Electrically Modulated Permeability Control of Bilayer Films

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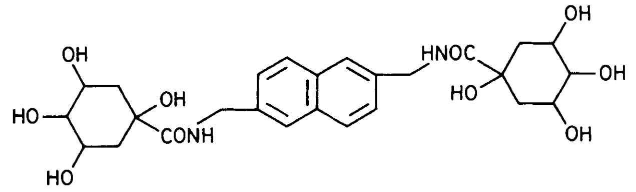
A polyion complex film was prepared by mixing aqueous solutions of dialkylammonium bilayers and poly(styrene sulphonate) and the permeability of the film could be reversibly controlled by the applied electric field.

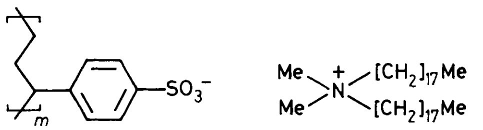
Immobilization of synthetic or natural lipid bilayers facilitates their use as novel functional materials. We have immobilized bilayers on a capsule membrane; the bilayers supported on the physically strong membrane act as a valve responding to stimuli from the outside.[1] Kunitake and co-workers recently prepared bilayer-immobilized films by various methods; polyion complexes,[2] blending with synthetic polymers,[3,4] casting on glass,[5] and Langmuir–Blodgett films.[6] Kajiyama and co-workers reported that the permeability of the bilayer-immobilized membrane was changed at the phase transition[4,6] and on photoirradiation.[7]

We report here that the permeability of a bilayer-immobilized film can be controlled reversibly by turning on and off an electric field across the membrane. In the case of cetyltrimethylammonium bromide (CTAB)-immobilized films, acetylcellulose films, and poly(methyl glutamate) films, permeabilities were not affected by the applied electric field.

The bilayer-immobilized, polyion-complex-film was pre-



(1)



$2C_{18}N^{+}2C_1$ - PSS^-

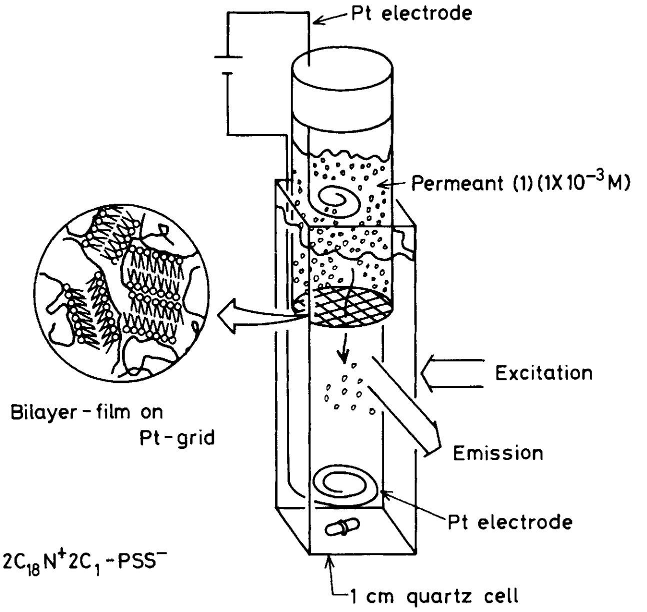


Figure 1. Fluorophotometric study of the permeation of (**1**) across the bilayer film.

pared by a slight modification of Kunitake's method.[2] An aqueous dispersion (2 ml) of dioctadecyldimethylammonium bromide ($2C_{18}N^+2C_1$, 3×10^{-5} mol) and an aqueous solution (2 ml) of sodium poly(styrene sulphonate) (PSS^-, 3×10^{-5} mol, M_r 2×10^6) were mixed at 70 °C, which is above the phase transition temperature, T_c of the $2C_{18}N^+2C_1$ bilayers. The precipitate was washed and purified by reprecipitation from chloroform with ethanol. The dried, white powder (recovery: 90%) was dissolved in chloroform and cast on a Pt-grid (100 mesh). The polyion complex film was transparent, physically strong, and water-insoluble.

The bilayer characteristics of the polyion complex film ($2C_{18}N^+2C_1$–PSS^-) were examined by differential scanning calorimetry (d.s.c.) and *X*-ray diffraction. The $2C_{18}N^+2C_1$–PSS^- film showed a sharp endothermic peak at 46 °C in water which was consistent with the phase transition temperature (45 °C) of aqueous $2C_{18}N^+2C_1$ bilayer vesicles. *X*-Ray analysis of the cast film showed a strong diffraction pattern with 38 Å spacing, consistent with the bimolecular length of $2C_{18}N^+2C_1$ amphiphiles. These structural data are similar to those observed in bilayer-corked capsule membranes[1] and clearly indicate that $2C_{18}N^+2C_1$ amphiphiles form extended lamellar structures in polyion complexes as well as other immobilized bilayer systems.[2—7] The thickness of the film was estimated to be 100 µm from scanning electron microscopy observations.

