

Electrochemical Behavior of Viologens with Long Alkyl Chains Depending on Their Concentrations and the Concentration of Micelles and Cyclodextrins

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The concentration dependence of the electrochemical behaviors of 1-methyl-1'-alkyl-4,4'-bipyridinium chloride ($C_1C_nV^{2+}$; $n=14, 16, 18$) was investigated using cyclic voltammetric, chronocoulometric and spectroelectrochemical techniques. The electrochemical behavior was investigated in terms of critical micelle concentrations (CMCs) of $C_1C_nV^{2+}$ determined by spectroscopic methods. The voltammetric behavior of these three surfactant viologens at lower and higher concentrations than their CMC varied: the relieved adsorption/precipitation of 1- e^- reduction product was observed for $C_1C_{14}V^{2+}$ with an increase in its concentration, whereas reorientation after adsorption/precipitation resulted in two anodic peak responses for $C_1C_{16}V^{+}$ and $C_1C_{18}V^{+}$. These phenomena were interpreted as the competition between electrodeposition and dissolution into the micelle. This was supported by the incorporation of $C_1C_{14}V^{+}$ into cetyltrimethylammonium bromide (CTAB) micelle despite their electrostatic repulsion. Stabilization of the viologen cation radical (V^+) by cyclodextrins (CDs) was also observed, where α -CD and methylated β -CD were more effective than β -CD in suppression of adsorption/dimerization of viologens having a long alkyl chain.

Introduction

Applications of electrochemistry in microheterogeneous fluids organized by surfactants have received a great deal of attentions, and the fundamental characterization of organized fluids, including films, has been studied extensively using electrochemical methods.¹ For this purpose viologens, 1,1'-disubstituted-4,4'-bipyridinium (V^{2+}) salts, have been used as electroactive species,²⁻¹⁵ where dimerization or electrodeposition of the viologen cation radical (V^+) and the comproportionation reaction between V^{2+} and its neutral form (V^0) often played important roles in the interpretation of experimental data. Kaifer and Bard,⁴ as well as others^{5,6} reported the electrochemistry of dimethylviologen (C_1C_1V) in the presence of sodium dodecylsulfate (SDS), sodium decylsulfate, Triton X-100, and cetyltrimethylammonium bromide (CTAB) micelles. Engelman and Evans reported the electrodeposition of alkyl sulfate salts of $C_1C_1V^{+}$.⁷ Asymmetric viologens, *e.g.*, methyl(or ethyl)alkylviologens (C_1C_nV or C_2C_nV), with enhanced hydrophobic properties rather than C_1C_1V have been used. Cotton and co-workers demonstrated the interaction between C_1C_nV and vesicles.⁸ Self assemblies or Langmuir-Blodgett films of $C_1C_{16}V$, $C_1C_{18}V$, $C_2C_{16}V$, and $C_2C_{18}V$ have been reported.⁹⁻¹¹ $C_1C_{14}V^{+}$ with and without CTAB was studied by spectroelectrochemistry.¹² Kaifer and co-workers worked on complexation of $C_2C_{16}V$ and $C_2C_{18}V$ with cyclodextrins (CDs).¹³ Such amphiphilic viologens are capable of forming micelles; thus, electrochemical behavior with and without formation of micelles would be interesting since both electrochemical probes and micelles are composed of the same compound.

Previously, we reported effects of the length of alkyl chains on dimerization^{16,17} of $C_1C_nV^{+}$ and effects of α -, β -, and γ -CDs on the formation of dimer of viologen cation rad-

icals.¹⁷⁻²⁰ In this study, we investigated the electrochemical behavior of $C_1C_nV^{2+}$ ($n=14, 16, 18$) solutions depending on their concentration and alkyl chain length of $C_1C_nV^{2+}$. The differences in electrochemical behavior around the critical micelle concentration (CMC) were interpreted in terms of the competition between electrodeposition and dissolution. In this regard, incorporation of $C_1C_nV^{+}$ into CTAB micelles and complexation of $C_1C_nV^{+}$ with α - and β -CDs as well as with β -CDs with some functional groups were also studied.

Experimental

Materials. Viologens used are chloride salts of 1-methyl-1'-alkyl-4,4'-bipyridinium ($C_1C_nV^{2+}$; $n=14, 16, 18$) dications. They were synthesized by refluxing 1-methyl-4,4'-bipyridinium iodides with 3 times excess amounts of the corresponding 1-bromoalkane ($C_nC_{2n+1}Br$; $n=14, 16, 18$; Tokyo Kasei) in acetonitrile followed by anion exchange with Cl^- .²¹ 1-Methyl-4,4'-bipyridinium iodide was obtained by a reaction of 4,4'-bipyridine (Aldrich) with iodomethane. Cetyltrimethylammonium bromide (CTAB) was obtained from Fluka and recrystallized twice in absolute ethanol before use. α - and β -CDs as well as sulfated β -CD (typical substitution of 7-11 per CD at random positions of -OHs) (Aldrich) and methylated β -CD (Cyclolab) were used as received. Aqueous solutions were prepared with reverse water purified by reverse osmosis, which was further purified by passing through a Millipore purification train.

