

## Poly(styrenesulfonate)의 존재하에서 3,3'-Dialkyl Oxacarbocyanines의 회합교란에 대한 Dialkyl 사슬길이 효과에 관한 연구

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### The Effect of Dialkyl Chain Length on the Disturbance of the Metachromasy of 3,3'-Dialkyl Oxacarbocyanines in the Presence of Poly(styrenesulfonate)

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The cationic dyes undergo a spectral change with increasing their concentrations in aqueous solution. This phenomenon has long been attributed to the formation of dimers or higher aggregates of these dyes in aqueous solution.<sup>1</sup> A similar change in spectrum has been observed when polyanions are added to a dilute aqueous solution of dyes.<sup>2-4</sup> This phenomenon is well known as metachromasy which can be explained on the basis of the aggregation of dyes on the surface of the polyanion chain.<sup>2-7</sup> Oxacarbocyanines belong to the family of polymethine dyes which show the metachromatic behaviours.

The kinetic study of the 3,3'-diethyl oxacarbocyanine in the presence of polyacrylic acid and that of the 3,3'-dipropyl oxacarbocyanine in the presence of poly(styrenesulfonate) have been carried out by the present authors using a stopped-flow method. We suggested the two-step mechanism by which dye molecules bind very rapidly to sites on polyanions, followed by a slow rearrangement of bound dye molecules on the surface of polyanions.<sup>7,8</sup>

The metachromasy induced by polyanions is disturbed by many factors, e.g., increase in temperature, high concentration of polyanions, presence of

electrolytes, urea, and various organic solvents.<sup>9,10</sup> Details of the mechanism on the disturbance of metachromasy by these various factors, however, still remain unclear because of its complexity.<sup>9,10</sup>

In the present work, we wish to report an effect of the dialkyl chain length of oxacarbocyanines on the disturbance of the metachromasy induced by poly(styrenesulfonate). Among the results, it has been revealed that the dialkyl chain length of dye affects the disturbance of metachromasy induced by excess polyanions.

#### EXPERIMENTAL

Poly(styrenesulfonate) sodium salt(PSS) was purchased from Polyscience. 3,3'-Dimethyl(DMOC), 3,3'-diethyl(DEOC), 3,3'-dipropyl(DPOC), and 3,3'-dihexyl oxacarbocyanine iodides(DHOC) were obtained from Aldrich. All materials were used without further purification.

The dye solutions were stored in borosilicate glass vessels covered with aluminum foil to exclude light and measurements were made as quickly as possible after preparation of the solutions in order to avoid errors to adsorption of the dye on the walls of the vessel. The preparation of all aque-

ous solutions of the dye was carried out in a dark room under a red safe light. Polyanion samples and dyes were separately dissolved in distilled water to prepare their stock solutions. Just prior to measurements of the absorption spectra, one part of the dye stock solution was mixed with one part of the polyanion stock solution. The P/D values were varied by adjusting the polyanion concentration at a fixed concentration of dye ( $1.4 \times 10^{-5}$  M).

Absorption spectral measurements were made on a Pye-Unicam SP8-400 spectrophotometer in cells of pathlength 1.0~10 mm. The kinetic studies were performed with the Otsuka Electronics RA-401 stopped-flow spectrophotometer equipped with Sibata WJ-15 model constant temperature circulating bath to keep the temperature in the reaction cell at  $20.0 \pm 0.1$  °C. The output from the instrument was fed to a NEC PC 9801 data processor. Typically, several runs were stored and averaged before final analysis.

## RESULTS AND DISCUSSION

Fig. 1 shows the absorption spectra of DMOC in the presence and absence of PSS. The absorption spectrum of DMOC in dilute aqueous solutions is characterized by a strong and sharp peak at 480 nm ( $\alpha$ -band) and a very slight shoulder at 460 nm ( $\beta$ -band). The absorption spectra of DMOC in the presence of PSS were measured at different P/D values. As a PSS solution is added to a fixed dilute DMOC solution, we can see that the shape of the spectrum is continuously changing; that is the absorbance of the  $\alpha$ -band decreases relative to that of  $\beta$ -band, and both the bands fall, while the absorbance of the band around 430 nm (metachromatic band) rises. As it was shown in Fig. 1, the metachromatic band is much broader and has a maximum shift of 50 nm toward the blue region of the spectrum. The wavelength of the metachromatic band reflects the magnitude of the stacking of the bound dyes; the shorter the wavelength of the metachromatic band, the stronger the stacking of the bound dyes.<sup>15</sup> The maximum

