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Electrochemical Studies of Viologens in Homogeneous Aqueous and Sodium Dodecyl Sulfate Micellar Solutions

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Cyclic voltammetric behavior of symmetric (dimethyl, diheptyl, dioctyl, dibenzyl) and asymmetric (methyloctyl, methyldodecyl, methylbenzyl) viologens was investigated in homogeneous aqueous solution and sodium dodecyl sulfate (SDS) micellar media. In SDS-free 0.1 M NaCl solutions, the reduction potential is less negative as the chain length of alkyl substituent is longer. This is due to the stabilization of the reduced cationic radical and neutral form of viologen by adsorption on electrode surface. The adsorbed species show the "aging-effect". With the exceptions of methyldodecyl viologen and methylbenzyl viologen, the viologens show strong tendency of conproportionation reaction between viologen dications and neutral forms. In cases of methyldodecyl viologen and methylbenzyl viologen, the conproportionation reaction is kinetically disfavored, though it is thermodynamically favorable. SDS micelles dissolve the adsorbed species and the viologens exhibit two reversible redox processes in SDS micellar solutions. The reduction potentials of viologens in SDS micellar solutions depend little on the length of alkyl chain. Benzyl-substituted viologens are more easily reduced than the alkyl substituted viologens, presumably due to electron-withdrawing character of benzyl group.

Introduction

1,1′-Disubstituted-4,4′-bipyridinium salts (viologens) are important class of compounds which show reversible redox character and have been used as herbicides,[1] as electron mediators in experimental schemes aimed at photochemical conversion of solar energy into hydrogen[2-4] and in reduction of organic substrates by variety of means,[5,6] and as materials for electrochromic displays.[7-8] Viologens undergo two successive one-electron reduction as shown below:[9]

$$V^{2+} \underset{}{\overset{E_1}{\rightleftarrows}} V^{\cdot +} \underset{}{\overset{E_2}{\rightleftarrows}} V^{\circ} \qquad (1)$$

The viologen monocation radical ($V^{\cdot +}$) is deeply blue colored with $\lambda_{max} \simeq 600$ nm, whereas V^{2+} shows its absorption maximum near 260 nm and that of V° is about 400 nm. In solution and at the surface of an electrode, dimerization of $V^{\cdot +}$, disproportionation reaction of $V^{\cdot +}$, and conproportionation reaction between V° and V^{2+} can take place.[9]

Since the reactions of reduced forms of viologen markedly influences the deposition and the color of the reduction products of viologens, understanding of the relative extent of the reactions is important for the use of viologens as active materials of electrochromic display. Also it must be recognized that the reactions can strongly affect the course of reactions in which viologens take part as electron mediators.

Cyclic voltammetry is a major mean for investigation of redox properties and reactivity of the electrogenerated species of viologens.[9] Symmetric dimethyl viologen ($C_1C_1V^{2+}$) and diheptyl viologen ($C_7C_7V^{2+}$) were widely studied. However, a few scattered reports which deal with asymmetric viologens have appeared. Barna and Fish[7d] reported an improved electrochromic display using 1-benzyl-1′-heptyl viologen, instead of $C_7C_7V^{2+}$. Lu *et al.*[10] showed that the chain length of alkyl substituent of viologens has a large effect on the cyclic voltammetric behavior of the compounds. From a resonance Raman study, they also demonstrated that the extents of dimerization and disproportionation reaction of reduced asymmetric viologens are different from those of symmetric viologens and depend on chain length of the alkyl substituent.[11]

Oxidative quenching reactions of photoexcited tris(2,2′-diimine)ruthenium(II) complexes with viologens in both homogeneous and microheterogeneous media have been studied intensively in relation to solar energy conversion into hydrogen.[2-4] Anionic surfactants such as sodium dodecyl sulfate (SDS),[12-14] polyelectrolytes,[15] and vesicle[16] media were found to give large effects on the electrochemical behavior of viologens, presumably due to hydrophobic and electrostatic

Table 1. Cathodic Peak Potentials (Volt vs SCE) of Viologens in 0.1 M NaCl and (0.1 M NaCl+20 mM SDS) Solutions at 25℃[a,b]

Viologen	0.1 M NaCl		0.1 M NaCl+20 mM SDS	
	E_1	E_2	E_1	E_2
$C_1C_1V^{2+}$	−0.71	−1.03	−0.67	−1.04
$C_7C_7V^{2+}$	−0.62	−0.75	−0.65[c]	−0.96[c]
$C_8C_8V^{2+}$	−0.56	−0.74	−0.65[c]	−0.95[c]
BBV^{2+}	−0.58	−0.76	−0.58[c]	−0.97[c]
$C_1C_8V^{2+}$	−0.72	−0.84	−0.66	−0.94
$C_1C_{12}V^{2+}$	−0.59	−0.78	−0.65	−1.07
C_1BV^{2+}	−0.66	−0.91	−0.60	−1.00

[a] At scan rate of 260 mV/s. [b] Adsorption of viologens and their reduction products on electrode surface prevented the calculation of thermodynamic redox potentials, but they are estimated to be 30 mV positive to the corresponding cathodic peak potentials. [c] Measured at 40°C.

interactions of viologens and/or their reduced species with the microparticles. The strong dependence of the quenching rate on the alkyl chain of viologens was attributed to the difference in the degree of embedment of viologens in the SDS micelle.[4,17,18] However, there is paucity of data for reduction potentials of viologens with different alkyl chain in the micellar solution to correlate the kinetic data with thermodynamic properties of the quenchers.

