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# STUDIES ON GAS TRANSPORT THROUGH DRY CELLULOSE ACETATE MEMBRANES PREPARED BY SOLVENT EXCHANGE TECHNIQUE

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## ABSTRACT

The mechanism of gas transport through pores on the surface of dry cellulose acetate membranes under pressure was identified for membranes prepared by the solvent exchange technique using pure gas permeation rate data. The pure gases were helium, methane and carbon dioxide. The variables involved in the membrane preparation are the shrinkage temperature, the first solvent, the second solvent and the combinations thereof. Different conditions of membrane preparation produce different pore sizes. Depending on this pore size, one of the following mechanisms becomes dominant: Knudsen, surface and size exclusion.

## INTRODUCTION

Dry cellulose acetate membranes have found applications in many industrial gas separation processes (1). When water-wet reverse osmosis membranes of cellulose acetate material are dried by two stage solvent exchange technique, where a water miscible solvent is used as a first solvent to replace water in the first stage and a volatile solvent is used as a second solvent to replace the first solvent in the second stage, there are many variables involved in the membrane preparation procedure. We have found that the shrinkage temperature, the solvents involved in the solvent exchange technique and the number of steps of water-first solvent exchange are some of the most important variables to be considered in the preparation of dry membranes (2). The choice of the solvents and the combination of chosen solvents are particularly important. As a criteria of the choice of the second solvent, we have proposed the interaction force working between the second solvent and polymeric materials in the presence of the first solvent (3).

In our latest work we have considered the molecular size of the first solvent and the boiling point of the second solvent as the important criteria for the choice of solvents on the basis of several assumptions concerning the functions of solvents during the membrane drying procedure (4).

This study is an extension of former work. The object of this study is to identify the transport mechanism by which gas molecules permeate through membranes of different pore sizes which are produced on the membrane surface under various conditions of membrane drying procedure. The permeation data of pure helium, methane and carbon dioxide gases are used to identify the most dominant flow mechanism in the membrane pore. It is expected that this work will elucidate the effect of the shrinkage temperature, the first solvent and the second solvent on the pore size of the dry membrane surface and will offer a means of controlling the pore size, gas flow mechanism and consequently the performance of dry cellulose acetate membranes.

## EXPERIMENTAL

The membranes used in the present investigation were cast from a solution of the following composition (wt.-%): cellulose acetate (Eastman 398-3) 17.0, acetone 69.2, magnesium perchlorate 1.45 and water 12.35 (5). 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 60s of the solvent evaporation time then heat-treated in hot water at the temperature ranging from 70 to 90°C for 10 minutes. 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") which is a nonsolvent for the membrane material. Then, the first solvent is replaced by a second solvent which 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 include methyl alcohol and ethyl alcohol. Second solvents used include carbon disulfide, isopropyl ether and hexane. The replacement of water in the membrane by the first solvent was by successive immersions in first solvent-water solutions (overnight for each immersion), and these were progressively more concentrated in the first solvent; i.e. 25, 50, 75, 100 vol%.

The equipment used in the present investigation and the details of the experimental procedure have been previously reported (6). Helium, methane and $CO_2$ were used as feed gases. Air in the reverse osmosis cells and in the feed gas line was removed by flushing them with the feed gas. All the experiments were conducted at room temperature and feed gas pressure was either 450 kPa or 2200 kPa abs. The gas permeation velocity was measured by using a bubble flow meter. All the pure gases were obtained from Matheson Canada with a specified purity of 99.9%.

## RESULTS AND DISCUSSION

In our previous work (4), the effect of the shrinkage temperature, of the first alcoholic solvent and the second volatile solvent on the performance of dry cellulose acetate membrane has been explained by considering that the pore size of membranes changes progressively in the process of membrane drying from a) the water-wet condition (pore size I), to b) alcohol-wet condition (pore size II), then to c) a condition under which membrane pores are filled with a volatile organic solvent (pore size III), and finally to d) a dry condition after evaporation of volatile solvent (pore size IV).

