease in product rate and relative increase in solute separation. These results are understandable on the basis that the quantity $a_w D_w$ is a measure of the rate of water penetration into the membrane phase during gelation in region 1 (Fig. 1), and a lower value of this quantity results in slower, and hence finer, precipitation of the polymer aggregates constituting the "skin" or the surface layer of the membrane, and ultimately in smaller average effective size of pores on the membrane surface.

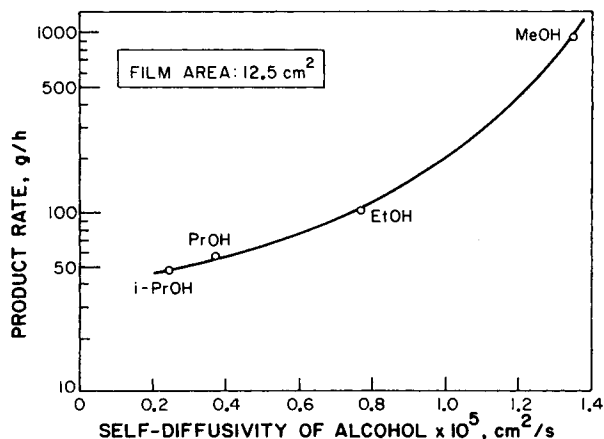


Fig. 2. Effect of self-diffusivity of alcohol in pure alcohol gelation medium on performance of resulting membranes. Operating pressure, 250 psig; NaCl concentration in feed solution, 300 ppm; feed flow rate, $400 \text{ cm}^3/\text{min}$; solvent evaporation period during film formation, $<5 \text{ sec}$.

Figure 2 gives a correlation of self-diffusivity of alcohol versus product rate obtained (Fig. 1) with pure alcohol as the gelation medium. The results show that the product rate increased with increase in self-diffusivity of alcohol, and the above two quantities are uniquely related. These results again illustrate the importance of the diffusivity of the penetrating species in the gelation medium, which controls the rate of precipitation of polymer aggregates constituting the surface layer of the resulting membrane.

The actual gelation environment involves a multicomponent system. The effective activity and diffusivity of each component in the total gelation environment contribute to the ultimate porous structure of the resulting membrane, and hence to its permeation characteristics. In addition, as the alcohol concentration in the gelation medium increases further beyond region 1 into regions 2 to 5 of 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) in the membrane matrix become progressively more important. As discussed in detail earlier,^{1,2} these factors also affect the size, number and distribution of nonsolvent swelling agent 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 to 5 of Figure 1, and the existence of maxima and/or minima in product rates in these regions indicate that the above factors include those having opposing tendencies in the direction of change of size, number, and distribution of pores in the membrane surface and the effective thickness of the membrane.

With respect to ethylene glycol (EG)-water gelation medium, the results given in Figure 1 show that product rates continued to drop with progressive increase in EG concentration in the gelation medium; the corresponding solute separation data passed through a maximum (93%) at EG mole fraction of 0.12. At higher EG concentrations, while solute separations dropped slowly, product rate data dropped steeply. At EG mole fraction of 0.5, product rate dropped to practically negligible value (<1.0 g/hr) while solute separation was still significant (20%). These results show that in the gelation environment involving EG-water gelation medium, water continued to be the major polymer precipitating agent throughout the EC concentrations studied, even though at mole fractions greater than 0.12, EG also accelerated significantly the rate of polymer precipitation, making the polymer aggregates (constituting the surface layer of the resulting membrane) coarser. The very low diffusivity of ethylene glycol probably accounts for the difference between the results obtained (Fig. 1) with EG-H₂O gelation medium and the other alcohol-water gelation mediums studied.

