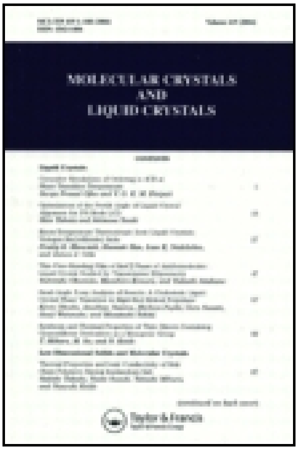

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MEASUREMENT OF THE DISPLACEMENT CURRENT ACROSS MONOLAYERS AT THE AIR-WATER INTERFACE USING KUHN-TYPE LB FILM APPARATUS

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Abstract A number of methods have been developed to investigate the physical properties of monolayers formed at the air-water interface. Among them, the displacement current method is appropriate for the investigation of the dynamic behavior of monolayers. The measuring system of displacement current method was constructed at home-made Kuhn type LB deposition apparatus using aluminum plate electrode. The currents induced by the dynamic motion of molecules were measured when the molecules were pressed by barrier. To verify the measuring system, we used 4-octyl-4′-(5-carboxy-pentamethyleneoxy)azobenzene molecules which has two remarkable variations of surface pressure of monolayer at the air-water interface. We can detect the two peaks of displacement currents which shows that the orientations of molecules are changed greatly at the state of these two remarkable changes of surface pressure.

INTRODUCTION

Molecular electronic device was a new concept in 1980s. But recently, it came to be familier to the reserchers in various fields. Especially, many researchers of electronic field have much intrests to find the functional behavior of organic molecules which can be aggregated as a monolayer film by using the Langmuir-Blodgett(LB) deposition method. LB deposition method was invented by I. Langmuir and K.B. Blodgett of General Electric Research Laboratory in 1930s and it was improved by H. Kuhn of Marks Flanck Laboratory in 1960s.[1] This improved one is called Kuhn-type LB film apparatus in which the moving barrier is drived by a mass of the weight. Recently, many other types of apparatuses were developed to drive the barrier by motor which is controlled by computer. Together with the improvement of these apparatuses, a number of techniques to investigate the physical properties of monolayers at the air-water interface were also developed. Among them, ellipsometric method, fluorescence microscopic method, surface potential measuring method and displacement current measuring method can be used to investigate the physical properties of monolayers at the air-water interface without destroying the monolayers.

M. Iwamoto of Tokyo Institute of Technology invented the displacement current measuring method.[2] This method has a simple mechanism constructed by two parallel plate electrodes to measure the current in order to investigate the electrical properties of monolayers at the air-water interface. In this method, displacement current due to a change of induced charge on an electrode suspended in air is measured together with a surface pressure-area isotherm with compressing the monolayer by barrier. Since the displacement current is generated only when the induced charge on the electrode suspended in air is changed with respect to time, the dynamic behavior of monolayers can be monitored by measuring the displacement current.

In this paper, we have constructed the displacement current measuring system at a home-made Kuhn-type LB film apparatus. We investigated the dynamic behavior of the polar molecules on the air-water interface by using azobenzene-containing long-chain fatty acids due to the compression of barrier.

EXPERIMENTS

Experimental Setup

Figure 1 shows the experimental setup. Kuhn-type LB apparatus was made by poly-tetra-fluoroethylene(PTFE). This LB apparatus and the current measuring circuit were placed in an electrically shielded box which was grounded to earth. The current measuring system was composed of a pair of electrodes and a sensitive electrometer(Keithley 617). Two aluminum plate electrodes were placed to be parallel to the surface of the water, and electrically connected each other through the electrometer. Electrode 1 was suspended in air by attaching to a micrometer and this electrode and the micrometer were electrically separated by inserting an insulator(PTFE bar) between them.[3] Electrode 2 was placed in the water. The area of each electrode was 36[cm^2]. The micrometer was used to adjust the distance between electrode 1 and the water surface accurately. The distance (d_1) from water surface to electrode 1 was 1[mm]. Electrode 1 was surrounded by aluminum shield plate to protect the effect of charges induced on the barrier. The PTFE barrier was known to have negative charges on the water from this experiment. The analog data of measured current was sent to the microcomputer through A/D converting interface card.