The following assumptions are made.

1. The separation factor increases when the pore size on the surface of the dry membrane (pore size IV) decreases.

2. The pore size on the surface of the water-wet membrane (pore size I) decreases with increase in the shrinkage temperature.

3. The pore size on the alcohol-wet membrane (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. The more remote is the pore size II from the critical value, the greater becomes the pore size IV.

5. The above critical value in the pore size II is unique to the second solvent and increases with increase in the boiling point of the latter solvent.

The assumptions 1 - 3 were justified in the previous paper (4). The assumptions 4 and 5 were also justified in the previous paper (4) on the basis of two opposing effects influencing the pore size II. By one effect, the order of pore size in the pore size II is retained in the pore size IV, while by the other effect, the order of pore size in the pore size II tends to be reversed in the pore size IV. The capillary forces present during removal of volatile solvent from the capillary pore give rise to the second effect. Applying the above assumptions to the experimental data on separation factors of membranes prepared using methyl alcohol and ethyl alcohol as the first solvent, the pore sizes involved in the alcohol-wet (pore size II) and in the dry membranes (pore size IV) can be described as illustrated in Fig. 1.

In Fig. 1-a, for example, ethyl alcohol and methyl alcohol have been used as the first solvent prior to the use of $CS_2$ as second solvent. Membranes from both ethyl alcohol and methyl alcohol solvent cover a certain range of pore size since water-wet membranes were shrunk at different temperatures prior to the solvent exchange with an alcohol. The pore size II of all the membranes involved in ethyl alcohol first solvent may be greater than those of methyl alcohol solvent by assumption 3. The critical value in pore size II is found in the middle of the range covered by membranes of ethyl alcohol as the first solvent. Looking further into Fig. 1, it is realized that the combinations of solvents can be classified into four patterns, $\alpha$ through $\delta$, which are illustrated in Fig. 2 for better understanding.

In Fig. 2 seven membranes are shown with different pore sizes. As membrane number decreases shrinkage temperature progressively increases and the pore size II decreases. The pore size IV which is shown parallel to the pore size II indicates that membrane 4 corresponds to the membrane with the smallest pore size IV and the critical pore size II. The pore size II and IV of the membrane 1 are almost the same, while the pore size II of membrane 7 is greatly reduced during solvent evaporation and a small pore size IV is achieved, which is however much larger than pore size IV of membrane 4. The ranges covered by membranes of different patterns are also shown in Fig. 2.

Pattern $\alpha$ example: methyl alcohol/$CS_2$ combination. The membrane pore size II is the smallest. However, there is little pore size reduction during the solvent evaporation process, and as a result the largest pore size IV is produced.

Pattern $\beta$ examples: methyl alcohol/isopropyl ether and ethyl alcohol/hexane combinations. The pore sizes II are on the right side of the critical pore size. The pore size IV decreases as the shrinkage temperature decreases.

Pattern $\gamma$ example: ethyl alcohol/$CS_2$ combination. The pore size II passes the critical pore size. The pore size IV decreases and increases again as shrinkage temperature decreases.

