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Dimer Formation of Viologen Derivatives and their Electrochromic Properties

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ABSTRACT

The electrochromic properties of 1,1′-diethyl-4,4′-bipyridinium dibromide (EV), 1,1′-dipropyl-4,4′-bipyridinium dibromide (PV), 1,1′-dibutyl-4,4′-bipyridinium dibromide (BV) and 1-ethyl-1′-butyl bipyridinium dibromide (EBV) were studied using a propylenecarbonate/methanol solution with Bu_4NBF_4 *as the supporting electrolyte. A monomer–dimer equilibrium is proposed to explain the observation that the EV and EBV cation radical solutions are violet at an applied voltage of 1.7–3.0 V, but become blue in the open-circuit condition.* © *1997 Elsevier Science Ltd. All rights reserved*

Keywords: Electrochromism, viologen, display, aggregation, ITO glass, electrochemistry.

INTRODUCTION

Viologens (*N*,*N*′-disubstituted-4,4′-bipyridinium dications) have been extensively studied in the past decade because of their potential as prototypical electron-transfer reagents,[1] herbicides[2] and materials for electrochromic displays (ECD).[3,4]

The reduction of the dication of viologens to a highly colored cation radical led us to propose its use as an organic electrochromic substance. Viologen

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undergoes a one-electron reduction to give a colored radical cation. The redox system of viologen is shown in Scheme 1.

Scheme 1.

In a previous study,[5] we reported a response-improved electrochromic two-color display using a propylenecarbonate(PC)/methanol solution incorporated with two viologens, i.e. 1,1′-dibenzyl-4,4′-bipyridinium difluoroborate and 1,1′-tetramethylene-bis-(1-benzyl-4,4′-bipyridinium)bromide, with Bu_4NBF_4 as supporting electrolyte. This electrochromic device changed in color from blue at an applied voltage 0.5–2.0 V to reddish-purple at 2.5 V, and the color could be controlled by the applied voltage.

In this paper, we report the electrochromic behavior of various symmetric and asymmetric viologens in PC/methanol solution and a correlation of the monomer–dimer equilibrium of viologens.

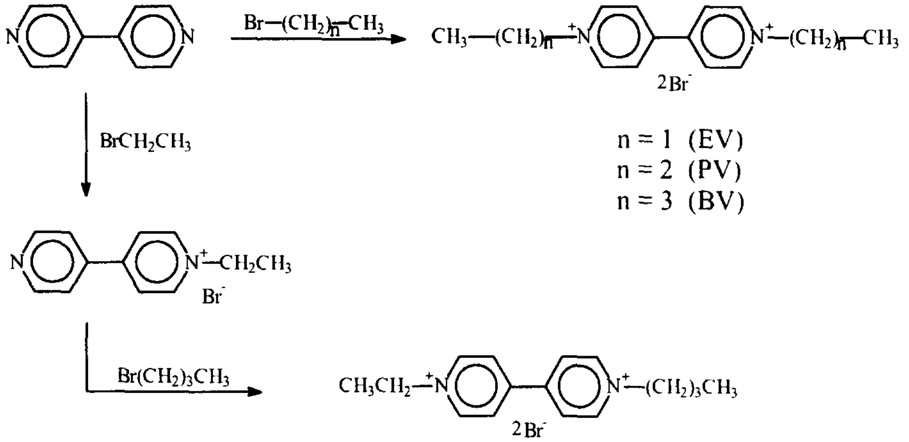
EXPERIMENTAL

Materials

4,4′-Bipyridyl (Aldrich) was used without further purification. 1,1′-Diethyl-4,4′-bipyridium dibromide (EV) was prepared as yellow crystals by refluxing an acetone solution of 4,4′-bipyridyl with 1-bromoethane. Other viologens, 1,1′-dipropyl-4,4′-bipyridinium dibromide (PV), 1,1′-dibutyl-4,4′-biypyridinium dibromide (BV), 1-ethyl-1′-butyl-4,4′-bipyridinium dibromide (EBV), were prepared by a similar procedure (Scheme 2).

