

# Studies on the Solvent Exchange Technique for Making Dry Cellulose Acetate Membranes for the Separation of Gaseous Mixtures\*

A. LUI and F. D. F. TALBOT, *Department of Chemical Engineering, University of Ottawa, Ottawa, K1N 6N5* and A. FOU DA, T. MATSUURA, and S. SOURIRAJAN,<sup>†</sup> *Division of Chemistry, National Research Council of Canada, Ottawa, K1A 0R6, Canada*

## Synopsis

The effect of the pore size on the surface of the water-wet reverse osmosis membrane and the solvents used in the solvent exchange process on the pore size of the resulting dry cellulose acetate membrane was studied with respect to the separation of a CO<sub>2</sub>/CH<sub>4</sub> mixture. It has been found that there is a critical pore size on the surface of wet membrane that results in the smallest pore size on the dry membrane and, consequently, in the highest separation factor. Such critical pore sizes become greater when the boiling point of the second solvent is increased.

## INTRODUCTION

This article is based on the concept of the pore on the surface layer of the membrane. The entire work is dedicated to control of the pore size to optimize the separation of the binary gas mixture as well as the permeation rate. The pore is defined as any space between nonbonded material entities in the membrane matrix through which space mass transport can take place. The equivalent diameter of such a pore is expressed by any distance (however small) greater than zero.<sup>1</sup>

Cellulose acetate membranes, when dried in a manner to preserve their porosity and the surface pore structure, showed higher permeation rates and significant separations for gaseous mixtures.<sup>2,3</sup> Many studies on membrane drying by solvent exchange and its industrial application in gas separations can also be found in the literature.<sup>4-9</sup>

To achieve a membrane of optimum pore size and pore size distribution that gives a high separation factor and a high permeation rate, a firm cause and effect relationship must be established between the variables involved in the membrane formation and the performance of these membranes. In the formation of cellulose acetate membranes we have determined that evaporation period, shrinkage temperature, and solvent or solvents used for the replacement of water in the membrane during the drying process are some of the more important factors affecting the ultimate pore size and the pore size distribution of the membrane.<sup>10</sup> Therefore, it was natural to study the effects

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<sup>†</sup>Present address: Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada.

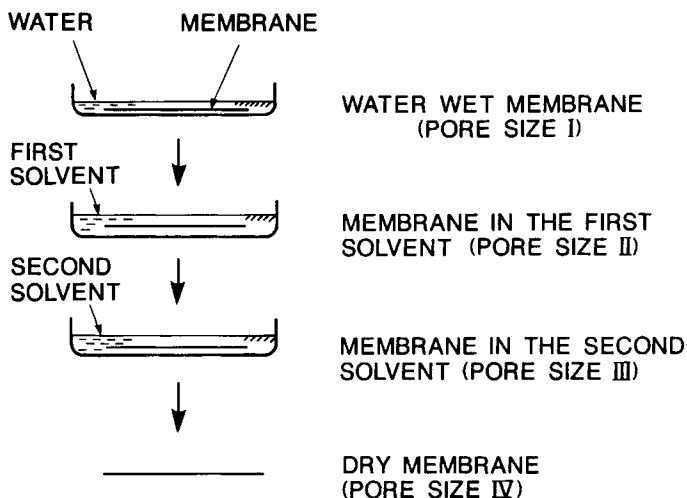


Fig. 1. Illustration of steps involved in the solvent exchange technique.

of various solvents used in the solvent exchange process of the membrane drying. This study was done using hydrogen/methane gas mixtures.<sup>11</sup> A similar study has been made by Ohya et al. with respect to the pure gas permeation through cellulose acetate membrane and the separation of several gas mixtures.<sup>12</sup>

In the multiphase solvent exchange technique, the water in the membrane is replaced by a water-soluble first solvent that is a nonsolvent for the membrane material. The first solvent is replaced by a second solvent that is volatile. The second solvent is subsequently air evaporated to obtain the dry membrane. A number of different organic liquids can be used as solvents. It is conjectured that the pore size on the membrane surface changes progressively during the process of solvent exchange; that is, that there are at least four stages affecting pore sizes involved in the membrane drying process. Figure 1 shows these stages with their corresponding pore sizes. They are:

