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Effect of a magnetic field on charge flow along the interface between phosphatidylcholine monolayer and water

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The specific conductivity along the interface between a phosphatidylcholine monolayer and a surface of pure water has been measured to be approx. 10^{-2} $\Omega^{-1} \cdot cm^{-1}$, which is assigned to be due mainly to protonic conduction (Sakurai, I. and Kawamura, Y. (1987) Biochim. Biophys. Acta 904, 405–409). To get further evidence for the charge flow mechanism along the interface, the effect of application of a magnetic field on the interface conductivity is investigated. On application of a magnetic field, electrical conductivity along the interface was increased or decreased by about 10% depending on the relative orientations of the electric and magnetic fields. The results can be interpreted by an orientational effect, which occurred due to the anisotropy of diamagnetic susceptibility of the monolayer, and the effect of Lorentz force exerted on moving protons, which results in a deflection of the charge pathway. The electrical conductivity of a surface monolayer depends upon the order and arrangement of the polar head network within the monolayer, as well as on the mobility of protons in the network.

Understanding the electrical properties of the surface of a biomembrane or a lipid bilayer provides us with additional insight into the biological function itself. However, previous reports on the electrical properties of biomembranes have focused primarily on the observation of charge transfer through biomembranes due to the penetration of ionic particles into them, as evidenced by the changing pH levels at the inner and outer region of a biomembrane.

On the other hand, the mechanism and the meaning of charge flow along the surface of the biological membrane have ever attracted not so much interest as charge flow through the membrane. The electrical properties along the surface of biomembranes should be important for the movement of ionic particles between the functional protein molecules arranged on the surface of biomembrane, the movement of which should be important for the activation of the protein molecules.

The existence of an efficient proton transfer pathway has been reported for phospholipid surface monolayers on pure water [1–3], which exists along the interface between the surface monolayer and pure water. To explain the electrical conduction in a bulk lipid/water system, an interfacial proton jump mechanism has been proposed [4]. We evaluated the specific electrical conductivity along that pathway as high as approx. 10^{-2} $\Omega^{-1} \cdot cm^{-1}$ for a monolayer/water system of synthetic phosphatidylcholine, L-DPPC (L-α-dipalmitoylphosphatidylcholine), at 25 °C.

In the present paper, an investigation on the effect of magnetic field on the electrical charge flow at L-DPPC/water interface is described. On application of magnetic field, a change in the electrical conductivity of the interface is observed. The results are interpreted to be due to an orientational effect on the monolayers polar headgroup network, and to the effect of the Lorentz force exerted on the charge carriers in the lipid monolayer/water interface by the magnetic field.

The phosphatidylcholine used in the present experiments was L-DPPC obtained from Sigma Co. Ltd., which was used as received without further purification.

Measurements of the lateral electrical properties of a lipid monolayer on water surface under a magnetic field were carried out by placing an experimental arrangement between the poles of an electric magnet.

As Fig. 1 illustrates, the experimental set up was fairly simple. A cylindrical glass vessel, with an inner diameter of 2.7 cm was used as the measuring cell. Two bright platinum electrode plates, 2.0 cm wide and 1.1 cm high, separated by a distance of 1.5 cm were affixed

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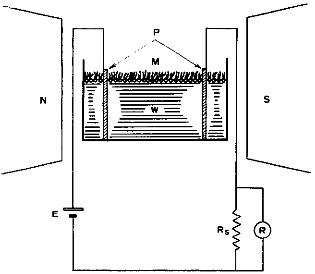

Fig. 1. Schematic illustration of the general experimental arrangement: M = monolayer, W = water, R = recorder, N and S = pole pieces of the electric magnet. In this illustration, the electrodes' setting is for configurations I and II (see the text and Fig. 3).

to the inside of the measuring cell. The measuring cell was connected in series with a voltage source and standard resistor (R_s) of 20 kΩ in order to monitor cell current. In all experiments, a 1.5 V dry battery was used as the dc voltage source.

