

## Development of LB Molecules Orientation Technology by Electric Field and Ultrasonic Vibration

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The merocyanine Dye (MC) molecules normally can produce stable Langmuir-Blodgett (LB) films by mixing with arachidic acid molecules. The higher optical and electronic functionalities, however, can be expected through making the film of sole MC molecule [1]. Our new technology aims to produce stabilized LB films with the sole MC molecule by applying the ultrasonic vibrations and electric field simultaneously to the MC Langmuir (L) film on the water surface. This paper evaluates the improved dense property of L film from the  $\pi$ -A curves based on the technology. The result shows a reduction, approx. 35% at maximum, in the average molecule occupation area under a constant surface pressure.

Keywords: LB film, orientation control of LB molecule, electric field, ultrasonic vibration,

### 1. INTRODUCTION

Dye molecules such as MC dyes and spiropyran dye can produce stable L and LB films when mixed with arachidic acid molecule. In this case, optical and electronic functions of the LB film may be lost in accordance with the fraction of arachidic acid that has an insulation property.

The ultimate purpose of this study is to develop the technology of fabricating an ideal structure of LB film. A Langmuir(L) film is known to form an island structure when it is spread on the surface of water in a LB trough. The fact that this operation causes generation of pinholes is also known. A countermeasure to this problem has usually been building-up of the LB film to cover these structural defects.

Further, a molecule with a long hydrophobic chain can be considered to be slant when spread on the surface of the water in LB trough. In this situation, the average molecule occupation area may become enlarged as a result that the hydrophobic chains of the adjacent molecules intertwine each other.

To solve the above problems, applying an external electric field "E" to a supernatant L molecule can generate an interaction energy of  $-\mu E$  and the molecule occupation area receives a torque in the electric field direction. This results in a displacement of molecules since the molecule is asymmetric and has an electric moment " $\mu$ " ( $= 4.85$  debye in MC) [2].

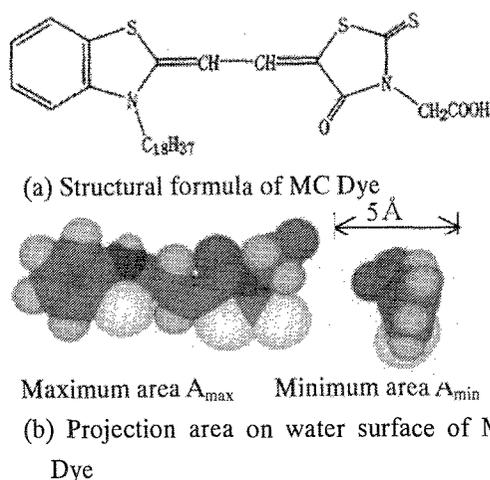


Fig.1 Structural formula and Projection area on water surface of Merocyanine Dye

Applying suitable ultrasonic vibrations to molecules on the water surface is another solution to the problem. This enables to suppress molecular aggregation leading to the island structure and helps to complete the electric field orientation as well as the formation of a L film free of the intertwining of hydrophobic chains. Consequently, the higher surface molecule density can be expected to be reached. This is named as the "electric orientation method".

### 2. COMPUTATION FOR MOLECULE OCCUPATION AREA BY 3-DEMENSIONAL MOLECULE MODEL

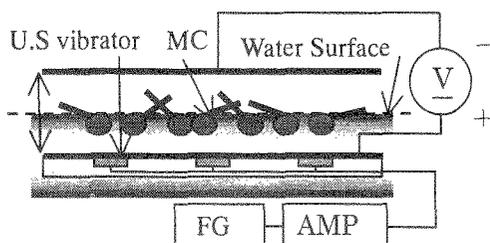


Fig.2 Control by electric field and ultrasonic Experiment composition

A computed simulation based on the 3-dimensional molecule model for MC dye molecule was performed to clarify the concept of the average molecule occupation area by the new LB film preparation technology [3] [4].

