

DEPRESSION OF THE COMPLEX FORMATION BETWEEN ZINC TETRAPHENYL-
PORPHYRINTRISULFONATE (Zn-TPPS₃) AND METHYLVIIOLOGEN BY
THE ADDITION OF SURFACTANT MICELLES

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Photoreduction of methylviologen was carried out by the irradiation of the system containing triethanolamine, Zn-TPPS₃, and methylviologen in the presence of sodium dodecyl sulfate (SDS). The reduction rate increased with methylviologen concentration and reached a constant value which was in contrast with the result observed in the absence of SDS. The result was explained by the depression of the complex formation between Zn-TPPS₃ and methylviologen which does not serve as a photosensitizer.

Photochemical redox systems containing electron donor, photosensitizer, electron carrier and catalyst have been proposed for the solar energy utilization.^{1,2)} In the course of our studies, Zn-TPPS₃ has exhibited particularly high activity for the accumulation of the reduced form of an electron carrier such as methylviologen.^{3,4)} The rate of the photoreduction of methylviologen increases with methylviologen concentration and then decreases at the higher concentration.⁵⁾ The decrease of the reduction rate at the higher concentration is caused by the complex formation between Zn-TPPS₃ and methylviologen, for the complex does not serve as a photosensitizer. In this letter we hope to describe the depression of the complex formation by the addition of surfactant.

General details of the experiments were given in the literature.⁵⁾ To measure the absorption spectrum, the sample solution (which consisted of methylviologen and Zn-TPPS₃ in Tris-HCl buffer (pH 7.0)) was deaerated by repeated freeze-pump-thaw cycles. In the photolysis triethanolamine as an electron donor was added anaerobically and then irradiated continuously with light from a 200 W tungsten lamp. Light of wavelength shorter than 390 nm was removed by Toshiba L-39 filter.

When Zn-TPPS₃ was mixed with methylviologen, the characteristic Soret absorption band (418 nm) decreased with the increase in the methylviologen concentration, and a new spectrum appeared which has a characteristic absorption band at 425 nm through isosbestic point at 422 nm. The concentration of the complex is determined by the method reported previously.^{5,6)}

Figure 1 shows the amount of the complex formed against methylviologen concentration. In the presence of SDS, the complex formation is fairly depressed, e.g., though the greater part (70%) of Zn-TPPS₃ is complexed with [MV²⁺] = 1.0 × 10⁻³ mol dm⁻³ in the absence of SDS, only 6% of Zn-TPPS₃ is complexed with the same methylviologen concentration in the presence of SDS.

The above results are explained by the electrostatic effect among the charges of micellar surface, Zn-TPPS₃ and methylviologen. As methylviologen is positively charged, methylviologen is favorable to attack negatively charged micellar surface. The positively charged methylviologen is adsorbed in the micellar surface and protected against attack of negatively charged Zn-TPPS₃ strong electrostatic repulsion between micellar surface and negatively charged Zn-TPPS₃.

Figure 2 show the photoreduction rate of methylviologen against its concentration. Even in the higher concentration of methylviologen, no decrease of the rate was observed. On the contrary, the rate decrease in the higher concentration was observed in the system without SDS.⁵⁾ The result in Fig. 2 also shows the depression of the complex formation in the presence of SDS.

References

- 1) J.R. Darwent, P. Douglas, A. Harriman, G. Porter, and M.C. Richoux, *Coord. Rev.*, **44**, 83 (1982), and references therein.
- 2) J. Kiwi, K. Kalyanasundaram, and M. Gratzel, *Struct. Bonding*, **49**, 37 (1982), and references therein.
- 3) I. Okura, M. Takeuchi, and N. Kim-Thuan, *Chem. Lett.*, **1980**, 765.
- 4) I. Okura, M. Takeuchi, and N. Kim-Thuan, *Photochem. Photobiol.*, **33**, 413 (1981).
- 5) I. Okura, S. Kusunoki, and S. Aono, *Bull. Chem. Soc. Jpn.*, **57**, 1184 (1984).
- 6) I. Okura, S. Kusunoki, and S. Aono, *Inorg. Chem.*, **22**, 3828 (1983).

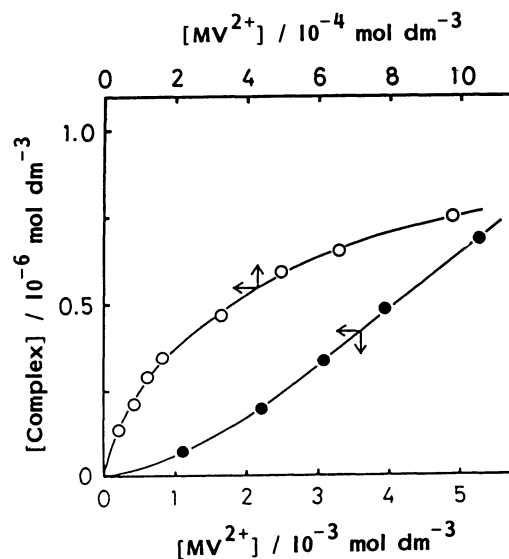


Fig. 1. Amount of complex against methylviologen concentration. The samples contain Zn-TPPS₃ (1.01 × 10⁻⁶ mol dm⁻³) and methylviologen. O: without SDS, ●: with SDS (1.60 × 10⁻² mol dm⁻³).

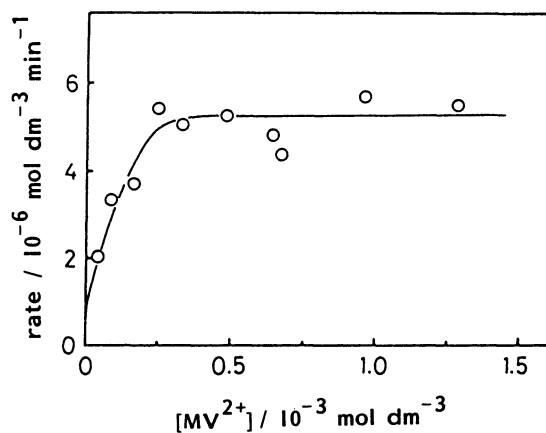


Fig. 2. Photoreduction rate of methylviologen against its concentration. The samples contain triethanolamine (7.41 × 10⁻² mol dm⁻³), Zn-TPPS₃ (7.57 × 10⁻² mol dm⁻³), methylviologen and SDS (1.60 × 10⁻² mol dm⁻³). The sample solution was irradiated by 200 W tungsten lamp at 30 °C.

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