Apparatus and procedures. Cyclic voltammetry (CV) and chronocoulometry (CC) were carried out with a BAS 100B electrochemical analyzer (Bioanalytical Systems). A 3 mm diameter glassy carbon (GC) disk electrode (BAS) and an $Ag|AgCl|3 M NaCl$ reference electrode (BAS) were used. CV measurements were carried out for >10 min after

immersing the electrode in solution under an N_2 atmosphere to provide equilibration time of self-aggregation of $C_1C_nV^{2+}$ on the electrode surface.¹⁴ A Hewlett-Packard 8452A diode array spectrophotometer was used to obtain absorption spectra of viologen dication using an ordinary cell (light pathlength: 1.0 cm). A spectroelectrochemical cell was assembled using a cover of a demountable rectangular cell (light pathlength: 100 μ m, Uvonic Cuvettes) and a piece of indium tin oxide (ITO) coated glass (Delta Technologies) as the working electrode.¹⁷ The potential appropriate for 1-e⁻ reduction of viologen was controlled potentiostatically with an AFRDE5 bipotentiostat (Pine Instruments). The solution prior to electrolysis was used as a blank for spectroelectrochemical measurements

Results and Discussion

Spectroscopic measurements of CMC of viologen dication. Spectroscopic determination of the critical micelle concentrations (CMCs) of surface-active viologens was introduced by Grätzel and co-workers.²² The absorption spectrum of a viologen dication has an absorption maxima near 260 nm. This absorption band is red-shifted when the viologens form an aggregate, and the red shift was observed at a longer wavelength within the tail of the main absorption band, e.g., 310 nm. Figure 1 shows a plot of absorption at 310 nm versus concentration of $C_1C_{14}VCl_2$ in 50 mM NaCl, where two discrete regions are observed. From the change of the slope, presumably due to the charge transfer absorption between viologens and counterions by aggregation,^{13,22} the CMC is obtained as 4×10^{-3} M. The results of such experiments for determining CMCs of viologens in 50 mM NaCl and 0.1 M KCl are summarized in Table 1. These values in 50 mM NaCl show good agreement with those reported by Kaifer and co-workers using surface tension measurements.¹³ The CMCs decreased by a decade for each addi-

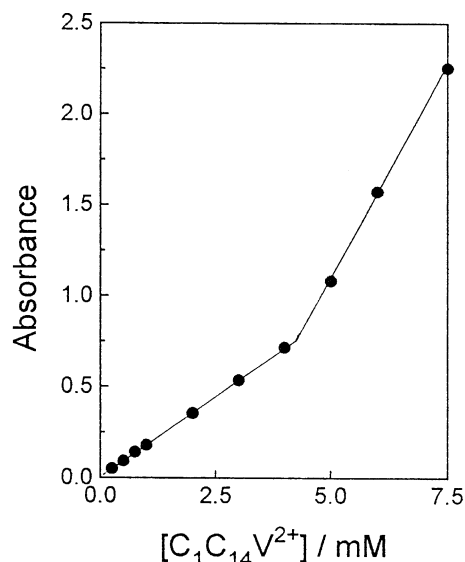


Figure 1. A plot of absorbance at 310 nm against the concentration of $C_1C_{14}V^{2+}$. Solutions contained 50 mM NaCl and the pathlength of the cell was 1 cm.

Table 1. Critical Micelle Concentrations (CMCs) of Viologens Determined by Spectroscopic Method. The CMCs in parenthesis are reported values using surface tension measurements from reference 13

Viologen	in 0.1 M KCl	in 0.05 M NaCl
$C_1C_{14}V^{2+}$		4×10^{-3} M
$C_1C_{16}V^{2+}$	3×10^{-4} M	5×10^{-4} M (4×10^{-4} M)
$C_1C_{18}V^{2+}$	3×10^{-5} M	5×10^{-5} M (3×10^{-5} M)

tional ethylene group in the alkyl chain. It is consistent with Traube's rule that the CMC decreases three fold for each additional methylene group in the chain.¹ The CMCs in 0.1 M KCl are smaller than those in 50 mM NaCl. This is due to a decrease in coulombic repulsion between adjacent head groups at higher ionic strength, which allows the aggregation of the viologens at lower concentrations.¹

Comparison of CMCs with chronocoulometry (CC). The change in the diffusion properties measured for an electroactive probe in micellar solutions is claimed to provide

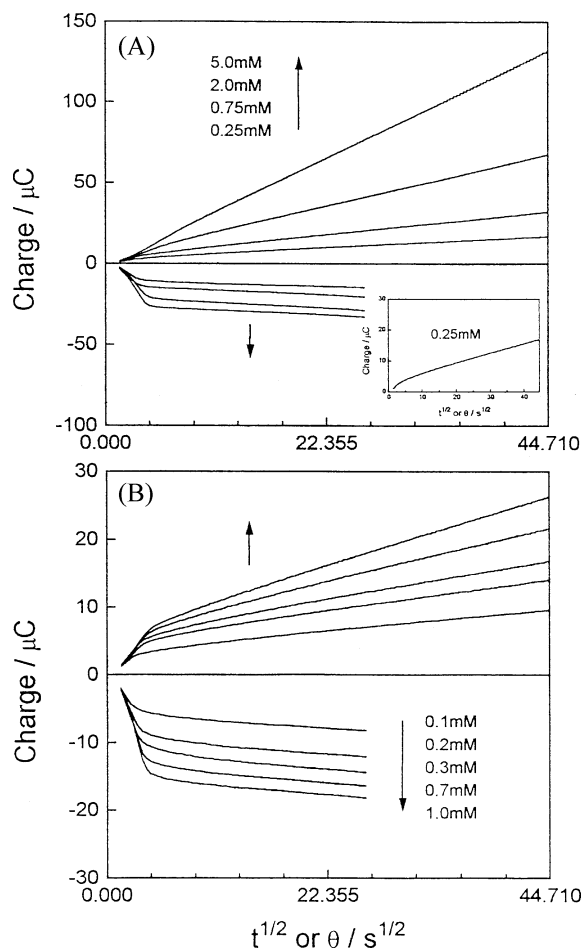


Figure 2. Double potential step chronocoulometric results in $C_1C_{14}V^{2+}$ (A) and $C_1C_{16}V^{2+}$ (B) solutions depending on their concentrations. Solutions contained 50 mM NaCl. Initial and final potentials were 0 V. Step potentials were -0.70 V for $C_1C_{14}V^{2+}$ and -0.65 V for $C_1C_{16}V^{2+}$, respectively. Switching time was 2s. The title of abscissa was represented as in reference 7.