In this paper, we compare the cyclic voltammetric behavior of various symmetric and asymmetric viologens in homogeneous aqueous and SDS micellar solutions. The reduction peak potentials of the viologens in the media are presented.

Experimental

Materials. The viologens and their abbreviations used in this investigation are the following: symmetric viologens are dimethyl viologen ($C_1C_1V^{2+}$), diheptyl viologen ($C_7C_7V^{2+}$), dioctyl viologen ($C_8C_8V^{2+}$), and dibenzyl viologen (BBV^{2+}); asymmetric viologens are 1-methyl-1'-octyl viologen ($C_1C_8V^{2+}$), 1-methyl-1'-dodecyl viologen ($C_1C_{12}V^{2+}$), and 1-methyl-1'-benzyl viologen (C_1BV^{2+}). The counter ion of these compounds was chloride. Except BBV^{2+} (Aldrich), the viologen chlorides were made in this laboratory by a procedure described elsewhere.[4] SDS (Fluka) was recrystallized three times from absolute ethanol after washing with diethyl ether. Water was deionized and then distilled in glass from acidic $KMnO_4$.

Electrochemistry. The cyclic voltammetric measurements were carried out with a Tacussel PRG 5 potentiostat and GSTP3 function generator. Voltammograms were recorded on a Rikadenki Model 21 T X-Y recorder. A glassy carbon electrode (Metrohm, A=0.0608 cm²) was used as a working electrode. The electrode was polished with a 0.1 μm alumina/water slurry before use. A platinum electrode was used as a counter electrode. Potential was recorded against a saturated calomel electrode (SCE). All the experiments were performed with the solution containing 0.1 M NaCl under the purified nitrogen atmosphere. Unless otherwise specified solution temperature was 25°C.

Results and Discussion

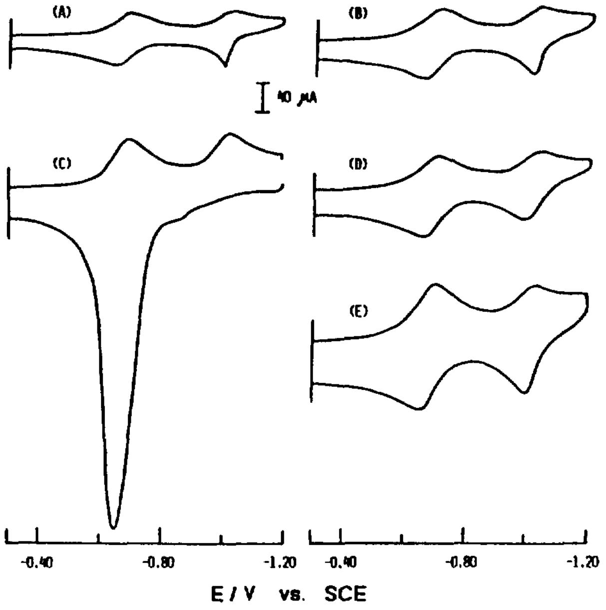

Figure 1. Cyclic voltammograms of 1.0×10^{-3} M $C_1C_1V^{2+}$ in 0.1 M NaCl solutions. Scan rates are (A), 65 mV/s; (B)-(D), 130 mV/s; (E), 260 mV/s. (C) is the voltammogram taken after electrolysis at −1.20 V for 90 s. Solution temperature for (D) was at 40℃ and others were at 25℃. All voltammograms are in the same current scale.

Redox potentials of viologen in homogeneous aqueous and 20 mM SDS micellar media are summarized in Table 1. We describe here electrochemical behavior of individual classes of viologns.

Symmetric Viologens in Homogeneous Aqueous Media. Cyclic voltammetric behavior of viologens was highly dependent on the chain length of the alkyl substituent. Figure 1 shows cyclic voltammograms of 1.0×10^{-3} M $C_1C_1V^{2+}$ containing 0.1 M NaCl taken at various scan rates. The cathodic scan exhibits two successive reduction waves at −0.71 and −1.03 V *vs* SCE. Also two anodic peaks are shown in backward scan. The peak-to-peak potential differences of the cathodic and anodic peaks are about 0.06 V for the first redox step and about 0.03 V for the second step.

