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The Oxygen Gas Permselectivity of Dried Cellulose Acetate Membranes

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Synopsis. The oxygen gas permselectivity of annealed cellulose di- and triacetate membranes were investigated. We have suggested that the permeation ratios of oxygen to nitrogen gases of these membranes attain 7—8 by annealing in air at 180 °C.

In recent years, cellulose diacetae membranes have came to play an important role in the reverse osmosis process. Therefore, there have been many investigations concerning the permselectivities for salts in aqueous solutions. However, the gas permselectivities of the cellulose acetate membranes have not been widely investigated. The cellulose diacetate membranes have, though, been found to show 2—3 times as much permeability to oxygen as to nitrogen.[1] Most polymer membranes thus far reported have oxygen permeation ratios to nitrogen ranging from 2 to 6.[2,3]

In this paper, we wish to report that the cellulose di- and triacetate membranes have a higher permeation ratio of oxygen gas than the reported values of this polymer, we have established this by investigating the conditions for the membrane preparation.

The cellulose di- and triacetate used in this study were Eastman's type E398-3 and Daicel's type LT-70 respectively. Two kinds of cellulose diacetate membranes, skinned and dense membrane, were prepared by the same procedure as in a previous paper.[4] Here, "skinned membrane" refers to the membrane consisting of a dense layer or skin, which is only 0.1 to 1.0 μm thick and which is responsible for the separation, on top of a highly porous structure which comprises about 99% of the overall thickness of the membrane. The skinned and dense membranes were both about 120 μm thick.

The cellulose triacetate dense membranes were prepared by a procedure essentially the same as that used for the cellulose diacetate dense membranes. In this case, the casting solvent consisted of 90 wt % dichloromethane and 10 wt % ethanol. The dense membranes were 10—30 μm thick. However, we could not make the skinned membrane of cellulose triacetate because we lack the knowledge of the most combination of solvents.

The skinned membranes were annealed in a water bath for 30 min at 80—90 °C and then freeze-dried in order to maintain the skinned structure of the membranes. The dense membranes were annealed in the air at 180 °C for 2 h.

The instrument for gas permeation measurment was driven by the pressure difference between the atmospheric and the diminished pressure; the gas permeation rates were calculated from the pressure change in the low-pressure region. Pure gases were used as the permeative gases.

The results of the gas permeation of the skinned membranes at 23 °C are shown in Fig. 1. In Fig. 1 the apparent gas permeation rates are used because the dense layer of the skinned membrane was not clear enough to be measured. Figure 1 shows some scatter, but this scatter seems to be result of the fluctuation in freeze-drying conditions. It is apparent from these results that the permeation ratio of oxygen to nitrogen increases with a decrease in the oxygen gas permeation rate, and with an increase in the annealing temperature; finally, it may reach the permeation ratio of the annealed dense membrane to be discussed below. It is also indicated that the non-annealed membranes deviate from this relationship, but the reason for this remains unknown.

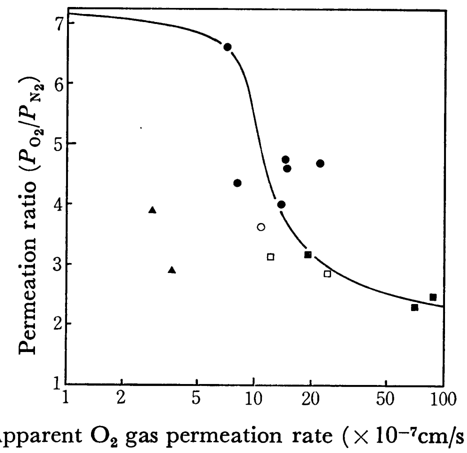

Fig. 1. Gas permeation property of skinned cellulose diacetate membranes.
▲: Non-annealed, ●: annealed at 90 °C, ○: annealed at 85 °C, □: annealed at 80 °C, ■: Gantzel's data.[1]

TABLE 1. GAS PERMEABILITY COEFFICIENTS OF DENSE CELLULOSE DIACETATE MEMBRANES

Annealing condition	Membrane thickness	P_{O_2} (cm^2/s cmHg)	P_{O_2}/P_{N_2}
Non-annealed	30 μ	0.72×10^{-10}	3.2
4 h at 180 °C	30	0.93	7.3
Gantzel's data	—	0.78	2.8

TABLE 2. GAS PERMEABILITY COEFFICIENTS OF DENSE CELLULOSE TRIACETATE MEMBRANES

Annealing condition	Membrane thickness	P_{O_2} (cm^2/s cmHg)	P_{O_2}/P_{N_2}
Non-annealed (1)	19 μ	1.6×10^{-10}	5.3
Non-annealed (2)	13	1.6	6.2
4 h at 180 °C (1)	18	1.9	7.8
4 h at 180 °C (3)	30	1.5	7.2

The results of the gas permeation of the dense membranes at 23 °C are shown in Tables 1 and 2. It can be noticed from these tables that upon the annealing of the dense membranes the oxygen gas permeation rates are not affected, while the permeation ratios increase, and that the permeation ratios of cellulose di- and triacetate membranes attain 7.3 and 7.8 respectively. It is noteworthy that the oxygen gas permeation rate of the cellulose triacetate membrane is about twice that of the cellulose diacetate membrane.

It is well known that the gas permselectivity of polymer membranes is determined by the gas solubilities and the gas-diffusion coefficients of the membranes. We measured the oxygen and nitrogen gas solubilities of these membranes, but could not recognize any difference in the solubilities between the non-annealed and annealed membranes.[5] Consequently, we assume that the annealing process mainly influences the diffusion of the gases, and that the pore radii[6] in the cellulose di- and triacetate membranes might be made smaller by the annealing process. This annealing process would have greater effect on the diffusion of nitrogen gas, whose molecular size is larger than that of oxygen gas; therefore, the oxygen permeation ratio would increase.

As has been mentioned above, the cellulose triacetate membrane has a high permeability and permselectivity. Consequently, if one succeeded in making the skinned membrane of cellulose triacetate, it may be expected to be an excellent membrane for separating oxygen gas from nitrogen gas.

References

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