The structural formula of used MC dye is shown in Fig. 1(a). and Fig. 1(b) shows the largest and smallest projection area of the hydrophilic group for MC molecule on the water surface in LB trough.

Both projection figures were arranged to contact approx. 50 molecules mutually and densely in a certain rectangle area. The computation result showed the occupation area per molecule as  $51 \text{ \AA}^2$  in maximum and  $21 \text{ \AA}^2$  in minimum.

The average molecule occupation area of the L film is within the range of  $A_{\max}$  to  $A_{\min}$  on the premises that there is no heat turbulence, the molecule is a rigid body and the average molecule occupation area of the L film is determined upon the projection area of the hydrophilic group of the LB molecule.

This avails to assume the following as the actual state of the L film:

- ① The projection area of the hydrophilic group in the molecule is either in the condition of  $A_{\max}$  or  $A_{\min}$  of Fig.1 (b), forming a solid film with adjacent hydrophobic groups being entangled each other.
- ② The molecule on the surface of the water is receiving heat turbulence.
- ③ The L film contains pinholes.
- ④ The angle between a hydrophilic group and a hydrophobic of the molecule are bent with angles of 0 to 90 degrees.

Here, items ① to ③ work as an increasing factor for the average molecule occupation area while item ④ does adversely.

The average molecule occupation area that

forms a solid film is  $\leq 52 \text{ \AA}^2$  as shown by the  $\pi \cdot A$  curve of MC molecule without the electric orientation control in Fig. 3. The value is almost similar to the average molecule occupancy area " $A_{\max}$ " obtained by the 3D simulation. This result just looks as if the hydrophilic group was in the status of " $A_{\max}$ " on the surface of the water.

However, in reality it should be considered that the hydrophobic groups become to entangle and the solid film is formed by the influence of items ① to ④. If it is the case, the molecule occupation area should become smaller by the electric orientation method as described above and well-controlled orientation of the L film will be realized.

### 3. EXPERIMENT

Fig. 2 shows the structure of a LB trough (Langmuir MINI trough manufactured by Joyce Loebel).

Three cells for ultrasonic vibration (Resonance frequency = 50.6 kHz, manufactured by Tokin Co. Ltd.) were installed on the upper stainless steel sheet in a box that is placed under the surface of water in the trough.

Two stainless steel sheets (thickness = 1 mm,  $150 \times 280$  mm each) were set by 10 mm above and below the water surface, respectively, facing each other. The ultrasonic vibration strength at the water surface was displayed as a relative value in the form of output voltage of the function generator (FG).

The MC molecule was dissolved in deployment solution at a concentration of 33m mol/L and the solution was spread on the water surface.

Applying an electric field between both electrodes, the supersonic vibration cells were driven with an amplifier output connected to FG. After applying 60 seconds of the ultrasonic vibrations, both power supplies were turned off and the  $\pi \cdot A$  curve was measured.

The  $\pi \cdot A$  curve was measured by varying electric field " $E$ " = 0 to 1500 mV/m and FG output voltage " $V$ " = 100 to 1500 mV/m for ultrasonic vibration. Comparison were made between these results and the reference  $\pi \cdot A$  curve that did not undergo the electric field and the ultrasonic vibrations.

