Oxygen Permselective Membranes from DNA-Lipid Complexes

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DNA-lipid complex membranes from highly purified DNA from salmon milt and cationic amphiphilic lipids showed a high permselectivity toward O₂. The permselectivity was dependent on types of cationic amphiphiles. The DNA-lipid complex membrane consisting of octadecyltrimethylammonium cation (C₁₈TMA) showed a high permselectivity of 26.9.

Key words: DNA-lipid complexes / gas separation / oxygen enrichment / permselectivity / salmon milt

1. Introduction

In Hokkaido, Japan, over 1,000 tons of DNA from salmon milt can be produced by a suitable extraction process although they are now being abandoned. DNA molecules carry an important biological information on genetics of living things with its double-stranded structure consisting of complementary nucleic acid base pairs. On the other hand, DNA molecules have a huge molecular weight so that DNA was reported to be promising polymeric materials to give durable films, and they have been studied in connection with optical devices, electric or ion conductivity, ion permeation, capture of metal ions and endocrine disruptors. It is an indispensable research subject to develop potential utilization of natural resources. Among many applications of DNA, the authors focused their attention on separation membranes made from DNA because membranes will play an important role in environmental and energy related processes. Oxygen/nitrogen separation from air is one of increasingly important membrane separation processes since oxygen-enriched air (OEA) is applied to medical use, chemical industry, refineries, and fermentation and biological digestion processes. Nitrogen-enriched air (NEA) is used in flammable-liquid storage tanks, tires, and so forth. This paper reports the oxygen/nitrogen separation behaviors through the membranes from DNA-lipid complexes.

2. Experimental Section

2.1 Materials

Fiberlike purified DNA sodium salt (DNA-Na) of 93 % from salmon milt (Nippon Chemical Feed Co.) was used. Cationic amphiphiles, such as dodecyltrimethylammonium chloride (n = 12) (C₁₂TMA), tetradecyltrimethylammonium chloride (n = 14) (C₁₄TMA), hexadecyltrimethylammonium chloride (n = 16) (C₁₆TMA), and octadecyltrimethylammonium chloride (n = 18) (C₁₈TMA), were used as received. Water purified with an ultrapure water system (Simpli Lab, Millipore S. A., Molsheim, France) was used for preparing the sample solution.

\[
\text{CH}_3 \quad \text{CH}_3\text{N}-(\text{CH}_2)_{n-1}\text{-CH}_3 \quad \text{CH}_3
\]

cationic amphiphiles \quad n

| C₁₂TMA | 12 |
| C₁₄TMA | 14 |
| C₁₆TMA | 16 |
| C₁₈TMA | 18 |

2.2 Preparation of membrane materials

4 g of DNA sodium salt was dissolved in a 2.00 dm³
of water, followed by shaking incubation overnight at ambient temperature. In the present study, the composition of the base pairs of the DNA-Na was not determined. Here 662.0, the average value of base pairs of DNA-Na, was adopted as an average molecular weight of the constitutional repeating unit (base pair). A 2.00 dm³ of aqueous DNA-Na solution was added to 2.00 dm³ of aqueous solution of ca. 2.2 equiv. mol of cationic amphiphiles (2.80 g of C₁₂TMA, 3.42 g of C₁₄TMA, 3.59 g of C₁₆TMA, 3.70 g of C₁₈TMA). DNA-lipid polyion complex was spontaneously precipitated. The precipitate was collected by filtration, washed with water, and then dried in vacuo at 30 °C. 4.69 - 5.39 g of white powder of DNA-lipid complexes were obtained.