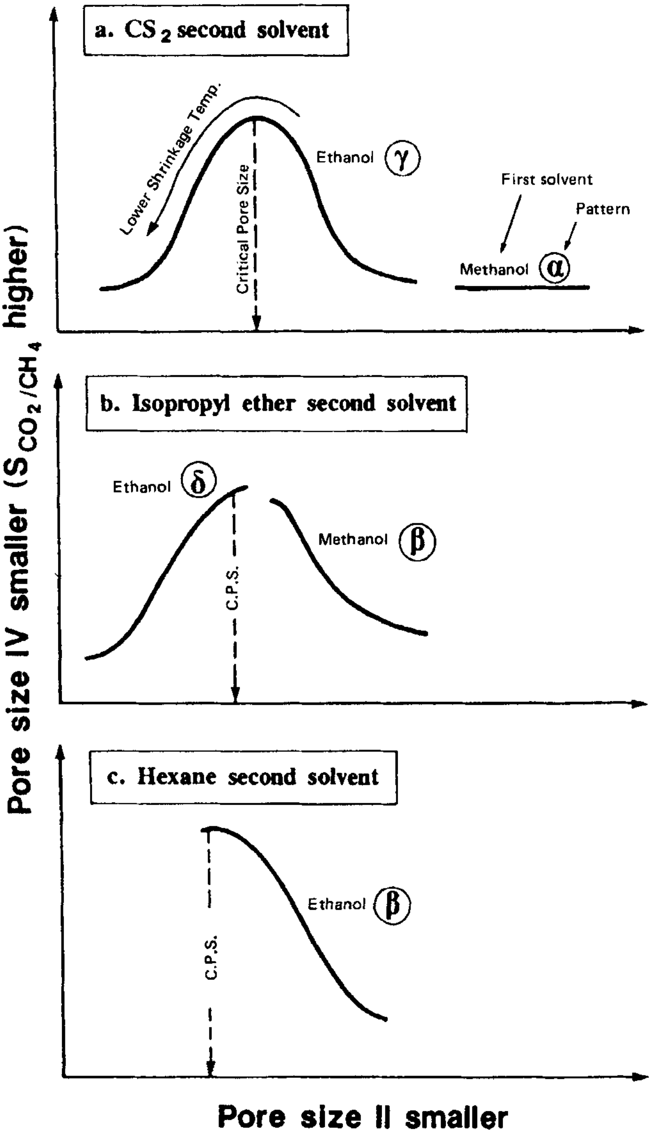

Fig. 1. Schematic representation of patterns in the change of the pore size produced by different combinations of first and second solvent. membranes, cellulose acetate; $S_{CO_2/CH_4}$ = separation factor of $CO_2/CH_4$ gas mixture

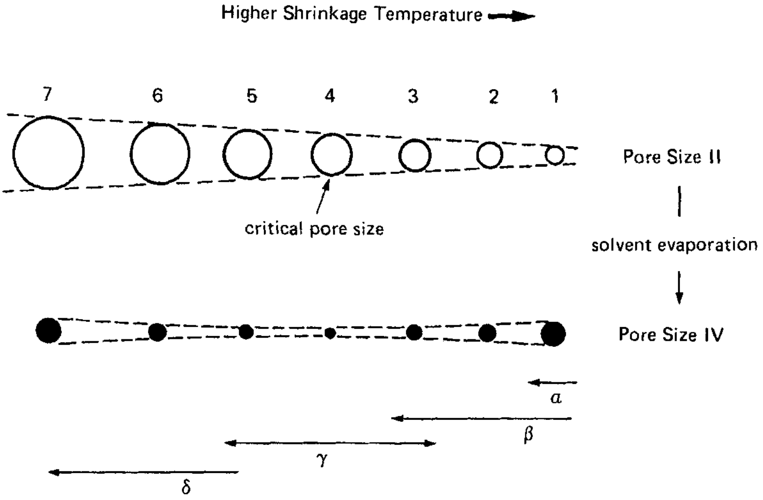

Fig. 2 Schematic representation of pore sizes and their change in alcohol-wet membranes and dry membranes, and the range of the pore size covered by each pattern.

Pattern δ example: ethyl alcohol/isopropyl ether combination. The pore size II is on the left side of the critical pore size. The pore size increases as shrinkage temperature decreases.

Table 1 and Figures 3 - 6 illustrate the pure $CO_2$ and methane gas permeation versus He gas permeation data for each membrane studied. These data reveal the nature of pores produced on the dry membrane. Prior to a thorough investigation of experimental results we should recall some basic characteristics of membrane gas transport. There are two important components for membrane gas transport. One is the Knudsen flow mechanism and the other is surface flow mechanism. According to the Knudsen flow mechanism the order in gas permeability is He > $CH_4$ > $CO_2$ since the flux is reciprocally proportional to the square root of gas molecular weights, which are 4, 16 and 44 for He, $CH_4$ and $CO_2$, respectively. The permeability of the gas ($mol/m^2 \cdot s \cdot Pa$) should remain constant regardless of the gas pressure. According to the surface flow mechanism, on the other hand, the order in the gas permeability is $CO_2$ > $CH_4$ since $CO_2$ is more strongly adsorbed to the cellulose acetate surface. Furthermore, the permeability should increase proportionally to the increase in the applied pressure. This