In order to observe the effect of the magnetic field on the electrical conductivity of the monolayer system, measurements were carried out by placing the platinum electrodes in four different settings (see Fig. 3). In setting I, the electrical field between the two electrodes is antiparallel to the magnetic field. In setting II, the two fields are parallel. In settings III and IV, the two fields are perpendicular with each other, but the direction of electric field is just opposite in the two settings while that of magnetic field is kept the same. Prior to each measurement, the glass cell was washed and filled with 2 cm^3 of pure water, which has a specific resistivity of approx. $1.7 \cdot 10^7$ Ω·cm. After having poured pure water into the glass measuring cell, a voltage drop, V_0, across R_s was recorded with and without a magnetic field of 7.5 kG. V_0 is proportional to the cell current without a surface monolayer, and along with the geometrical factor of the cell, gives us the conductivity of the water used.

When the initial transient current change had subsided, one drop of 0.01 g of L-DPPC/chloroform solution with a concentration of 0.2 wt% was placed on the water surface. The drop of solution spread swiftly on the surface and as soon as the L-DPPC monolayer had developed on the water surface, V_0 suddenly increased by ΔV (see Fig. 2). The magnitude of ΔV, which corresponds to the increase of cell current on expanding the surface monolayer, gives the electrical conductivity along the interface as has been discussed in Ref. 1. The magnitude of ΔV depends slightly on the origin and geometrical factor of platinum plate and/or the lot of phosphatidylcholine, giving a slightly different value of the interface conductivity. The order of magnitude, however, remains the same.

We previously calculated that a lipid concentration of 0.014 wt% was required in order to cover the entire surface of the water within the present measuring cell with a surface monolayer [1]. A concentration in excess of 0.014 wt% did not effect ΔV. When a more concentrated solution was used to expand a surface monolayer, the excess molecules aggregated making an 'island' on the surface and went down to the bottom of the cell remaining, probably, a monolayer on the water surface [1]. The lateral pressure of the resulting monolayer was approx. 40 to 43 dyne/cm and the monolayer existed in a crystalline form [1].

ΔV remained constant for approx. 10–20 min. Fig. 2 represents a typical record of voltage across R_s against time for the L-DPPC at about 20 °C. Further details of this experimental procedure were described elsewhere [1]. The ΔV values, which are proportional to the conductance of the interface region between the polar headgroup network of the monolayer and water, were measured under each of the four different settings of the electrical field in relation to the magnetic field. The results are illustrated in Fig. 3, where ΔV is the averaged value of about 20 measurements under each of the four electrode settings in relation to the magnetic field. We found that placing a drop of L-DPPC/chloroform solution on the water surface and developing a monolayer under the magnetic field gave slightly different ΔV values from that obtained without the magnetic field. The change in ΔV with different settings of the two fields were small. When the magnetic field is weak, the effect of the magnetic field on ΔV is also small. Accordingly, when the interface region was exposed to a magnetic field of only 3.9 kG or 1.2 kG, there was not sufficient observable interaction with the magnetic field

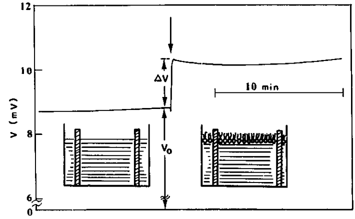

Fig. 2. Typical record of the voltage drop across R_s for L-DPPC monolayer from 0.2 wt% chloroform solution at 25 °C, $E = 1.5$ V dc, and without magnetic field. The arrow indicates the point where the L-DPPC/chloroform solution was put on the water's surface.

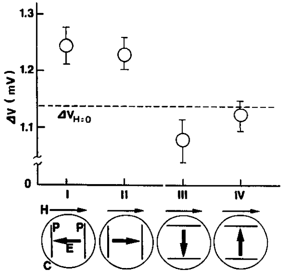

Fig. 3. Four different settings of the electrical (*E*, thick arrow) and the magnetic (*H*, thin arrow) fields (bottom) and average values of ΔV obtained for each of the four different settings at 20 ° C (top). In the bottom, C is the measuring cell, P are the electrodes. The symbols I, II, III and IV are for the identification of each setting. In the top, the broken line represents the value of ΔV obtained without magnetic field and the vertical lines for each of the four points represent the standard deviation obtained from 20 experiments.

to make the effect of it on the resulting ΔV values reliable.

