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Electrical Conduction of Black Foam Films Formed by Lysophospholipids

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The lateral film conductivity along the polar head-groups and the core thickness of film have been measured on the black foam films formed from aqueous solution of 1-palmitoyl-*sn*-glycero-3-phosphocholine and 1-lauroyl-*sn*-glycero-3-phosphoethanolamine without and with different concentration of NaCl and $CaCl_2$. It is found that conductivity of each film depends on the core thickness and the type and the concentration of added electrolyte.

Phosphatidylcholines (PC) and phosphatidylethanolamines (PE) are major and essential membrane phospholipids. Significant differences in phase behaviour and in the physico-chemical properties of PC and PE have been reported in spite of both phospholipids have zwitterionic polar groups and similar molecular structures.$^{1-4)}$

In this study lateral conductivities parallel to the film surface have been measured on the equilibrium foam films formed from respective aqueous solutions of synthetic 1-palmitoyl-*sn*-glycero-3-phosphocholine (lysoPC) and synthetic 1-lauroyl-*sn*-glycero-3-phosphoethanolamine (lysoPE) without and with NaCl and $CaCl_2$. Each electrolyte is added up to 1 M (1 M = 1 mol dm^{-3}). In addition aqueous core thicknesses (d_2) of the equilibrium films and bulk conductivities (κ) of the film-forming solutions have been separately measured. The results are discussed based on the three-layer model which consists of two surface monolayers enclosed an aqueous core.

Figure 1 schematically shows a measuring cell and a block diagram of apparatus for conductivity measurements on thin films.$^{5)}$ Film conductivity (κ_f), i.e. conductivity of a film with a length of 1 cm and a width of 1 cm was measured using the apparatus and the cell having a pair of bright platinum-ring electrode 14.5 mm inside diameter. The cell having the film-forming solution was placed in a thermostat at 30 °C in the case of lysoPC films and 32 °C in the case of lysoPE films. After the equilibrium inside the cell is established, a vertical cylindrical film was formed between the electrodes by removing a part of the solution. The measurements were made with alternating current, input voltage 10 or 100 mV and 20 Hz.

On the other hand, the thickness (d_2) of aqueous core in the equilibrium foam film was determined from measurement of the absorbance at absorption band for liquid water

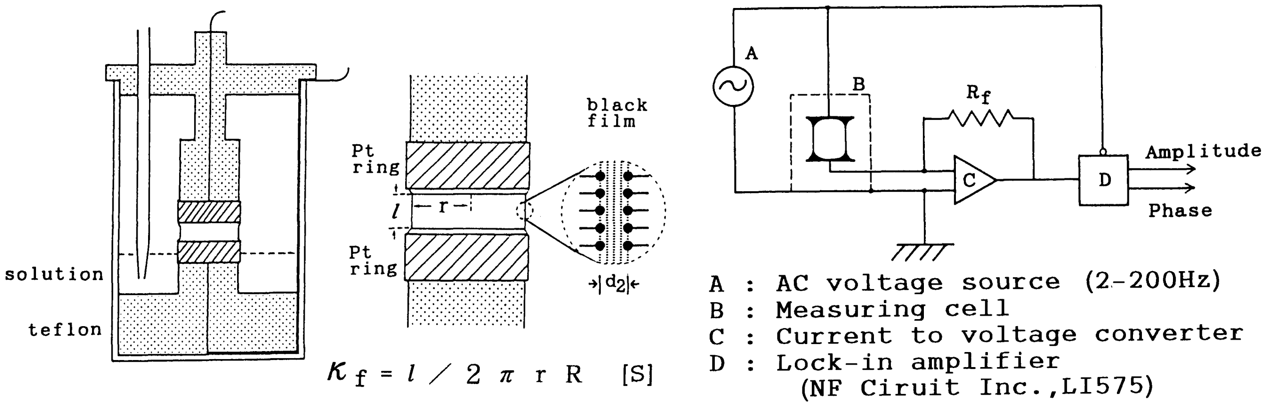

Fig.1. A measuring cell having the three-layer structure of black film and a block diagram of apparatus of conductivity measurements.

