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PERMEATION PROPERTY OF BUILT-UP THIN FILM OF ARTIFICIAL LIPID WITH HYDROPHILIC AND HYDROPHOBIC SURFACES

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Artificial lipid was spread on water surface as a monomolecular layer and the monolayer was built up on the polymeric film. The built-up film was formed by the bimolecular layer structure and exhibited the crystal-liquid crystal phase transition. In the case of the built-up film with the hydrophilic surface contacting with a salt solution, the diffusive permeability coefficient, P of K^+ ion increased discontinuously about 100 times over the range of crystal-liquid crystal phase transition temperature, T_C. In the case of that with the hydrophobic surface, the slope of the P vs. 1/T plot increased with a break at T_C.

Artificial lipids exhibit the bimolecular membrane structure and the characteristics of both thermotropic and lyotropic mesomorphisms in a similar manner to biological phospholipids.1) Also, we reported that the permeability coefficients of water and ions through the polymer/artificial lipid composite membrane increased with a distinct jump at the neighborhood of crystal-liquid crystal phase transition temperature, T_C.2,3) Since amphiphiles are spread on water surface as a monomolecular film, their ultra-thin films can be built up on a substrate by depositing the monomolecular layer successively.4) The thin film prepared by the Langmuir-Blodgett method(L-B film) is advantageous for investigating the permeation properties of artificial lipids.

The purpose of this paper is to investigate the multilayer structure and permeation properties of K^+ ion for the built-up thin films of artificial lipid with the hydrophilic and the hydrophobic surfaces.

Artificial lipid used was dioctadecyldimethylammonium bromide(DOAB). A chloroform-hexane mixture solution of DOAB was spread on the surface of pure water(pH=7.0) at 289 and 293 K. The volume ratio of chloroform

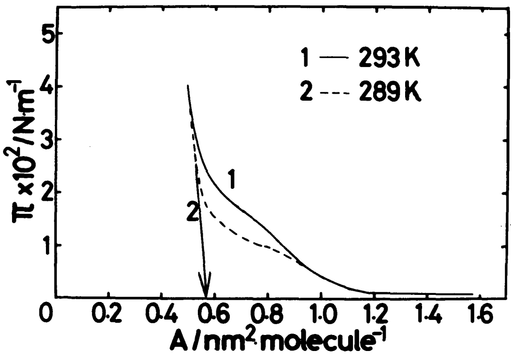

Fig.1. π - A curves for DOAB monomolecular film at 289 and 293 K.

to hexane was 1 : 4. The Wilhelmy type of film balance with a thin hanging glass plate was employed in order to measure the magnitude of surface pressure, π as a function of molecular area, A. Its sensitivity was within 7×10^{-5} $\mathrm{Nm^{-1}}$. Figure 1 shows the π-A curves for DOAB monolayer. It is apparent from Fig. 1 that DOAB monolayer is the condensed film at π of 2.95×10^{-2} $\mathrm{Nm^{-1}}$. This magnitude of π is equal to the surface pressure of oleic acid which was used for a piston oil. The dimension of unit cell has been determined for the single crystal of DOAB.5) The lattice constants of the triclinic system are a(molecular axis) 3.810 nm, b = 0.789 nm, c = 0.742 nm, $\alpha = 104.4°$, $\beta = 103.1°$ and $\gamma = 74.9°$. On the basis of these lattice constants of DOAB, the molecular area at the condensed film shown by the arrow in Fig. 1 corresponds well to the occupied area by one hydrophilic group of DOAB.

Multilayers of DOAB were built-up on the polymeric film according to the Langmuir-Blodgett method.4) The polymeric film used was the ultra-filtration membrane of poly(tetrafluoroethylene) with average pore size of 0.22 μm(Fluoropore; FP-022). The surface of FP-022 was coated with thin hydrophobic poly(butadiene) (PBD) layer of about 10 - 20 μm in thickness. The monolayer of DOAB on an aqueous subphase was kept at the constant pressure of 2.95×10^{-2} $\mathrm{Nm^{-1}}$ using oleic acid as the piston oil. The temperature of a subphase was controlled at 289 K during the preparation of the thin film. The two kinds of ultra-thin film with the hydrophilic and the hydrophobic surfaces were built-up on FP-022 coated with a thin PBD layer, that is, the polar head group or the alkyl group faces to the air side in the outermost layer, respectively. In the case of the Langmuir-Blodgett method(the vertical dipping method), the alkyl chains face to the outer direction after raising up the polymer substrate, resulting in the formation of the hydrophobic surface. For the preparation of the built-up film with the hydrophilic surface, DOAB monolayer was transferred by the horizontal lifting method6,7) on the thin film built-up by the Langmuir-Blodgett method mentioned above.

