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OXYGEN ENRICHMENT BY FLUOROCARBON BILAYER FILMS[1)]

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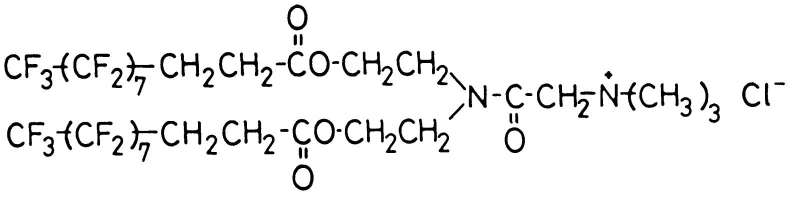
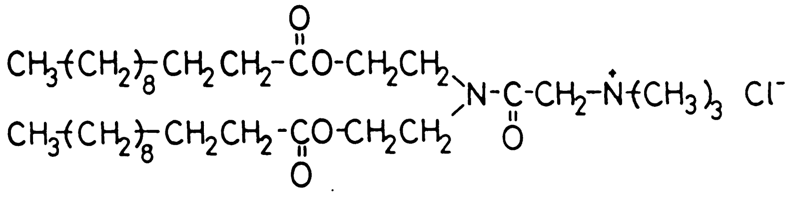
Casting of aqueous fluorocarbon bilayers with and without poly(vinyl alcohol) produced self-supporting films in which the bilayers are aligned parallel to the film plane. Permeation of O_2 through these films was faster by factors of 2.4 to 2.7 than that of N_2.

Single-chain and double-chain amphiphiles which possess long perfluoroalkyl chains in the hydrophobic portion can form stable bilayer membranes in water.[2)] The fluorocarbon bilayers thus obtained are similar to the hydrocarbon counterpart in the aggregation behavior.[3)]

Liquid fluorocarbons have been investigated as artificial blood (oxygen carrier)[4)] since they dissolve molecular oxygen very well. This affinity is one of the important factors in development of polymer membranes used for oxygen enrichment. Recently, Washizu et al.[5)] prepared a ternary composite membrane (polymer/liquid-crystal/fluorocarbon) which exhibits a large permeability coefficient for O_2 and a large separation factor for O_2 and N_2. In order to examine the permeation of O_2 through the fluorocarbon bilayer and its hydrocarbon counterpart, we immobilized $2C_8^FC_3$-de-C_2N^+ and $2C_{12}$-de-C_2N^+ with and without poly(vinyl alcohol)(PVA). We have reported that the bilayer characteristics of hydrocarbon amphiphiles are preserved in the cast films.[6,7)]



$2C_8^FC_3$-de-C_2N^+



$2C_{12}$-de-C_2N^+

The amphiphiles were prepared by the standard procedures.[8] They were shown to form vesicles by electron microscopy (sample, 10 mM in water; staining agent, uranyl acetate), and endothermic peaks due to the crystal-to-liquid crystal phase transition were found at 75 °C ($2C_8^FC_3$-de-C_2N^+) and 21 °C ($2C_{12}$-de-C_2N^+) in differential scanning calorimetry (instrument, Daini-Seikosha SSC 560). These data support strongly the existence of the bilayer structure.

Immobilization was conducted as follows. Given amounts of amphiphiles were dispersed in water by sonication, and the dispersions were mixed with aqueous PVA when necessary. The mixtures were cast in Petri dishes at room temperature. Transparent films were obtained after drying in vacuo. Figure 1 shows a scanning electron micrograph of the cross section of a $2C_8^FC_3$-de-C_2N^+(83 wt%)/PVA cast film. The formation of layer structures parallel to the film plane is observed. An analogous SEM picture was obtained for a single-component cast film of $2C_8^FC_3$-de-C_2N^+. DSC measurement of the film indicated the phase transition at 89°C, which is 14°C higher than that observed for the corresponding aqueous bilayer. Immobilization usually enhances the phase transition temperature (T_C), probably due to partial dehydration and/or formation of highly extended lamellae.[7]

The X-ray diffraction data are consistent with the SEM observation. When the incident X-ray beam was parallel to the film plane which was held vertically, highly oriented diffractions corresponding to bilayer spacings were observed along the equator (Fig. 2). These structural data prove that the fluorocarbon amphiphile forms extended bilayer lamellae parallel to the film plane and also, their thermal and structural properties are intrinsically the same as those of the corresponding aqueous bilayer.