Table 1. Permeability Data on Dry Cellulose Acetate Membrane Prepared by Shrinkage Temperature of 85°C and Methyl alcohol/$CS_2$ Combination (Pattern $\alpha$ in Figure 2)

| Operating pressure, kPa abs. | Permeability x $10^{11}$, mol/$m^2$.s.Pa | | |
|---|---|---|---|
| | He | $CH_4$ | $CO_2$ |
| 450 | 13.13 | 10.47 | 6.89 |
| 2200 | -- | 11.67 | 6.95 |

effect is often interpreted as plasticization of polymeric materials by $CO_2$ gases.

Table 1 shows the data of a membrane prepared by the combination of methyl alcohol/$CS_2$ (pattern $\alpha$). Apparently, the order in the permeability is He > $CH_4$ > $CO_2$ and the permeabilities of $CH_4$ and $CO_2$ do not change significantly at a higher operating pressure, indicating the Knudsen flow is dominating. Therefore, the membrane of pattern $\alpha$ (corresponding to membrane 1 in Fig. 2) has a very large pore size. Figures 3 and 4 show the data from membranes prepared by combinations of methyl alcohol/isopropyl ether and ethyl alcohol/hexane, respectively, both belonging to pattern $\beta$ which covers from membrane 1 to membrane 3 in Figure 2. The highest shrinkage temperature corresponds to the membrane with the largest pore.

Both Fig. 3 and Fig. 4 show that the permeability of all gases decrease as shrinkage temperature decreases though a notably exceptional point (membrane shrunk at 70°C in Fig. 4) is found. The largest pores (at shrinkage temperature of 85°C in Fig. 3 and 90°C in Fig. 4) show the Knudsen mechanism ($CH_4$ permeability > $CO_2$ permeability), while for the rest of the membranes the order in $CH_4$ and $CO_2$ permeabilities are reversed, indicating that the dominant gas transport is through the surface flow mechanism. This is confirmed by the effect of the operating pressure. Referring to Fig. 3, the permeability of the membrane shrunk at 85°C (of the largest pore size) decreases slightly for all gases, while permeability data increase with increase in pressure for the rest of membranes. The increase in $CO_2$ gas flux is, however, most remarkable, indicating surface flow contribution is the most important with respect to $CO_2$ gas. Similar data have been obtained from membranes involved in Fig. 4. These data clearly