- Pore size (I) which corresponds to the pore size on the surface of water wet membranes
- Pore size (II) which corresponds to the pore size on the surface of membranes after replacement of water by the first solvent
- Pore size (III) which corresponds to the pore size on the surface of membranes after replacement of the first solvent by the second solvent
- Pore size (IV) which corresponds to the pore size on the surface of the finally obtained dry membranes

The objective of this study is to clarify the effect of the first and second solvent on the change of pore sizes at each step of solvent exchange, and on pore sizes of the dry membranes ultimately produced. For this purpose, water-wet membranes of different pore sizes (I), were produced by applying *seven different shrinkage temperatures*. Furthermore, *three alcohols* as the first solvent and *four volatile organic solvents* as the second solvent were

chosen as variables involved in the preparation of dry cellulose acetate membranes. The separation of  $\text{CO}_2/\text{CH}_4$  gas mixtures was chosen to evaluate the effect of the membrane pore size on the performance of dry membranes. Both experimental data and discussions based thereupon are presented.

### EXPERIMENTAL

The membranes used in the present investigation were cast from a solution of the following composition (wt%): cellulose acetate (Eastman 398-3) 17, acetone 69.2, magnesium perchlorate 1.45, and water 12.35.<sup>13</sup> All membranes were cast to equal nominal thickness. The temperatures of the casting solution and the casting atmosphere were kept constant at 10°C and 30°C, respectively. The relative humidity of the atmosphere was maintained at 65%. Membranes were gelled in ice cold water after 60 s of solvent evaporation time and then shrunk in hot water at temperatures ranging from 60 to 95°C. These membranes were then dried by a multiple solvent exchange technique. In this technique the water in the membrane is first replaced by a water-miscible solvent (called the "first solvent") that is a nonsolvent for the membrane material. Then, the first solvent is replaced by a second solvent that is volatile. The second solvent is subsequently air evaporated to obtain the dry membrane. A number of different organic liquids can be used as solvents. First solvents used included methyl alcohol, ethyl alcohol, and isopropyl alcohol. Second solvents used included carbon disulfide, isopropyl ether, hexane, and toluene. The replacement of water in the membrane by the first solvent was done by successive immersion in first solvent-water solutions, and these were progressively more concentrated in the first solvent; that is, 25, 50, 75, 100 vol% aqueous solution of the first solvents were used for the successive solvent replacement.

The equipment used in the present investigation and details of the experimental procedure have been previously reported.<sup>10,11</sup> Air in the reverse osmosis cells and in the gas feed line was removed by flushing with the feed gas mixture of  $\text{CO}_2$  and methane. The mole fraction of  $\text{CO}_2$  in the feed gas mixture was set equal to 0.9 in all experiments. All experiments were conducted at room temperature and the feed pressure was varied in the range of 345 to 2200 kPa abs. The composition of gas was measured by gas chromatography using Spectra-Physics SP7100 model equipped with a Porapak Q column. The accuracy involved in gas composition analysis was  $\pm 1\%$ . All the gases (pure and mixed) were obtained from Matheson Canada with a specified purity of 99.9%.

## RESULTS AND DISCUSSION

### Experimental Data

Typical experimental data are presented in Figures 2-5. In each figure the separation factor  $S_{12}$  defined as