the diffusion properties of the micelles themselves.¹ Since these viologens contained electroactive functional groups we monitored the chronocoulometric behavior depending on their bulk concentrations. Figure 2 shows plots of the charge versus $(\text{time})^{1/2}$ depending on the total concentrations of $\text{C}_1\text{C}_n\text{V}^{2+}$ in 50 mM NaCl solutions as the results of double potential step experiments. There are two discrete regions during the forward step: > 0.1 s after the potential step owing to the adsorption/precipitation of $\text{C}_1\text{C}_n\text{V}^{2+}$ on the electrode surface; however, the plot obeys the Cottrell equation for times 0.1 to 2.0 s.²³ Thus, the slope of charge vs. $(\text{time})^{1/2}$ in 0.1-2.0 s divided by the bulk concentration of viologen (slope/C_o^*) is proportional to the square root of the apparent diffusion coefficient. Plots of slope/C_o^* vs. C_o^* for the forward steps are shown in Figure 3. Interestingly, the (slope/C_o^*) approaches zero virtually at concentrations higher than 3 mM and 0.5 mM for $\text{C}_1\text{C}_{14}\text{V}^{2+}$ and $\text{C}_1\text{C}_{16}\text{V}^{2+}$, respectively, which corresponds to the CMC values obtained by spectroscopic methods (Table 1). The flat region with increasing bulk viologen concentrations may be attributed to the formation of micelles at those concentrations. For $\text{C}_1\text{C}_{18}\text{V}^{2+}$, such a change was observed at *ca.* 0.1 mM, which was hard to measure. The discontinuity of slope/C_o^* during the reverse step was observed at the same concentration as during the

forward step. The CMC of $\text{C}_1\text{C}_n\text{V}^{+}$, however, should be smaller than that of $\text{C}_1\text{C}_n\text{V}^{2+}$ owing to the relief in electrostatic repulsion among the positively charged head groups and an increase in their hydrophobic character. It seems that $\text{C}_1\text{C}_n\text{V}^{+}$ species ($n = 14$) favor adsorption/precipitation rather than the formation of $\text{C}_1\text{C}_n\text{V}^{+}$ micelles, whereas $\text{C}_1\text{C}_n\text{V}^{+}$ could form the mixed micelle of $\text{C}_1\text{C}_n\text{V}^{2+}/\text{C}_1\text{C}_n\text{V}^{+}$ if there exist $\text{C}_1\text{C}_n\text{V}^{2+}$ micelles.¹³ The parallelism of the tendencies of dimerization and adsorption/precipitation of $\text{C}_1\text{C}_n\text{V}^{+}$ ($n \leq 10$) was reported, suggesting that dependence of K_D values on alkyl substituents arises from adsorption, rather than the interaction between alkyl chains in the dimer.^{8,17}

At this point, we would like to mention one feature of double potential chronocoulometric experiments for 1-e^- reduction followed by re-oxidation in 1 mM $\text{C}_1\text{C}_n\text{V}^{2+}$ solutions. For $\text{C}_1\text{C}_n\text{V}^{2+}$ ($n=1$ to 10) the forward step showed linear response implying the 1-e^- reduction process of $\text{C}_1\text{C}_n\text{V}^{2+}$ was diffusion controlled; however, the reverse step for $\text{C}_1\text{C}_n\text{V}^{2+}$ ($n \geq 9$) showed two discrete regions due to the deposition of $\text{C}_1\text{C}_n\text{V}^{+}$ ($n \geq 9$) on the electrode during the forward step.^{7,17} For $\text{C}_1\text{C}_n\text{V}^{2+}$ ($n=14, 16, 18$), both forward and reverse steps showed two discrete regions, which can be interpreted as deposition of both $\text{C}_1\text{C}_n\text{V}^{+}$ and $\text{C}_1\text{C}_n\text{V}^{2+}$, although the deposition of the former is larger than the latter. It can be used as a measure of hydrophobicity of amphiphilic species containing electroactive species.

Cyclic voltammetry (CV) depending on bulk concentrations. The effects of bulk concentrations on CVs in 50 mM NaCl solutions are illustrated in Figure 4. Both the changes of the first cathodic peak potential (E_{pc1}) of $\text{C}_1\text{C}_{14}\text{V}^{2+}$ (Figure 4A) and the ratio of the corresponding anodic peak current to the first cathodic peak current (i_{pa1}/i_{pc1}) are very interesting: E_{pc1} shifts in a positive direction with increasing bulk concentrations up to 3 mM and it shifts to the opposite direction with increasing concentration thereafter; the abrupt change of the slope of i_{pa1}/i_{pc1} vs. $[\text{C}_1\text{C}_{14}\text{V}^{2+}]$ is also found near 3 mM (Figure 5). These results suggest that the deposition of $\text{C}_1\text{C}_{14}\text{V}^{+}$ on the electrode is predominant when $C_o^* < 3$ mM whereas $\text{C}_1\text{C}_{14}\text{V}^{+}$ zips away from the electrode by some mechanism when $C_o^* > 3$. It thus changes the potential to a negative value by relieving adsorption/precipitation at higher C_o^* . The plausible mechanism seems to be dissolution of $\text{C}_1\text{C}_{14}\text{V}^{+}$ inside the micelle of $\text{C}_1\text{C}_{14}\text{V}^{2+}$, which is supported by incorporation of $\text{C}_1\text{C}_{14}\text{V}^{+}$ into CTAB micelles (*vide supra*).

