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# Chlorophyll a Langmuir-blodgett 박막의 특성에 관한 연구

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## A Study on Characteristics of Chlorophyll a Langmuir-Blodgett film

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#### **INTRODUCTION**

The photochemical and photophysical behavior of biological pigments have been important subjects in the fields of photobiology and photochemistry. In connection with the photosynthetic primary process as well as light energy conversion, chlorophyll a (Chl a) has been one of the most widely studied pigments [1-3]. Also Chl a plays an essential role in both plant and bacterial photosynthesis, exhibiting a functional duality as energy collector and primary electron carrier [4].

In this study, we investigated the Chl *a* Langmuir-Blodgett (LB) film formation and determined the optimal condition for the Chl *a* LB film fabrication. To verify the dependence of the temperature condition, after the various  $\pi$ -A isotherms were obtained at various temperature respectively the Chl *a* LB films were fabricated onto the quartz substrate. It was investigated the Chl *a* LB films onto the substrate were formed well by UV-visible spectroscopy and the surface morphology of Chl *a* LB film onto substrate was analyzed by using Atomic Force Microscopy (AFM).

## **EXPERIMENTAL DETAILS**

Chlorophyll *a* (Chl *a*, extracted from spinach) and Chloroform were purchased from Sigma Chemical Company. (St. Louis, USA). The LB film deposition of Chl *a* was carried out with a circular-type Langmuir trough (Model 2011, Nima Tech, UK). Chl *a* molecules were dissolved into chloroform at a concentration of 0.2 mg/ml, and stocked in a frozen state at  $-20^{\circ}$ C without light illumination.

The Chl *a* solution was then carefully applied onto the aqueous subphase (deionized distilled water) with various temparature. The monolayer was compressed until a collapse occurred thereby producing the surface pressure-area ( $\pi$ -A) isotherm of Chl *a*. The deposition of the Chl *a* LB films was started with an upward stroke. The dipping speeds of up-downward strokes for the Chl *a* LB film deposition were 5 mm/min. The extent formation of Chl *a* LB films onto substrate was measures using UV-visible spectrophotometer (Jasco V-500, JAPAN). The surface morphology of Chl *a* LB film onto substrate was analyzed by AFM (Auto Probe CP, PSI, USA).

#### **RESULTS AND DISCUSSION**

In LB film formation, the Chl *a* molecules that spread onto subphase have gaseous state dynamic and the molecules in interface were sensitively affected with temperature dependence. In Fig 1.,  $\pi$ -A isotherm of Chl *a* LB films with optimal temperature (25°C) were shown. This figure shows that the surface pressure constantly increased until it reached about 20 mN/m as the monolayer was compressed. The collapse of monolayer was found at around 36 mN/m. Langmuir monolayers has gaseous state above 115 Å<sup>2</sup>/molecule, liquid-expand (LE) state at 115~70 Å<sup>2</sup>/molecule, liquid-condensed (LC) state at 70~38 Å<sup>2</sup>/molecule, and solid-like (SL) state below 38 Å<sup>2</sup> / molecule.



Fig 1.  $\pi$  -A isotherm of Chl *a* monolayer at air-water interface (25°C)

In order to confirm the deposition of Chl *a* monolayers onto a solid substrate, the absorption of the Chl *a* LB films was measured. The absorption spectrum of the Chl *a* solution is shown in Fig. 2. It has a broad band ranging from 400-700 nm with two peaks at around 435 nm and 665 nm.



For the absorption spectrum of LB film, quartz was used as the substrate and a bare-quartz plate was used as the reference. Based on the obtained  $\pi$ -A isotherm, in all experiments, the Chl *a* monolayers were deposited at 25 mN/m. It was investigated by UV-visible absorption spectrum that Chl *a* LB films deposited onto quartz substrate were formed well. As shown in Fig. 3.



Fig. 3. Absorption spectra of Chl a LB films

The UV-visible absorption spectrum of Chl a LB films deposited onto the quartz substrate at various layer shows that absorbance intensity peak was proportionally increased according to increasing Chl a layers. It was also known that there were slight red-shifts by 10-20 nm in the LB films. These results

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could be due to the close-packed structure of Chl *a* LB films. Accordingly, it can be deduced that the Chl *a* monolayers were well transferred onto the solid substrate, with maintaining their spectroscopic properties.



Fig. 4. AFM images of Chl a LB films deposited onto the gold substrate at  $25^{\circ}$ C : (a) 1  $\mu$ m, (b) 0.5  $\mu$ m, (c) 0.2  $\mu$ m.

To verify the film formation, surface morphology of Chl a LB films was obtained by AFM. In Fig 4, various scan size AFM morphology was shown. In Fig. 4 (c), Chl a LB film has 50 nm scale moleculer cluster. It is indicated that the Chl a molecules were aggregate before Langmuir monolayer formation onto the aquoeus subphase. The chemisorption and physisorption of Chl a molecule-subphase effect to the Chl a aggregation. Thus, the aggregation degree could be controlled by the pH.

## **References**

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