Fig. 3 plots each of the obtained average values of ΔV values for the four different electrode settings under a magnetic field of 7.5 kG, as well as those of ΔV obtained without any magnetic field. For convenience, average values for the settings I, II, III and IV are expressed as ΔV_{I}, ΔV_{II}, ΔV_{III} and ΔV_{IV}, respectively. Measurements which carried out without application of the magnetic field are expressed as $\Delta V_{\mathrm{H}=0}$.

By plotting the various values of ΔV as in Fig. 3, we can easily summarize the present results by the following relationship: $(\Delta V_{\mathrm{I}} \cong \Delta V_{\mathrm{II}}) > \Delta V_{\mathrm{H}=0} > (\Delta V_{\mathrm{III}} < \Delta V_{\mathrm{IV}})$, i.e. (i) ΔV_{I} is nearly equal to ΔV_{II}, (ii) ΔV_{I} and ΔV_{II} are larger than $\Delta V_{\mathrm{H}=0}$, while ΔV_{III} and ΔV_{IV} are smaller than $\Delta V_{\mathrm{H}=0}$, and (iii) ΔV_{III} is slightly smaller than ΔV_{IV}.

We can list up two possible effects of the magnetic field on the surface monolayer system. The one is the orientational effect of the magnetic field which occurred due to the diamagnetic anisotropy of the surface monolayer. The other is the effect of Lorentz force exerted on moving charge carriers in the magnetic field. In the following we will discuss the two in turn.

The result (i) shows that the inversion of the magnetic field relative to the electrical field does not induce any change on the magnetic field effect observed on these configurations of the fields. This implies the orientational effect of the magnetic field, *H*, through the anisotropy of diamagnetic susceptibility, since the effect depends on H^2 and the inversion of the field direction does not affect anisotropic magnetic energy, *F*, given by

$$F = \tfrac{1}{2} v \Delta\chi H^2$$

In this equation, v and $\Delta\chi$ represent the volume of an orienting unit and the magnitude of diamagnetic susceptibility anisotropy of it, respectively. As the orienting unit, we may take a surface monolayer plate of about 100 μm in lateral dimension, since observation through an electron and optical microscopes show that surface monolayers are not a completely homogeneous mono-molecular film but of a mosaic structure with the lateral dimension of each mosaic domain is to be about 100 μm [5,6]. As for $\Delta\chi$ of phosphatidylcholines, a value of $\Delta\chi \cong 10^{-7}$ cgs in the case of a single crystal of L-DPPC in a xylene suspension [7], $\Delta\chi \cong 10^{-9}$ cgs in the case of L_{α} phase egg yolk phosphatidylcholine [8] and $\Delta\chi \cong 10^{-11}$ cgs in the myelin figures of egg yolk phosphatidylcholine [9] are reported.

Using these values of $\Delta\chi$ and assuming the size of the orienting unit to be of 100 μm in diameter (i.e., the lateral dimension of a mosaic) and of 30 Å in thickness (i.e., the thickness of surface monolayer), we can make a rough estimate of *F*. The values of *F* thus obtained ranges between 10^{-10} and 10^{-12} erg for $H = 7.5$ kG. The thermal energy kT at 25°C, on the other hand, is in the order of 10^{-14} erg, so the following relationship is concluded for the present case: $kT \ll F$. This suggests that *F* is sufficient to orient the mosaic of phosphatidylcholine monolayer on the water surface under the experimental conditions. Consequently, the result (ii) can be attributed probably to a biaxial orientation of the mosaic domain. Indeed a biaxial orientation of L-DPPC plate like crystallites has been observed under a magnetic field [7]. The dipoles at polar heads of phosphatidylcholine within each mosaic domain make a herring-bone type arrangement in the monolayer plane [10], and they become oriented by the magnetic field. Therefore, in the configurations I and II, it is possible for the polar headgroup network in the interface region to favourably orient for an enhancement of protonic conduction through the hydrogen bonds in the network, whereas in the configurations III and IV the orientation of electric dipoles is not favourable for protonic conduction, since in the latter case the magnetic orientation of the mosaic domain relative to the electrical field differs $\pi/2$ compared to the former case. At the present stage of the study, however, the detailed mechanism of orientation effect is not clear.