Effect of Shrinkage Temperature on the Average Size of Pores on the Membrane Surface

Figure 3 gives the effect of shrinking membranes in hot water for 10 min on product rates, with respect to membranes obtained by using MeOH-H₂O, PrOH-H₂O, and *iso*-PrOH-H₂O gelation mediums. The mole fraction of alcohol in the gelation medium was 0.5 in all cases, and the solvent evaporation period during film formation was 10 sec for all the membranes tested. For comparison, the corresponding performance data for membranes made with pure water gelation medium are also given in Figure 3. For the latter membranes, solute separation increased and product rate decreased with increase in shrinkage temperature; this observation is in accordance with common experience^{13,14} which is explicable on the basis of decrease of average pore size on the membrane surface with increase in shrinkage temperature as a result of movement of closely packed polymer segments still closer together due to polymer-polymer attraction. In the case of membranes made with alcohol-water gelation mediums, the average pore size on the membrane surface in the as-cast condition was sufficiently big so that product rate was high and solute separation was negligible in all cases; with increase in shrinkage temperature, solute separations were still negligible and product rates increased as shown in Figure 3. The latter observation is significant, and it is understandable on the following basis. In the as-cast condition, the randomly precipitated polymer segments on the membrane surface are sufficiently far apart and hence the average pore size on the membrane surface is sufficiently big to give a high product rate and practically no solute separation; with increase in shrinkage temperature, the polymer segments which are relatively closer together move a little still closer together (because of polymer-polymer attraction) thus increasing the size of a sufficient number of original void spaces between polymer segments, which results in bigger average size of pores on the membrane surface and increased product rate with no detectable change in solute separation for the test feed solution used. This phenomenon can be expected to happen as the average pore size on the membrane surface in the as-cast condition is sufficiently big and the original pore size distribution is sufficiently nonuniform.

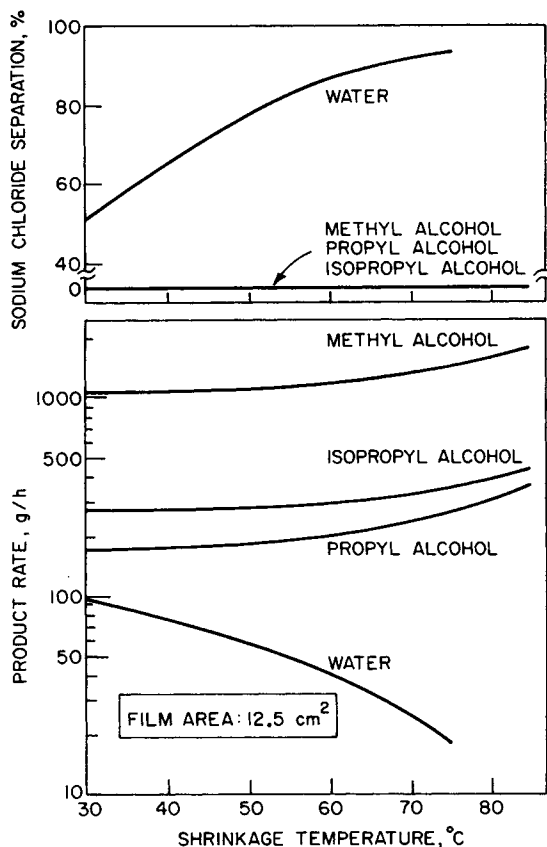


Fig. 3. Effect of shrinkage temperature on membrane performance. Gelation medium, water or 50 mole % indicated alcohol; operating pressure, 250 psig; NaCl concentration in feed solution, 300 ppm; feed flow rate, 400 cm³/min; solvent evaporation period during film formation, 10 sec.

CONCLUSION

The use of alcohol-water gelation mediums opens a new means of generating membranes with different surface porosities for reverse osmosis and ultrafiltration applications. Detailed cause and effect studies on variations of size and distribution of pores with different gelation conditions can lead to useful physicochemical criteria for the choice of gelation mediums for specific membrane applications.

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GARY R. GILDERT
TAKESHI MATSUURA
S. SOURIRAJAN

Division of Chemistry
National Research Council of Canada
Ottawa, Canada K1A 0R9

Received November 7, 1978