It has been accepted that the redox peak near −0.70 V corresponds to the first redox reaction Eq. (2) of $C_1C_1V^{2+}$. The peak near −1.0 V was generally considered to be the reduction of $C_1C_1V^{\cdot +}$ as represented in Eq. (3).[9-16]

$$C_1C_1V^{2+}+e^-=C_1C_1V^{\cdot +} \tag{2}$$

$$C_1C_1V^{\cdot +}+e^-=C_1C_1V^{\circ} \tag{3}$$

The methyl viologen cationic radical ($C_1C_1V^{\cdot +}$) is known to form a dimer in aqueous media.[15,19-21] Heyrovsky claimed that the actual reduction potential of $C_1C_1V^{\cdot +}$ is −1.35 V and the voltammetric peak of $C_1C_1V^{2+}$ observed at −1.0 V is due to the reduction of dication dimer, $(C_1C_1V^{\cdot +})_2$.[19] Kosower and Cotter[20] estimated the equilibrium constant for the dimerization reaction of diethyl viologen cation radicals as 380 M^{-1} in 1 M KCl. Considering hydrophobic and electrostatic effects on the dimerization reaction, the equilibrium constant for $C_1C_1V^{\cdot +}$ in 0.1 M NaCl should be much smaller than 380 M^{-1}. Quintela *et al.*[15] reported extensive dimerization of electrogenerated $C_1C_1V^{\cdot +}$ in SDS media of the concentration slightly above the critical micelle concentration (cmc: 1.0 mM) of the surfactant. In 0.1 mM SDS solution, they estimated the ratio of dimer to monomer (D/M) is 0.21. Considering premicellar association of $C_1C_1V^{\cdot +}$ with dodecyl sulfate anion,[12] the D/M ratio in the absence of SDS should be much less than 0.21. Thus we assign the voltammetric peak at −1.0 V to the second reduction of the viologen Eq. (3).

The oxidation peak near −1.0 V, which corresponds to the oxidation of $C_1C_1V^{\circ}$, is sharper than the other peaks. This is a typical pattern of a cyclic voltammogram where the reduction product is adsorbed. As the scan rate is getting faster, the desorption peak becomes less sharp, indicating that the adsorption process is slow. Raising the solution temperature from 25℃ to 40℃ (Figure 1D) results in little change in reduction peaks, but the peak corresponding to the first oxidation of $C_1C_1V^{\circ}$ shows slight anodic shift exhibiting the peak-to-peak potential difference of the second redox peaks as 0.06 V. Also, the sharp desorption peak is not observed at 40℃. These observations indicate that no significant electrode adsorption of $C_1C_1V^{\circ}$ occurs at 40℃, presumably due to small enthalpy of adsorption.

The cyclic voltammogram of the first anodic scan after electrolysis of $C_1C_1V^{2+}$ at −1.20 V *vs* SCE for 90 s is shown in Figure 1C. The oxidation peak of $C_1C_1V^{\circ}$ is virtually undetected. Instead, a large oxidation peak of $C_1C_1V^{\cdot +}$ is seen at the same potential observed in normal cyclic voltammograms. This implies that most of $C_1C_1V^{\circ}$ electrogenerated during electrolysis undergo conproportionation reaction with $C_1C_1V^{2+}$, Eq. (4).

$$C_1C_1V^{2-} + C_1C_1V^{\circ} = 2C_1C_1V^{\cdot +} \quad (4)$$

Thermodynamically, the equilibrium constant of the reaction (4) is related to the two redox potentials by Eq. (5):

$$K_{comp} = \exp[-(E_2 - E_1)F/RT] \quad (5)$$

Taking E_1 and E_2 for the reduction of $C_1C_1V^{2+}$ as −0.68 and −1.00 V, respectively, K_{comp} is calculated to be 5.8×10^5, which agrees well with the reported value of 3.8×10^5.[13]

There has been some controversy whether $C_1C_1^{\cdot +}$ is adsorbed on the electrode or not. Kobayashi *et al.*[22] from a polarographic work and Datta and his coworkers[23] from a spectro-electrochemical study using a carbon electrode claimed that the radical cation of the dimethyl viologen is adsorbed on the surface of electrodes. On the other hand, our previous works[12] and the works of Kaifer and Bard[13] did not reveal any evidence for the adsorption of $C_1C_1V^{\cdot +}$ in homogeneous aqueous media. In the presence of SDS below cmc, the cation radical is co-adsorbed with dodecyl sulfate anion (*vide infra*). The observations of 0.06 V for peak-to-peak potential difference in cyclic voltammogram or the first redox step and the same potential for oxidation of $C_1C_1V^{\cdot +}$ in both cyclic voltammograms taken normally and taken after interruption at −1.20 V seem to indicate that $C_1C_1V^{\cdot +}$ is not adsorbed.