### 4. RESULTS AND DISCUSSION

#### 4-a. Ultrasonic Vibration Dependency

The  $\pi \cdot A$  curve under the ultrasonic vibrations

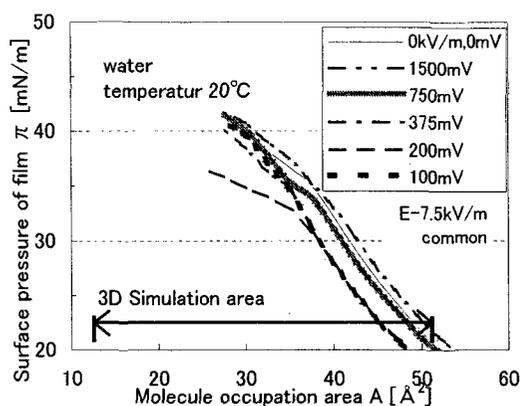


Fig.3 FG output dependability of  $\pi \cdot A$  Curve

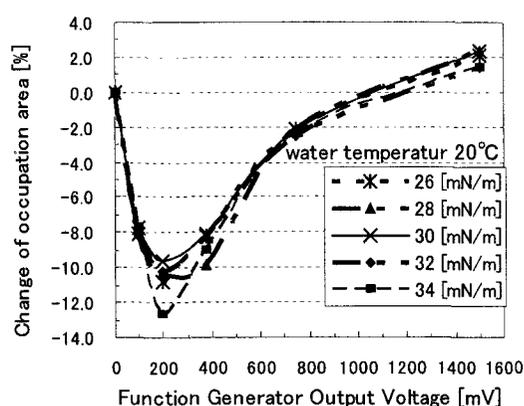


Fig.5 Change rate of A to F.G out put

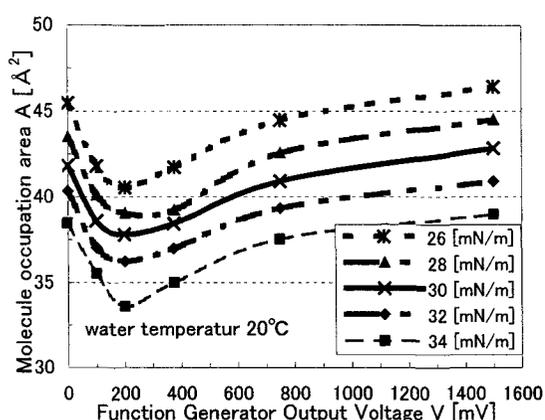


Fig.4 Characteristic of A to FG out put

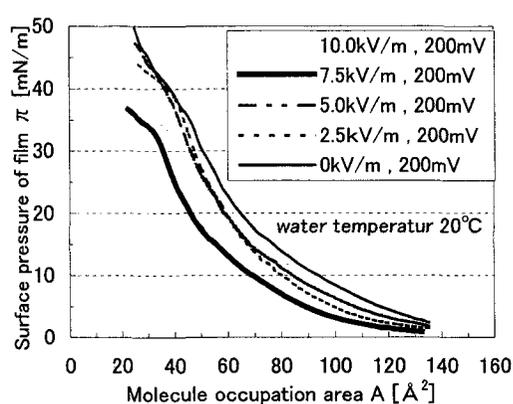


Fig.6 Electrical field dependability of  $\pi \cdot A$  Curve

was measured when the electric field between the electrodes was fixed to 7.5 kV/m as shown in Fig.3. The average molecule occupation area at constant surface pressure  $>20$  mN/m decreased in comparison with that of the film without applied ultrasonic vibration in the range of FG output 100 to 375 mV. If the FG output is  $\leq 750$  mV, the molecule on the water surface is considered to dissolve entanglement and is oriented through the ultrasonic vibrations.

In contrast to this, the molecular are tended to increase with FG output. This characteristic change is clearly exhibited in Fig. 4 with the relationship of the molecule occupation area and the FG output at constant surface pressures.

The latter phenomenon can be considered that the vibration torque given to the molecule exceeded the orientation torque made by electric field. The molecule on the water thereby becomes a highly disturbed state with the hydrophobic groups of adjacent molecules keeping in touch each other and intertwining compared to the status of no ultrasonic vibrations.

Fig. 5 shows the rate (%) of change in

occupation area for each surface pressure as a function of applied electric field.

Fig. 6 reveals that the average molecule occupation area at same surface pressure changes by controlling the molecule orientations. The minimum point of each curve can be seen at FG output = 200 mV, its surface pressure was 34 mN/m, and the reduction rate was approx. 12%.