Subsequently, permeations of O_2 and N_2 gases through the cast film were measured at 30°C by the volumetric method (high vacuum method).[9] Figure 3 summarizes permeability coefficients (P_{O_2} and P_{N_2}) and the separation factor ($\alpha = P_{O_2}/P_{N_2}$) for a series of the $2C_8^FC_3$-de-C_2N^+/PVA blend film. It is apparent that P_{O_2} and P_{N_2} are enhanced by incorporation of the fluorocarbon bilayer. Since the degree of enhancement of P_{O_2} is larger than that of P_{N_2}, the magnitude of α reaches 2.7 at the 10 wt% fluorocarbon content. Though the P values are enhanced drastically by further increases in the fluorocarbon content, the α value remains constant at 2.3 - 2.6. The magnitude of P_{O_2} for the pure fluorocarbon film reaches 1.7×10^{-8} $cm^3(STP)\cdot cm^{-1}\cdot s^{-1}\cdot cmHg^{-1}$ (26°C) which is 5800 times larger than that of PVA film. The permeation naturally becomes even more efficient at higher temperature : $P_{O_2} = 2.2 \times 10^{-8}$ $cm^3(STP)\cdot cm^{-1}\cdot s^{-1}\cdot cmHg^{-1}$ and $\alpha = 2.3$ for $2C_8^FC_3$-de-C_2N^+(83 wt%)/PVA at 100 °C.

On the other hand, when the hydrocarbon bilayer of $2C_{12}$-de-C_2N^+(50 wt%) was used in place of the fluorocarbon, the separation factor did not exceed that of a pure PVA film ($\alpha = 1.3$), and P_{O_2} was enhanced only three times at 30 °C.

In conclusion, the fluorocarbon bilayer can be immobilized without loosing the bilayer structure and the cast film thus obtained (with or without polymer binder) is effective for oxygen enrichment.

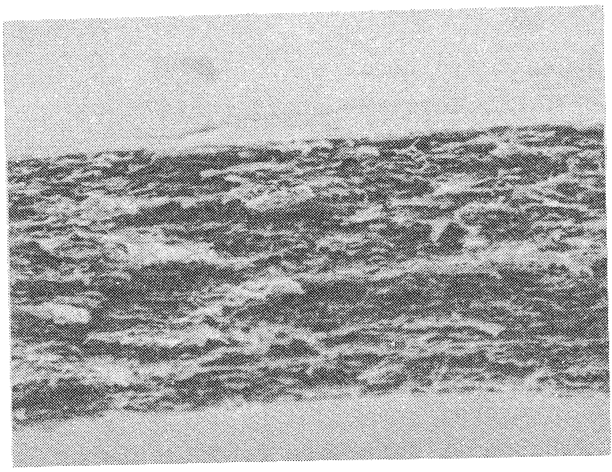


Fig. 1. Scanning electron micrograph of a $2C^F_8C_3$-de-C_2N^+ (83wt%)/PVA film. (scale = 20 μm)

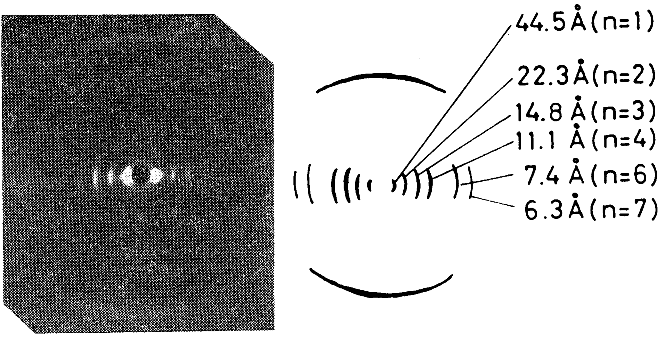


Fig. 2. Wide angle X-ray diffraction of a $2C^F_8C_3$-de-C_2N^+(83wt%)/PVA film.

