

The Measurement of Maxwell Displacement Current of Phospholipid Monolayers on the Water Surface

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ABSTRACT

The organization of phospholipid monolayers and their monolayers mixed with fatty acid containing azobenzene on the water surface was investigated by means of the displacement current measurement method. The phase transition from the gaseous phase to the gaseous-fluid phase which accompanies the polar ordering of phospholipid molecules was detected in the range of immeasurably low surface pressure. The molecular area which gives the onset of the transition was determined for phospholipid monolayers. The Maxwell displacement current (MDC) pulses were generated across mixed monolayers due to the photoisomerization of fatty acid containing azobenzene by alternating irradiation of ultraviolet and visible light, because the condensation of pure azobenzene monolayers was loosened by the introduction of phospholipids into the monolayers. The displacement currents generated during light irradiation were also investigated in connection with monolayer compression cycles. It was found that the maximum of MDC appeared at the molecular area just before the initial rise of surface pressure in compression cycles.

I. Introduction

Monolayers of lipid on the water surface have attracted much attention not only as models of biological membranes, but also as precursors of multilayer systems promising many technical applications¹⁾. We have been investigating the reorganization of monolayers on the water surface by means of displacement current measurement method, which allows molecular motions to be probed without destroying the

monolayers. This method can give essential information on the polar orientation order in monolayers.

Recently, much attention has been paid to the artificial lipid membranes containing azobenzene derivatives as a model of visual light processing because of their similarity to biological membranes²⁾. The azobenzene derivatives undergo reversible cis-trans photoisomerization in the artificial membranes, because the condensation of pure azobenzene monolayers is loosened by the introduction of phospholipids into

the monolayers, and the molecular aggregation in pure azobenzene monolayers is also weakened by the introduction of phospholipids. Molecular switching between cis and trans-forms in mono- and multilayer systems containing azobenzene is of particular interest in physics, chemistry and electronics, because of the possible applications to optical memories and information storage devices³⁾.

In the present paper, we investigated the reorganization of phospholipid monolayers and the molecular motion even in the range of immeasurably low surface pressure by means of the MDC. We then discuss the charge flow and displacement currents generated by photois-

omerization in phospholipid and fatty acid containing azobenzene mixed monolayer systems on the water surface.

II. Materials and Experimental Method

1. Materials and Experimental Setup

L- α -Dilauryl phosphatidylcholine (denoted as DLPC) and 4-octyl-4'-(5-carboxyl-pentamethyleneoxy)-azobenzene (denoted as 8A5H) were commercially supplied by Sigma and Dojin Kagaku, respectively, and they were then used in present investigation as received without further purification. The chemical structures of these molecules are shown in Fig. 1. The DLPC phospholipid molecule has one phosphatidylcholine head group (hydrophilic group) and two long saturated alkyl chains with a carbonyl group (hydrophobic group). Figure 2. shows a schematic diagram of the experimental setup used here. It was the same as that previously used⁴⁾. Briefly, the setup consisted of a Wilhelmy-type film balance, a 500W Xenon lamp source, and electrodes 1 and 2 which were connected to each other through a sensitive ammeter. Electrode 1 was suspended in air parallel to the water surface and electrode 2 was immersed in the water subphase. Electrode 1 was a transparent electrode whose working area was 44.5 cm². The spacing between electrode 1 and the water surface was 1.0mm. The water subphase (pH 5.8) was kept at a temperature of 20 \pm 1 $^{\circ}$ C.