We also investigated micellar effects on CVs of $\text{C}_1\text{C}_{16}\text{V}^{2+}$ and $\text{C}_1\text{C}_{18}\text{V}^{2+}$ around the CMC determined spectroscopic method. In Figure 4B, the E_{pc1} of $\text{C}_1\text{C}_{16}\text{V}^{2+}$ shifts in a positive direction at the higher concentration than at 0.5 mM, which is probably related to the electrodeposition of 1-e^- reduction product,²⁴ but the reason of the opposite trend at the lower concentration is unclear now. For $\text{C}_1\text{C}_{16}\text{V}^{2+}$ and $\text{C}_1\text{C}_{18}\text{V}^{2+}$, the anodic peak corresponding to the first cathodic peak is separated into two peaks as the concentration increases at a potential scan rate of 50 mV/s (Figure 4B and C). It is attributed to a so-called aging effect due to the reorientation or the phase transition process after precipita-

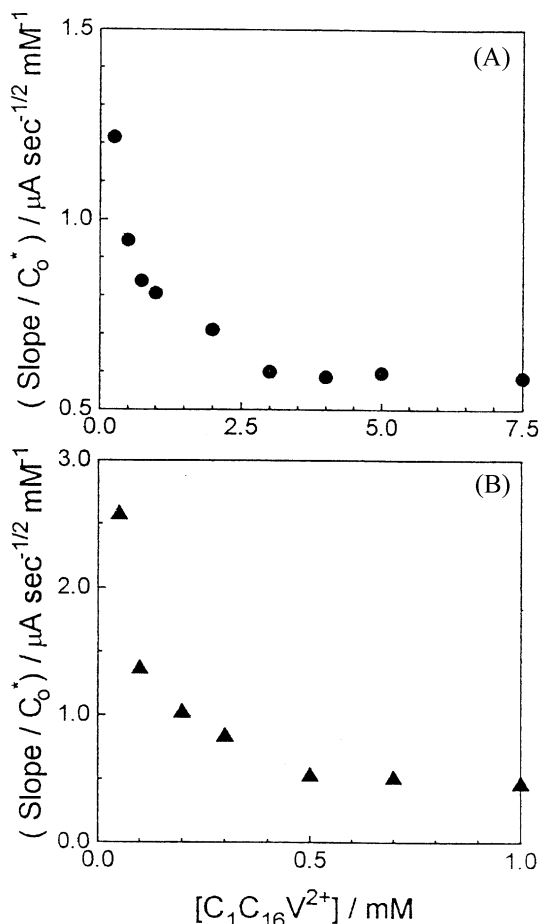


Figure 3. The plots of slope/C_o^* (see text) against the concentration of $\text{C}_1\text{C}_{14}\text{V}^{2+}$ (A) and $\text{C}_1\text{C}_{16}\text{V}^{2+}$ (B), respectively, from the data shown in Figure 2. Some of the data were not shown in Figure 2.

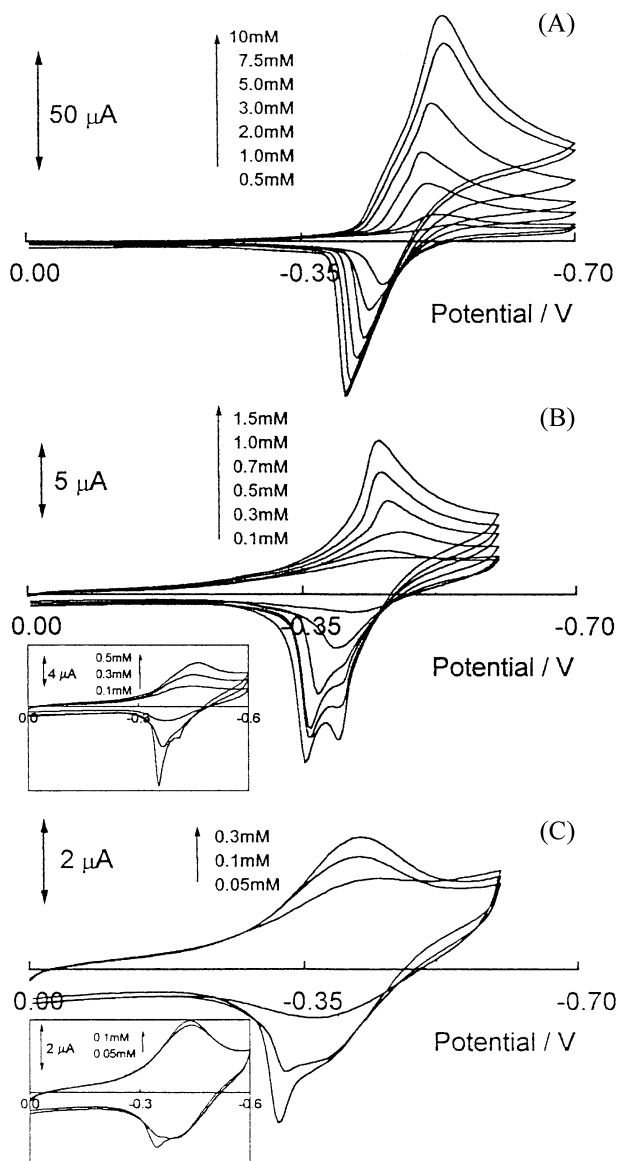


Figure 4. Effects of concentrations on CVs of $C_1C_{14}V^{2+}$ (A), $C_1C_{16}V^{2+}$ (B), and $C_1C_{18}V^{2+}$ (C), respectively. Solutions contained 50 mM NaCl and GC electrode (area=0.07 cm²) was used. The potential scan rate was 50 mV/s. (inset: solutions contained 0.1 M KCl).