It has been reported that cyclic voltammetric behavior of $C_7C_7V^{2+}$ is strongly influenced by the solution composition, electrode materials, and the scan rate.[7c,16,24–26] Figure 2 shows cyclic voltammograms of $C_7C_7V^{2+}$ taken with a glassy carbon electrode (GCE) at various scan rates and different temperatures. Cathodic scan exhibits two reduction peaks (*a, c*) at −0.62 and −0.75 V when the scan rate is relatively low, while two shoulders (*a, b*) at −0.62 and −0.67 V and a peak (*c*) at −0.75 V are seen at fast scan (for designation of peaks, refer to Figures 2B and 2C). The peaks *a* and *c* correspond to two one-electron reduction reactions. According to Brunink *et al.* the shoulder *b* is attributed to the reduction of charge-transfer complex between viologen dication and cation radical.[7c] Oxidation peaks are more dependent on scan rate: for example, at scan rate of 65 mV/s, three peaks (*d, e, f*) appear at −0.37, −0.50 and −0.64 V: by increasing the scan rate, the peak at −0.64 V is replaced by another peak *g* near −0.69 V. Raising the solution temperature to 40℃ from 25℃ reduces the oxidation peak *d* and enhances the peak *g*.

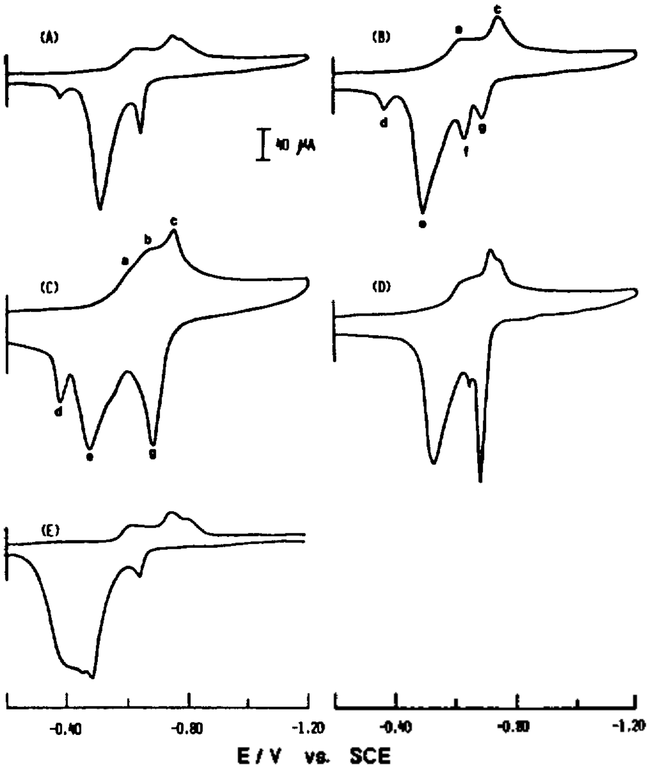

Figure 2. Cyclic voltammograms of 1.0×10^{-3} M $C_7C_7V^{2-}$ in 0.1 M NaCl solutions. Scan rates are (A), 65 mV/s; (B), 130 mV/s; (C), 260 mV/s; (D) and (E), 130 mV/s. (E) is the voltammogram taken after electrolysis at −1.20 V for 90 s. Solution temperature for (D) was at 40℃ and others were at 25℃. Bar (I) denotes 40 μA and all voltammograms are in the same current scale.

It is well known that diheptyl viologen radical ($C_7C_7V^{\cdot +}$) salt and neutral viologen ($C_7C_7V^{\circ}$) form insoluble films on the electrode surface.[7] The peaks *c-f* are sharper than the peak *a* as the redox reactions take place from the deposited films. The dependence of the adsorption-related peaks on the scan rate is ascribed to so-called 'aging-effect' which states reorientation or phase transition of the viologen film after initial formation by electrochemical reaction.[7c,24–26] The oxidation peaks *d* and *f* might be ascribable to the two one-electron redox reactions of aged film, as they are observed

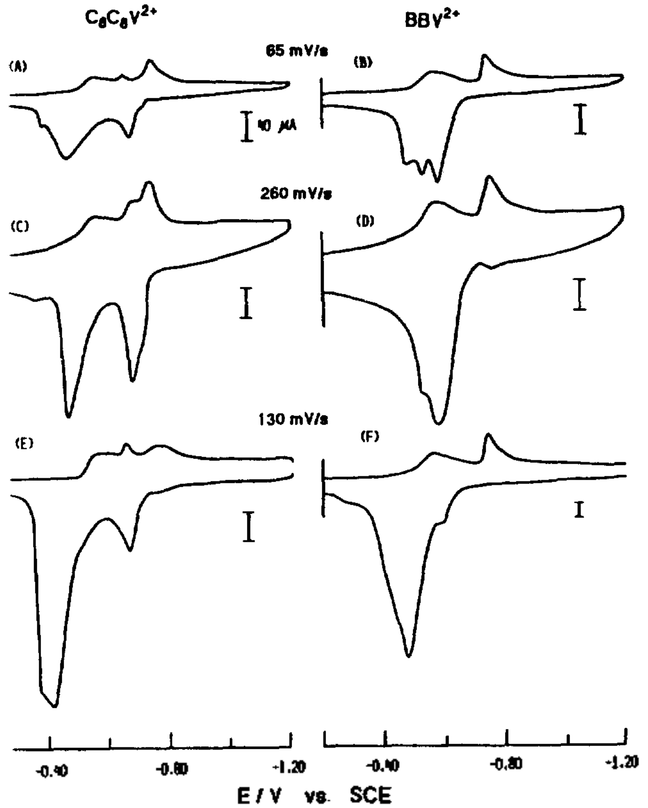

Figure 3. Cyclic voltammograms of 1.0×10^{-3} M $C_8C_8V^{2+}$ (A, C, E) and 1.0×10^{-3} M BBV^{2+} (B, D, F). Scan rates are 65 mV/s (A, B), 260 mV/s (C, D). (E) and (F) and taken with scan rate of 130 mV/s after interruption at −1.20 V for 90 s. Bars (I) denote 40 μA.