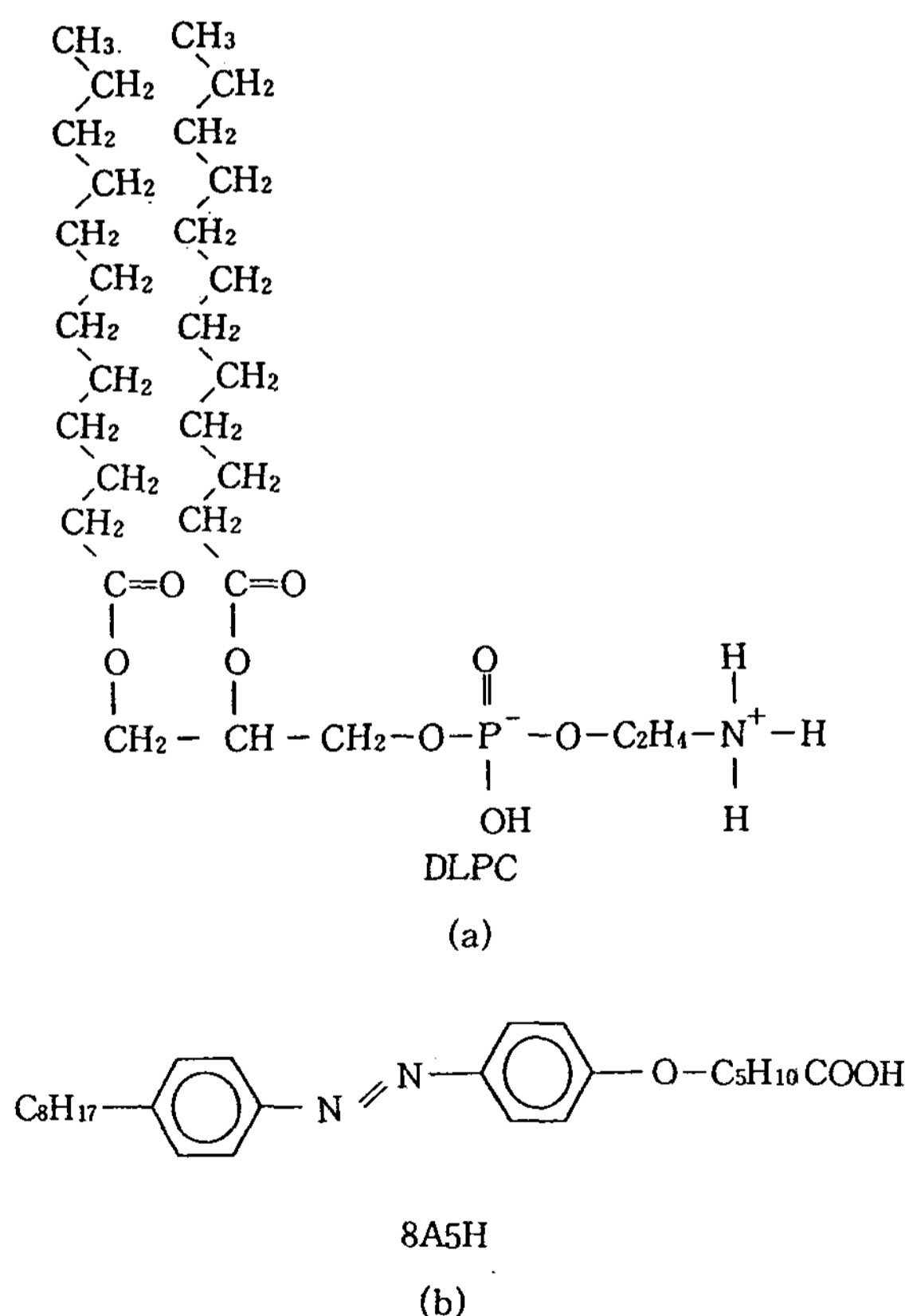


Fig. 1. Molecules used in the present study.
(a) DLPC and (b) 8A5H.

2. MDC Measurement

Monolayers composed of DLPC and 8A5H in molar ratios of 2:1, 1:1 and 1:2 were spread from chloroform solutions with a concentration of 0.2mol/liter on the surface of pure water in a Langmuir trough (150 \times 730mm) using a microsyringe. The monolayers formed on the water surface were compressed with constant barrier