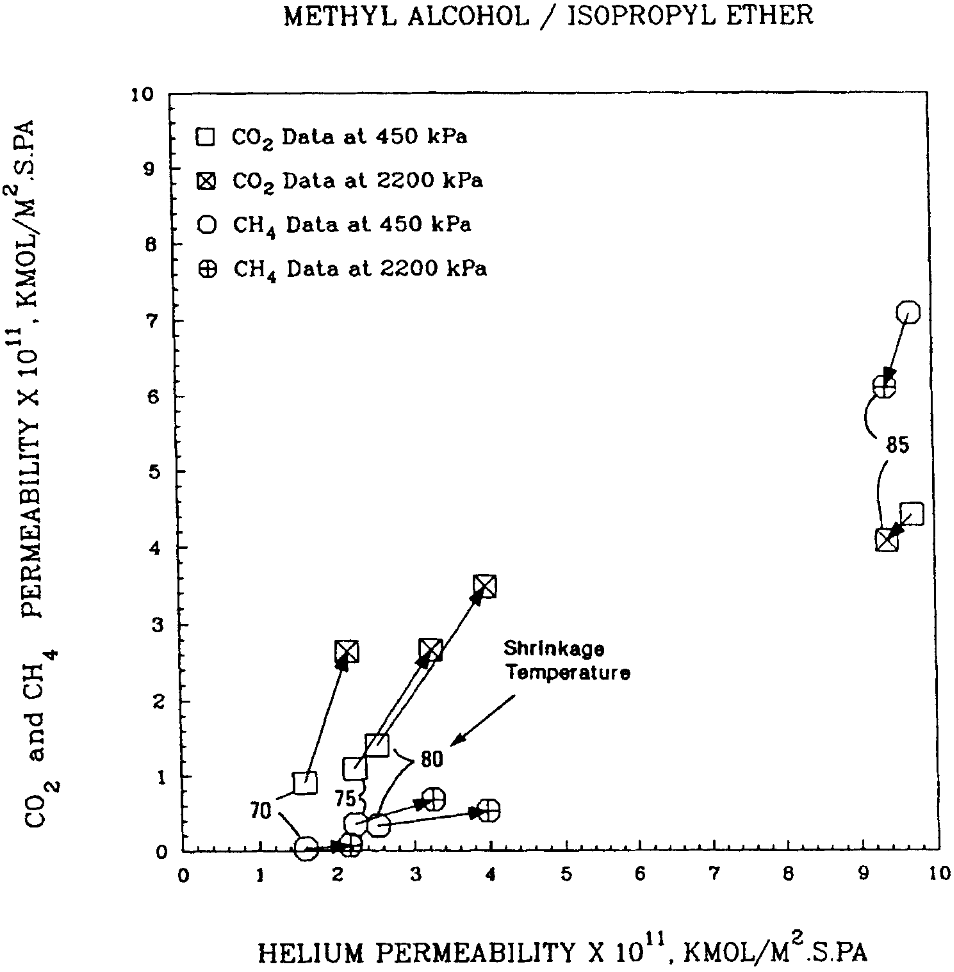

Fig. 3. Permeability data of dry cellulose acetate membranes prepared by different shrinkage temperatures (°C) and methyl alcohol/isopropyl ether combination.