only when the scan rate is low. The peak *g* is related to the reduction peak *c* and could be assigned to the oxidation of neutral viologen which did not undergo phase transition. From the dependence of temperature and scan rate, the peak *d* is assigned to the oxidation of dimer $(C_7C_7V^{\cdot +})_2$. Like $C_1C_1V^{2+}$, strong tendency of conproportionation reaction between $C_7C_7V^{\circ}$ and $C_7C_7V^{2+}$ is observed.

Cyclic voltammogram of $C_8C_8V^{2+}$ (Figure 3) is similar to that of $C_7C_7V^{2+}$. However, a few noticeable differences are observed (Figures 3A, 3C, 3E). One is that the potential corresponding to reduction of $C_8C_8V^{2+}$ to $C_8C_8V^{\cdot +}$ (*ca.* −0.56 V) is less negative than the corresponding value for $C_7C_7V^{2+}$, −0.62 V. The other is that the oxidation peak *f*, which is assigned to the oxidation of aged $C_8C_8V^{\circ}$ film, persists while the peak *g* appears as a shoulder at scan rate of 260 mV/s. These results imply that the rate of phase transition of the reduced viologen film is much faster for dioctyl viologen than for diheptyl viologen.

Cyclic voltammograms of BBV^{2+} (Figure 3B, 3D and 3F) shows two one-electron reduction peaks at −0.58 and −0.75 V. The oxidation peaks are strongly influenced by scan rate. At relatively low scan rate, three anodic peaks are observed at *ca.* −0.49, −0.54 and −0.59 V. As the scan rate increases, the −0.59 V peak becomes more important and the −0.49 V peak becomes less significant. An additional small peak at *ca.* −0.76 V appears when scan rate is 260 mV/s, which can be assigned to the oxidation of BBV° to $BBV^{\cdot +}$. Cyclic voltammogram taken at 40℃ with the scan rate of 130 mV/s showed sharp spikes at −0.54 (large) and −0.61 V (small), but other oxidation peaks were not found (voltammogram is not shown). The first anodic scan after interruption at −1.20 V for 90 s revealed a shoulder at *ca.* −0.60 V, and a large peak at *ca.* −0.48 V (Figure 3F). Potentials and assignments of the voltammetric peaks of BBV^{2+} as well as those of $C_7C_7V^{2+}$ and $C_8C_8V^{2+}$ are summarized in Table 2.

The first reduction peak potentials of $C_7C_7V^{2+}$ and BBV^{2+} are in good agreement with previous reports.[25-27] However, the potentials of second reduction obtained in this study are about 0.1 V positive to the reported values. This is presumably due to different solvent systems: other workers used high concentration of KBr, typically 0.3 M, whereas we used 0.1 M NaCl; viologen cation radicals form stable precipitates with Br^- stabilizing the cation radical salt against further reduction.

Asymmetric Viologens in Homogeneous Aqueous Solutions. Figure 4 compares cyclic voltammograms of $C_1C_8V^{2+}$, $C_1C_{12}V^{2+}$ and C_1BV^{2+}. The voltammogram of $C_1C_8V^{2+}$ exhibits three reduction peaks at −0.72, −0.84 and

Table 2. Peak Potentials of Cyclic Voltammograms for Symmetric Dialkyl Viologens on a Glassy Carbon Electrode in Aqueous 0.1 M NaCl Solutions

Peak	Potentials (V *vs.* SCE)						Assignment
	Scan Rate=65 mV/s			Scan Rate=260 mV/s			
	$C_7C_7V^{2+}$	$C_8C_8V^{2+}$	BBV^{2+}	$C_7C_7V^{2+}$	$C_8C_8V^{2+}$	BBV^{2+}	
			Cathodic				
a	−0.62	−0.56	−0.58	−0.62(s)	−0.56	−0.58	$V^{2+} \rightarrow V^{\cdot +}$ (ad)
b		−0.65	−0.67(s)	−0.67	−0.75		Redn of CT[7c]
c	−0.75	−0.74	−0.75	−0.75	−0.74	−0.76	$V^{\cdot +}(ad) \rightarrow V^{\circ}(ad)$
			Anodic				
d	−0.37	−0.38		−0.37	−0.36		$(V^{\cdot +})_2 \rightarrow V^{2+}$
e	−0.50	−0.46	−0.49*, −0.54	−0.47	−0.46	−0.53	$V^{\cdot +}(ad) \rightarrow V^{2+}$
f	−0.64	−0.67	−0.59	−	−0.67	−0.58	$V^{\circ}(ag) \rightarrow V^{\cdot +}(ad)$
g				−0.69	−0.71(s)	−0.76	$V^{\circ}(ad) \rightarrow V^{\cdot +}(ad)$

*Oxidation of reoriented (aged) $BBV^{\cdot +}$ to BBV^{2+}, **(ad) and (ag) denote electrode adsorbed and aged films, respectively.