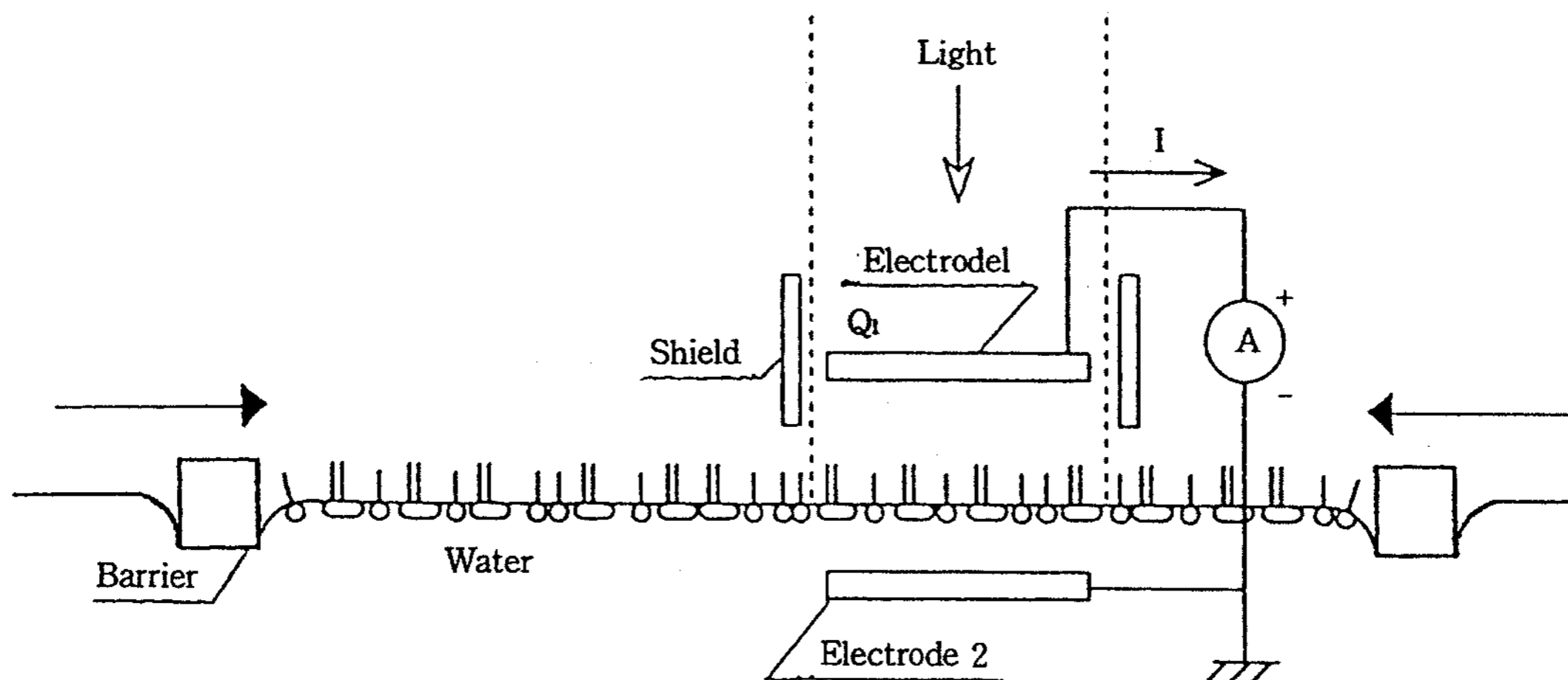


Fig. 2. Schematic diagram of the experimental setup used for the present study.

velocity of 40.0mm/min using two moving barriers. After spreading the solution of phospholipid and 8A5H mixed molecules onto the surface of water, we let it stand 10min to evaporate the chloroform and to form a stable monolayer on the water surface. The displacement current-molecular area ($I-A$) isotherm was monitored together with the surface pressure-molecular area ($\pi-A$) isotherm during the monolayer compression. In the present experiment, we compressed and expanded monolayers cyclically and recorded the $\pi-A$ and $I-A$ isotherms. Charge flowing through the ammeter (ΔQ_1) was also monitored with the $I-A$ isotherm. The MDC induced by photoisomerization was also measured in a manner similar to that in our previous study except that we measured MDCs for monolayers compressed in the compression cycles⁴ by irradiating monolayers successively with ultraviolet (UV, λ_1) and visible light (λ_2) outputs of the Xenon lamp through appropriate band-pass filters. The intensity of UV(360nm in wavelength) and visible (450 nm in wavelength) light was 2.52 and 0.120 mW/cm², respectively.

III. Results and Discussion

1. MDC Measurement by DLPC Monolayer Compression

Figure 3. show an example of the MDC across DLPC monolayer in the range of immeasurably low surface pressure. The monolayer was compressed in the range of molecular area A from 200 to 40Å² by moving the barriers at a speed of 40mm/min. At the beginning of the compression, the MDC was not generated across DLPC monolayers. Although the surface pressure change was not detected for molecular areas $A > 90\text{Å}^2$ and the MDC was generated at $A < 120\text{Å}^2$ for DLPC monolayers. Regions 1 and 2 were divided at the area per molecule A_i at which the MDC flow was initiated by monolayer compression. The molecular areas(A_i) used here was $A_i = 130 \pm 10\text{Å}^2$ for DLPC. It was found that the onset of the generation of the MDC depended on the length of the hydrophobic alkyl chains in phospholipids, and the molecular area A_i increased as the length of the alkyl chains increased.