$$S_{12} = \frac{X_{13}/X_{23}}{X_{12}/X_{22}} \quad (1)$$

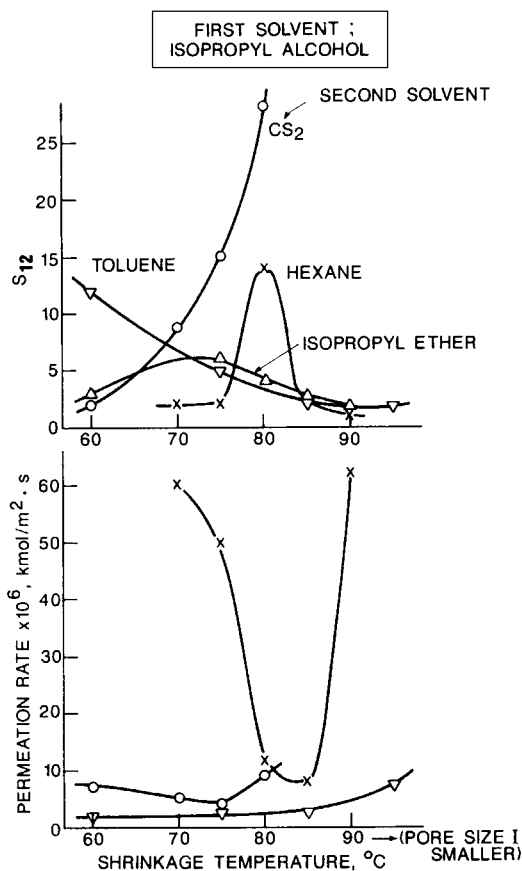


Fig. 2. Effect of shrinkage temperature and of the second solvent used in the solvent exchange technique on the separation factor and the product permeation rate. Membranes: material, cellulose acetate 398-3; first solvent, isopropyl alcohol; second solvent, as specified in the figure. Operating conditions: temperature, room;  $\text{CO}_2$  mole fraction in feed, 0.9; pressure, 2200 kPa abs.

where:

$X_{13}$  = mole fraction of  $\text{CO}_2$  in product gas

$X_{23}$  = mole fraction of  $\text{CH}_4$  in product gas

$X_{12}$  = mole fraction of  $\text{CO}_2$  in feed gas

$X_{22}$  = mole fraction of  $\text{CH}_4$  in feed gas

and the permeation rate are given as a function of the shrinkage temperature. The operating conditions under which these experiments were performed are all specified in the figure captions.

The experimental results shown in Figure 2 were obtained when isopropyl alcohol was used as a first solvent while changing the second solvent. By observing the separation factor in Figure 2 the following remarks can be made:

1. When carbon disulfide is used as a second solvent the separation factor increases with increase in shrinkage temperature.

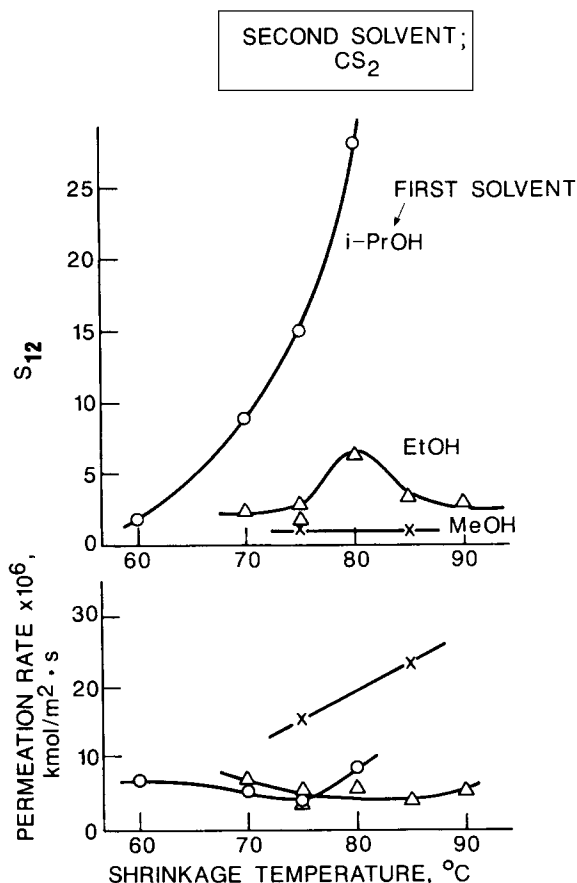


Fig. 3. Effect of shrinkage temperature and of the first solvent used in the solvent exchange technique on the separation factor and the product permeation rate. Membranes: material, cellulose acetate 398-3; second solvent,  $\text{CS}_2$ ; first solvent, as specified in the figure. Operating conditions: same as Figure 2 except the pressure for ethyl alcohol and methyl alcohol first solvent is 345 kPa abs.

2. When isopropyl ether and hexane are the second solvent, the separation factor passes through a maximum as the shrinkage temperature is increased.
3. When toluene is the second solvent, the separation factor decreases with increase in the shrinkage temperature.