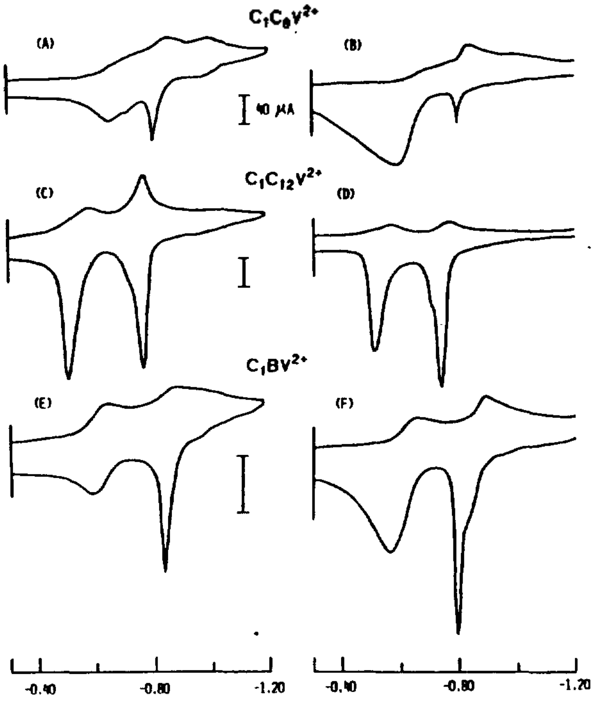

Figure 4. Cyclic voltammograms of 2.0×10^{-3} M $C_1C_8V^{2+}$ (A, B), 0.72×10^{-3} M $C_1C_{12}V^{2+}$ (C, D), and 0.72×10^{-3} M C_1BV^{2+} (E, F). Left (A, C, E) voltammograms are normal voltammograms, and Right (B, D, F) are those taken after interruption at −1.2 V for 90 s. Scan rates were 130 mV/s. Bars (I) indicate 40 μA.

−0.99 V. In anodic scan of $C_1C_8V^{2+}$ solution at high scan rate, three corresponding oxidation peaks are seen at −0.66, −0.81 and −0.96 V. The two pairs of redox peaks near −0.70 and −0.82 V agree well with a report by Lu *et al.*[10] and might be ascribed to the two successive one-electron redox processes of $C_1C_8V^{2+}$ involving electrode-adsorbed $C_1C_8V^{\cdot +}$ salt. The reduction peak at −0.99 V and the corresponding oxidation peak at −0.96 V were not noticed by Lu *et al.*[10] and could be due to the reduction of $C_1C_8V^{\cdot +}$ which did not adsorb on electrode. However, additional experiments are clearly needed for less speculative explanation. When the scan rate is low, an additional small oxidation peak is observed at −0.73 V. This seems to be the oxidation peaks of $C_1C_8V^{\circ}$ film after reorientation or phase transition. As other symmetric viologens, the current for oxidation of $C_1C_8V^{\cdot +}$ is much greater than that of $C_1C_8V^{\circ}$ indicating strong tendency of conproportionation reaction between $C_1C_8V^{2+}$ and $C_1C_8V^{\circ}$.

In agreement with previous reports,[10,12] cyclic voltammogram of $C_1C_{12}V^{2+}$ displays two well-separated redox peaks: the cathodic peak potentials are −0.59 and −0.78 V, whereas the anodic peak potentials are −0.52 and −0.77 V. At slow scan rate, the another oxidation peak from 'aged' $C_1C_{12}V^{\circ}$ appears in the vicinity of second redox step. Interestingly, the peak currents of two oxidation steps for this viologen are similar in magnitude. This implies that the conproportionation reaction (4) does not occur in significant extent for this viologen, though the reaction is thermodynamically favorable: K_{comp} is calculated to be 42 from reduction peak potentials.