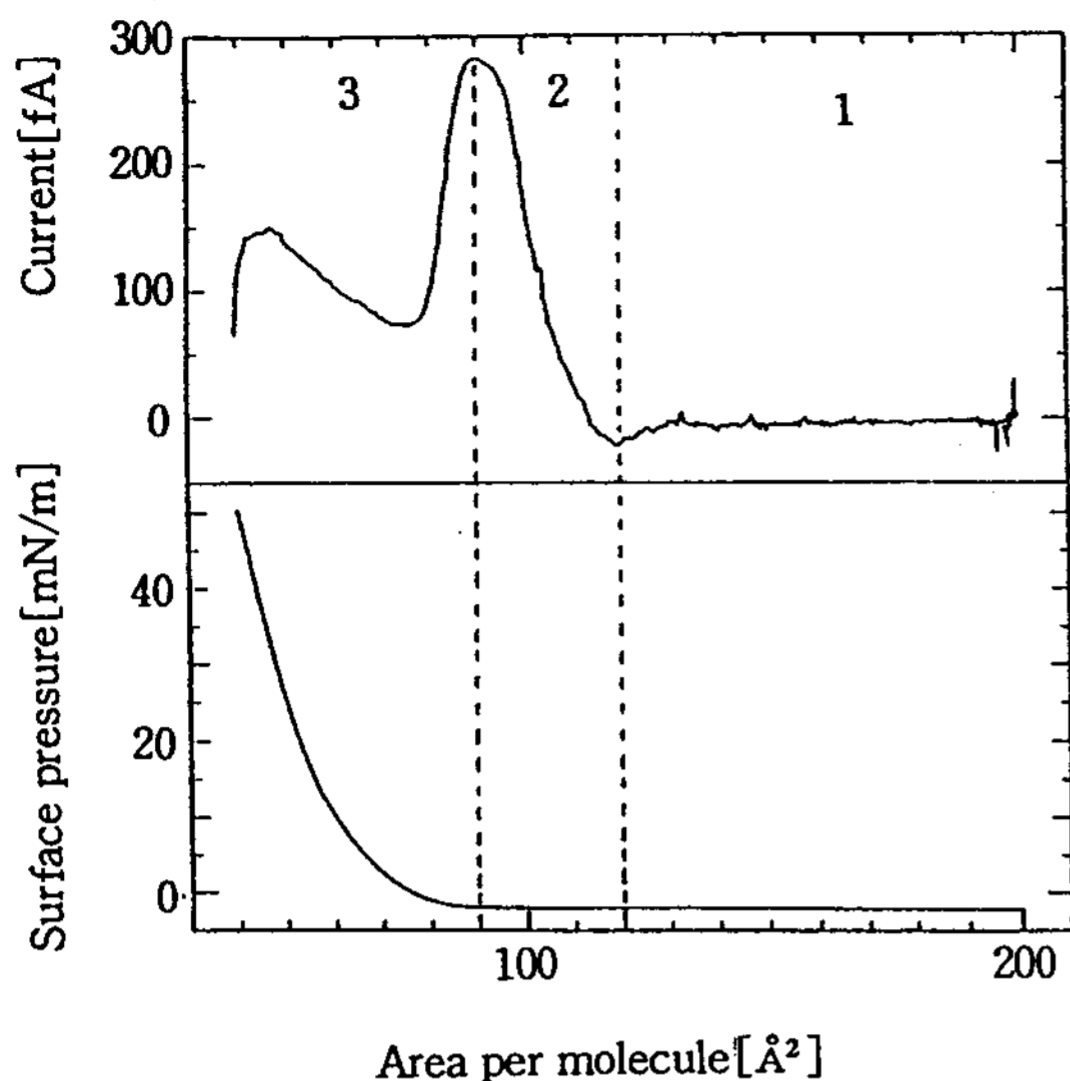


Fig. 3. A typical example of the displacement current measurement for DLPC monolayers on the surface with monolayer compression in the range of immeasurably low surface pressure: π -A and I -A Isotherms (from bottom to top).