In general, the product permeation rate shows a tendency to decrease with increase in the separation factor. An exceptional case is for  $\text{CS}_2$  as the second solvent where both separation factor and the permeation rate increase with the increase of the shrinkage temperature from 75 to 80°C.

The experimental results shown in Figure 3 were obtained when the second solvent was fixed to  $\text{CS}_2$  and the first solvent was changed. The figure shows that the separation is quite dependent on the first solvent as it increases monotonically with the shrinkage temperature in case of isopropyl alcohol,

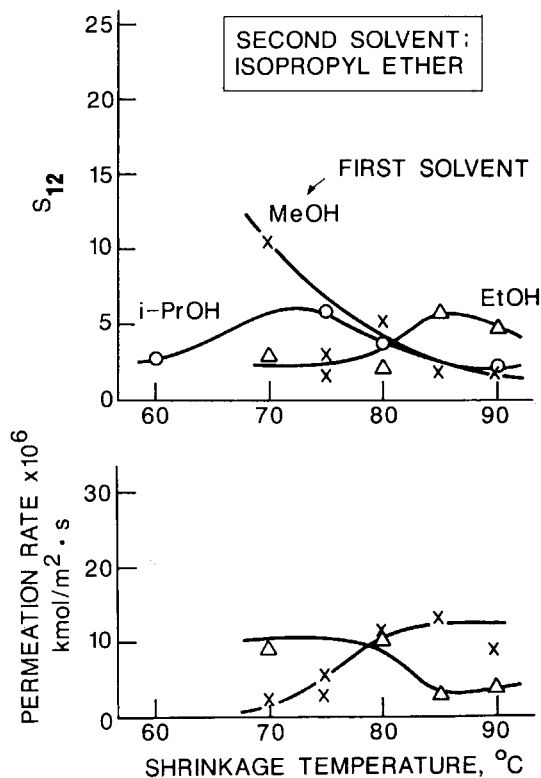


Fig. 4. Effect of shrinkage temperature and of the first solvent used in the solvent exchange technique on the separation factor and the product permeation rate. Membranes: material, cellulose acetate 398-3; second solvent, isopropyl ether; first solvent, as specified in the figure. Operating conditions: same as Figure 3.

passes through a maximum when ethyl alcohol is used, and remains constant when methyl alcohol is used as a first solvent.

Figure 4 shows the results obtained when the first solvent is changed while the second solvent is fixed to isopropyl ether. The separation factor passes through a maximum value with increase in the shrinkage temperature when the first solvent is either isopropyl alcohol or ethyl alcohol. The separation factor decreases with increase in the shrinkage temperature when the first solvent is methyl alcohol.

Figure 5 shows the experimental results obtained when the first solvent is changed while the second solvent is fixed to hexane. The separation factor passes through a maximum, decreases, and remains constant as the shrinkage temperature increases when isopropyl alcohol, ethyl alcohol, and methyl alcohol, respectively, is used for the first solvent.

Generally, the product permeation rate decreases with increase in the separation factor in all above experimental results.

#### Assumptions to Explain the Experimental Data

To explain the experimental results described above, the presence of the "pore" on the membrane surface is assumed. The definition of the pore has

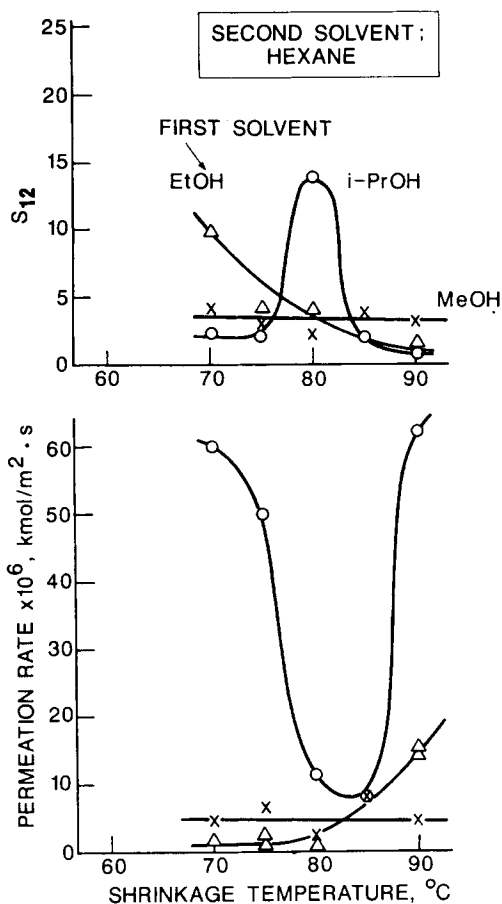


Fig. 5. Effect of shrinkage temperature and of the first solvent used in the solvent exchange technique on the separation factor and the product permeation rate. Membranes: material, cellulose acetate 398-3; second solvent, hexane; first solvent as specified in the figure. Operating conditions: same as Figure 3.