The regular stacking of the L-B film and the molecular chain orientation were confirmed on the basis of the small angle X-ray scattering (SAXS) technique. Figure 2 shows the SAXS photographs of the DOAB thin film built up on the PBD film as a function of the number of bilayers, N. The incident X-ray beam was parallel to the film surface which was set vertically as shown in the lower part of Fig. 2. Fairly sharp scattering patterns corresponding to the long spacing of 3.68 nm were observed on equator in the case above N = 6. The diffraction intensity increased with an increase in N. The long spacing of 3.68 nm corresponds to that of DOAB bilayer. It has been reported that the

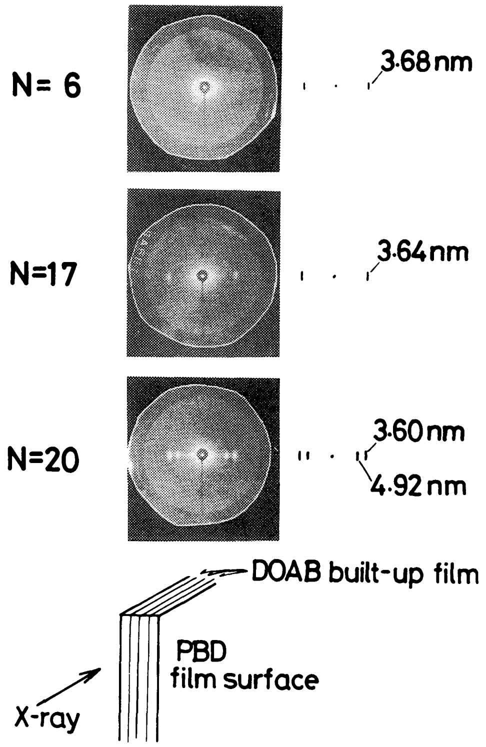

Fig.2.X-ray photographs of built-up film of DOAB on PBD. N represents number of bilayer.

membrane structure with the long spacing of 3.6 nm is generally stable in the state of DOAB bimolecular layer in which DOAB molecular axis is tilted to their bilayer surface.1) This SAXS result clearly indicates that DOAB monolayers were deposited successively in a regular stacking state and also, the molecular orientation in the DOAB bilayer is considerably high. In the case of N= 20, the long spacing of 4.92 nm was observed in addition to that of 3.60 nm. This magnitude corresponds to a bimolecular length of DOAB estimated by using of the CPK model on the assumption of the planar zigzag conformation of dialkyl groups.1) Though the existence of the long spacing of 4.9 nm may suggest that there are two types of relatively stable membrane structures within the DOAB built-up film, it is undoubted that a fairly regular stacking of DOAB monolayer was formed on the basis of the narrow SAXS intensity distribution along the azimuthal angle as shown in Fig. 2.

Differential scanning calorimetry(DSC) study showed the crystal-liquid crystal phase transition behavior for the built-up film of DOAB. Figure 3 shows the DSC curves for them with hydrophilic and hydrophobic surfaces. The magnitude of T_c for the built-up film with the hydrophilic surface was comparable to that of DOAB liposome(324 K)1) in which the polar head group faces to the water phase. On the other hand, T_c for it with hydrophobic surface was shifted to a slightly lower temperature side. It is reasonable to consider that the built-up film with the hydrophobic surface is relatively unstable in the case of reverse aggregation of DOAB molecules in which alkyl chains in the outermost layer face to the air side and the hydrophobic PBD film surface. Therefore, T_cs for the built-up film with the hydrophilic and the hydrophobic surfaces were observed in the temperature range of 318 - 325 K and of 315 - 320 K, respectively, as shown in Fig. 3.

