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ABSORPTION SPECTRA AND PHOTOEMISSION OF CHLOROPHYLL-B MULTILAYERS

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The monolayer of chlorophyll (Chl) b at the air/water interface has been examined by pressure – area isotherm and film thickness. Furthermore, with the multilayer of Chl b on the solid surface the visible absorption spectra and the external photoelectric effect in the vacuum ultraviolet region have been studied. The energy diagram has been proposed.

By the use of monolayer and multilayer techniques, thin films with well-defined orientation of molecules can be obtained. Previously, with anthraquinone derivatives containing long alkyl chains the authors have reported that the different types of orientation of the chromophores can be realized in the surface films, depending on variation in the numbers and relative positions of the long substituent groups, and that spectroscopic properties of these built-up multilayers can be approximately related to the orderly array of the oriented chromophores.[1,2]

It is generally supposed that photosynthesis takes place in the chloroplast where chlorophylls and other pigments are incorporated into highly organized lamellar structure. Katz has suggested that photoconduction in chlorophyll lamellar systems may play a significant role in the primary photoprocess.[3] The concept of chlorophyll aggregate with layered structure has stimulated numerous progressive studies on the mono- and multilayers of chlorophylls as a simplified model for the chloroplast.[4] For instance, the measurements of spectroscopic and photoelectric properties of the chlorophyll multilayers have led to some useful informations about the aggregation of the porphyrin chromophore and the transfer mechanism of the excitation energy in the photosynthetic system.[5-9] In most cases these studies have been concerned with Chl a, whereas the study on the mono- and multilayers of Chl b has been scarcely noted.

In the present work, the monolayer of Chl b spread at the air/water interface has been examined by surface pressure – area characteristics, and its multilayer deposited on solid supports has been studied by measurements of film thickness, visible absorption spectra and external photoelectric effect in the vacuum ultraviolet region. From the result of the latter, the energy diagram in the thin films has been proposed.

Materials: Chl a and Chl b were extracted from fresh spinach leaves and purified by chromatography on a sugar column, according to the method reported by others.[4,10] The purity and the chemical stability were checked spectroscopically on the basis of the data reported by Trurnit and Colmano[6] and confirmed to be fairly good.

Procedures: Monolayers were spread from the benzene solution on the surface of distilled water (pH 6). A modified Wilhelmy type of film balance, which consists of a thin hanging glass plate connected with a digital precesion balance, was used for measurement of surface pressure. The monolayer of Chl b was transferred onto the solid surface by the Langmuir-Blodgett technique under surface pressure of 29.5 dyn/cm, using oleic acid as a piston oil.11) The film thickness was measured by the interference of sodium D line for the two to ten layers deposited on the chromium-plated steel plate which had been precoated with the stepped gauge of barium stearate multilayers.12) For the measurements of visible absorption spectra, the multilayer was deposited on the quartz plate precoated with a monolayer of ferric stearate and a Shimazu multipurpose spectrophotometer (model MPS-50) was used. The photoemission current was measured by a Cary 31 vibrating-reed electrometer with a Seya-Namioka-type vacuum ultraviolet monochrometer connected with a Hinteregger-type hydrogen discharge lamp. The multilayer deposited onto a copper disk was fixed at the center of the collector which was a glass sphere coated with a conducting layer of colloidal graphite (Aquadag) on the inside. The spectral dependence of the photoemission yield was measured under an applied potential of 10 V enough to collect all the photoemitted electrons, and the current – voltage characteristics were observed by a spherical retarding method. The details of arrangement for the photoelectric measurements have been reported previously.13) All experiments were performed in a dark room at 10 – 15 °C.

Figure 1 shows the pressure – area isotherm of Chl *b* monolayer as compared with that of Chl *a*, the latter being in good agreement with the data reported by others.6,7) The collapse pressure for Chl *b* is higher than that for Chl *a*. This can be attributed to the difference in the substituent on the porphyrin ring, since it is rather hydrophilic -CHO group for Chl *b*, while it is hydrophobic -CH_3 group for Chl *a*. From the fact that the limiting areas (the extrapolated area at zero pressure for condensed region) of Chl *a* and Chl *b* have the same value of 104 $Å^2$/molecule, the porphyrin plane which is about 225 $Å^2$ in dimensions seems to be inclined at about 50 degrees to the surface in both cases.