already been given in the Introduction. The size of the pore so defined is supposed to be affected by the change in the membrane morphology as well as the configuration of the polymeric molecules, of which the membrane is constructed. Supposing that polymeric molecules are building blocks of the film, the spaces created between such blocks have to be affected by their assemblage. The variables involved in the formation of dry cellulose acetate membranes are supposed to affect the assembling of polymer molecules in the film, and consequently the size of the spaces created between polymer molecules. This view is particularly valid when the polymer is in the glassy state.

It is sometimes conjectured that the morphology of the "dense" polymer film is the same no matter under what conditions the film is made. The difference in the performance data from different membranes is caused primarily by the difference in the contribution to the transport of gas molecules from the "defect" in the membrane, which is synonymous to pinholes on the membrane surface. The authors disagree with this view because simple evidence to deny such a view can be presented. Starting from the same cellulose

TABLE I  
Comparison of Pure Gas Permeability Data for Two Dry Cellulose Acetate Membranes

Permeant gas	Permeability $\times 10^{5a}$ mol/s	
	Film 1	Film 2
Helium	0.835	1.80
Carbon dioxide	1.05	2.56
Methane	0.170	0.030

<sup>a</sup> Operating pressure, 2068 kPag (= 300 psig); operating temperature, 25°C; effective film area, 10.2 cm<sup>2</sup>.

acetate material, we were able to produce two different dry membranes under different drying conditions. The permeation rate data obtained for both membranes are shown in Table I. If the higher values of the permeation rate of helium and carbon dioxide of film 2 as compared with those of film 1 are due to the presence of pinholes in film 2, the permeation rate in film 2 should also be higher with respect to methane. Table I shows that there is a significant decrease in methane permeation rate through film 2. The above data indicate clearly that the sizes of the channels through which gas transport takes place differ for each of the films studied, and different mechanisms are involved. Such changes in the channel sizes have been obviously caused by changed conditions of preparing dry cellulose acetate membranes. The size of such channels is called the pore size in this article.

Based on the concept of the pore and the pore size so defined, the experimental data given in Figure 2-5 can be explained uniformly and consistently on the basis of the following assumptions:

1. The separation factor increases when the pore size on the surface of dry membranes (corresponding to the pore size (IV) according to Fig. 1) decreases.
2. The pore size on the surface of the water-wet membrane [corresponding to the pore size (I)] decreases with increase in the shrinkage temperature.
3. The pore size on the surface of the membrane after replacement of water by the first alcoholic solvent [corresponding to the pore size (II)] increases with increase in the molecular size of alcohol solvent.
4. There is a critical value in the pore size (II) from which the smallest pore size (IV) is produced on the surface of the resulting dry membrane. When the pore size (II) becomes further from the critical value either to the larger or the smaller side, the pore size (IV) becomes progressively greater.
5. The above critical value of the pore size (II) is unique to the second solvent and increases with increase in the boiling point of the second solvent.

As mentioned earlier, the results shown in Figure 2 were obtained when the first solvent was fixed to isopropyl alcohol. Therefore, the shrinkage temperature shown on the abscissa, which represents the scale for the pore size of water-wet membranes [the pore size (I)] according to our second assumption, can also represent the scale of the pore size (II) of the membrane after replacement of water by the first solvent.