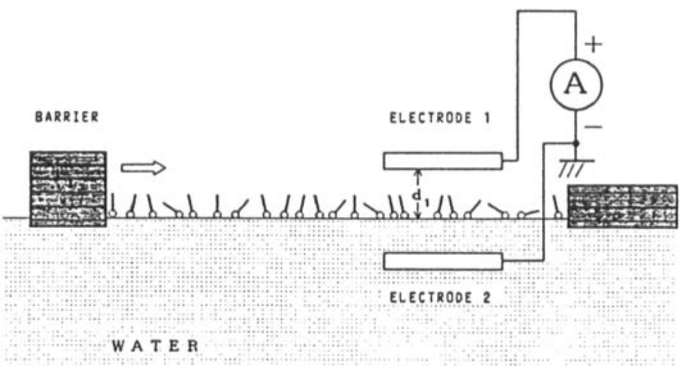

FIGURE 1 The experimental setup.

In a conventional Kuhn-type LB apparatus, it is hard to move the barrier continuously to the both direction of the front and the rear, because the barrier is pulled only to the front direction by a gravitational weight which is connected to the barrier by a thin thread. When the barrier begins to compress molecules, the surface pressure of a monolayer increases immediately to the maximum value which is determined by a mass of the weight.
For the reasons, we had to modify the driving mechanism of barrier to apply the principle of the displacement current measuring method in Kuhn-type apparatus. A massive weight was hung on with a

thread to move the barrier toward the rear direction of apparatus and a motor driven round bar was used to wind the thread to move the barrier to both direction.

In many improved LB apparatuses the barrier position can be easily monitored by computer. But in a Kuhn-type LB apparatus, the barrier is very sensitive to a friction, because it floats on the water and is driven by a small weight. So it is not easy to attach some device on it to detect the barrier position continuously. We designed a device to monitor the barrier position without disturbing the motion of the barrier. A high resistive narrow trench of water which has the same length of the LB trap was placed at one side of the LB trap. D.C. voltage was applied on both end of this water trench. From the negative terminal of the battery we connected a fine and flexible conductor whose one end was immersed in the water of trench. The immersed end of the conductor moved with the barrier and did the role of sliding contact of this water resistor. The voltage drop between the sliding contact and the positive terminal of the battery was linearly changed with the position of the barrier. We measured the voltage by computer and the area/molecule was calculated using this voltage.

Material and Experimental Procedure

Azobenzene-containing long-chain fatty acids (4-octyl-4′-(5-carboxyl-pentamethy leneoxy)-azobenzene) denoted by 8A5H was purchased from Dojindo Lab.Co.of Japan.
Figure 2 shows the molecular structure of this fatty acid.
The fatty acid was used as received in this experiment. The spreading solvent was commercial spectroscopic grade chloroform.
The concentration of fatty acid solution was 6×10^{-4}M/l.
The LB trap was filled with deionized water. 5 minutes after the spread of solution on a pure water subphase, the compression of the monolayer was begun. When the monolayer was compressed the measured value of the displacement current was sent to microcomputer.

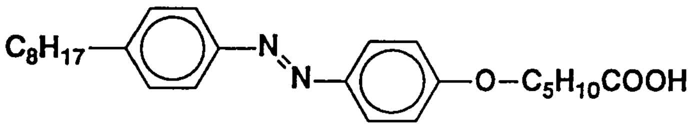

FIGURE 2 Molecular structure of 8A5H.

RESULTS AND DISCUSSION

Surface Pressure-Area Isotherm

Figure 2 shows the π-A isotherm of monolayer of the fatty acid(8A5H) on pure water. The π-A isotherm of 8A5H have plateau region at 5dyne/cm. This result agree with the work of Kawai et al who concluded the reason of this plateau region to the transition of the monolayer from a liquid crystalline state to a gel state.[4] This plateau region of the π-A isotherm of monolayer of the fatty acid(8A5H) is very useful for certifying our displacement current measuring system of Kuhn-type LB apparatus, because there must be some differences of the displacement current between the plateus region and other steeply increasing regions.

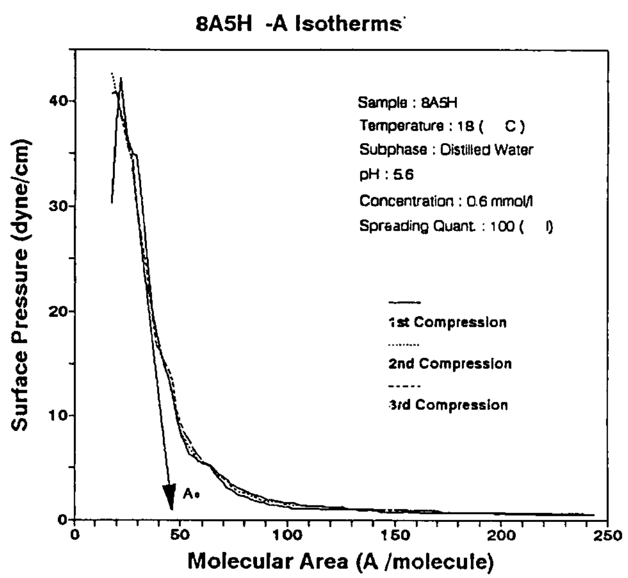

FIGURE 3 π-A Isotherm of 8A5H monolayer on the water subface.