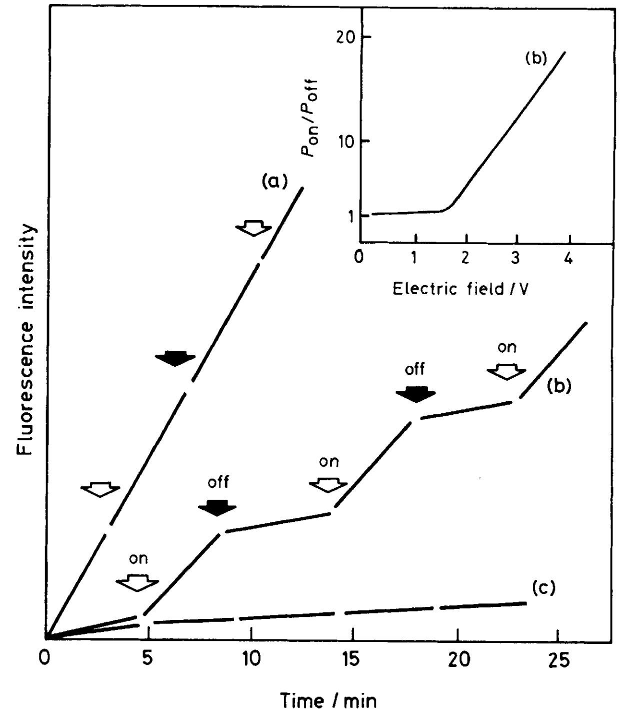


Figure 2. Electrically modulated permeability control of the fluorescent probe (**1**) across bilayer films. (a) CTA^+–PSS^- film at 55 °C; (b) $2C_{18}N^+2C_1$–PSS^- film at 55 °C; (c) $2C_{18}N^+2C_1$–PSS^- film at 25 °C. The external D.C. voltage (3 V) was applied from Pt electrodes across the film. The insert shows the variation of the permeation rate enhancement (P_{on}/P_{off}) of the $2C_{18}N^+2C_1$–PSS^- film at 55 °C with applied electric field.

The permeation of the freely water-soluble, nonionic fluorescent probe (**1**) across the $2C_{18}N^+2C_1$–PSS^- films cast on Pt-grid (100 mesh) was followed fluorophotometrically as shown in Figure 1; typical time dependences of the permeation under an intermittent electrical field are shown in Figure 2. A nonionic permeant was chosen to avoid the effect of both electro-osmosis and electro-static interaction with the bilayer film. The permeation of probe (**1**) was very slow in the absence of an electric field (P 1.5×10^{-9} cm^2 s^{-1}), but with an applied voltage of 3 V between two Pt electrodes across the membrane at 55 °C (above T_c = 46 °C) of the bilayers, the permeability was immediately enhanced by a factor of 10 (P 1.7×10^{-8} cm^2 s^{-1}) and reverted to the original slow rate when the potential was turned off even after a long duration (1—10 min). This permeability control could be reproduced repeatedly without damaging the polyion complex films at 55 °C. This permeability enhancement at 55 °C was observed only with a voltage of >1.7 V between the two electrodes (corresponding to a voltage of 0.5 V across the membrane with a thickness of 100 µm; 50 V/cm), and increased proportionally with increasing electric field in the range 1.7—4 V (see insert to Figure 2).

The permeation of probe (**1**) at 25 °C was not affected by the electric field in the range 0—6 V in contrast to the effects at 55 °C. Experiments at various temperatures showed that the electro-sensitive permeation occurred only in the fluid, liquid crystalline state of the bilayer-film above T_c, but not in the solid state below T_c. The electrosensitive permeation at 55 °C (above T_c), but not at 25 °C (below T_c) (Figure 2), can thus be concluded as being due to the phase transition of the bilayers in the polyion complex film.

Upon application of an electric field across the membrane, the bilayers in the polyion complex film act as a capacitor because of the poor conductivity of the lipid bilayers. With an electric field greater than the threshold value (1.7 V), the transmembrane potential could produce transient pores in the bilayers only in the fluid state above T_c. When the CTA^+–PSS^- film prepared from the monoalkyl surfactant cetyltrimethylammonium bromide was employed, electrically induced permeability enhancement was not observed with an applied voltage in the range 0—4 V at 55 °C. Permeations across normal polymer films such as acetylcellulose and poly(methyl glutamate) were insensitive to applied voltage (0—6 V). Eisenberg and Grodzinsky observed a very small effect of the electric field on the permeability of collagen films.[8] We have reported that the efflux of NaCl from a bilayer-corked capsule membrane was reversibly controlled by an external electric field.[9] These results clearly indicate that fluid bilayers are very important in forming channels or pores through membranes on the application of a transmembrane potential and this is believed to play a major role in biological membranes.

Physically strong, bilayer-immobilized films which respond to transmembrane potential may provide a new tool for studying models of biological synaptics and controlled-release drug delivery systems.

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