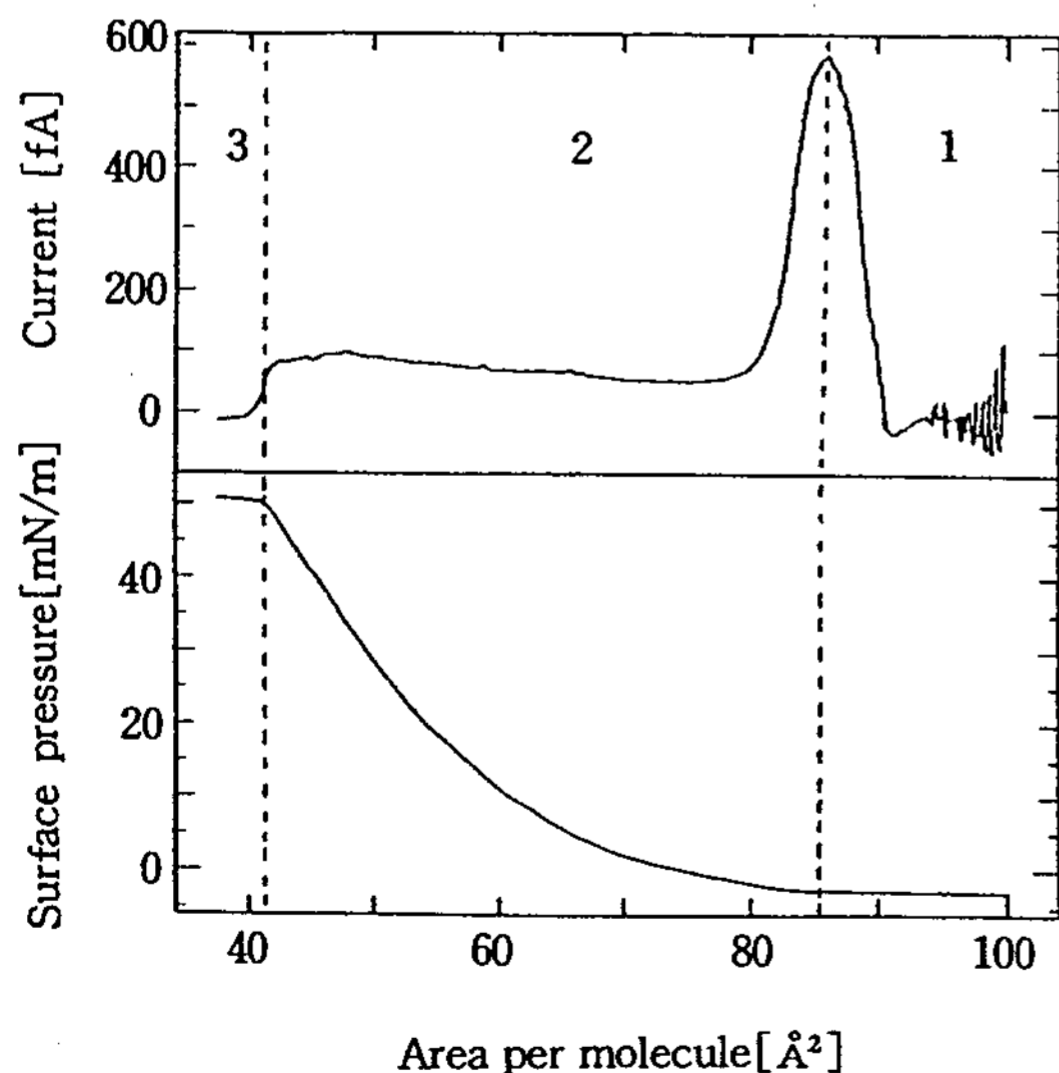


Fig. 4. A typical example of the displacement current measurement for DLPC monolayers on the surface with monolayer compression: π -A and I -A Isotherms (from bottom to top).

Figure 4. show the MDC for DLPC monolayers in the range of molecular area $A < A_i$. The monolayers were compressed in the range of area per molecule A from ca. 100 to 38 \AA^2 . The I - A isotherm strongly depended on the lipids. Briefly, for DLPC monolayers, one large MDC peak appeared during the monolayer compression.