tion of viologen cation radicals.⁸ Thus, at faster scan rates (≥ 1 V/s), the separation of anodic peaks is not observed and i_{pc1} is proportional to the scan rate (Figure 6). It also means that the major contribution to the current under this experimental condition is from the electrodeposited species rather than the bulk species.²⁴ Buttry and co-workers reported the EQCM study of adsorption of ferrocenylmethyl-dimethyl-alkyl-ammonium salts, where species with alkyl chains of ≤ 14 carbons desorbed from the electrode during oxidation while that of 18 carbons remained adsorbed.²⁵ Similar effects were observed by Kaifer and co-workers.¹¹ The reason for different voltammetric behavior between $C_1C_{14}V^{2+}$ and $C_1C_{16}V^{2+}/C_1C_{18}V^{2+}$ can be attributed to the fact that the relatively strong interaction between $C_1C_nV^+$ ($n=16, 18$) compared with that between $C_1C_{14}V^+$ hinders dissolution of

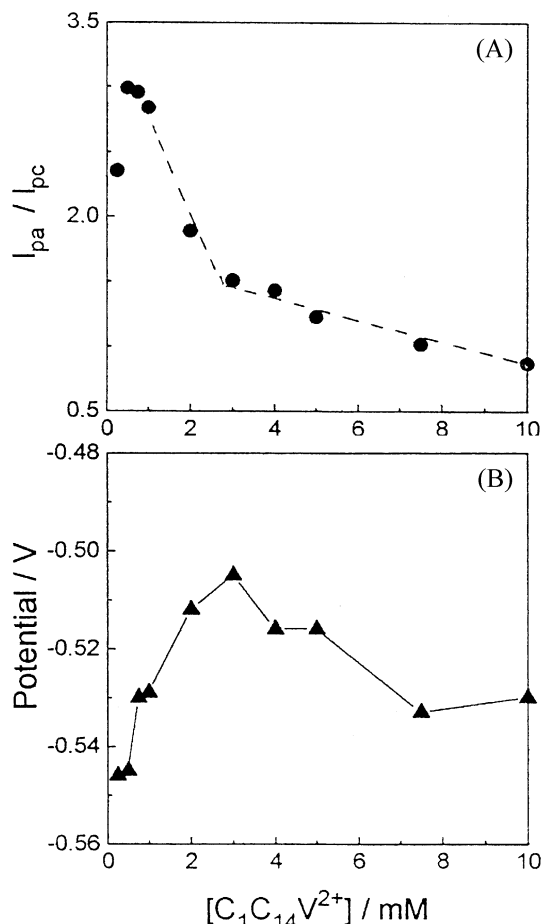


Figure 5. Changes of i_{pa1}/i_{pc1} (A) and E_{pc1} (B) as a function of $[C_1C_{14}V^{2+}]$ in Figure 4A.

viologen cation radicals inside the $C_1C_nV^{2+}$ micelles. With an increase in the ionic strength (in 0.1M KCl) of $C_1C_{16}V^{2+}$ and $C_1C_{18}V^{2+}$ solutions such an anodic peak separation arises at lower concentrations (insets of Figure 4). Since the increase of hydrophobicity of amphiphilic species drives

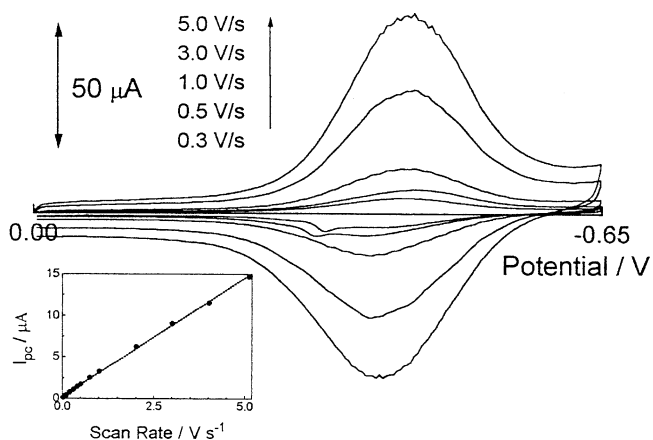


Figure 6. Effects of the potential scan rates on CVs in an aqueous solution containing 0.3 mM $C_1C_{18}V^{2+}$ and 50 mM NaCl. A GC electrode (area=0.07 cm²) and the option of IR compensation were used. (inset: a plot of i_{pc1} against the potential scan rates)

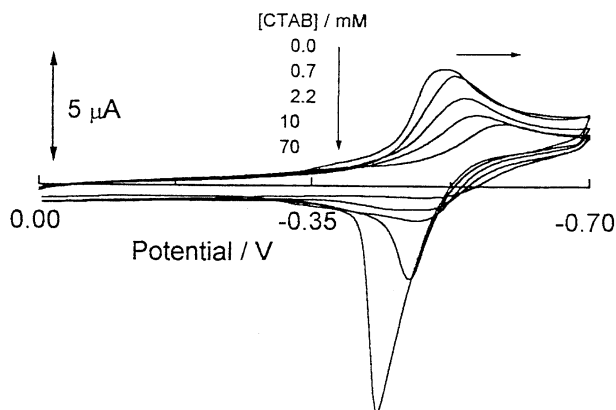


Figure 7. Effect of added [CTAB] on CVs at a GC electrode (area=0.07 cm²) in an aqueous solution containing 1 mM C₁C₁₄V²⁺ and 0.1 M KCl. The potential scan rate was 50 mV/s.

there is a relationship between CMC and observation of the aging effects in CVs with moderate scan rates (≤ 500 mV/s) for C₁C₁₆V⁺ and C₁C₁₈V⁺.