If the magnetic field of 7.5 kG was applied to the monolayer after it had developed on the water surface, no field effect was observed in ΔV. Once the monolayer has been expanded on the water surface, the steric hindrance between mosaic domains may suppress the free rotation of domains under the magnetic field. Consequently, the magnetic orientation only occurs during the expansion of monolayers.

The result (iii) is difficult to explain as a manifestation of the magnetic orientation effect since ΔV_{III} and ΔV_{IV} seem to differ from each other, i.e. ΔV_{III} is slightly smaller than ΔV_{IV}, and the two fields are perpendicular with each other. The configurations of two fields for ΔV_{III} and ΔV_{IV} imply that the result comes from the effect of Lorentz force. Indeed, the Lorentz force acting on the charge current is such that in the configuration III, the charge pathway is deflected upward. Consequently, the charges which flow in the interface between the polar headgroup network of phosphatidylcholine and water may be trapped in the network. In the configuration IV, on the other hand, the charge pathway may be deflected downward by the Lorentz force. Despite this action by Lorentz force, all of the charges in the pathway can arrive at the opposing electrode, and, accordingly, ΔV_{IV} can show a larger value than that of ΔV_{III}.

Next, we will roughly estimate how much of the charge pathway can be expected to be deflected by that much of a magnetic field of 7.5 kG. To carry out an order estimation of the effect, we assume that the conductivity σ of the interface region of the monolayer system can be approximated by a free-charge-gas model as $\sigma \cong ne^2\tau/m$, where n represents the number of charged particles per unit volume, e the charge of particle, τ the collision time, and m the mass of the particle. By use of the values $\sigma \approx 10^{-2}\ \Omega^{-1}\cdot\mathrm{cm}^{-1}$ evaluated from experimental results as described previously [1], $n \approx 6\cdot 10^{17}\ \mathrm{cm}^{-3}$ evaluated from an assumed surface pH value 3 [2,3], $e \approx 1.6\cdot 10^{-19}$ C, and $m \approx 1.7\cdot 10^{-24}$ g for proton, τ is estimated as $1.1\cdot 10^{-13}$ s. This is roughly compatible with the collision time of a proton jump through a hydrogen bond. Assuming the drift velocity, v of particle to be the thermal average, i.e. $v \approx (2kT/m)^{1/2} \approx 2\cdot 10^5$ cm/s, we can obtain a rough estimate of the mean free path, l, of the particle to be $l \approx v\tau \approx 2\cdot 10^{-8}$ cm, which corresponds well to a hydrogen bond length. The estimation of the magnitude of deflection length of the particle perpendicular to the water surface after a particle had travelled the distance between the two electrodes, which was $d \approx 1$ cm, is easily carried out based upon the elementary electromagnetic theory. The magnitude of deflection of a particle perpendicular to the monolayer, during the travelling time $T \approx d/v \approx 10^{-5}$ s, is estimated to be $\approx 600\cdot 10^{-8}$ cm. If the charged particles are assumed to be electrons, then the deflected length becomes a value more than 2000-times larger than would be the case were the charged particles protons. Still, with such a large deflection distance it is difficult to explain why the difference between ΔV_{III} and ΔV_{IV} is so slight. It follows then, that the charged particles could be protons, and the magnetic field of 7.5 kG is strong enough for a charge carrier to be deflected away from the conduction pathway.

Thus the magnetic field effects on the lateral electrical conduction along the lipid surface monolayer can be consistently interpreted by protonic conduction process. As reported before [1], the observation of the isotope effect on the conduction behaviour strongly suggests that charge carriers are protons. We can roughly estimate the diffusion constant D of charge carriers along the surface monolayer from the present electrical measurements, which is $D \approx l^2/2\tau \approx 10^{-2}\ \mathrm{cm}^2/\mathrm{s}$. The apparent diffusion constant thus obtained is compatible with that evaluated by Teissié et al. [3] to explain the result of a diffusion experiment.

In conclusion, the observed magnetic field effects result from an orientation effect which is caused by the diamagnetic anisotropy on the surface monolayer as well as from the Lorentz force acting upon moving protons. The electrical conductivity parallel with the magnetic field is slightly increased by the orientational effect. This behaviour implies that the charge flow along the interface region between the L-DPPC surface monolayer and pure water depends upon the order and arrangement of the polar head network within the surface monolayer.

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