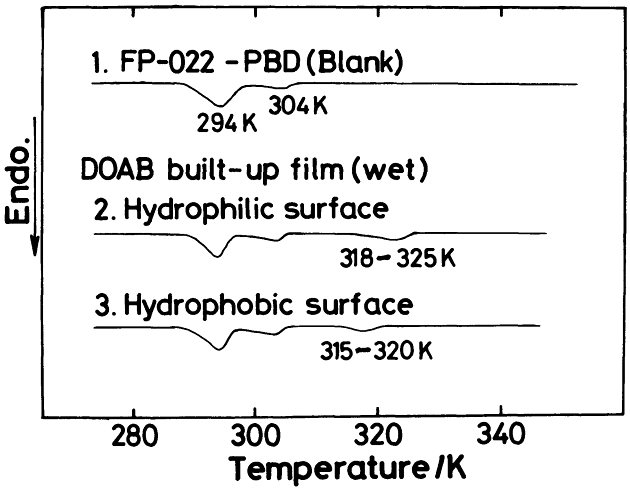

Fig.3.DSC curves of DOAB built-up films with hydrophilic and hydrophobic surfaces.

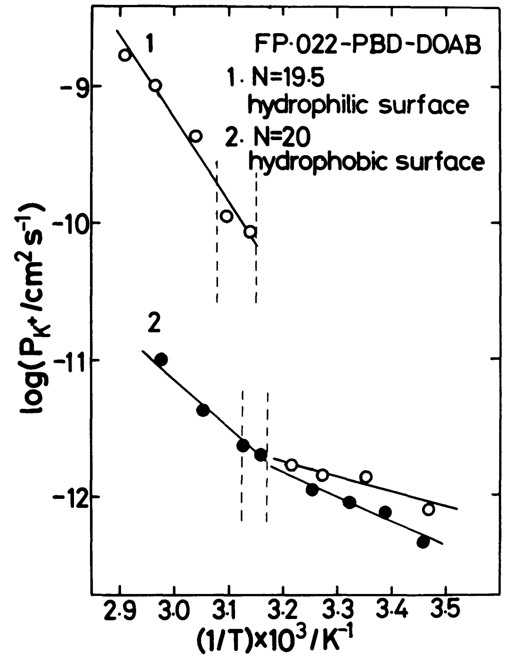

Fig.4. Temperature dependences of K^+ ion permeability coefficient for DOAB built-up films with hydrophilic and hydrophobic surfaces.

The permeation property of K^+ ion for the built up film of DOAB on the polymeric film was investigated by applying a normal osmosis method using 1 mol dm^{-3} aqueous solution of KCl and water separated by the membrane. K^+ ion permeability was determined from the time dependences of the concentration change evaluated with atomic absorption spectrophotometry. Figure 4 shows the Arrhenius plots of the permeability coefficient, P of K^+ ion for the built-up DOAB thin film with the hydrophilic and the hydrophobic surfaces. The ranges between two broken lines represent the T_c regions observed by DSC. The Arrhenius plot shows that the permeability of K^+ ion through the thin film has a positive activation energy and its magnitude ranges from 80 to 130 kJ mol^{-1}. This magnitude clearly indicates that the permeation of K^+ ion is mainly controlled by the diffusion of vacancy of free volume in the DOAB thin film. Therefore, the built-up DOAB thin film can be handled as a homogeneous medium or a dense membrane without pinhole as long as ion permeation is considered. In the case of the built-up film with the hydrophobic surface contacting with a salt solution (case 2 in Fig. 4), the relation of P_{K^+} vs. 1/T revealed a break at T_c. On the other hand, in the case of the built-up film with the hydrophilic one(case 1 in Fig. 4), P_{K^+} exhibited a discontinuous increase by approximately 100 times over a T_c range. The diffusion coefficients of K^+ ion through these thin films with the hydrophobic and the hydrophilic surfaces are nearly comparable each other above T_c, because they have almost same chemical nature and thickness. Therefore, above T_c the solubility characteristics of K^+ ion into the thin film surface mainly contribute to the remarkable difference of P_{K^+} between these thin films, because charged ions are more easily sorbed to the film with the hydrophilic surface than that with hydrophobic one. In this way, the ion permeation process is predominantly affected by solubility rather than diffusion above T_c. On the other hand, below T_c, the diffusivity of ions through thin films is very small and is the rate-determining process for permeation, since the built-up DOAB film is in a crystalline state.

In conclusion, the built-up thin films of artificial lipid with the hydrophilic and the hydrophobic surfaces were formed on the polymeric substrate in regular stacking and orientation states. Their surface states remarkably affect the membrane permeability of K^+ ion. The built-up film with the hydrophilic surface exhibited a distinct jump of P_{K^+} by about 100 times over a T_c range.

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