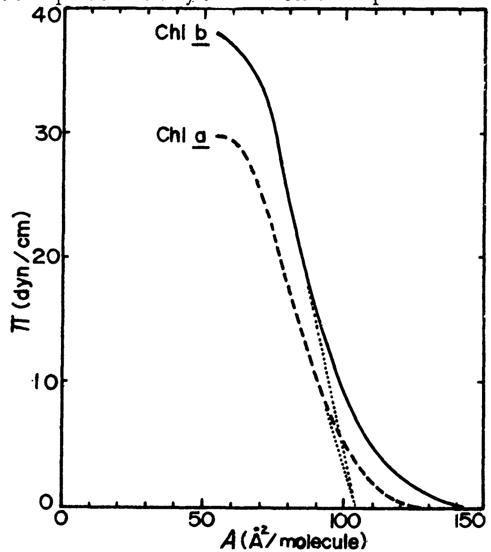

Fig.1. Pressure – area curves for Chl *a* and Chl *b* at 15 °C.

The monolayer of Chl *b* can be transferred onto the solid plate in both down and up trips (Y-film). The optically measured thickness per single layer was found to be about 24 Å in contrast with 14 Å, early data by Langmuir.14) From the results of area and thickness, two possible types of molecular orientation can be considered for the layered structure: one in which the porphyrin ring and the phytol chain are folded in hairpin type with ester linkage being anchored, and the other in which the phytol chain (probably with some helical form) stands on the lamellar plane hanging the tilted porphyrin ring, the molecule as a whole being a spoon type. Even though the former is preferable in the monolayer on water, the latter which leads to close parallel stacking of porphyrin rings may be possible in the multilayer on solid since change of the molecular configuration would occur during the transferring process.

The visible absorption spectrum for the multilayer of Chl *b* is shown in Fig.2, comparing with the spectrum of the ether solution. The absorbances of both blue and red bands were found to be directly proportional to the number of layers and the value per single layer at the red band was 0.007, which is comparable to that for the multilayer of Chl *a*.15) In each band for the film spectrum the peak position shifts towards longer wavelength with band broadening and lowering of peak maximum, which corresponds to the results reported for the monolayer at the air/water interface.6) These spectral characteristics can be related to the orderly array of the oriented porphyrin rings in each layer.

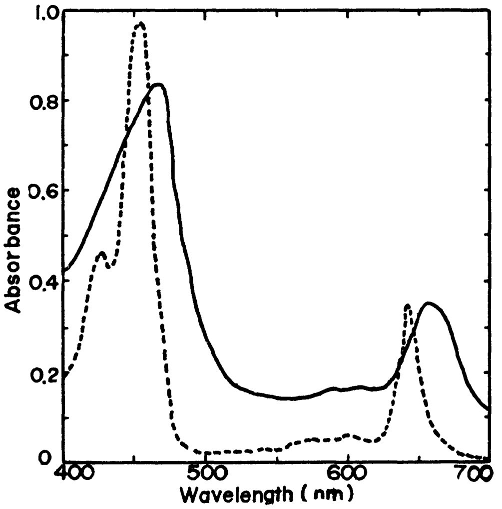

Fig.2. Visible absorption spectra of Chl b in multilayer (—— 50 layers) and in ether solution (------).

Figure 3 shows the spectral distributions of the quantum yield for the multilayer of Chl b (200 layers), as compared with the casting films of Chl a and Chl b by evaporation of the benzene solutions, the latter being similar to the data of Dam et al.16) A little difference in the shape of the spectral dependence of the quantum yield between the multilayer and the casting film may reflect different aggregations of the molecules. In the region near the threshold point, as shown in the insert of Fig.3, the results are in good agreement with the semiempirical cube-power law, $Y \propto (h\nu - E_{th})^3$, where E_{th} is the threshold energy of photoemission.17) Thus, the threshold values extraporated from the cube-root plots are found to be 5.25 eV for Chl b and 5.1 eV for Chl a. For the film of Chl a obtained by evaporation of the chloroform solution the value of 4.8 eV was reported by Vilesov et al.18)