The I - A isotherms corresponded well to the trace of the π - A isotherms. Judging from the trace of the MDC obtained in the experiment, we divided I - A and π - A isotherms as in the figure. In this study, regions 1-3 were examined. The magnitude of the MDC current generated in region 3 was inversely proportional to A^2 .

2. MDC Measurement by Mixed Monolayer Compression

Figure 5. show an example of MDCs across DLPC and 8A5H mixed monolayers during the first monolayer compression cycle. Curves 1, 2 and 3 show the experimental results for DLPC and 8A5H mixed monolayers in molar ratios of 2:1, 1:1 and 1:2, respectively. Mixed monolayers were compressed in the range of molecular area A from 133.4 to 25 \AA^2 by two barriers at a speed of 40 mm/min , where the molecular area A is defined as

$$A = \frac{S(A)}{N_A + N_B}$$

Here $S(A)$ is the area, where monolayers are formed, N_A and N_B are the number of DLPC and 8A5H molecules on the area $S(A)$.

At the beginning of the first compression, MDC was not generated across DLPC and 8A5H mixed monolayers. However, one MDC peak was generated in the range of molecular area before the initial rise of surface pressure.

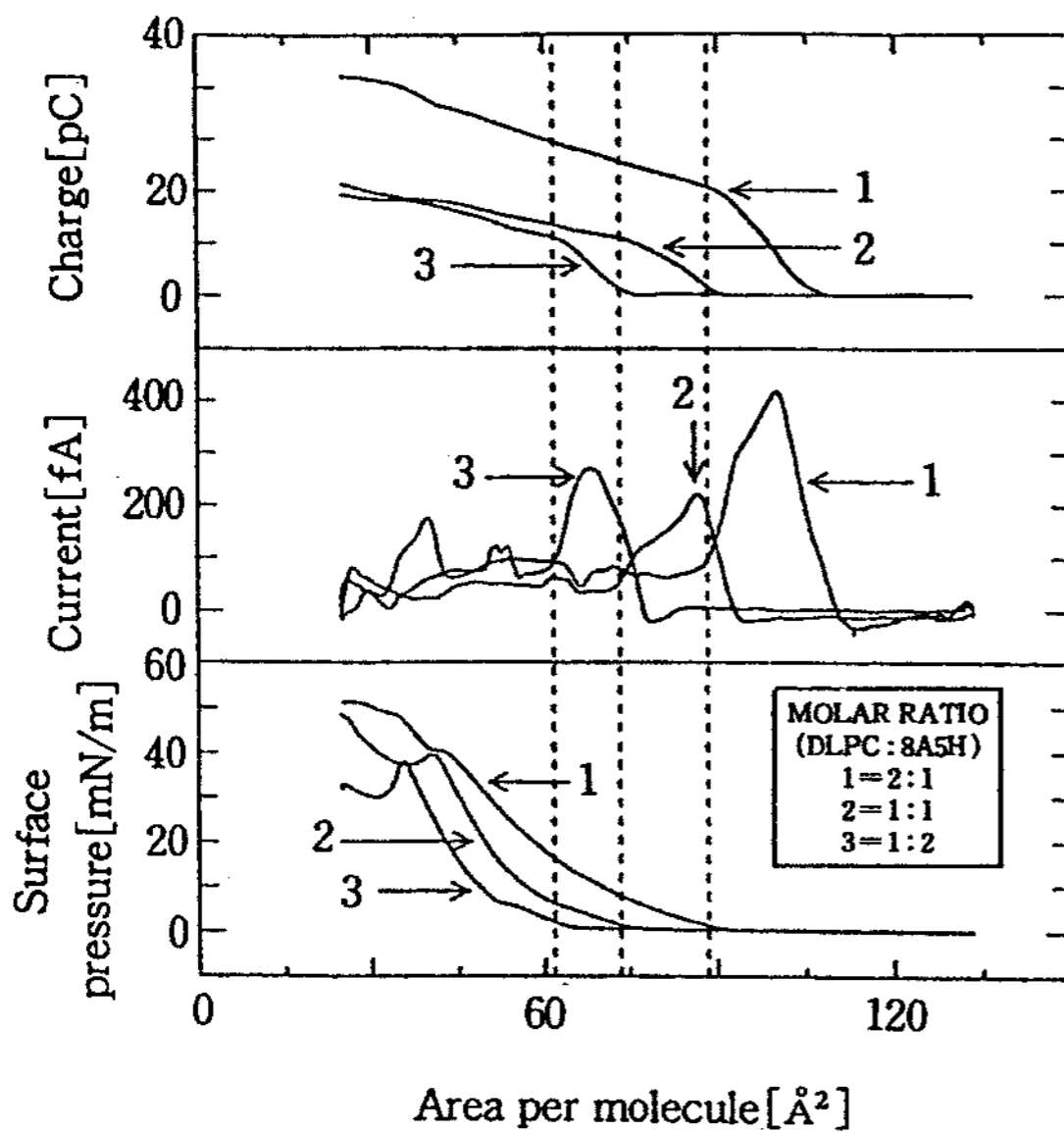


Fig. 5. Charge, Current and Surface pressure—Area curves of DLPC—8A5H mixed monolayers composed of the various molar ratios at the compression.

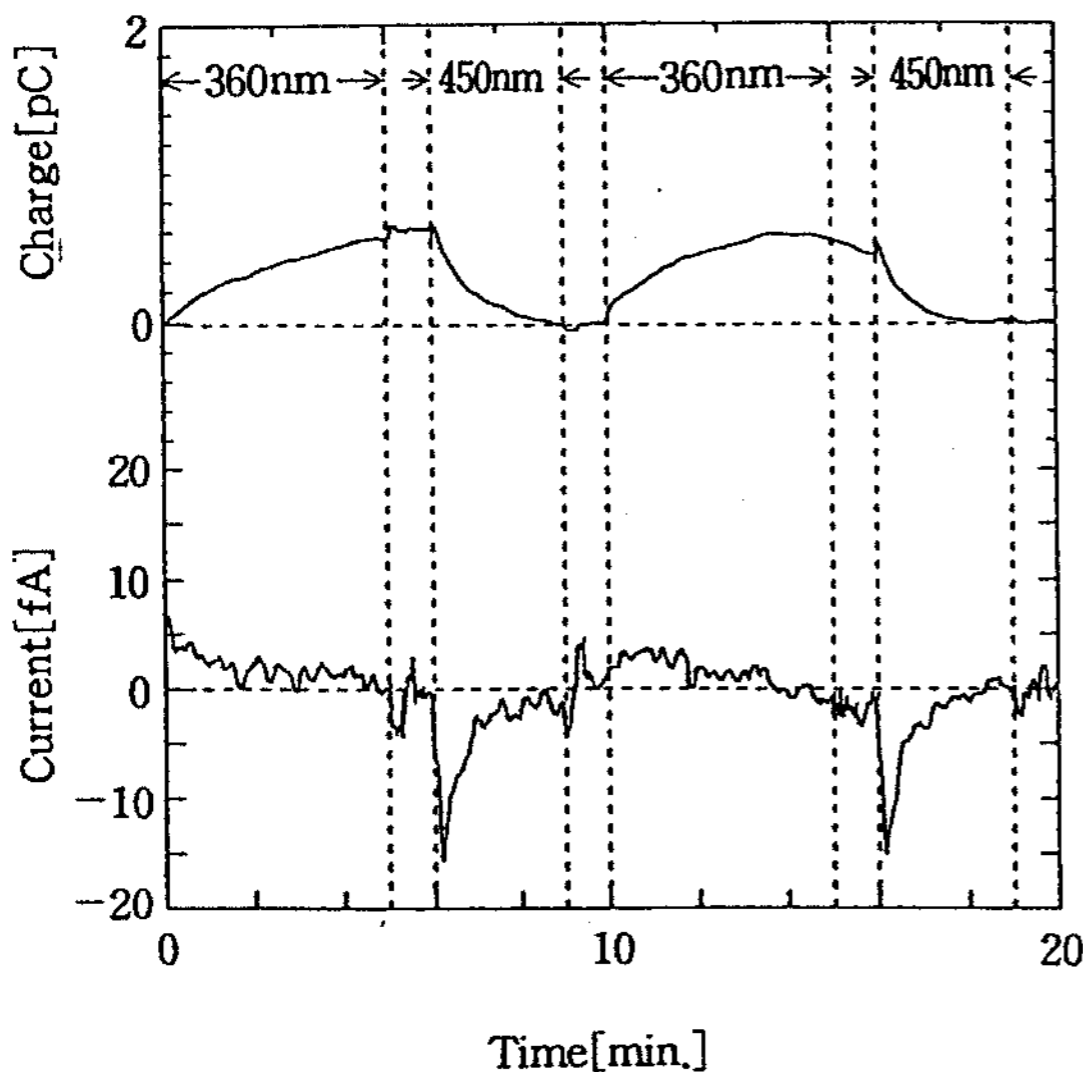


Fig. 6. A typical example of the displacement current across DLPC—8A5H mixed monolayers of the trans type with a molar ratio of 2 vs. 1 by the alternating photoirradiation at the molecular area of 90 \AA^2 for the compression.