#### 4-b. Electric Field Control of Molecule Orientation

The dependence of the average molecule occupation area on electric field strength was investigated under the fixed FG output of 200mV. Fig. 6 compares the results with the  $\pi \cdot A$  curves.

In comparison with  $E = 0$  kV/m, surface pressure of film applied with the electric field tends to decrease at constant molecule occupation area. The film pressure gives lowest value of  $E = 7.5$  kV/m while it shows increasing tendency in  $E=10.0$  kV/m in comparison with the status of  $E = 0$  kV/m.

Namely, Fig. 6 shows that the surface pressure at same molecule occupation area decreases more for the film that was applied the electric field and

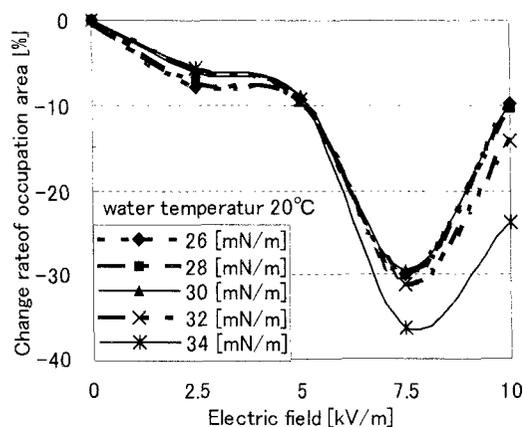


Fig.7 Characteristic of A to Electric field

the ultrasonic vibrations than for the film that was applied the ultrasonic vibration solely.

It can be considered that the contacting portions of the MC hydrophobic chains has increased since hydrophobic chains vibrate with confused directions as the result of the vibrations applied without directing the electric torque toward the electric field.

Also, the electric field strength dependence of the average molecule occupation area is interpreted as below. Fig. 7 re-illustrated Fig. 6 in terms of the relationship of the change (%) of the average molecule occupation area "A" and FG output at constant surface pressure  $\pi$ , in which the changing rate of reference is set as 0% when ultrasonic vibrations with FG output = 200 mV is applied while the value of electric field is zero.

Fig.7 shows the fact that the average molecule occupation area still more decreases at same surface pressure by combination of ultrasonic vibrations and electric field. Especially, a drastic drop takes place at  $E = 5.0$  to  $7.5$  kV/m with its maximum reduction being approx. 35%. This is considered due to a situation of that the induced torque of the molecule caused by the electric field exceeded the contact-frictional resistance of the hydrophobic chains on application of the electric field of this specific range.

On the contrary, occupation area A increases increasing in  $E = 10.0$  kV/m since a large moment along the direction of electric field is applied to the molecule and its hydrophobic chain was oriented in a nearly perpendicular form. Hydrophilic groups of the molecule, on the other hand, there by adjoined on a straight line and they were opposed to each other by the repulsive power of the dipole charge of the molecule, resulting in a substantial separation

interval between molecules.

Fig.7 implies that when the ultrasonic vibrations are carried out without applied electric field, the average molecule occupation area increases compared with the case where the electric field is applied. This is possibly due to an increase in the contact portion between hydrophobic chains of adjacent molecules that must be laid down with molecular vibration when ultrasonic vibrations alone were applied with no applied electric field.

Consequently, positive effect on the molecular orientation in the MC Langmuir film, by simultaneously applying the electric field and the ultrasonic vibration, was found in regards to the subjects of ③ and ④ in section 2.

## 5. CONCLUSION

This research has demonstrated that the denser molecule arrangement in Langmuir film preparation can be realized with reduction of the average molecule occupation area to maximum approx. 35% by giving the torque for orientation to the supernatant molecule in the presence of suitable ultrasonic vibrations and electric field intensity.

Our technology is expected to realize preparation of highly organized films composed of sole functional molecule, which have conventionally been manufactured in the form of mixed mono layer films. The technology "electric orientation method" is also promising for making new LB films, for examples, with highly improved optical absorption efficiency with use of J-aggregates.

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