### 2.3 Membrane preparation

A 0.6 g of DNA-lipid complex was dissolved in 60 g of CHCl₃/EtOH (4/1, wt./wt.) solution. The DNA-lipid complex solution thus prepared was poured into a flat-laboratory dish (105 mm diameter), followed by immersing a PTFE membrane filter (T-100A090C; diameter, 90 mm; pore radius, 1.00 μm; porosity, 0.79; Advantec Mfs, Inc.) into the cast solution. And then the flat-laboratory dish was evacuated in a desiccator so that the cast solution could thoroughly penetrate into pores in the PTFE membrane filter. The solvent was allowed to evaporate at ambient temperature and atmospheric pressure. The thickness of membrane thus prepared was 76 ~ 133 μm. The thickness of the PTFE membrane filter itself was nominally 75 μm, which was confirmed in the present study. From this, it was concluded that the PTFE membrane filter was impregnated with DNA-lipid complex.

### 2.4 Gas permeation

The permeation of O₂ and N₂ through membranes were measured at 25 °C by the vacuum-pressure method using a K-315N-01 gas permeation instrument (Tsukubarakaseiki Co.). The feed gas pressure was fixed to be around 79.5 cmHg (106 kPa) and the initial pressure of the permeate side was kept below 3.8 × 10⁻³ cmHg (5 Pa). The effective membrane area was determined to be 2.41 cm², taking into account the porosity of PTFE membrane filter. From the steady-state straight line of the permeation curve, the permeability coefficient P was calculated18, 19. Permeability coefficients of O₂ and N₂ in the present study were average data obtained from three to four different measurements.

The ideal separation factor (α_O₂/N₂) is defined by

\[ \alpha_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}} \]

where P_O₂ and P_N₂ are permeability coefficients of pure O₂ and pure N₂, respectively.

### 3. Results and Discussion

Since mechanical properties of DNA-lipid complex films20 are reported to be satisfactory for gas permeation, gas permeation experiments were carried out with DNA-lipid complex membranes, which were supported by a PTFE porous membrane filter. Table summarizes permeability coefficients of O₂ and N₂, and ideal separation factor. Those four types of DNA-lipid complex membranes transported O₂ in preference to N₂, and permselectivity toward O₂ reached 26.9 for the DNA-lipid complex membrane derived from DNA-C₁₈TMA having octadecyltrimethylammonium cation as a counter ion. The permselectivity toward O₂ increased with increasing in carbon numbers of cationic amphiphile.

A tradeoff relationship is often observed between permeability and permselectivity in membrane transport. In other words, highly permeable membrane gives low permselectivity and vice versa. The upper bound line for the relationship between permeability coefficient and permselectivity have been reported for several binary gas mixtures by Robeson21. Fig. shows the relationship between permeability coefficient of O₂
Fig. Relationship between permeability coefficient of oxygen and oxygen-nitrogen permselectivity for DNA-lipid complex membranes. (The upper bound line is from ref. [21]; 1 Barrer = 1 × 10⁻¹⁰ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹.)

and permselectivity toward O₂ for the four types of DNA-lipid complex membranes together with Robeson’s upper bound line. The data points for the present membranes, excepting DNA-C₁₂TMA membrane, are above the upper bound line drawn for conventional polymers by Robeson. Especially DNA-C₁₈TMA membrane showed a high permselectivity toward O₂. From the table and the figure, it is expected that a DNA-lipid complex membrane consisting of higher alkyltrimethylammonium cation, of which carbon number of longest alkyl group is over 18, could show a higher permselectivity toward O₂ in O₂/N₂ gas separation.

From the chemical structures of DNA-lipid complex, it is expected that DNA-lipid complex membranes show high permeability coefficients toward CO₂. To this end, single gas permeation through the DNA-C₁₈TMA membrane was also investigated. The ideal separation factor toward CO₂ for the DNA-C₁₈TMA membrane (αₐ₉/₉₂), for instance, was determined to be 19.2.

4. Conclusions

DNA-lipid complex membranes from highly purified DNA from salmon milt and cationic amphiphilic lipids showed a high permselectivity toward O₂. The permselectivity was dependent on types of amphiphiles. The DNA-lipid complex membrane consisting of octadecyltrimethylammonium cation (C₁₈TMA) showed a high permselectivity of 26.9. This suggests that DNA-lipid complex membranes could be applicable to oxygen-enriched air (OEA) production for medical use, chemical industry, refineries, and fermentation and biological digestion processes.

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