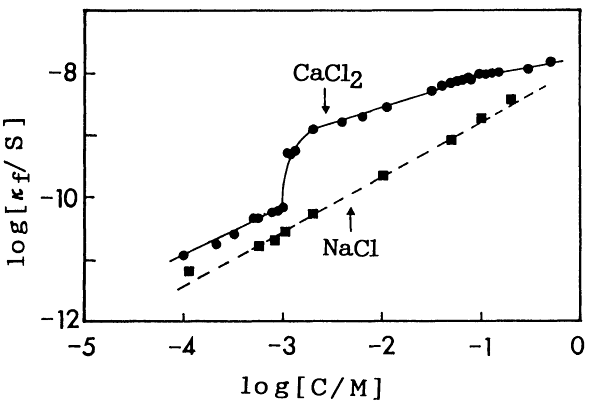

Fig.2. Effect of NaCl and $CaCl_2$ concentrations(C) on the film conductivity of lysoPC at 30 °C.

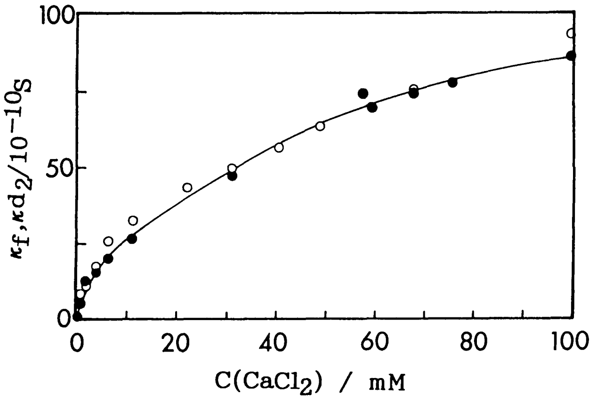

Fig.3. Effect of $CaCl_2$ concentration on the κ_f(●) and κd_2 (○)in the case of lysoPC at 30 °C.

assigned to the fundamental OH-streching frequency at 3400 cm^{-1},using Nicolet 740 equipped with an InSb detector. The spectra were obtained with 300 – 800 scans and spectral resolution 4 cm^{-1}. A molar absorption coefficient of 150 was used to convert the IR absorbance in 3400 cm^{-1} into an equivalent thickness of aqueous core by using Lambert – Beer law. Details have been described in the preceding paper.$^{6)}$

Figure 2 shows the film conductivities of lysoPC equilibrium films against $CaCl_2$ and NaCl concentrations of film-forming solutions. Included in Fig. 3 for comparison are κ_f and κd_2 of lysoPC equilibrium films against $CaCl_2$ concentration. Here the value of κd_2 corresponds to the contribution of the aqueous core to κ_f, assuming that the film-forming solution is in the core of black film. The aqueous solution of pure lysoPC possesses negligible κ of 1.4×10^{-6} $Scm^{-1}$and κ_f of pure lysoPC films is 2.6×10^{-12} S at 30 °C. Figure 4 gives κ_f and κd_2 of lysoPE equilibrium films against $CaCl_2$ concentration of film-forming solutions. The values of κ and κ_f for pure lysoPE are 2.4×10^{-6} Scm^{-1} and 3.9×10^{-11}S at 32 °C, respectively. Included in Fig. 5 for comparison are κ_f and κd_2 for equilibrium films of lysoPC and lysoPE against NaCl concentration of film-forming solutions.

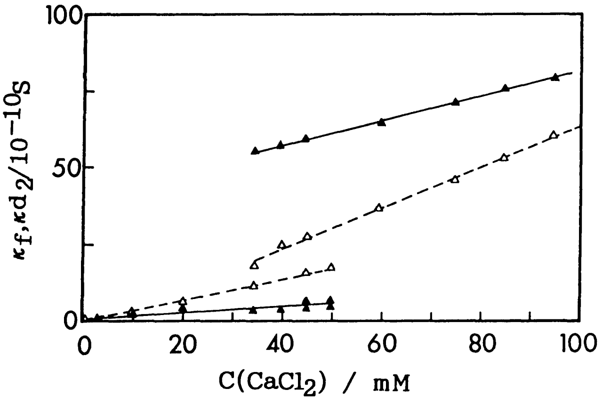

Fig.4. Effect of $CaCl_2$ concentration on the κ_f (—▲—) and κd_2 (--△--) in the case of lysoPE at 32 °C.

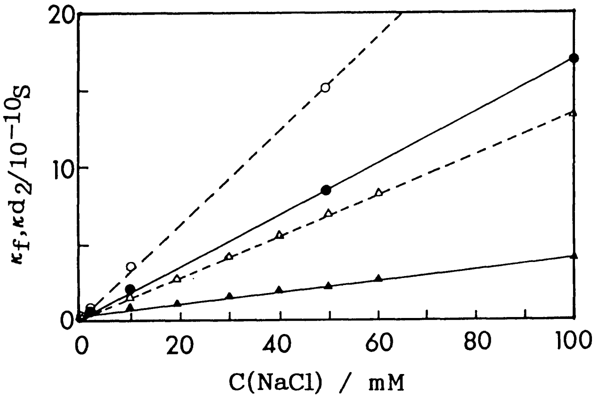

Fig.5. Effect of NaCl concentration on the κ_f and κd_2 of lysoPC(—●—, --○--) and lysoPE(—▲—, --△--).

