

Electrochemical Study on the Dimerization of $2e^-$ -Reduced N',N'' -(Trimethylene)bis(N-methyl-4,4'-bipyridinium) Ion within Zeolite Cavities

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N,N' -Disubstituted-4,4'-bipyridinium salts, known as viologen (V^{2+}), have been used as electron mediators, herbicides, an active component of electrochromic display, and electron acceptor moiety in supramolecular systems.¹ One-electron reduced viologen, $V^{\cdot+}$, is known to dimerize in solution,²⁻⁶ and the dimerization affects physico-chemical properties and thus applicabilities of viologens. To control monomer-dimer equilibria of $V^{\cdot+}$, cyclodextrins (CDs) have been used most frequently.³⁻⁶ However, because of hydrophobic characters and small cavity volumes of CDs, effects of CDs on the dimerization of $V^{\cdot+}$ is usually observed with viologens with long alkyl chains.

Zeolites have well-defined framework structures with cavities of varying dimensions depending on the types. Viologens are easily incorporated into zeolite cavities by ion-exchange.⁷ It is expected that the dimerization behavior of $V^{\cdot+}$ is highly dependent on the cavity dimensions and a study on the dimerization within zeolite cavities might provide new insights into the dimerization of $V^{\cdot+}$. There have been some reports on the redox chemistry of the methyl viologen in clays⁸ and zeolites,^{7b} however, few reports dealt in the dimerization of $V^{\cdot+}$ except the methyl viologen extensively.

In this report, we wish to present the dimerization reaction between viologen moieties of $2e^-$ reduced N',N'' -(trimethylene)bis(N-methyl-4,4'-bipyridinium) ion, $C_1V^{2+}-C_3-VC_1^{2+}$, inside the cavities of zeolite-L (channel diameter: 7.1 Å) and ZSM-5 (channel diameter: 5.5 Å) studied by electrochemical methods. $C_1V^{2+}-C_3-VC_1^{2+}$ was chosen because its $2e^-$ reduced species has been reported to form an intramolecular dimer nearly quantitatively,⁹ but the intramolecular dimerization is expected to be hindered in the restricted space of zeolite channels.

Experimental Section

Zeolite-L (ELZ-L, Lot No. 961687041001-S) was purchased from Union Carbide. ZSM-5 with the Si/Al ratio of 13.5 was a gift from ALSI-PENTA Zeolite GmbH. An iodide salt of N',N'' -(trimethylene)bis(N-methyl-4,4'-bipyridinium), $C_1V^{2+}-C_3-VC_1^{2+} \cdot 4I^-$, was synthesized^{9b} and ion-exchanged⁷ into zeolite-L and ZSM-5 using the reported procedures. The concentration of $C_1V^{2+}-C_3-VC_1^{2+}$ were calculated using $\epsilon = 4.4 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$ at 257 nm.^{9b} The zeolite modified elec-

trode (ZME) was prepared by transferring 10 μL of the viologen-exchanged zeolite dispersion solution (zeolite 5.0 mg, carbon paste 5.0 mg and polystyrene 1.0 mg in 0.4 mL THF)¹⁰ onto the surface of a glassy carbon electrode (BAS, area of 0.07 cm^2) followed by drying. Cyclic voltammetry (CV) experiments were carried out with the modified electrode and an Ag | AgCl | 3M NaCl reference electrode (BAS) in 0.1 M KCl solution using a BAS 100B electrochemical analyzer. For the spectroelectrochemical experiments, 40 μL of the viologen-exchanged zeolite dispersion solution (zeolite 5.0 mg in 0.4 mL H_2O) was transferred onto ITO glass (Delta, working area of 0.50 cm^2) and dried. A 15 μL aliquot of polystyrene (1.0 mg)/THF (0.4 mL) mixture was then dropped on the surface to enhance the binding.¹⁰ A spectroelectrochemical cell was constructed using the ITO electrode coated with viologen-exchanged zeolite in aqueous solutions containing only supporting electrolyte, and absorption spectra of $C_1V^{\cdot+}-C_3-VC_1^{\cdot+}$ /zeolite were taken with a HP 8452 diode array spectrometer after electrolysis at an appropriate potential.^{5a}

Results and Discussion

The absorption spectrum of $2e^-$ reduced bisviologen, $C_1V^{\cdot+}-C_3-VC_1^{\cdot+}$, in an aqueous solution shows characteristic bands at 361 and 534 nm with a shoulder at 504 nm as shown in Figure 1A. This is the spectrum of the intramolecular dimer, $C_3[C_1V^{\cdot+}]_2$.^{5c} This spectrum is somewhat different from that of intermolecular dimer of viologen radical cations ($[C_1C_1-V^{\cdot+}]_2$), where no shoulder peaks are exhibited.³⁻⁶