Preparation of the ECD cell

The ECD cell consisted of two glass sheets (3 cm × 3 cm) separated by a 0.1 mm thickness spacer of PET film. The glass sheets were coated on one side with transparent conductive electrodes of indium-doped tin oxide (ITO), and these sides were placed so as to face each other on the inside of the cell and sealed with an insulating epoxide resin. Prior to the final sealing, the space between the electrodes was filled with a PC/MeOH solution of 0.196 mmol EV and 1.5 mmol tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as electrolyte.



(EBV)

Scheme 2.

RESULTS AND DISCUSSION

Viologens are now widely established as a useful class of organic electrochromic compounds. The reduction of the viologen dication to a highly colored cation radical led us to propose its use in such applications.

The absorption spectra of the colored EV cell produced on the cathode after electrocoloration are shown in Fig. 1; the threshold voltage for the coloration is about 1.7 V for EV. In the EV system, the prominent peak appears at 530 nm and the colour is violet. The absorbance of this

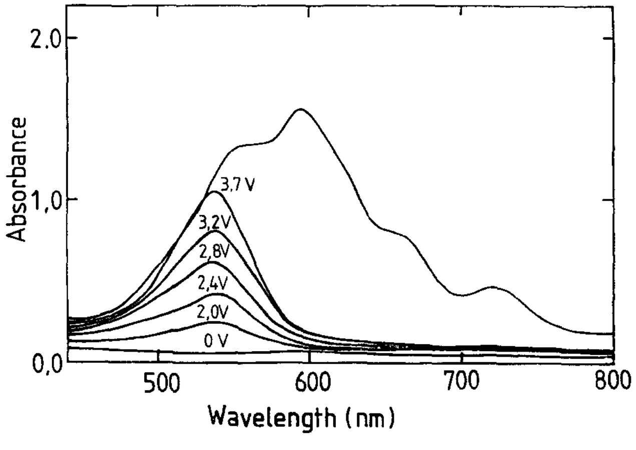


Fig. 1. Absorption spectra of the colored EV cell as a function of applied voltage

increased significantly depending on the increment of the applied voltage. At an applied voltage of 1.7–3.4 V in the EV cell, the absorption maximum was observed at around 530 nm and the color was violet, but in open-circuit condition the absorption maximum appeared at 600 nm and the color was blue, and then rapidly bleached colorless. Schwarz[6] has examined the spectra of solutions of the methyl viologen radical cation produced electrochemically over the concentration range in which an obvious color change occurs and confirmed the idea that a monomer–dimer equilibrium is involved. This equilibrium is expressed as eqn (1), in which $MV^{\cdot +}$ is the methyl viologen cation radical.

$$(MV^{\cdot +})_2 \leftrightarrow 2MV^{\cdot +} \qquad (1)$$

Quantitative studies on this dimerization have been carried out by absorption spectroscopy using the chemical reduction method.[7,8]

There are several reports dealing with the dimerization of viologens. Some reports[9] assigned the 365 nm and 560 nm bands as those of the dimer and the 600 nm band as that of the monomer, data somewhat different from the spectra evaluated by other workers. The change in the UV–visible spectrum of the PC/methanol solution of reduced EV with change in voltage shows very similar behavior to that obtained for an aqueous medium of reduced methyl viologen. In this latter spectrum, it was found that the monomer radical cations (λ_{max} 600 nm) were in equilibrium with the dimer molecule (λ_{max} 365 and 560 nm).

In PC/methanol solution of reduced EV, the λ_{max} values are very close to those of reduced methyl viologen, so it is feasible, by analogy, to postulate a similar monomer–dimer equilibrium.

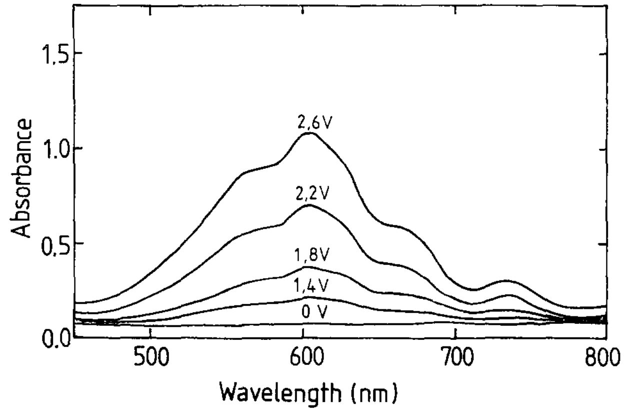


Fig. 2. Absorption spectra of the colored PV cell as a function of applied voltage.