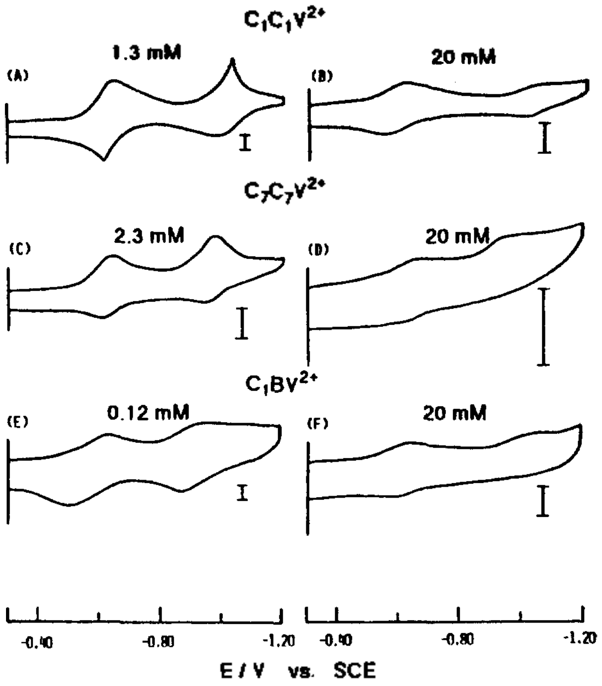

Figure 5. Cyclic voltammograms of 1.0×10^{-3} M $C_1C_1V^{2+}$ (A, B), 1.0×10^{-3} M $C_7C_7V^{2+}$ (C, D) and 0.72×10^{-3} M C_1BV^{2+} (E, F) in the presence of SDS. Scan rates are 130 mV/s. Bars (I) represent 20 μA. The concentrations of SDS are shown. (D) was taken at 40℃ and others were at 25℃.

The cathodic peaks for C_1BV^{2+} are observed at −0.66 and −0.91 V, while the corresponding anodic peaks are observed at −0.60 and −0.85 V. As other viologens investigated in this study, the second oxidation peak appears as a sharp spike, indicative of adsorption of C_1BV°. In the range of scan rate of 32.5-260 mV/s, no significant change in peak potentials is observed with variation of scan rate. Contrary to this, the first anodic scan after interruption for 90 s at −1.2 V shows a broad oxidation peak at −0.56 V, a 0.04 V positive shift from the corresponding value in normal cyclic voltammogram, and a sharp spike at −0.79 V. The second oxidation peak observed in normal cyclic voltammogram at −0.85 V appears only as a shoulder. This indicates that the C_1BV° adsorbed on electrode surface slowly undergoes phase transition and $C_1BV^{\cdot +}$ generated from oxidation of the aged C_1BV° may have proper orientation to adhere one electrode surface. Similar to $C_1C_{12}V^{2+}$, the conproportionation reaction between dication and neutral species is not significant for this viologen.

Cyclic Voltammetric Behavior in SDS Solutions and Effect of Alkyl Substituent on the Reduction Potentials. At concentration of SDS near cmc of the surfactant, the cyclic voltammogram of $C_1C_1V^{2+}$ exhibits sharp peaks for the second reduction and the first oxidation (Figure 5A). This is in agreement with the results of Kaifer and Bard[13] and is due to adsorption of premicellar aggregate of $C_1C_1V^{\cdot +}$/dodecyl sulfate anion.[12] At higher concentration of SDS (Figure 5B), the two pairs of the redox peaks show the normal shape expected for those controlled by diffusion.

However, the potentials of the peaks are significantly different from the corresponding values measured in SDS-free solution: the first redox peaks show anodic shift of *ca.* 0.04 V and the second redox peaks exhibit cathodic shift of about 0.10 V. These behaviors agree well with our earlier findings from polarographic studies[12] and results of Kaifer and Bard,[13] and indicate that $C_1C_1V^{\cdot +}$ is more stabilized in SDS micellar phase than $C_1C_1V^{2+}$ or $C_1C_1V^{0}$. Several studies have shown strong association of $C_1C_1V^{2+}$ with SDS micelle.[12,13,28,29] The reported binding constant, varies from 900 to 70,000 M^{-1}.[28,29] Whatever the binding constant it is clear that the binding with SDS micelle is stronger for $C_1C_1V^{\cdot +}$ than for the dicationic or neutral form of the viologen.

$C_7C_7V^{2+}$, $C_8C_8V^{2+}$, and BBV^{2+} form precipitates with SDS at low SDS concentration. For solutions of these viologens, we raised temperature to 40℃ to dissolve the precipitates. When the SDS concentration is about 2.0 mM in 1.0 mM viologen solutions, the solutions were still cloudy but the adsorption related peaks were disappeared and two reversible redox processes were shown in cyclic voltammograms. Figure 5C and 5D show cyclic voltammograms of 1.0×10^{-3} M $C_7C_7V^{2+}$ in the presence of 2.3 and 20.0 mM SDS, respectively. In contrast to the behavior of $C_1C_1V^{2+}$, redox potentials of $C_7C_7V^{2+}$ and $C_8C_8V^{2+}$ shift to more negative direction by the presence of SDS, and little difference between these two viologens is found. This indicates that the less negative redox potentials in homogeneous aqueous media for the symmetric viologen with long alkyl chains, with respect to $C_1C_1V^{2+}$, mainly arise from stabilization of radical cation salt and neutral viologen by adsorption on the electrode.

