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J-aggregate to J-aggregate relaxations in langmuir films of amphiphilic merocyanine dye derivatives studied by optimum difference spectrum method

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Abstract

Langmuir (L) films of amphiphilic merocyanine dye derivatives (DS and DSe) mixed with arachidic acid have been prepared on a Mg^{2+}-containing aqueous subphase. Time evolution of the molar absorption coefficient (ε) spectra observed for them has shown that J-aggregates with relatively large red shifts (ca. 2800 cm^{-1}) are the majorities at the initial stage, but J-aggregates with smaller shifts (ca. 2400 cm^{-1}) become major within few minutes of compression. Isosbestic points clearly seen in the time evolution of the spectra imply those films include no other appreciable components. A similar phenomenon has been observed for DS films on Ca^{2+}-containing subphase. The pure spectra of the initial and final J-aggregates have been extracted from the experimentally obtained ε spectra by employing the optimum difference spectrum (ODS) method. Semi-quantitative discussion based on the extracted pure spectra has suggested that the observed phenomena are structural relaxations, i.e., changes in the molecular arrangements in the J-aggregates, and that the interactions between the static dipoles born by the dye molecules are not the main driving force of the J-aggregation of DS and DSe.

Keywords: J-aggregate; Relaxation; Langmuir film; Spectrum analysis

1. Introduction

J-aggregates [1] have attracted much attention and been studied intensively by many researchers because of their fascinating optical properties: a red-shifted and narrowed electronic absorption band (J-band), enhanced photoluminescence, and a very small Stokes shift. J-aggregate to J-aggregate relaxations are interesting phenomena from both the technological and scientific viewpoints, since they may be used for information storage, and may reflect the mechanism of J-aggregation.

An amphiphilic merocyanine dye derivative, 3-carboxymethyl-5-[2-(3-octadecyl-2(3H)-benzothiazolylidene)ethylidene]-2-thioxo-4-thiazolidinone (DS) [2] and its derivative of DSe [3–5] (Fig. 1) form J-aggregates in their pure and mixed Langmuir (L) films [6] prepared upon appropriate aqueous subphases. These L films are suited for studying the J-aggregates under variation of physical and chemical conditions such as the surface pressure and salts dissolved in the subphase. In fact, the dependence of the spectral features of the J-band upon the cation species in the subphase was intensively studied for L films of DS by Yoneyama et al. [7] and Miyata et al. [8] and for those of DSe by Kawaguchi and Iwata [3–5]. These authors found that the J-band spectrum depends on time in some cases, but were not interested in the mechanism of the observed spectral changes and then did not report detailed data. Recently, Kato et al. [9,10] have reported a thermal J-aggregate-to-J-aggregate transition in DS films upon a subphase containing both Cd^{2+} and Mg^{2+}. They are interested in the transition mechanism and performing extensive studies, but in their case both of the physical and chemical conditions, i.e., the temperature and the cation species associating with the L films, are varied and the mechanism may be complicated.

This work aims at providing a new insight into the mechanism of the spectral changes taking place in L films of DS and DSe under constant chemical conditions. With this purpose, the spectral changes have been observed in detail and the recorded

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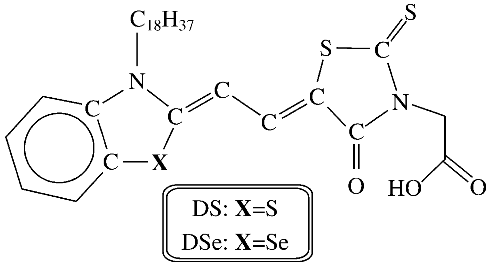

Fig. 1. Chemical structures of amphiphilic merocyanine dye derivatives used in this work.

spectra have been analyzed carefully. The followings are the keys in this work that enable significant extension of the past studies in Refs. [3–5,7,8]. (i) Drawing molar absorption coefficient (ε) spectra instead of usual absorbance spectra. This can be done by simultaneous recording of the surface area and the absorbance spectrum of an L film under a finite surface pressure. In addition, the effect of side reactions could be neglected with restricting the period of time for observation to several minutes. (Then, the word "final" in this work is used to indicate quasi-stable states realized in the short periods of time. Long-time effects, such as reported in Ref. [8], cannot be discussed in this way.) (ii) Analyzing the obtained ε spectra by the optimum difference spectrum (ODS) method, which is a recently proposed [11–14] powerful tool for analyzing two-component spectra. It is based on the least-squares regression and gives the maximum likelihood estimators of the difference between the pure spectra of the components as ODS, even when the components' quantities in the samples are unknown. Pure spectra of J-aggregates have been extracted through the analyses. (iii) Semi-quantitative discussion upon the relationship between the shift due to J-aggregation (J-shift) and the number of dye molecules in the aggregation (aggregation number).