Incorporation of C₁C₁₄V⁺ into CTAB micelles. To support the possibility of dissolution of C₁C₁₄V⁺ in C₁C₁₄V²⁺ micelles, we investigated incorporation of C₁C₁₄V⁺ into a positively charged ionic micelle, or CTAB micelle. Effects of concentration of CTAB on CVs in 0.1 M KCl solutions are illustrated in Figure 7, where i_{pa1}/i_{pc1} decreases with increasing concentrations of CTAB and smaller than unity at [CTAB] ≥ 2.2 mM. This observation leads to two conclusions: one is that the C₁C₁₄V⁺ is easy to incorporate into CTAB micelles; the other is that CTAB micelles associate more strongly with C₁C₁₄V⁺ than with C₁C₁₄V²⁺ at higher [CTAB] due to the decrease in electrostatic repulsion between head groups. In Figure 7, E_{pc1} shifts to the negative direction with increasing [CTAB]. The positive shift of the potential should be observed if C₁C₁₄V⁺ has a higher binding affinity to the hosts than C₁C₁₄V²⁺ and C₁C₁₄V⁺ is free from adsorption/precipitation or the interaction of the latter is weaker than the former. Previously, we reported such potential shifts in interactions of β -CD depending on the oxidation states of C₁C₇V²⁺.¹⁸ It suggests the stabilization of C₁C₁₄V⁺ in CTAB micelles; however, the direction of potential shift is reverse due to electrodeposition. Overall, these CV responses show tendencies similar to those of C₁C₁₄V²⁺ solutions at $C_o^* > 3$ mM.

Incorporation of C₁C₁₄V⁺ into CTAB micelles is clearly shown by spectroelectrochemical experiments (Figure 8). The absorption spectrum of the 1-e⁻ reduction product of C₁C₁₄V²⁺ without CTAB shows the absorption characteristic of the dimer of viologen cation radicals near 360 nm and 520 nm and only hints of the presence of monomer at 396 nm as a shoulder peak.^{2,13,15-20,26} As the concentration of CTAB increases, absorption bands of the monomer viologen cation radical at 396 nm and 604 nm are enhanced gradually. The absorption band near 360 nm, however, increases at lower [CTAB] and then decreases at higher [CTAB]. An isosbestic point, ca. 550 nm, is still evident at higher [CTAB] as viologen/ α -CD complexation takes place.¹⁷ This observation has

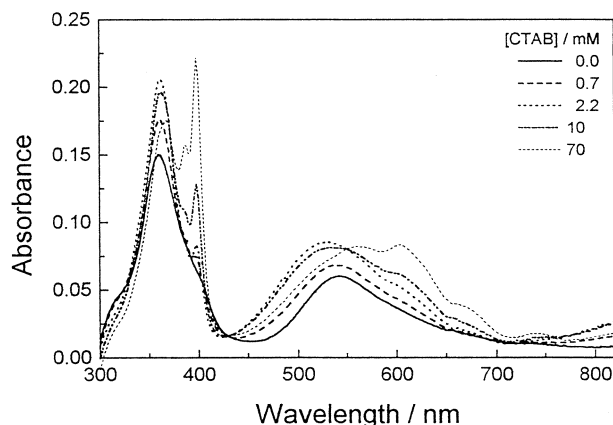
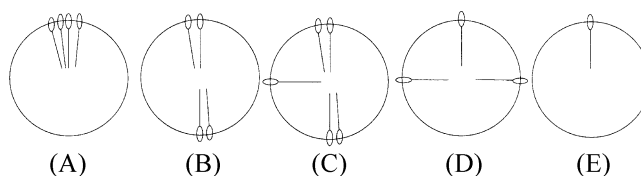


Figure 8. Effect of added [CTAB] on the spectra of the 1-e⁻ reduction product of C₁C₁₄V²⁺. Solutions contained 0.94 mM C₁C₁₄V²⁺ and 0.1 M KCl. The cell thickness was 100 μ m.

a four-fold meaning: (1) the hydrophobic C₁C₁₄V⁺ species dissolved from the electrode into CTAB micelle even at lower [CTAB]; (2) there exists monomer-dimer-like equilibria of C₁C₁₄V⁺ by the incorporation of the viologens with CTAB micelles at higher [CTAB]; (3) the existence of an isosbestic point indicates that the absorption spectra of uncomplexed and CTAB-complexed species are in equilibrium; (4) electrodeposition is preferred to the formation of C₁C₁₄V⁺ micelles without CTAB under this experimental condition. Previously, we reported that the absorbance of C₁C₉V⁺ and C₁C₁₀V⁺ spectra was near 70% of that calculated using molar absorption coefficients of viologens that are free from deposition.¹⁷ One of the possible reasons for this discrepancy would be due to adsorption/precipitation of the reduced viologens on the electrode surface: the electrodeposited molecule beneath of another adsorbed molecules is in the shadow of the molecule of the top-layer and does not contribute to the light absorbing. Thus, it renders less absorbance for the systems than what is expected when the molecules are fully dispersed in solution.

Monomer-dimer equilibria of C₁C₁₄V⁺ by the incorporation of the viologens into CTAB micelles can be explained as following. Stabilization of C₁C₁₄V⁺ in sodium dodecylsulfate (SDS) micelles was reported.^{4,5} Usually charged ionic solutes can have strong coulombic attraction to surfaces of oppositely charged micelles. This work, however, demonstrates another example of charged repulsion between ions



Scheme 1. Schematic Representation of Incorporation of C₁C₁₄V⁺ in CTAB Micelles (circle). A and B might show a similar spectrum to that of the dimer, while D and E might show a similar spectrum to that of the monomer in the UV-vis region. C might show a spectrum of a mixture of a monomer and dimers.

and ionic micelles of the same charge, which can be overcome by strong hydrophobic interactions.¹² Incorporation of $C_1C_{14}V^{+}$ into CTAB micelles is postulated as in Scheme 1, considering that the spectrum of the $C_1C_{14}V^{+}$ solution containing electrodeposited species is similar to that of the dimer in the UV-vis region and dimer is a basic unit of aggregation.