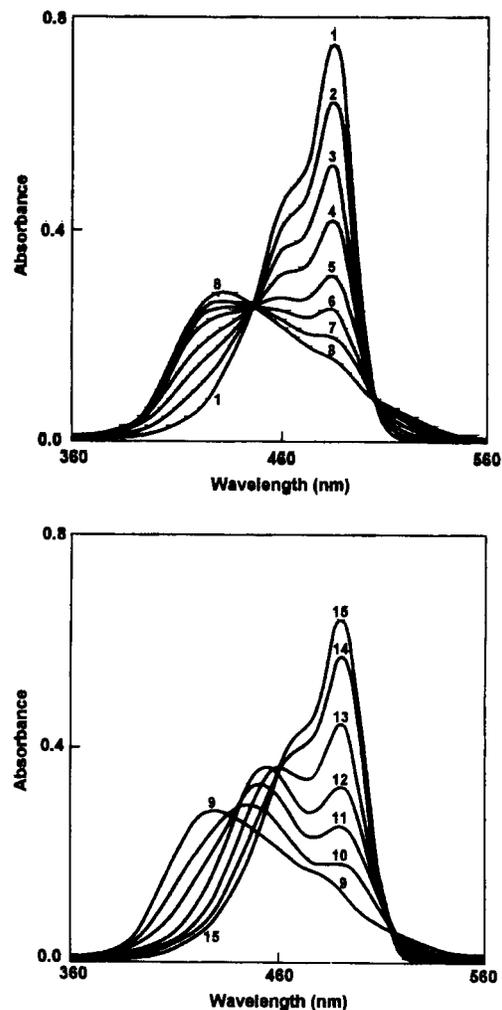


Fig. 1. The absorption spectra of DMOC-PSS system with the various P/D at pH 8.0 (tris-HCl buffer). [DMOC] =  $1.4 \times 10^{-5}$  M (fixed), P/D; 1) 0.0, 2) 0.1, 3) 0.3, 4) 0.4, 5) 0.5, 6) 0.6, 7) 0.8, 8) 1.0, 9) 1.0, 10) 4.0, 11) 6.0, 12) 8.0, 13) 10.0, 14) 40.0, 15) 80.0.

metachromasy occurred at P/D=1. We suggest that the absorption band near 430 nm induced by adding PSS arises from the aggregation of dyes bound to PSS chain. By further increasing P/D values, the  $\alpha$ -band reappears with 2 nm red shift of its maximum, and in the same time, the metachromatic band is gradually substituted by a new one ( $\beta$ -band) with a maximum 20 nm red shifted. The highly aggregated DMOC induced by PSS was easily destroyed at relatively high P/D values.

Similar spectral changes were observed when DEOC, DPOC, and DHOC were used as dye molecules.

The disturbance of metachromasy by a large excess of polyanion is due to the formation of bound monomers after the occurrence of redistribution of aggregated dyes over the excessive binding site.<sup>9,10</sup> Unfortunately, because of the similarities of the spectral aspects of dyes in the presence of large excess of PSS, the effects of the variation of dialkyl chain length on the disturbance of metachromasy could not be found by using the absorption spectrophotometric method. A stopped-flow kinetic method, however, allowed us to have a further discussion on the disturbance of metachromasy by a large excess of PSS.

To investigate the effect of dialkyl chain length of oxcarbocyanines on the disturbance of metachromasy, we measured the rate of the formation of a bound monomer with a stopped-flow method. The kinetics of the formation of a bound monomer was studied by monitoring the rate of the formation of a bound monomer induced by a newly added polyanion. When a dye-PSS solution at P/D=1 was mixed with a solution of excess PSS only, a transient increase of the absorbance of  $\alpha$ -band was observed at 482 nm for the DMOC-PSS system

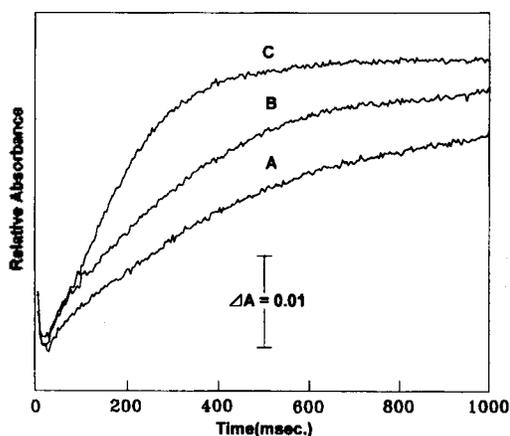
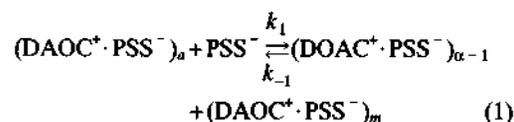