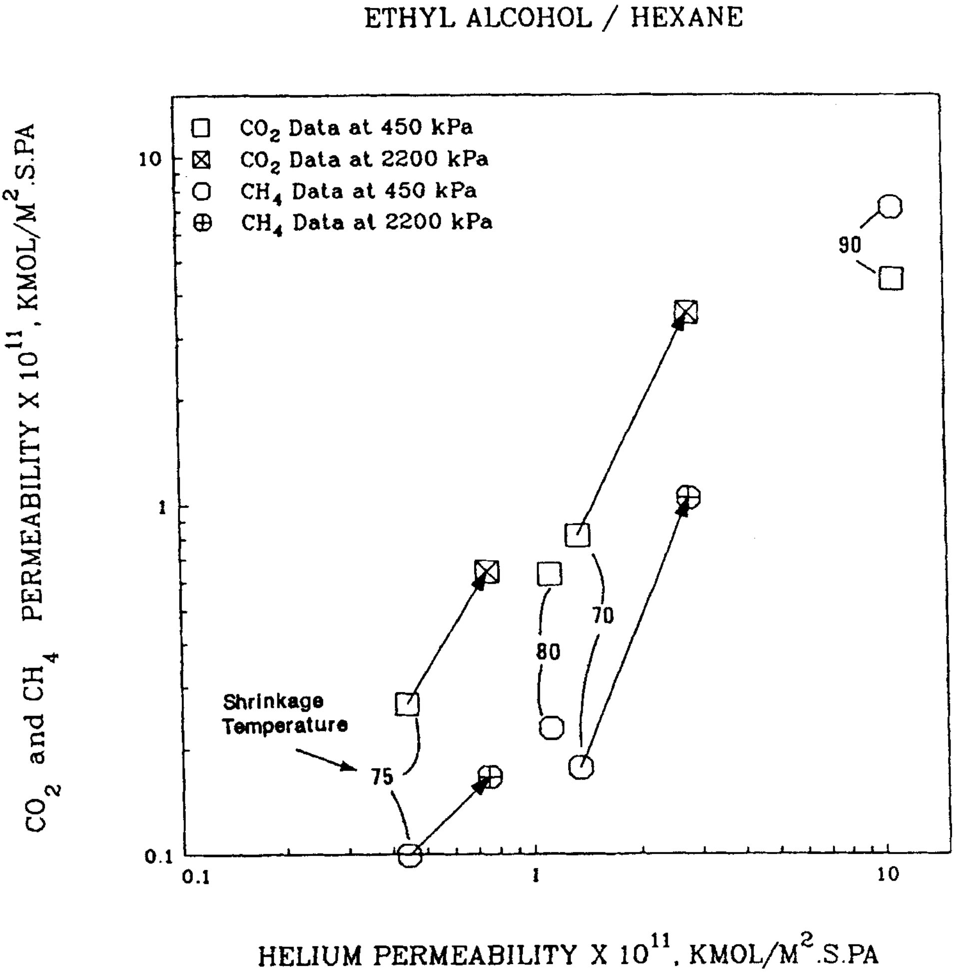

Fig. 4. Permeability data of dry cellulose acetate membranes prepared by different shrinkage temperatures (°C) and ethyl alcohol/hexane combination.

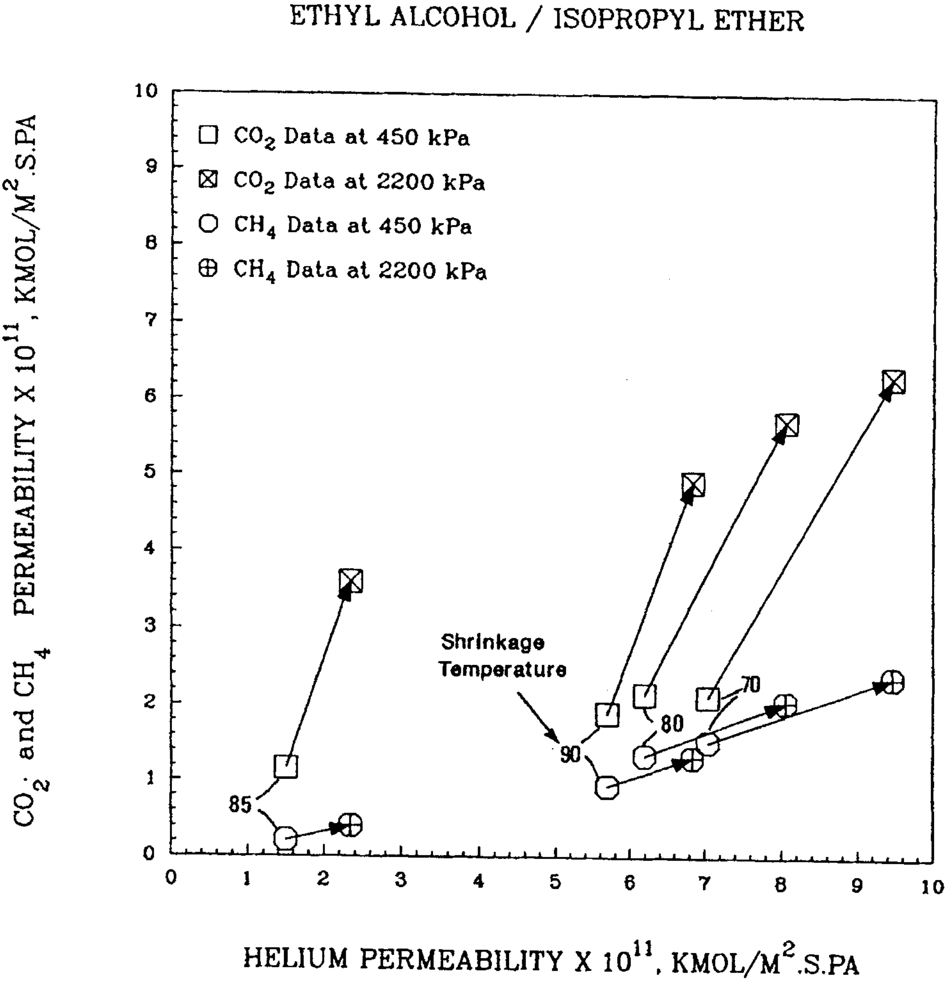

Fig. 5. Permeability data of dry cellulose acetate membranes prepared by different shrinkage temperatures (°C) and ethyl alcohol/isopropyl ether combination.