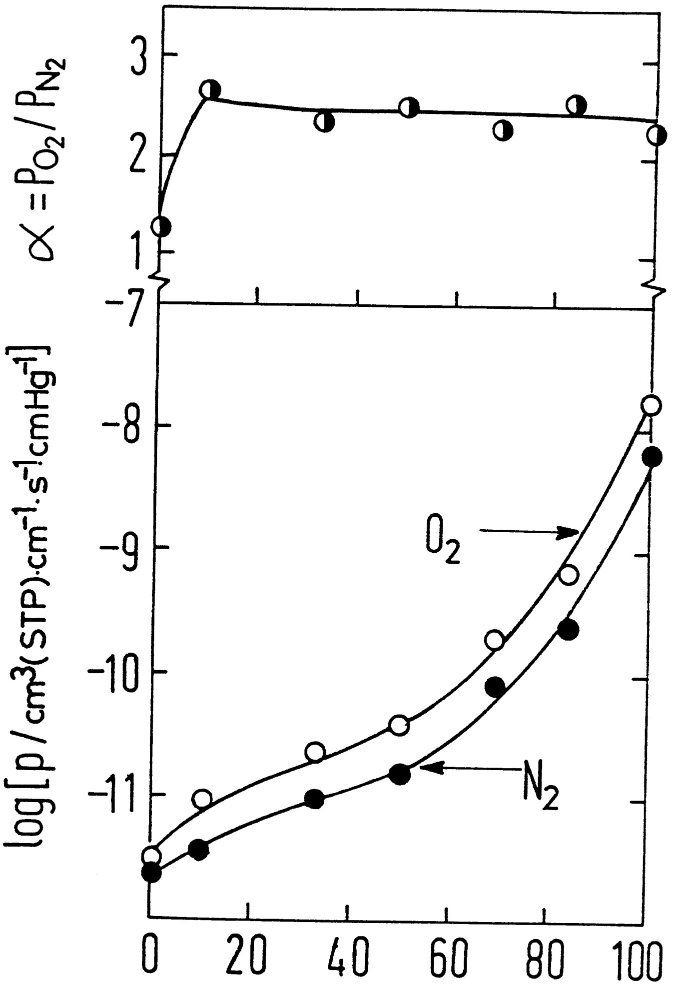


Fig. 3. Permeability coefficient and separation factor of bilayer/PVA cast film. 30 °C, film thickness 20-60 μm, bilayer : $2C^F_8C_3$-de-C_2N^+.

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8) 2H,2H,3H,3H-Perfluoroundecanoic acid and dodecanoic acid were condensed with diethanolamine by the azeotropic removal of water, and the product diesters were allowed to react with chloroacetyl chloride and subsequently with trimethylamine. The final product was identified by IR and NMR spectroscopies. $2C_8^FC_3$-de-C_2N^+; colorless powder, mp 78→184°C (the arrow indicates the liquid-crystalline region), Found; C 30.49, H 2.44, N 2.32%. Calad for $C_{31}H_{27}O_5N_2F_{34}Cl\cdot 2.0H_2O$; C 30.40, H 2.55, N 2.29%. $2C_{12}$-de-C_2N^+; colorless powder, mp 60→81°C, Found; C 64.02, H 10.87, N 4.52%. Calcd for $C_{33}H_{65}O_5N_2Cl\cdot 1.0H_2O$; C 63.59, H 10.83, N 4.49%.

9) The permeation experiments were conducted according to the procedure of Barrer and Skirrow.10) The bilayer/PVA blend films were directly placed in a steel cell. In the absence of PVA, bilayer films were cast on MF-Millipore filters (pore size, 0.025 μm) and used as such in the permeation experiment.

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