Furthermore, with the multilayer of Chl b the current – voltage characteristics of photoemission under monochromatic radiations are shown in Fig.4(a), where the ordinates are normalized with the saturation current, $I_s = 1.0$. The value of the saturation voltage V_s, which corresponds to the contact-potential difference between the emitter and the collector, is found to be about one volt. The differentiation of the V – I characteristics, as shown in Fig.4(b), gives the kinetic energy distribution curves of photoelectrons. It is observed that a group of slow electrons at about 1.2 eV remains stationary irrespective of the incident photon energies and other groups of fast electrons appear depending upon the photon energies, in contrast to the result reported for the casting film of Chl a in which only one group of slow electrons (0.3 – 0.5 eV) was exhibited.19)

Finally, assuming that the thin film of Chl b is an intrinsic semiconductor, the

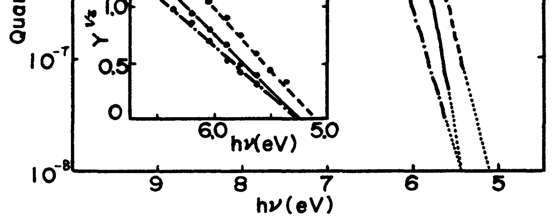

Fig.3. Spectral distribution of the photoemission yield for Chl b multilayer (——) and the films obtained by evaporation of benzene solutions of Chl a (------) and Chl b (—·—·—).

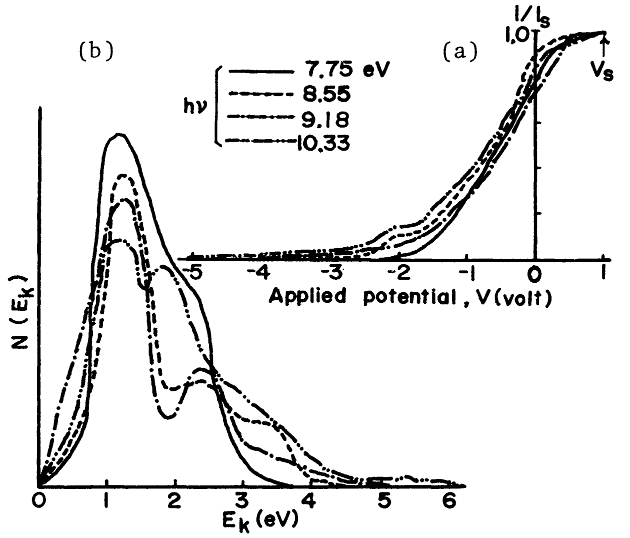

Fig.4. (a) Current – voltage relation, and (b) energy distribution curves for Chl b multilayer.

energy diagram can be obtained from the observed values of E_{th} and V_s, as shown in Fig.5. The band-gap energy, E_g, is given as follows:

$$E_g = 2\ (E_{th} + eV_s - \Phi_c),$$

where Φ_c is the work function of the collector. Thus, the value of E_g for the multilayer of Chl b is obtained to be 3.02 eV by setting Φ_c = 4.74 eV for Aquadag. For the crystalline Chl b, however, Rosenberg$^{20)}$ and Eley$^{21)}$ reported that the value of E_g was about 1.45 eV based on the results of the temperature dependence of the conductivity. The E_g value for cytochrome c_3, hemoprotein, is found to be about 3.1 eV.$^{22)}$ As the result of the present study, the work function of Chl b multilayer is found to be 3.74 eV, which is remarkably larger than the value of Φ = 0.7 eV estimated from the analysis of tunnelling conductivity for the multilayer of Chl a.$^{23)}$

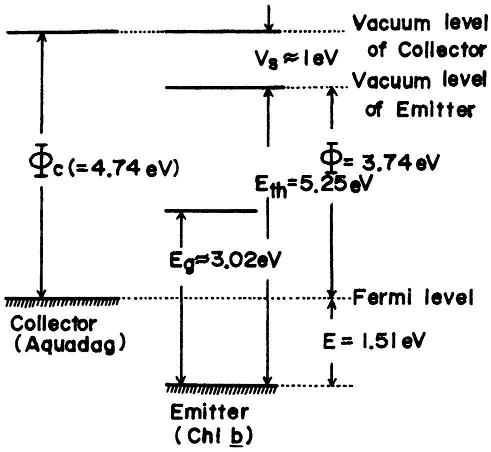

Fig.5. Schematic diagram for the external photoelectric process of Chl b multilayer.

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