Fig. 2. The absorbance changes(at 482 nm) when DMOC-PSS solution at P/D=1 is mixed with different concentrations of PSS at 1 mM tris-HCl buffer and 20 °C. (A) 10-fold excess, (B) 40-fold excess, (C) 80-fold excess over the dye concentration( $1.4 \times 10^{-5}$  M).

(Fig. 2). These signals represent the formation of a bound monomer on a newly added polymer chain.

To interpret the present data, we propose the following kinetic equation for the formation of bound monomers.



In this equation,  $k_1$  and  $k_{-1}$  are the forward reaction constant and the backward reaction constant, respectively.  $(\text{DAOC}^+ \cdot \text{PSS}^-)_a$  and  $(\text{DAOC}^+ \cdot \text{PSS}^-)_m$  denote the aggregated and monomeric states of a bound dye of dialkyl oxcarbocyanine (DAOC), respectively. In order to obtain the forward rate constant of eq. 1 from the observed change of absorbance, we assume the followings; The extinction coefficients of bound aggregate are very close at the peak of a bound monomer around 482 nm, and bound monomers and aggregates are located on the linear polyanion chain of PSS. Under these circumstances, the increase of absorbance at the bound-monomer peak,  $\Delta A_{482}$ , is directly related to the increase of the amount of bound monomer,

$$(d\Delta A_{482}/dt) = \Delta \epsilon [d(\text{DAOC}^+ \cdot \text{PSS}^-)_m]/dt \quad (2)$$

where  $\Delta \epsilon$  is equal to  $\epsilon(\text{DAOC}^+ \cdot \text{PSS}^-)_m - \epsilon(\text{DAOC}^+ \cdot \text{PSS}^-)_a$ .  $\Delta \epsilon$  is taken to be  $5.7 \times 10^4$  L/mol·cm for DMOC. We obtained the initial rate by changing the amount of added PSS from  $1.4 \times 10^{-4}$  to  $1.12 \times 10^{-2}$  M to find that the initial rate is approximately proportional to the added PSS concentration. These results indicate that the reaction (1) may proceed via the direct transfer of a bound dye from one site to another of polyanion, but not by way of desorption to a bulk medium. In the latter case, the rate would be independent of [PSS].

Fig. 3 shows the bimolecular rate constants of eq. 1,  $k_1$ , for DMOC, DEOC, DPOC, and DHOC. The rate constants,  $k_1$ , decreases with an increase of dialkyl chain lengths(n). This result implies that the dialkyl chain length of dyes plays an important role in the rate of the formation of bound monomer. When the aggregate state is stabilized due to the hydrophobic interaction, it is expected that the

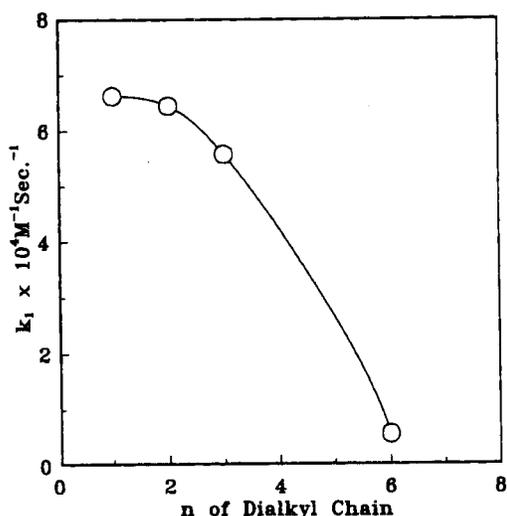


Fig. 3. The dependences of  $k_1$  on the dialkyl chain length( $n$ ) of oxacarboyanines.

rate of formation of a bound monomer would be decreased with the increase of dialkyl chain length resulted in the increase of hydrophobic effect.

In conclusion, our results reveal that the disturbance of metachromasy by a large excess of polyanion is due to the formation of bound monomers and that the rate of formation of a bound monomer depends on the dialkyl chain length of dye. Further studies are required to delineate the mechanism by which the length of dialkyl chain of

oxacarboyanine affects the disturbance of metachromasy by a large excess of polyanion.

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