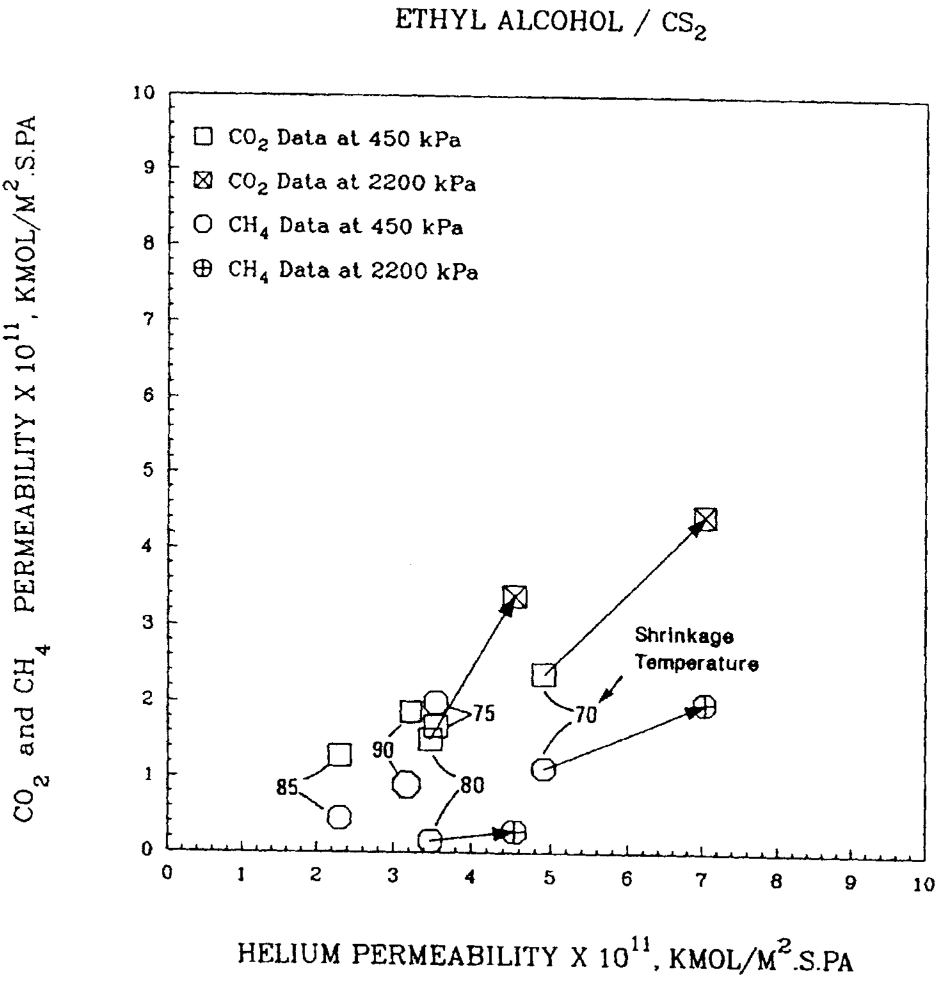

Fig. 6 Permeability data of dry cellulose acetate membranes prepared by different shrinkage temperatures (°C) and ethyl alcohol/$CS_2$ combination.

indicate that the Knudsen mechanism is observed only for membrane of the highest shrinkage temperature (indicated in Fig. 2 as membrane 1) and surface flow is dominant for the rest of the membrane pores. The presence of exceptional data in Fig. 4 (70°C) might indicate that ethyl alcohol/hexane combination belongs to pattern $\gamma$ rather than pattern $\beta$.