Experiments Using Conventional Kuhn-type Apparatus.

Figure 4 shows the barrier motion of the conventional Kuhn-type LB apparatus. When the barrier began to compress the molecules, the area of the spreaded molecules was decreased immediately to the minimum value within 20 seconds. This result shows that it is hard to measure the displacement current of monolayers at the phases of gas and liquid by using the conventional Kuhn-type LB trap. Thus, we found the necessity for the modification of driving mechanism of barrier. Nevertheless this result gave us the possibility of measurement of the position of barrier using our method.

Figure 5 shows the displacement current which was measured after 20 seconds from the beginning of compression. At this state, we can assume that the barrier moves very slowly toward the electrode as the result of Figure 4. But the direction of the displacement current of Figure 5 does not agree with the theory of the displacement current measuring method. After we found this phenomena, we surrounded the electrode 1 by an aluminum shield plate and then the negative current was disapeared. From this result, we found the fact that the PTFE barrier has negative charges on it, and when it comes closer to electrode 1 the negative displacement current is indused.

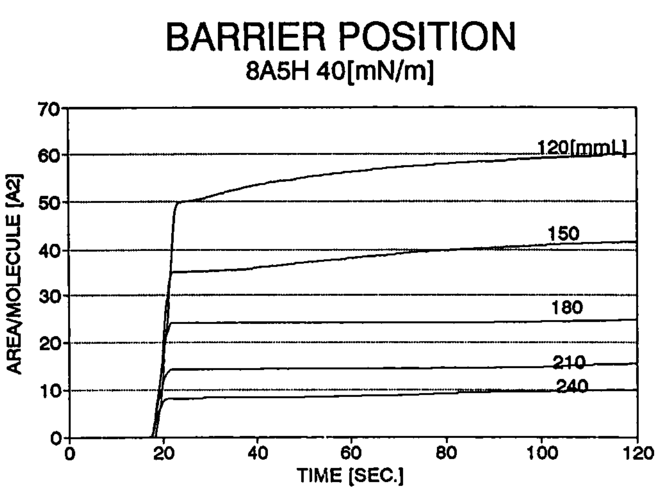

FIGURE 4 Change of area of the conventional Kuhn-type LB trap.

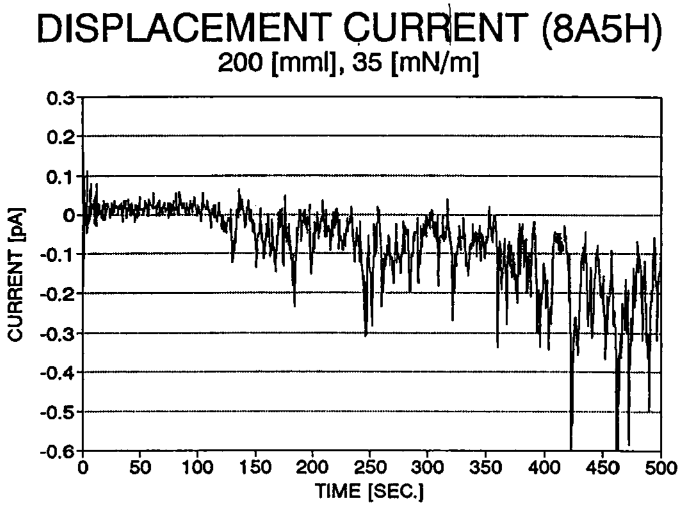

FIGURE 5 Displacement current induced by the charges on the PTFE barrier.

Displacement Current Measured by Using Modified Kuhn-type Apparatus.

Figure 6 is an experimental result of measurement of the displacement current without monolayer on the water surface. This result shows that the air gap between the electrode 1 and the water surface is a good insulator.

