Inorganica Chimica Acta, *116* (1986) L53–L54

Depression of the Complex Formation Between Zinc Tetraphenylporphyrintrisulfonate (Zn–TPPS$_3{}^{3-}$) and Viologen by the Addition of Surfactant Micelles

ICHIRO OKURA*, TATSUYA KITA, SHIGETOSHI AONO and NARUHIKO KAJI

Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

(Received February 12, 1986)

Photochemical redox systems containing electron donor, photosensitizer, electron carrier and catalyst have been proposed for solar energy utilization [1, 2]. In the course of our studies, Zn–TPPS$_3{}^{3-}$ 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, but after reaching a peak it decreases with subsequently higher concentrations [5]. The same phenomenon is observed in the case of PVS. The decrease of the reduction rate at high concentrations is caused by the complex formation between Zn–TPPS$_3{}^{3-}$ and viologen, which is not photoactive. At high viologen concentration, Zn–TPPS$_3{}^{3-}$ does not exhibit high activity in itself as a photosensitizer. By the addition of surfactant, however, the depression of the complex formation was observed. In this paper we hope to describe the effect of the surfactant on complex formation.

Experimental

General details of the experiments have been reported in the literature [5]. To measure the absorption spectra, the sample solution (which consisted of viologen and Zn–TPPS$_3{}^{3-}$ 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 wavelengths shorter than 390 nm was removed by Toshiba L-39 filter.

Results and Discussion

When Zn–TPPS$_3{}^{3-}$ was mixed with methylviologen, the characteristic Soret absorption band (418 nm) decreased with increasing methylviologen concentration, and a new spectrum appeared which has a characteristic absorption band at 425 nm through an isosbestic point at 422 nm. It is known that the new spectrum is caused by the 1:1 complex formation between Zn–TPPS$_3{}^{3-}$ and methylviologen [5, 6]. In the presence of SDS, the complex formation was fairly depressed, and the complex was observed only at much higher concentrations of methylviologen, compared to the system without SDS.

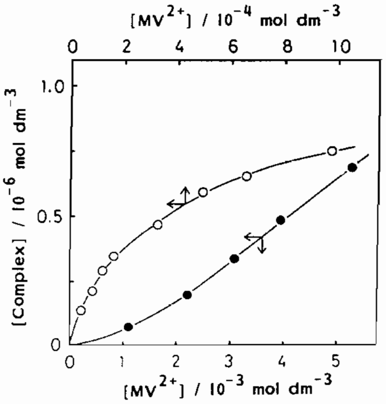

Fig. 1. Amount of complex against methylviologen concentration. The samples contain Zn–TPPS$_3{}^{3-}$ (1.01×10^{-6} mol dm^{-3}) and methylviologen. ○: without SDS, ●: with SDS (1.60×10^{-2} mol dm^{-3}).

Figure 1 shows the amount of the complexes formed against methylviologen concentration. The concentration of the complex is determined by the method reported previously [5, 6]. In the presence of SDS, the complex formation is fairly depressed; e.g., though the greater part (78%) of Zn–TPPS$_3{}^{3-}$ is complexed with [MV^{2+}] = 1.0×10^{-3} mol dm^{-3} in the absence of SDS, only 6% of Zn–TPPS$_3{}^{3-}$ 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 the micellar surface, Zn–TPPS$_3{}^{3-}$ and methylviologen. As methylviologen is positively charged, methylviologen is favorable to attack the negatively-charged micellar surface. The positively-charged methylviologen is adsorbed on the micellar surface [7] (the ratio of methylviologen concentrations in micelles against the one in the bulk was 3.3×10^3, and the ratio of reduced methylviologen concentrations in micelles against the one in the bulk was 3.3×10^2) and is protected against attack of negatively charged Zn–TPPS$_3{}^{3-}$ by strong electrostatic repulsion between the micellar surface and negatively-charged Zn–TPPS$_3{}^{3-}$.

In the case of PVS, the complex formation between Zn–TPPS$_3{}^{3-}$ is not depressed even in the presence of SDS. This result is also explained by the

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

electrostatic effect among the charges of the micellar surface, Zn–$TPPS_3{}^{3-}$ and PVS. As the charge of PVS is neutral in the oxidized form, PVS exists in bulk (water-phase) and is not adsorbed on the micellar surface. Thus, no effect of SDS is observed in the PVS system.

Figure 2 shows the photoreduction rate of methylviologen against its concentration. Even at high concentrations of methylviologen, no decrease of the rate was observed. On the contrary, the rate decrease at high concentrations 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.

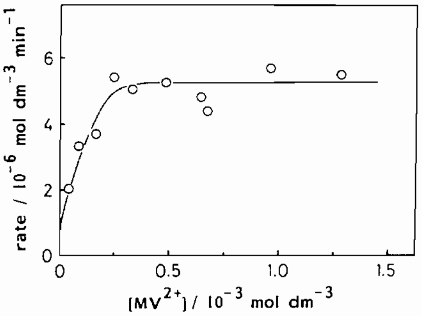

Fig. 2. Photoreduction rate of methylviologen against its concentration. The samples contain triethanolamine (7.41×10^{-2} mol dm^{-3}), Zn–$TPPS_3{}^{3-}$ (7.57×10^{-2} mol dm^{-3}), methylviologen and SDS (1.60×10^{-2} mol dm^{-3}). The sample solution was irradiated by a 200 W tungsten lamp at 30 °C.

Acknowledgements

We express our appreciation to Professor T. Keii and Professor Y. Ono for their stimulating and helpful discussions.

References

1 J. R. Darwent, P. Douglas, A. Harriman, G. Porter and M. C. Richoux, *Coord. Chem. Rev., 44,* 83 (1982), and refs. therein.
2 J. Kiwi, K. Kalyanasundaram and M. Gratzel, *Struct. Bonding (Berlin), 49,* 37 (1982), and refs. therein.
3 I. Okura, M. Takeuchi and N. Kim-Thuan, *Chem. Lett.,* 765 (1980).
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).
7 K. Suga and S. Aoyagi, *Abstr. Annual Meeting of Japan Electrochemical Society,* 1984, p. 18–19.