Figure 5 shows the data from membranes prepared by using the combination of ethyl alcohol/isopropyl ether, which belongs to pattern $\delta$. As shown in Fig. 2 the pore size should increase with decrease in shrinkage temperature. Figure 5 shows that this is the case except for the membrane shrunk at 90°C. This exceptional point might be indicating that ehtyl alcohol/isopropyl ether combination belongs to pattern $\gamma$ with a critical temperature of 85°C. Apparently, the membrane shrunk at 70°C possesses the largest size corresponding to membrane 7 in Figure 2. Furthermore, all membranes involved demonstrated the action of the surface flow mechanism. Therefore, pores on membranes 1 and 7 which are the largest pores at two ends of a series of pore sizes IV (see Fig. 2) are of a completely different nature. The pore size IV of membrane 1 retains the pore size II and is significantly larger than the pore size IV of membrane 7, which is produced as a result of a significant reduction of the pore size II. The former membrane shows the Knudsen flow mechanism while the latter shows the surface flow mechanism.

Lastly, the results from membranes belonging to pattern $\gamma$ (combination of ethyl alcohol/$CS_2$) are shown in Fig. 6. As shown in Fig. 2 this pattern is intermediate between patterns $\beta$ and $\delta$, passing through critical pore size II and the minimum pore size IV as shrinkage temperature decreases. This trend is best observed in the methane permeability data, which has the order of

$$70°C > 75°C > 80°C < 85°C < 90°C$$

showing a minimum at the middle of the range of shrinkage temperature as expected from Fig. 2. The orders in the flux of $CO_2$ and helium are not exactly the same as that of $CH_4$. The reason is as follows. When we compare the kinetic radii of gas molecules (7) involved in this study, methane is $1.92 \times 10^{-10}$ m and carbon dioxide is more of a cylindrical shape with radius of $1.65 \times 10^{-10}$ m. Helium is of course the smallest and the kinetic radius of $1.30 \times 10^{-10}$ m. Therefore, the effective molecule size for transport in the membrane pore is largest for $CH_4$ molecule. The results in Figure 6 indicate that the pore obtained by the 80°C shrinkage temperature has such a small size that the permeation of $CH_4$ is almost completely prevented. The permeation of $CO_2$ and helium, on the other hand, are allowed and their permeabilities are higher than those at the shrinkage temperature of 85°C, probably due to the presence of a thin active skin layer. With very small pores and a thin active skin layer this membrane is the most suitable for $CO_2/CH_4$ separation. More complete data of $CO_2/CH_4$ separation factors experimentally observed were presented elsewhere (8). Reflecting the small pore size, $CH_4$

permeability is almost unchanged while $CO_2$ permeability increases significantly with increase in operating pressure. All of the membranes in this series show surface flow mechanisms.

## CONCLUSION

As assumed in our previous work, there is a critical value in pore size II of alcohol-wet membrane from which the smallest pore size IV on the dry membrane is resulted. The further apart is the pore size II from the critical value, the greater becomes the pore size IV on the dry membrane surface. Bearing in mind the above assumptions, the following conclusions have been drawn from our experimental observations.

1) Knudsen flow is dominant in the largest pore size IV on the dry cellulose acetate membrane which results from the smallest pore size II (corresponding to membrane 1 on Fig. 2).

2) Surface flow mechanism is dominant in the other extreme of the largest pore size IV, i.e. the pore size IV produced from the largest pore size II (membrane 7 in Fig. 2). Because significant size reduction is involved, this pore size IV is smaller than the pore size IV of membrane 1 in Fig. 2.

3) Surface flow is also dominant for the rest of the pore sizes.

4) Methane molecules are rejected by the smallest pore size IV on the dry membrane which results from the critical pore size II (membrane 4 in Fig. 2) by size exclusion mechanism due to the largest size of methane molecule among all permeant gases studied in this work.

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