2. Experimental

The merocyanine dyes (DS and DSe, Fig. 1) and arachidic acid (AA) were purchased from the Japanese Research Institute for Photosensitizing Dyes Co. and Fluka Co., respectively, and were used without further purification. Pure or AA-mixed (1:1 molar ratio) solutions of the dyes were made using spectroscopic grade chloroform as the solvent. The concentration of the dyes was ca. 5×10^{-4} mol/l. These solutions were spread on a subphase contained in a Lauda Filmwaage trough under air at 20 °C. The initial area of the subphase surface was 500 cm^2 and the amount of the spread solution was 0.14 or 0.10 cm^3 in the pure or mixed case, respectively. The L films were compressed to condensed states in ca. 180 s. Aqueous 4×10^{-4} mol/l solutions of $MgCl_2$ and $CaCl_2$ were used as subphase, after adding $KHCO_3$ ($3–5 \times 10^{-6}$ mol/l). The pH value of these solutions kept in the trough was 6–7. Water with a resistivity greater than 1.8×10^7 Ω cm was prepared by using a Millipore Milli-Q system.

The electronic absorption spectra of the Langmuir films were recorded by a WRM-10TP polychrometer of Jasco Co. Ltd. with a halogen lamp as a light source and a bundle of optical fibers as a probe. The probing light emitted from the bundle propagates into the water subphase at normal incidence and was reflected by a mirror put on the bottom of the trough and then was collected by the bundle. The molar absorption coefficient, ε, of a dye in its Langmuir film was obtained through $\varepsilon(\lambda) = -1/2 \times 10^{-17} N_A A \log_{10}[I(\lambda)/I_0(\lambda)]$, where I and I_0 are the intensities of the detected light with and without the film, respectively, at the wavelength of λ. N_A is the Avogadro number and A [nm^2] is the area per dye molecule. Note that A is *not* the so-called "limited area," but the actual area observed at the same time of the optical measurement.

3. Results and discussion

3.1. Changes in J-bands

Figs. 2 and 3 show time evolution of the molar absorption coefficient (ε) spectra of DS–AA and DSe–AA mixed L films, respectively, prepared on the surface of an aqueous solution of $MgCl_2$ and kept under a surface pressure of $\pi = 25$ mN/m. To neglect spectral changes due to side reactions, such as discoloration of the dyes, only the spectra observed within restricted periods of time are displayed in these figures. During these periods of time, the area per dye molecule, which is obtained by simply dividing the film area by the number of the dye molecules (and then not the area occupied by a dye molecule), gradually decreases from 0.73 to 0.70 nm^2 and from 0.70 to 0.68 nm^2, respectively, in the DS–AA and DSe–AA films. (These decreases in the areas are not asymptotic and

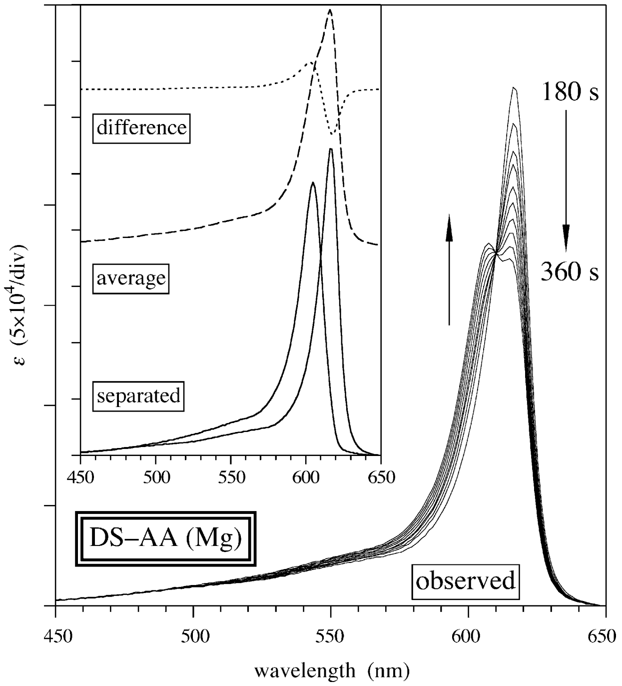

Fig. 2. Time evolution of the molar absorption coefficient (ε) spectrum observed for a DS–AA 1:1 (molar ratio) mixed Langmuir film prepared upon a Mg^{2+}-containing subphase kept under a surface pressure of 25 mN/m. Inset: extraction of pure spectra of two types of J-aggregate based on the optimum difference spectrum (ODS) method. Average and difference spectra are also indicated.