We can decompose each spectra of the mixture of viologen radical monomers and dimers into monomer and dimer components by the linear combination of the respective spectra based on Scheme 1 (detailed procedure is described elsewhere¹⁷). The concentrations of the dimer were calculated using the relationship $[\text{dimer}] = \{[\text{viologen}]_{\text{total}} [\text{monomer}]\} / 2$. The spectrum obtained at $[\text{CTAB}] = 10 \text{ mM}$ contains 0.26 (0.24 mM) of monomer fraction and 0.74 (0.35 mM) of dimer fraction, while that at $[\text{CTAB}] = 70 \text{ mM}$ has 0.51 (0.48 mM) of monomer fraction and 0.49 (0.23 mM) of dimer fraction. Although the micelle concentration increases by more than 7 times (CMC^{26} of CTAB without electrolyte is ca. 1 mM), the fraction of monomer only doubles. This implies that the relative contribution of structure C or D to monomer fraction at $[\text{CTAB}] = 10 \text{ mM}$ is larger than that at $[\text{CTAB}] = 70 \text{ mM}$. It also reflects that the interaction between $C_1C_{14}V^{+}$ - $C_1C_{14}V^{+}$ is stronger than that between $C_1C_{14}V^{+}$ -CTAB. Clearly, one of the reasons that the spectrum of $C_1C_{14}V^{+}$ at 70 mM of $[\text{CTAB}]$ does not show a fully monomer spectrum is $[\text{micelle}] / [C_1C_{14}V^{+}] < 1$. A similar behavior was also observed for $C_1C_{16}V^{2+}$ and $C_1C_{18}V^{2+}$ solutions, but to a lower extent.

Effects of Cyclodextrins (CDs). The effects of α - and β -CDs on the $C_1C_{14}V^{2+}/C_1C_{14}V^{+}$ redox couple are shown in Figure 9, where both deposition and dissolution by inclusion complexation are involved. Inhibition of electrodeposition

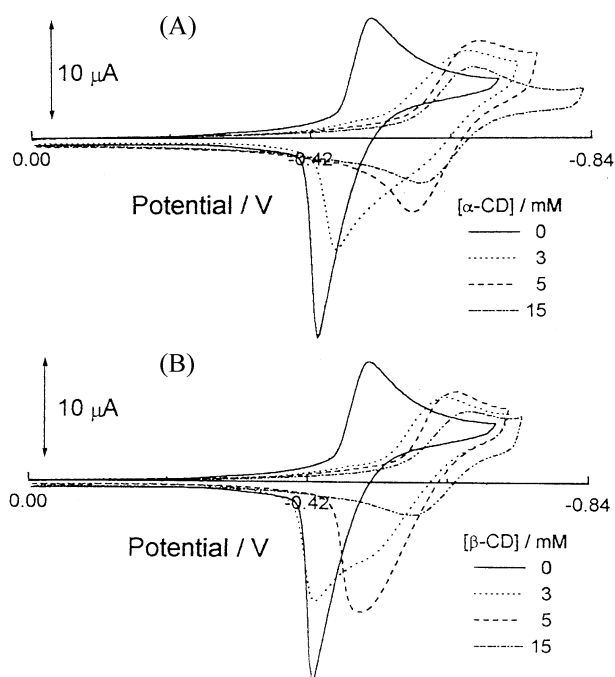


Figure 9. Effect of added $[\alpha\text{-CD}]$ (A) and $[\beta\text{-CD}]$ (B) on CVs. Solutions contained 2 mM $C_1C_{14}V^{2+}$ and 0.1 M KCl.

of $C_1C_{14}V^{+}$ by complexation with CD shifts the reduction potential to a more negative direction as in the presence of CTAB; however, α -CD is more effective in inhibition of deposition than β -CD, judging from the gradual change of the anodic peak current depending on $[\text{CD}]$.

This is also supported by spectroelectrochemical experiments (Figure 10), where α -CD is clearly more effective in the suppression of dimerization than β -CD. The spectra were taken at 75% of the exhaustive electrolysis because of the instability of the base line during the prolonged electrolysis time. It is presumably due to the scattered radiation by the lower solubility of viologen-CD complexes.¹³ The stronger effect of α -CD than that of β -CD coincides with Kaifer and co-worker's report using $C_2C_{16}V^{2+}$ and $C_2C_{18}V^{2+}$ solution,¹³ but they claimed that β -CD is unable to prevent the dimerization of $C_2C_{16}V^{+}$ and $C_2C_{18}V^{+}$. It can be explained in terms of competition between adsorption/precipitation and dissolution/inclusion. The relative strength of the former increases remarkably as the number of carbon atoms in the alkyl chain increases from 14 to 16. Note, however, that β -CD is more effective in suppression of the formation of the viologen radical dimer for $C_1C_nV^{+}$ ($n \leq 8$) than α -CD.^{18,28} This implies that the intrinsic binding affinity of the alkyl chain with α -CD is larger than that with β -CD due to tighter complexation, but β -CD has an additional effect in suppression of dimer formation due to inclusion of a part of the bipyridine ring. The former prevails in complexation with viologens containing long alkyl chains, while β -CD surpasses α -CD for those containing short alkyl chains by the latter. For the inhibition of the precipitation of $C_1C_{14}V^{+}$,