That is, one MDC peak is observed in the range of molecular area $A > 87 \text{ \AA}^2$ in curve 1, in the range of $A > 73 \text{ \AA}^2$ in curve 2, and in the range of 63 \AA^2 in curve 3. The charge ΔQ_1 gives a kink at the molecular area corresponding to the onset of the initial rise of the surface pressure.

3. Displacement Current Generated by the Photoirradiation

The displacement current was never generated by photoirradiation when monolayers were not formed on a water surface⁵⁾. Similarly, the displacement current was never generated from pure DLPC monolayers on a water surface by the photoirradiation, because the monolayers were not photoreactive⁶⁾. In contrast, the displacement current was generated from the DLPC—8A5H mixed monolayers by the alternating photoirradiation with UV light ($\lambda_1 = 360 \text{ nm}$) and visible light ($\lambda_2 = 450 \text{ nm}$).

Figure 6. shows a typical example of the displacement current generated from the DLPC and 8A5H mixed monolayers in molar ratio of 2 : 1. Figure 6 was obtained at the molecular area of around 90 \AA^2 just before the initial rise of the surface pressure during the monolayer compression cycle. Similar experimental results were obtained in the entire range of the molecular area for the compression cycles. In other words, the displacement current was generated in the whole of the molecular area, although the magnitude of the current changed as a function of molecular area A . Briefly, the alternating UV and visible light irradiation generated displacement current flowing in a direction from electrode 1 to electrode 2 (defined as the positive direction) when UV irradiation was applied and in the opposite direction from electrode 2 to electrode 1 (defined as the negative direction) when visible light was applied. The total charge flowing through the circuit during

irradiation with visible light was almost the same as that flowing during irradiation with UV light. On the other hand, the photoirradiation twice in succession with visible or ultraviolet light (not shown) never generated the displacement current.

As we mentioned above, displacement current is generated from the mixed monolayer systems in the whole range of the molecular area by the alternating photoirradiation with UV and visible light. In contrast, displacement current was not generated by the alternating photoirradiation from pure 8A5H monolayers after the liquid-crystalline transition, possibly because of the closely packed condensation of 8A5H molecules and high aggregation of 8A5H molecules among them⁷⁾. We concluded that the introduction of phospholipids into pure 8A5H monolayers is very effective in the generation of MDC by photoisomerization of 8A5H molecules.

IV. Conclusions

In the present paper, we applied the Maxwell displacement current measuring method to examine the generation of MDC due to the cis-trans photoisomerization in phospholipid-fatty acid containing azobenzene mixed mon-

olayer systems on the water surface. It was found that the introduction of DLPC molecules into a pure azobenzene monolayer gives a direct effect on the generation of displacement current due to cis-trans photoisomerization. Finally, We concluded that the maximum of MDC appeared at the molecular area just before the initial rise of surface pressure in compression cycles.

References

1. Roberts, G., "Langmuir-Blodgett Films", Plenum, New York(1991).
2. Yamaguchi, H. and Nakanishi, H., Proceedings of Sixth International Conference on Organized Molecular Films, p-14b. 7, p.485 (1993).
3. Ashwell, G. J., Nature 347, 617(1990).
4. Naruse, H., Onishi, K., Iwamoto, M., Ichimura, K., Seki, T. and Tamaki, T., Jpn. J. Appl. Phys. 32, 2832(1993).
5. M. Iwamoto, Y. Majima, H. Naruse, T. Noguchi, and H. Fuwa, J. Chem. Phys. 95, 8561 (1991).
6. Lee, K. S. and Iwamoto, M., J. Coll. Inter. Sci., 177, 414(1996).
7. Iwamoto, M., Majima, Y., and Naruse, H., J. Appl. Phys., 72, 1631(1992).