Figure 7 shows the displacement current measured during the compression of a 8A5H monolayer. Since this current measurement was not executed with the simultaneous measurement of π-A isotherm, it is hard to analyze the result exactly. But we need to notice to the two peaks of current which appear at points of 160 and 175 seconds, respectively. As we discussed about Figure 2, there is a plateau region of π-A isotherm of 8A5H and we can assume that the two peaks of current occurs at just before and after the plateau region of π-A sotherm. To prove this assumtion, we are trying to measure the displacement current of monolayers of stearic acid(C_{18}) which has a simple π-A isotherm, and also we are now improving the measuring system to measure π-A isotherm simultaneously with displacement current.

Figure 8 shows that the negative current is flowing when the monolayer is extended just after the compression by reversing the direction of the barrier. This result coincide with the experimental result obtained by Y. Majima.[5]

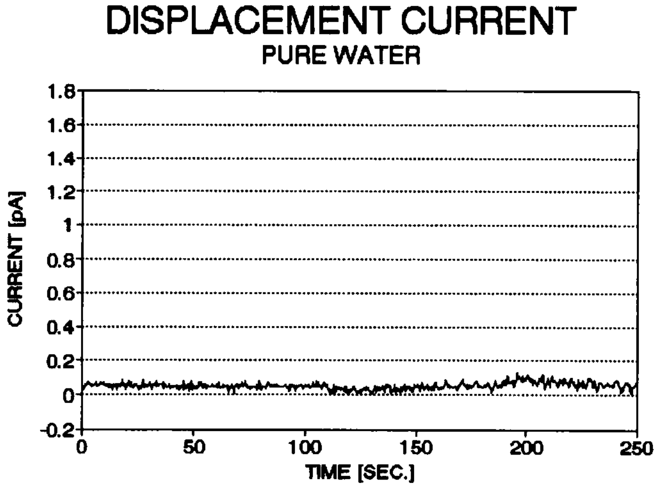

FIGURE 6 Displacement current measured without monolayer on water surface.

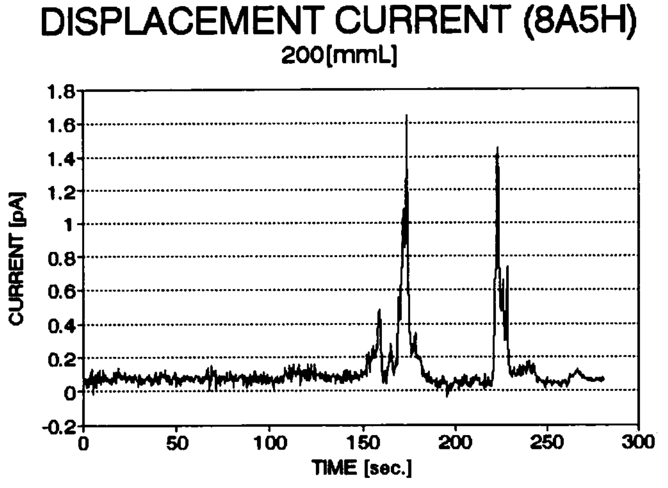

FIGURE 7 Displacement current measured for a 8A5H monolayer.

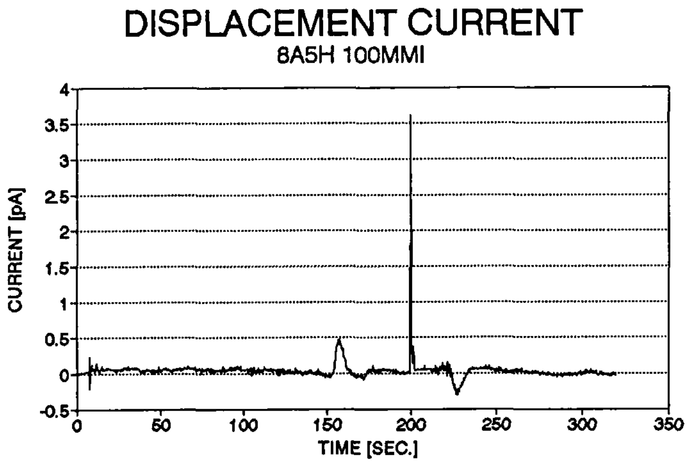

FIGURE 8 Displacement current measured for a 8A5H monolayer. (Monolayer was expended after the compression, the large peak at 200sec. is a noise by motor switching)

CONCLUSIONS

In the present paper, we used the Kuhn-type LB apparatus to measure the displacement current of monolayers on the air-water interface. We can measured the displacement currents which monitor the structural changes of monolayers.
We conclude that the displacement current measuring method can be easily applied to the Kuhn-type LB apparatus by modifying the barrier system.

ACKNOWLEDGMENTS

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