The second reduction potential of BBV^{2+} shows similar large negtive shift upon addition of SDS. However, the first reduction potential of the viologen is little affected by the presence of SDS and is lowest among the viologens studied. This strongly suggests that the BBV^{2+} is intrinsically more easily reduced, presumably due to electron-withdrawing character of benzyl group, than the viologens with alkyl groups. It is also likely that the first reduction potential of BBV^{2+} in SDS-free medium is not significantly influenced by precipitation of $BBV^{\cdot +}$ salt. This is supported by absence of noticeable counter ion effect on the first reduction potential of BBV^{2+},[27] which is in marked contrast to the behavior of $C_7C_7V^{2+}$.[24]

Unlike symmetric viologens, asymmetric viologens do not precipitate with SDS. This can be attributed to the formation of cation/anion mixed micelle[30] between SDS and the amphiphilic viologens, which behave as typical surfactant molecules:[31,32] the reported cmc of $C_1C_{12}V^{2+}$ is 2.0×10^{-2} M.[31] For these viologens, the adsorption-related peaks in cyclic voltammograms are not observed even at concentration of SDS far below cmc of the surfactant as shown in Figure 5E for C_1BV^{2+}. This can be taken as an evidence of mixed micellization between the viologens and SDS (Details on the formation of viologen/SDS mixed micelle will be reported elsewhere.)

In SDS micellar solutions, the values of reduction potentials of asymmetric viologens are similar to the values of symmetric viologens. Again, the viologen with benzyl substituent shows less negative first reduction potential than those with alkyl chains. It is also apparent that the stabilization of $C_1C_{12}V^{\cdot +}$ salt by electrode adsorption is the main cause for the observation of the first reduction potential of $C_1C_{12}V^{2+}$ in SDS-free solution at positive potential with respect to that in SDS solution. It is interesting to note from Table 1 that the first reduction potentials of symmetric and asymmetric alkyl viologens are similar in SDS solution. This supports the idea that only the alkyl chains of the viologens are inserted into SDS micelle and the bipyridinium moiety is exposed to bulk aqueous phase.[4,17,18]

In SDS micellar solutions, the order of easiness for the first reduction of asymmetric viologens in $C_1BV^{2+} < C_1C_{12}V^{2+} \leq C_1C_8V^{2+}$, which is the reverse order of the rate of electron-transfer quenching of $Ru(bpy)_3^{2+}$ by the viologens.[4] This strongly implies that the difference in rate of the quenching reaction mainly arises from the difference in reducibility of the electron acceptors, viologens.

In conclusion, the reduction potentials of viologens in homogeneous aqueous solutions depend strongly on the chain length of alkyl substituent. This is mainly due to stabilization of the reduced viologen cation radical salt and neutral form by deposition on the electrode surface. The deposited species undergo phase transition. With the exceptions of $C_1C_{12}V^{2+}$ and C_1BV^{2+}, the conproportionation reaction between dications and neutrl forms of viologens is favored kinetically as well as thermodynamically. The corresponding reactions for $C_1C_{12}V^{2+}$ and C_1BV^{2+} are thermodynamically favorable but kinetically disfavored. The electrode-adsorbed species dissolve in SDS micelles and cyclic voltammograms of viologens exhibit two reversible redox processes in SDS micellar media. The reduciton potentials of viologen in the micellar solutions depend little on the alkyl substituent. The first reduction potential of benzyl-substituted viologens is less negative than the corresponding values for alkyl-substituted viologens, due to electron-withdrawing character of benzyl group.

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Synthesis and Catalytic Properties of Ruthenium(III) Unsymmetrical Schiff Base Complexes

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Ruthenium(III) unsymmetrical Schiff base complexes, [Ru(CHBPH-TP)Cl_2] and K[Ru(CHBPH-HB)Cl_2] were synthesized, where CHBPH-TP and CHBPH-HB are 5-chloro-2-hydroxybenzophenonethiophencarba aldehydephenylenediimine and 5-chloro-2-hydroxybenzophenonehydroxybenzophenonephenylenediimine. These Schiff bases were obtained from the reactions of 5-chloro-2-hydroxybenzophenone (CHB) and 2-Thiophenecarbaldehyde (TP) or hyroxybenzophenone (HB) and 1,2-diaminobenzene. Elemental analysis, conductivity and infrared studies of the complexes suggest an octahedral geometry around ruthenium. Magnetic moments of the complexes indicate a single unpaired electron in a low spin d^5 configuration. The complexes are capable of catalyzing the oxidation of styrene with sodium hypochlorite in the presence of phase transfer agent. Oxidative cleavage of C=C bond is the major reaction pathway to form benzaldehyde for styrene oxidation.

Introduction

Symmetric tetradentate Schiff base complexes have been used extensively as macrocycle models,[1] while unsymmetric complexes are required to model the irregular binding of peptides. Unsymmetric complexes are very important in biological systems as well as in industrial catalysis and are interesting also from theoretical point of view.[2]

Kusta *et al.* obtained several metal complexes with unsymmetrical Schiff bases by reacting Cu(II), Ni(II), Pd(II) salt

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