The absorption spectrum of $C_1V^{\cdot+}-C_3-VC_1^{\cdot+}$ incorporated into zeolite-L (Figure 1B) also shows a very similar feature as that in homogeneous solution (Figure 1A) except a small peak near 400 nm¹¹; the peak at 396 nm is due to viologen radical cation monomer.⁶ This implies that $C_1V^{\cdot+}-C_3-VC_1^{\cdot+}$ exists mostly as a dimeric form inside zeolite-L under the experimental condition.¹² Zeolite-L has a lobed channel type structure with *ca.* 7 Å cavity opening and maximum *ca.* 13 Å lobe inside diameter. This dimension may not be large enough to provide the space for folding of N-methyl-4,4'-bipyridinium moiety of intramolecular dimer, *i.e.*, from open structure of $C_1V^{2+}-C_3-VC_1^{2+}$ (29 Å) to folded structure of $C_3[C_1V^{\cdot+}]_2$ of intramolecular dimer upon electroreduction. To ascertain whether the spectrum as shown in Figure 1 is possible for intermolecular dimer in the cavity of zeolite-L, we examined the spectrum of $1e^-$ -reduced methyl viologen

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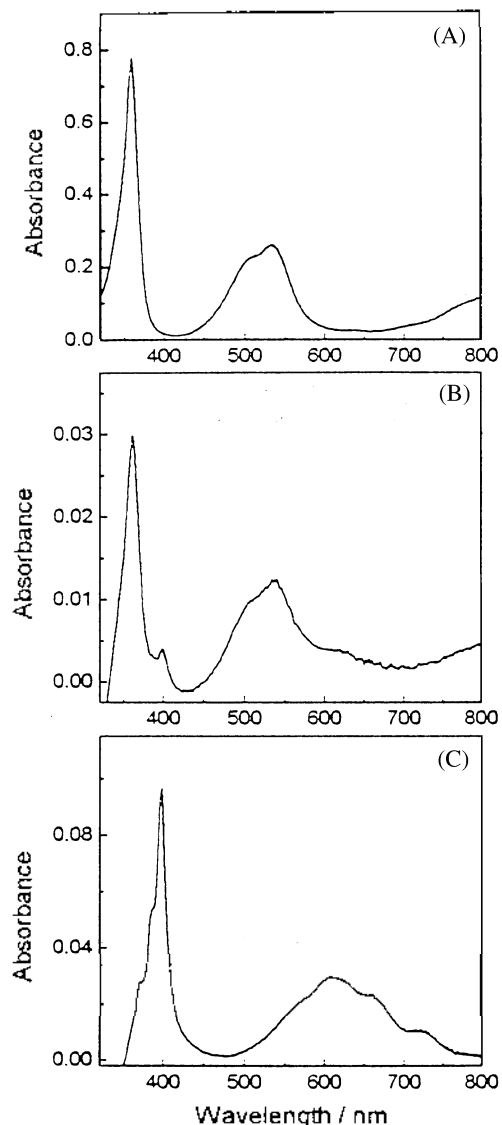


Figure 1. Absorption spectra of $C_1V^{2+}-C_3-VC_1^{2+}$ in an aqueous solution (A, 1 mM), $C_1V^{2+}-C_3-VC_1^{2+}$ incorporated into zeolite L (B, Loading: 1.4×10^{-4} mol/g) and $C_1V^{2+}-C_3-VC_1^{2+}$ incorporated into ZSM-5 in 0.1 M KCl solution (C, Loading: 1.7×10^{-4} mol/g).

encapsulated in zeolite-L. Unlike in solution, essentially the same spectrum as shown in Figure 1 was observed.

The formation of intermolecular dimer in zeolite-L is supported by cyclic voltammetry (CV) experiments. CV of $C_1V^{2+}-C_3-VC_1^{2+}$ in zeolite-L is observed to be highly dependent on the extent of loading of the bisviologen as shown in Figure 2. At low loading, the CV of $C_1V^{2+}-C_3-VC_1^{2+}$ /zeolite-L is very similar to that of methyl viologen in homogeneous solution showing the first reduction peak near -0.68 V. However, the first reduction peak is observed near -0.53 V for samples of high loading. The positive shift in reduction potential of $C_1V^{2+}-C_3-VC_1^{2+}$ in zeolite-L at high loading is attributed to the stabilization of the reduced form upon dimerization. Such dependence of the reduction behavior of $C_1V^{2+}-C_3-VC_1^{2+}$ on the extent of loading is not expected for the intramolecular dimerization. We thus conclude that the