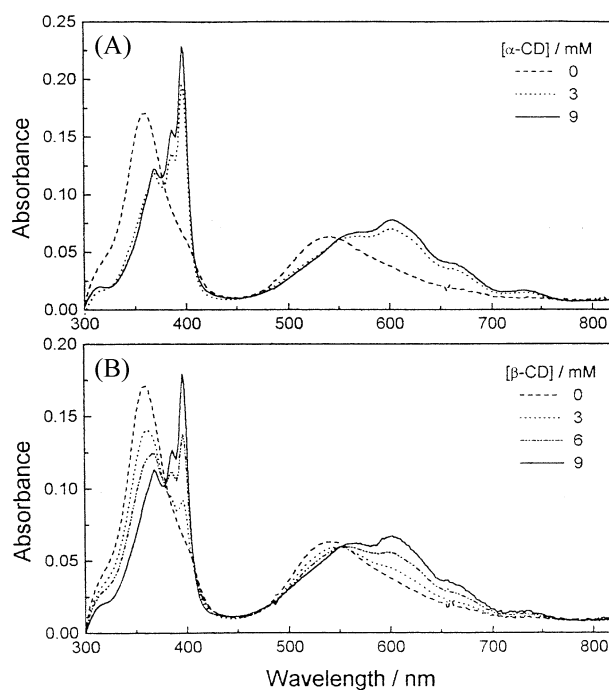


Figure 10. Effect of added $[\alpha\text{-CD}]$ (A) and $[\beta\text{-CD}]$ (B) on the spectra of the 1-e^- reduction product of $C_1C_{14}V^{2+}$. Solutions contained 1 mM $C_1C_{14}V^{2+}$ and 0.1 M KCl. The cell thickness was 100 μm . Spectra were taken at 75% of the exhaustive electrolysis (see text).

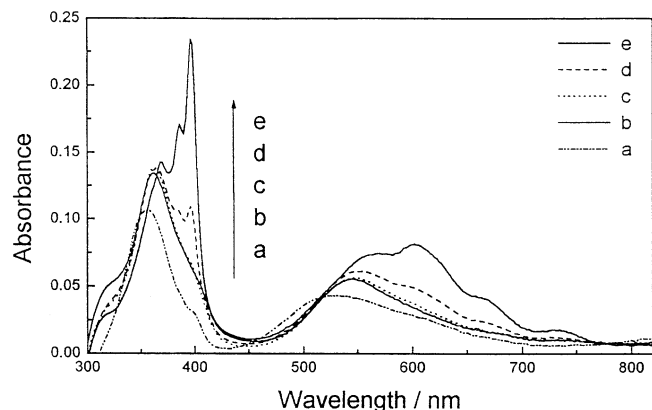


Figure 11. Spectra of the 1-e⁻ reduction product of C₁C₁₈V²⁺ with 9 mM of sulfated β-CD (a), without CD (b), with 9 mM of β-CD (c), with 9 mM of methylated β-CD (d) and with 15 mM of methylated β-CD (e). Solutions contained 1 mM C₁C₁₈V²⁺ and 0.1 M KCl. Other conditions are same as those in Figure 10.

CTAB is more effective than cyclodextrins (compare Figure 7 with Figure 9).

As mentioned earlier, one of the reasons for the failure of the suppression of dimerization of C₂C₁₈V⁺ is the limited solubility of the C₂C₁₈V⁺-(β-CD) complex. It is visualized in Figure 11, where three different types of β-CDs are used, *i.e.*, ordinary, methylated and sulfated β-CDs, for the electro-generated C₁C₁₈V⁺. The spectrum of C₁C₁₈V⁺ in the presence of 9 mM of sulfated β-CD indicates more aggregation than in the absence of CD (spectra a and b). It can be explained in terms of electrostatic attraction as seen in the case for the C₁C₁V⁺ in the presence of SDS.⁴ The difference between the spectra of C₁C₁₈V⁺ with 9 mM of β-CD and without β-CD (spectra c and b) is negligible, as claimed by Kaifer and co-workers.¹³ On the other hand, the spectrum of C₁C₁₈V⁺ with 9 mM of methylated β-CD shows a small absorption peak at 396 nm, *i.e.*, a hint of disruption of the aggregation (spectrum d). The dimerization and/or aggregation of C₁C₁₈V⁺ were virtually suppressed upon the addition of methylated β-CD up to 15 mM (spectrum e). The stronger effect of methylated β-CD compared with β-CD is attributed to the higher solubility of the C₁C₁₈V⁺-(methylated β-CD) complex compared with the C₁C₁₈V⁺-(β-CD) complex and the elongation of the length of the β-CD cavity, the inclusion site, by methylation.

Conclusions

We have demonstrated the differences in electrochemical behaviors of surfactant viologens (C₁C_nV²⁺; n=14, 16, 18) between concentrations below and above CMC. The *i*_{pa1}/*i*_{pc1} ratio decreases with an increase in [C₁C₁₄V²⁺], while the aging effects are more pronounced for C₁C₁₆V²⁺ and C₁C₁₈V²⁺ solutions. This was interpreted as the competition between adsorption/precipitation and dissolution/incorporation into micelles of C₁C_nV²⁺. Our interpretation was supported by the incorporation of C₁C₁₄V⁺ into CTAB micelles and complexation with CDs.

For this study we provide five additional pieces of information as follows. First, we report three different types of double potential chronocoulometric data depending on n of C₁C_nV²⁺. Second, we report the incorporation of ions and ionic micelles of the same charge despite the electrostatic repulsion. Third, the relative efficiencies of suppression of viologen radical dimers between α- and β-CDs are dependent on the length of alkyl chains of C₁C_nV⁺ (for n≤14, α-CD is more effective than β-CD, whereas the tendency is opposite for n≥8). Fourth, CTAB is more effective than CDs for the dissolution of the amphiphilic C₁C₁₄V⁺ species by forming mixed micelles, where the interaction between C₁C₁₄V⁺-C₁C₁₄V⁺ is stronger than that between C₁C₁₄V⁺-CTAB. Fifth, methylated β-CD is more effective in the suppression of the dimerization of C₁C_nV⁺ than β-CD, whereas sulfated β-CD shows the opposite effect due to electrostatic interactions.

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