Looking at Figure 2 it is found that the critical pore size (II) which results in the smallest pore size (IV) on the dry membrane surface, and which consequently results in the highest separation factor by our first assumption, is that of the membrane shrunk at the temperature above 80°C when the second solvent is CS<sub>2</sub>. Note that the boiling point of CS<sub>2</sub> is 46.5°C, the lowest among all second solvents studied. The shrinkage temperature at which the highest separation factor is obtained seems to be below 60°C with respect to toluene, whose boiling point is 110.8°C and the highest among all solvents studied. The results obtained with respect to isopropyl ether and hexane, whose boiling points are 68.0°C and 68.8°C, respectively, lie between those of CS<sub>2</sub> and toluene and show real maxima in the separation factor–shrinkage temperature correlation. Thus, the shrinkage temperature at which the highest separation factor is obtained shifts from a higher value to a lower one when the boiling point of the second solvent is increased. This implies that the critical pore size (II) increases with increase in the boiling point. The presence of the critical pore size (II) and its shift with the boiling point have been stated as assumption 4 and assumption 5. Therefore, assumptions 1, 2, 4, and 5 are consistent with all the data for separation factors given in Figure 2. Generally for each solvent the highest separation factor corresponds to the lower product permeation rate, which is also consistent with the first assumption.

It should be noted, however, that the separation factor and the product rate should have no unique correlation with each other, since the latter value

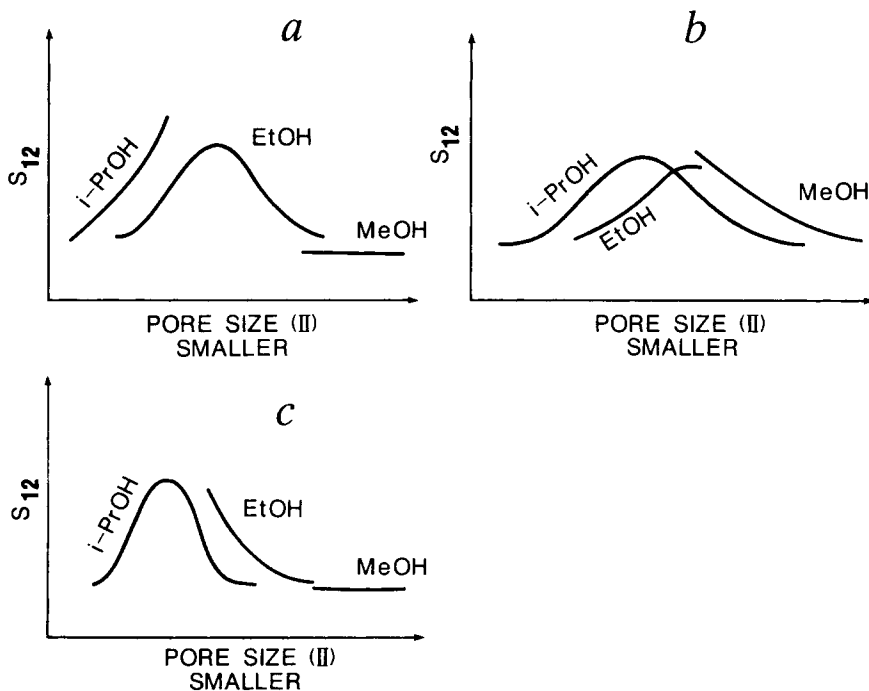


Fig. 6. The range of pore size corresponding to each first solvent and its relative position to the critical pore size.

depends also on the thickness of the active layer of the asymmetric membrane.

The results given in Figure 3 can be explained by introducing the third assumption. Since the order in the size of alcoholic molecules used as the first solvent is isopropyl alcohol > ethyl alcohol > methyl alcohol, the range of the pore size (II) on the surface of the membrane after replacement of water by the first solvent becomes also progressively smaller in the order isopropyl alcohol > ethyl alcohol > methyl alcohol as illustrated in Figure 6(a). It should be noted that membranes shrunk at different temperatures are involved within each first solvent and, therefore, the pore size (II) corresponding to each solvent covers a certain range. Assuming further that the critical pore size (II), which leads to the highest separation factor when the membrane is dried, is in the middle of the range covered by ethyl alcohol solvent [see Fig. 6(a)] the ranges of the pore size (II) covered by isopropyl alcohol and methyl alcohol can be on both sides of the critical value in the pore size (II). The increase in the separation factor with increase in the shrinkage temperature, when isopropyl alcohol is the first solvent, is understandable if the pore size (II) of membranes replaced by isopropyl alcohol solvent lies on the left shoulder of ethyl alcohol curve [in Fig. 6(a)]. Likewise, the constant separation factors obtained for methyl alcohol as the first solvent is understandable when the pore size (II) of these membranes is significantly less than those of ethyl alcohol. That the experimental results on the separation factor,  $S_{12}$ , given in Figures 4 and 5 can be explained by Figure 6(b) and Figure 6(c), respectively, is self-explanatory. Thus all the experimental data presented in Figures 2-5 can be explained on the basis of assumptions 1 to 5.