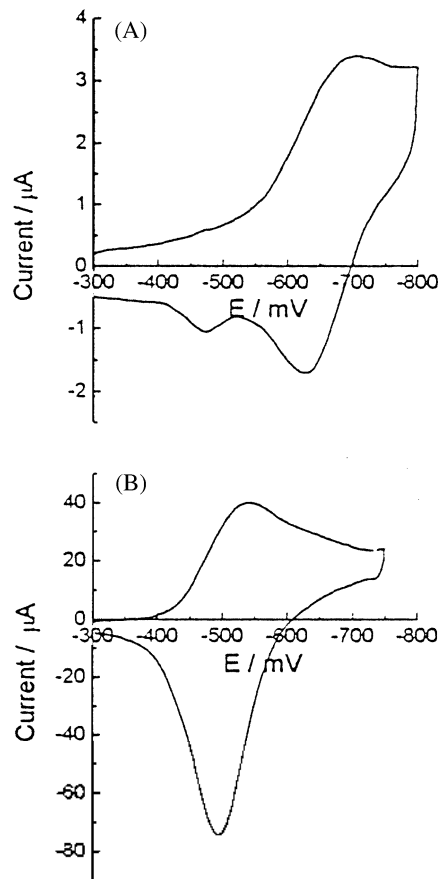


Figure 2. Cyclic voltammetric waves of $C_1V^{2+}-C_3-VC_1^{2+}$ /zeolite-L modified electrode in 0.1 M KCl solution with scan rate of 0.1 V/s. Loading: 7.1×10^{-6} mol/g (A); 1.7×10^{-4} mol/g (B).

viologen dimer in zeolite-L is of intermolecular nature.

The absorption spectrum of $2e^-$ -reduced $C_1V^{2+}-C_3-VC_1^{2+}$ (Figure 1C) in ZSM-5 is that of a typical monomeric form of V^{1+} , where the characteristic absorption bands at 396 and 604 nm with vibronic shoulders are shown.¹⁻⁶ This implies that the channel size of ZSM-5 is too small to form intramolecular as well as intermolecular dimer.

Finally, we like to discuss the spectral shape of viologen radical cation dimers in terms of their structures. In homogeneous solutions, the intermolecular dimer shows a band near 530 nm without any structural features. However, intramolecular dimers formed from bisviologen linked with trimethylene and pentamethylene chains, and intermolecular dimers of the reduced viologens induced by γ -CD exhibits a shoulder at around 510 nm.^{5c} An X-ray crystallographic study on the crystals of the methyl viologen radical cation with PF_6^- indicated that the axis of bipyridinium moieties in the dimer are staggered by 37° .¹³ Such a staggered arrangement of the bipyridinium moiety does not seem to be feasible in zeolite-L due to the small cavity size. Thus, it is highly probable that the appearance of the shoulder in *ca.* 530 nm peak of viologen dimer may be ascribed to the change of the arrangement of bipyridine rings from staggered to parallel.¹⁴

In conclusion, this study demonstrated that the control of intramolecular and intermolecular dimerization as well as

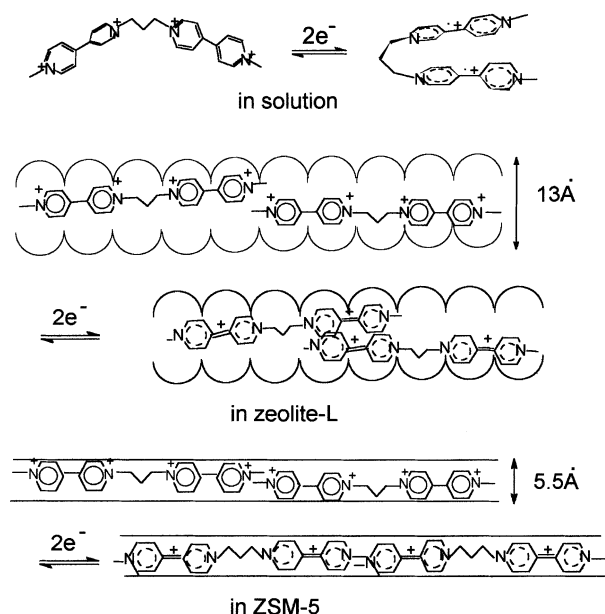


Figure 3. Schematic diagram for intramolecular dimerization of $C_1V^+-C_3-VC_1^+$ in solution (top), intermolecular dimerization in zeolite-L (middle), and suppression of dimerization of $C_1V^+C_3-VC_1^+$ in ZSM-5 (bottom).

the suppression of dimerization of $C_1V^+-C_3-VC_1^+$ are possible using different types of zeolites with electrochemical reduction (Figure 3). The radical cation of $C_1V^+-C_3-VC_1^+$ formed an intermolecular dimer in zeolite-L, where the appearance of a shoulder peak at *ca.* 530 nm was discussed in terms of the arrangement of bipyridine rings in dimer.

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- We also took the absorption spectra of the reduced viologen incorporated in zeolite by diffuse reflectance mode. However, the spectra by transmittance mode gave better signal to noise, presumably due to decrease of scattering by zeolite particles upon wetting.
- Zeolite-L-encapsulated $C_1V^+-C_3-VC_1^+$ prepared by solvated electrons showed its characteristic monomeric bands at dry state, but it showed dimeric bands upon hydration. This implies that the dimerization undergoes upon reduction at hydrated state. Details are discussed in reference 14.
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