The type of the equilibrium film and its thickness strongly depend on the concentration and the type of added electrolyte as well as the type of lipid. In lysoPC films, the addition of NaCl exhibits no effect on the core thicknesses of equilibrium films which are Newton black films (NBF) with constant core thickness of 2.5 nm and are observed in the range of the measured concentrations up to 1 M NaCl. Whereas, in the addition of $CaCl_2$ the equilibrium films are NBF with constant core thickness of 2.5 nm at concentration below about 1.1 mM, equilibrium silver films (SF) with core thicknesses from 24 to 15 nm at about 1 – 4 mM, common black films (CBF) with core thicknesses from 15 to 2.5 nm at about 5 mM – 0.2 M and again NBF with 2.5 nm thickness at higher concentrations than about 0.2 to 1 M.

In lysoPE films, when NaCl concentrations of film-forming solutions are above 30 mM, NBF always appears within the thicker film and it extends. At lower concentrations than about 20 mM, however, sometimes NBF appears in the thicker film and extends; at other times no trace of black film appeared even after several hours and the film remains SF. Only the results for NBF are shown in Fig. 5. The core thicknesses of these NBF are very thin, 1.2 nm, and are independent of NaCl concentration. In the addition of $CaCl_2$, at concentrations below about 3 mM sometimes NBF appears and extends, sometimes the film remains SF. In the range of 6 – 30 mM NBF always appears and extends. In the 35 – 50 mM range the equilibrium film is sometimes NBF, sometimes CBF. And in the range of 60 – 85 mM the equilibrium film is only CBF and in the 95 mM – 1 M range the type of black film can not be judged with the naked eye. Further, core thicknesses vary depending on $CaCl_2$ concentration, i.e. 1.2 nm at concentrations below 30 mM and 2.5 nm from 50 mM up to at least

250 mM.

As seen in Figs. 2-5, film conductivities for the equilibrium films of lysoPC and lysoPE greatly depend on their core thicknesses. In Fig. 2 the discontinuous increase of κ_f at about 1 mM $CaCl_2$ in lysoPC film corresponds to the transition from NBF to thicker film (SF). The results of κ_f in Fig. 4 also indicate that in the case of lysoPE the transition of film thickness occurs over 35 – 50 mM $CaCl_2$, which is in agreement with the observation with the naked eye. Film conductivities also depend on the conductivities of film-forming solutions. For example, in NBF, d_2 is independent of electrolyte concentrations, but in both lysoPC and lysoPE films κ_f varies in proportion to the electrolyte concentrations, as shown in Fig. 5. For comparison, we also carried out the conductivity measurement for the κ_f of the NBF formed from sodium dodecylsulfate (SDS) solution containing NaCl.$^{5)}$ In the NBF of SDS, κ_f are very little affected by increasing NaCl concentration, which is distinct from NBF of lysoPC and lysoPE as mentioned above.

It is thought that film conductivity consists of a sum of the contribution from aqueous core and two interfaces of monolayer/aqueous core. So κ_f of both lipids are compared with κd_2. In Figs. 3,4 and 5, it is found that for the NBF of both lipids $\kappa_f < \kappa d_2$, whereas for the CBF the results of both lipids are different, namely, $\kappa_f = \kappa d_2$ for the CBF and the equilibrium SF of lysoPC, whereas $\kappa_f > \kappa d_2$ for the CBF of lysoPE. The results may be interpreted as follows. First, the mobilities of ions are considerably reduced within the NBF of both lipids. Second, assuming that the conductivity in the core of CBF and equilibrium SF is equal to that of the film-forming solution, the contribution to κ_f from monolayer/aqueous core interface is negligible in lysoPC film, but in lysoPE film it is large. This finding in lysoPE films may be correlated to the existence of a two-dimensional hydrogen-bond network formed between the monolayer headgroups and adjacent water molecules.$^{4)}$ However it should be noted that lysoPE film leads to a much reduced swelling by $CaCl_2$ in contrast to lysoPC film which results in a large swelling, as described above. Therefore, it may be considered that the increase of ionic concentration in the aqueous core due to overlapping of diffuse double layers are larger in lysoPE than in lysoPC films. The precise mechanism is not yet clear.

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