### Validity of Assumptions Made

The first assumption can be justified since the surface flow mechanism is the only mechanism among all gas transport mechanisms through porous media, including Knudsen, slip, viscous, and surface flow mechanisms, which contributes significantly to the separation of the gas mixture.<sup>14</sup> When the pore size becomes smaller the surface flow contribution becomes greater, and thus the increase in the separation factor is expected. The second assumption has been concluded in our earlier report.<sup>15</sup> The third assumption is justified by a small increase in the pore size occurring when water is replaced by methyl or ethyl alcohol solvent.<sup>16,17</sup> The fourth and fifth assumptions require some explanations.

The presence of a critical value in the pore size (II) which results in the smallest value in the pore size (IV) and consequently the highest separation factor implies the presence of two opposing effects on the pore size (IV) when the pore size (II) is changed. Namely, the decrease in the latter value may either decrease or increase the pore size (IV) and consequently may either increase or decrease the separation factor. It is easy to understand the effect to increase the separation factor, since a smaller value in the pore size (II) may most logically result in a smaller value in the pore size (IV). The other effect requires further consideration. It is known that when a capillary pore of a small diameter is filled by liquid, a negative pressure prevails in the pore and a force is exerted on the capillary wall to decrease the pore size.<sup>18</sup> This is

particularly true when the liquid can wet the membrane surface effectively. When the liquid is removed rapidly under these circumstances, the pore size is reduced. Sometimes the pore may completely collapse. When the liquid is removed slowly, on the other hand, the pore size may retain the initial value. Briefly, the degree of the reduction in the pore size depends on the speed of removing the liquid from inside the pore. This speed further depends on the diffusion rate of the liquid through the pore, which is governed by the size of the pore. When the pore size is large, the liquid diffusion in the pore is rapid and the degree of pore size reduction is greater. It should be noted that the pore-filling liquid used in the foregoing discussion corresponds to the second solvent and is removed by evaporation in this work. Thus, we may expect a larger degree of the pore size reduction and a smaller pore (IV) on the dry membrane surface resulting from a larger pore size (II or III) on the surface of the membrane before evaporation, according to the above mechanism. These two opposing effects result in a critical value in the pore size (II) from which the smallest value in the pore size (IV) after evaporation is achieved. The fourth assumption on the presence of the critical pore size (II) is thus justified.

Furthermore, when the boiling point of the second solvent increases, the driving force applied on the second solvent to be removed from the pore is lowered. Therefore, in order to obtain a sufficiently high diffusion rate the pore size must be larger. As a consequence, the same degree of the pore size reduction can be achieved only for a greater pore size (II). This results in the shift of the critical value in the pore size (II) to a greater value. The fifth assumption can therefore also be justified.

## CONCLUSION

The pore size on the surface of water-wet reverse osmosis membranes, the choice of the first and the second solvents are important factors to govern the pore size of dry membranes used for gas separations. It is concluded that there is a critical value in the pore size on the surface of the wet membrane from which the smallest pore size on the surface of the dry membrane is obtained and consequently the highest separation factor can be achieved. Such a critical pore size depends on the boiling point of the second solvent used in the solvent exchange technique. This conclusion has to be further tested by conducting the membrane drying procedure under various circumstances, such as at different temperatures and under different vapor pressures of the second solvent in the drying atmosphere, and by measuring the performance data of the resulting membranes. It would also be desirable to dry membranes with other solvents than those used in this work to confirm the above conclusion. It should be noted that the above conclusion does not necessarily deny the effect of the interaction force between the second solvent and the polymeric material on the pore size and the pore size distribution, which has been concluded in our earlier work.<sup>11</sup> The latter aspect has to be also further investigated.

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