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단 신

Oxacarbocyanine의 두 알킬 사슬이 3,3'-Dialkyl Oxacarbocyanine과 Poly(styrenesulfonate)의 상호작용에 미치는 효과

李 弘*·裵賢玉
원광대학교 자연과학대 화학과
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The Effect of Dialkyl Chain Length of Oxacarbocyanine on the Interaction between 3,3'-Dialkyl Oxacarbocyanine and Poly(styrenesulfonate)

Hong Lee* and Hyun-Ock Pae
Department of Chemistry, WonKwang University, Iksan 570-749, Korea
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The main feature of the binding of cationic dyes to biopolymers or to synthetic polyanions is the *metachromasy*, which is a change of the absorption spectrum.[1] This effect has been suggested as due to different binding modes of the dye molecules on the substrate, and owing to its ability in evidencing particular structures, it has proved helpful in the technique of biological tissue staining.[2] In addition, some of these dyes bear similarities with some antibiotic molecules. These facts are valuable reasons to address research to the study of the interaction mechanism between dyes and polyanionic substrates.[3~10]

The interactions of dyes with many biopolyanions or synthetic polyanions have been studied in view of *stacking* model.[1~3,5~10] This phenomenon of *stacking* has been interpreted as follows; dye molecules bound to the polyanions may be sufficiently closely located on the polyanion to interact with one another to form aggregates analogous to those found in free dye solution.[5~10] Many static studies of *stacking* have been carried out to establish a plausible *stacking* model.[5~10] However, effects of dialkyl chain length of dye on the *stacking* have not been studied. Therefore, we studied the effect of dialkyl chain length of oxacarbocyanine on the interaction between 3,3'-dialkyl oxacarbocyanine and poly(styrenesulfonate). The following dialkyl groups of oxacarbocyanines, *i.e.*, 3,3'-dimethyl, 3,3'-diethyl, 3,3'-dipropyl, and 3,3'-dihexyl, were used.

EXPERIMENTAL

Materials. All dyes were purchased from Aldrich Co. and poly(styrenesulfonate) sodium salt (PSS) was obtained from Polyscience Co.. All materials were used without further purification.

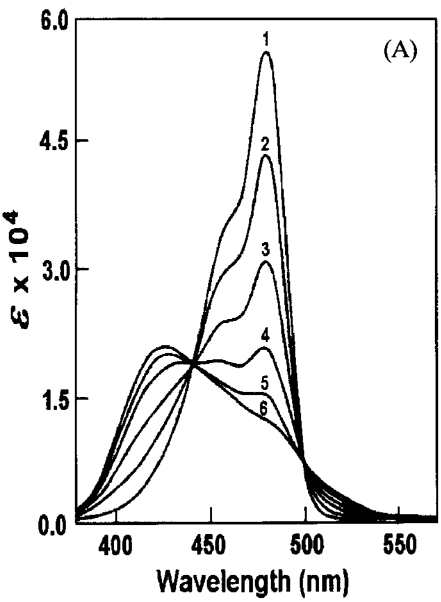
Measurements. PSS and dyes were separately dissolved in distilled water to prepare their stock solutions. Just prior to measurements of absorption spectra, one part of the dye stock solution was added to one part of the PSS solution and the mixture was maintained at a given temperature for 15 min. The concentration ratio between polyanion and dye solutions (P/D) was varied by adjusting the polyanion concentration at a fixed dye concentration (1.4×10^{-5} M). Absorption spectra were measured in a 1-cm quartz cell which was placed in a water jacket maintained at a working temperature. A Pye-Unicam SP-800 spectrophotometer was used.

RESULTS AND DISCUSSION

The absorption spectra of 3,3'-dialkyl oxacarbocyanine in the presence of PSS were measured at different P/D values (P/D values were varied by adjusting the polyanion concentration at a fixed dye concentration (1.4×10^{-5} M)). *Fig.* 1(a) shows typical spectral changes of 3,3'-dimethyl oxacarbocyanine in the absence and presence of PSS. The intensity at 480 nm (α-band) decreases with an increase in P/D values up to about 1, while an intensity at 430 nm comes to a distinct band, a metachromatic band. Further increase in P/D value results in an inversion in the spectral changes; α-band increases with a decrease in a metachromatic band (*Fig.* 1(b)). Similar spectral changes were observed when 3,3'-diethyl, 3,3'-dipropyl, and 3,3'-dihexyl oxacarbocyanine were used as dye molecules. However, the wavelength of the metachromatic band is the characteristic of each dye.

It has been proposed that by adding polyanions to a dilute aqueous solution of cationic dyes, such as acridine orange, the dye molecules were held sufficiently close together on the surface of the polyanion to allow them to interact to form aggregates.[1,5~10] Furthermore, the *stacking* theory predicts that the disappearance of the metachromatic band at large P/D value can be ascribed to the redistribution of the aggregated dyes over the excessive binding sites.[1] Thus, the appearance of metachromatic band at 430 nm can be ascribed to the *stacking* of bound dyes on the surface of PSS and the disappearance of that at high P/D values is thought to arise mainly from the redistribution of aggregated dye molecules over the anionic sites of the freshly added PSS.