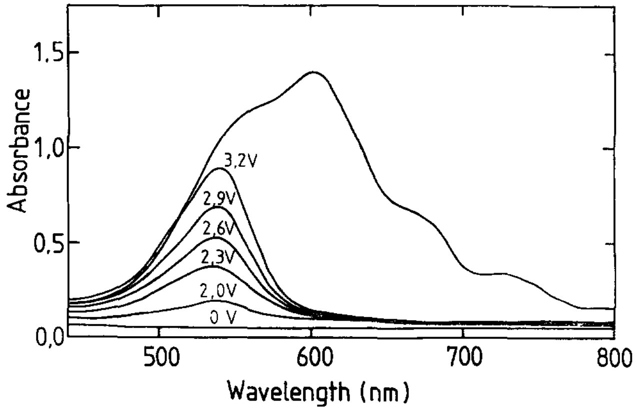


Fig. 3. Absorption spectra of the colored EBV cell as a function of applied voltage.

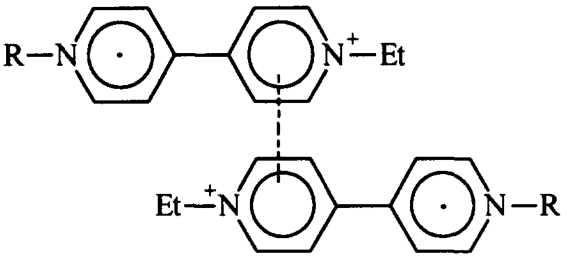
Figure 2 shows the optical density (OD) change of the PV cell as a function of the applied voltage; the optical density increases with increase in the applied voltage and the color is blue. At an applied voltage of 1.4–2.5 V in the PV cell, an absorption peak at around 600 nm is apparent (as that of monomer) and the color is blue.

It was noted that no dimer absorption was present in the electrogenerated PV solution. As shown in Fig. 2, the spectrum obtained by electrolysis of PV differed from that of the EV radical cation and a similar trend was observed in the BV system.

The length of alkyl chain has a significant influence on the formation of the viologen dimer and we therefore conclude that the longer the length of the alkyl chain, the weaker the force aggregating the viologens.

Figure 3 shows the absorption spectra of reduced EBV in PC/methanol solution for different applied voltages. The close similarity between these spectra (Fig. 3) and the spectrum shown in Fig. 1 leads us to conclude that the ethyl moiety is attributable to formation of dimer.

We propose that the dimer of the radical cation of the viologens exists in a head to head structure with two monomer molecules (by π-interactions). See Structure 1.



We have also investigated the formation of dimer in relation to the size of counter ion. The ECD cell containing 1,1′-diethyl-4,4′-dipyridinium diiodide colored blue at 2.0 V but changed colorless in the open-circuit condition. As mentioned above, the reduced EV exhibited monomer–dimer equilibrium. However, on replacement of bromide by iodide as the counter ion, monomer–dimer equilibrium behavior was not observed. This is almost certainly due to steric hindrance factors inhibiting formation of the dimer. It is therefore concluded that the formation of dimer is markedly affected by the size of the counter ions.

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REFERENCES

1. Bird, C. L. & Kuhn, A. T., *Chem. Soc. Rev.*, **10** (1981) 49.
2. Summers, L. A., *Bipyridinium Herbicides*. Academic Press, New York, 1980.
3. Bruinink, J., Kregting, C. G. A. & Ponjee, J. J., *J. Electrochem. Soc.*, **124** (1977) 1854.
4. Yasuda, A., Mori, H. & Seto, J., *J. Appl. Electrochem.*, **17** (1987) 5687.
5. Kim, S. H., Bae, J. S. & Hwang, S. H., *Dyes and Pigments* **2** (1996) 89.
6. Schwarz, W. H. Jr., Ph.D. Thesis, University of Wisconsin, 1961.
7. Kosowar, E. M. & Cotler, J. L., *J. Am. Chem. Soc.*, **86** (1964) 5524.
8. Stargasdt, J. F. & Hawkridge, F. M., *Anal. Chim. Acta*, **146** (1983) 1.
9. Meisel, D., Mulac, A. & Matheson, M. S., *J. Phys. Chem.*, **85** (1981) 179.