The wavelength of metachromatic band (λ_{meta}) for 3,3'-dimethyl, 3,3'-diethyl, 3,3'-dipropyl, and 3,3'-dihexyl oxacarbocyanine was 430, 440, 442, and 460 nm, respectively, at P/D value of unit (*Fig.* 2). Thus, it can be seen that the dye which has a shorter dialkyl group gives a shorter λ_{meta}. The wavelength of the metachromatic band reflects the magnitude of the *stacking* of bound dyes;[5~10] the shorter the wavelength of the metachromatic band, the stronger the *stacking* of the bound dyes. Thus, it is quite likely that the dye which has a longer dialkyl group can not be in more compact *stacking*



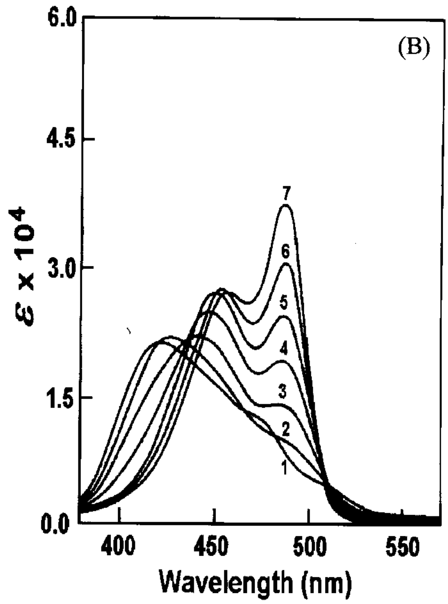


Fig. 1. (A) and (B). Typical absorption spectra of 3,3'-dimethyl oxacarbocyanine in the presence of PSS at various P/D values. [3,3'-Dimethyl oxacarbocyanine]=1.4×10^{-5} M. P/D=1) 0.0, 2) 0.2, 3) 0.4, 4) 0.6, 5) 0.8, 6) 1.0, 7) 2.0, 8) 5.0, 9) 10.0, 10) 20.0, 11) 30.0, 12) 40.0, 13) 50.0.

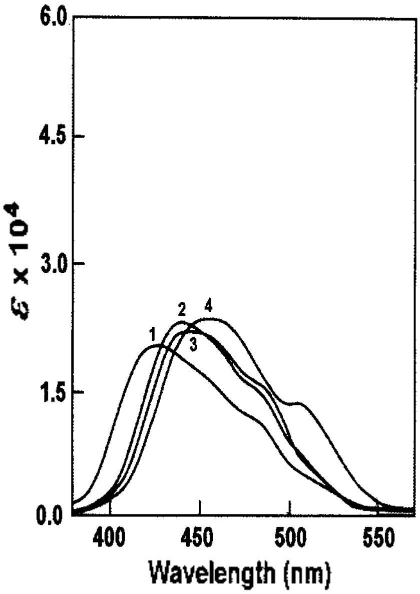


Fig. 2. Effect of dialkyl chain length on the metachromatic band induced by PSS at P/D=1. 1) 3,3'-Dimethyl, 2) 3,3'-diethyl, 3) 3,3'-dipropyl, 4) 3,3'-dihexyl oxacarbocyanine.

state due to the steric hindrance between bound dyes on the surface of PSS.

CONCLUSION

By utilizing the absorption spectra that the metachromatic band of 3,3-dialkyl oxacarbocyanine is characteristic of its *stacking* state depending on the dialkyl chain length, we have shown that the steric hindrance induced by dialkyl chain of dye plays an important role in the *stacking* of bound dyes onto the surface of polyanion; the shorter the dialkyl chain, the stronger the *stacking* of the bound dyes.

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REFERENCES

1. Bradley, D. F.; Wolf, M. K. *Nat. Acad. Sci. U. S.*, **1959**, *45*, 944.
2. Hammes, G. G.; Hubbard, C. D. *J. Phys. Chem.* **1966**, *70*, 1615.
3. Yamagishi, A.; Soma, M. *J. Phys. Chem.* **1981**, *85*, 3090.
4. Yamagishi, A.; Masul, T.; Watanabe, F. *J. Phys. Chem.* **1981**, *85*, 281.
5. Yamagishi, A.; Watanabe, F. *J. Phys. Chem.* **1981**, *85*, 2129.
6. Taniguchi, M.; Yamagishi, A. *J. Phys. Chem.* **1990**, *94*, 2534.
7. Shirai, M.; Nagatsuka, T.; Tanaka, M. *Makromol. Chem.* **1977**, *178*, 37.
8. Shirai, M.; Nagatsuka, T.; Tanaka, M. *Makromol. Chem.* **1978**, *179*, 173.
9. Shirai, M.; Tanaka, M. *J. Polym. Sci.* **1976**, *14*, 343.
10. Shirai, M.; Nagatsuka, T.; Tanaka, M. *J. Polym. Sci.* **1977**, *15*, 2083.