Electrochemical Studies on the Methylviologen-Sodium Dodecyl Sulfate Solution in the Presence of MgCl₂

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요 약: 100 mM NaCl+27 mM MgCl₂ 용액에서, 도데실산나트륨 (SDS)의 유무에 따른 1.0 mM 메틸비올로겐 (MV²⁺)의 전기화학적 거동을 연구하였다. ΔEp(산화와 환원 봉우리 전위 간의 차이) 대 -log[SDS]로 도시한 그림에서 두 선의 교차점을 임계미셀농도 (CMC)로 결정하였다. Mg²⁺가 첨가되면, 유리단소전극에 대한 효과적인 MV⁺⁺의 접근이 가능해지고 미셀형성도 지연되었다.

Abstract: Electrochemical behaviours on 1.0 mM methylviologen (MV²⁺) in 100 mM NaCl+27 mM MgCl₂ solution, without and with sodium dodecyl sulfate (SDS), were studied. The intersection of two lines on ΔEp (the difference between the anodic, Epa, and the cathodic, Epc, peak potentials) of the first and second redox waves vs. -log[SDS] plot was determined as a critical micelle concentration (CMC). When Mg²⁺ was added, the effective access of MV⁺⁺ to the glassy carbon electrode surface became possible and the formation of micelles was retarded.

Key words: Methylviologen, Sodium dodecyl sulfate, Critical micelle concentration, Double layer, Ionic strength, Formation of micelles

1. INTRODUCTION

Since Michaelis reported the electrochemical behaviour for viologens (1,1'-disubstituted 4,4'-bipyridinium ions),¹ the extensive studies have been achieved for viologens. The radical cations of viologens have been widely used for laser photolysis technique,² photochemistry,³,⁴ fluorescence,⁵-⁷ Raman spectroscopy,⁸ and electrochromism⁹-¹¹ due to the intermolecular photo-induced electron transfer.¹²-¹⁵

Park et al.¹⁶ and Kaifer et al.¹⁷,¹⁸ reported the electrochemical studies of MV²⁺-SDS solution in the presence of NaCl. Recently it was reported that divalent cation such as Mg²⁺ markedly shifts the SDS-dependent activation profiles to a lower concentration range in a biological analysis.¹⁹

In this paper, thus, we have studied electrochemical behaviours of MV²⁺-SDS in 100 mM NaCl+27 mM MgCl₂ aqueous solution using cyclic voltammetry (CV). Especially, electrochemical behavior at the concentration of SDS near CMC of MV²⁺-SDS solution has been addressed. The struc-
ture of the double layer around a glassy carbon disk electrode (GC) resulting from MV$^{2+}$-SDS interaction has been rationalized using the model proposed by Jaramillo et al.$^{20,21}$

2. EXPERIMENTS

MV$^{2+}$ was recrystallized from methanol and dried at 80°C in vacuum oven. SDS and NaCl were obtained from Aldrich and used without further purification. Doubly distilled water was used to prepare all solutions. Surface tension measurement was carried out using CSC-Du Noüy (CAT. No. 70535) tensiometer. CMC by tensiometry was measured by plotting surface tension values as a function of concentration (−log[SDS])$^{22}$ at 25±0.2°C. A glassy carbon disk (BAS, MF-2012) with a geometric area of 0.0788 cm$^2$ was used as a working electrode. It was polished with 0.05 μm γ alumina/water slurry on a felt surface and then cleaned in an ultrasonic chamber filled to doubly distilled water for 2 min. A saturated calomel electrode (SCE) (BAS, MF-2055) and a platinum wire (BAS, MW-1032) were used as a reference electrode and an auxiliary electrode, respectively. All experiments were performed under a purified nitrogen atmosphere at 25±0.2°C.

3. RESULTS AND DISCUSSION

![Fig. 1. Cyclic voltammograms for 1.0 mM MV$^{2+}$ in 100 mM NaCl+27 mM MgCl$_2$ without (a) and with (b) 2.5 mM SDS at 25.0±0.2°C. Scan rate=100 mV/sec.](image)

Cyclic voltammograms of 1.0 mM MV$^{2+}$ in 100 mM NaCl+27 mM MgCl$_2$ solution, without and with SDS, are shown in Fig. 1. Data for the redox waves of MV$^{3+}/$MV$^{2+}$ and MV$^{4+}/$MV$^{3+}$ are shown with increasing the concentration of SDS in Table 1.

In the absence of SDS, two successive reduction waves of MV$^{3+}$ to MV$^{2+}$ take place at −714 (MV$^{2+}$→MV$^{+}$) and −1043 mV (MV$^{+}$→MV$^{0}$) vs. SCE. In the backward scan, two successive reoxidation waves of MV$^{0}$ to MV$^{3+}$ occur at −1009 (MV$^{0}$→MV$^{+}$) and −662 mV (MV$^{+}$→MV$^{2+}$). Each formal potential $E_{1/2}$ taken as the midpoint of $E_{pa}$ and $E_{pc}$ is −688 and −1026 mV. From values of $\Delta E_p$ and $i_{pa}/i_{pc}$ (anodic per cathodic peak current), the first and second redox couples are electrochemically quasi-reversible. On the other hand, the oxidation peak (MV$^{0}$)

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<th>$\Delta E_p$ (mV)</th>
<th>$-E_{1/2}$ (mV)</th>
<th>$i_{pa}$ (μA)</th>
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transfer slower (i.e., a increase on ΔE_p)\textsuperscript{23}
In the first couple (MV\textsuperscript{+/-2+}), on the other hand, 
i_{pa} decreases up to 3.0 mM SDS because of the increase of the
electrode surface screening with the increasing in the number of monomers, but increases
at 3.5–7.0 mM SDS range above that concentration
(see Table 1). This is due to the decrease of the elec-
trode surface screening, because monomers around
the electrode become dynamic to form micelles.
When the concentration of SDS is reached at 10
mM, i_{pa} decreases due to the decrease in the number
of MV\textsuperscript{+} per micelles.\textsuperscript{23} In the second redox couple
(MV\textsuperscript{0/+}), i_{pc} can be also explained in a similar way
as mentioned above. On the other hand, the peak A
in Fig. 3 was observed when [SDS]≤0.7 mM. In
absence of MgCl\textsubscript{2} (only, in presence of 100 mM
NaCl), this peak showed only a trace when [SDS]≤
1.0 mM. The oxidation peak A might be ascribable
to the electron reaction of aged film as noticed by
Park et al.\textsuperscript{12} This peak current was increased as the
scan rate (at 20–200 mV/sec range) decreases.

3.1. Interaction between both MV\textsuperscript{+/-2+} and MV\textsuperscript{0/+}
ions, and SDS
The Nernst equation for the reversible 1e\textsuperscript{-} redox
reaction of free and associated (or adsorbed) species
can be written as

\[ E_{a}^{\prime} - E_{a}^{\prime \prime} = 0.059 \log (K_{a}K_{a}) \]  \hspace{1cm} (1)
\[ E_{a}^{\prime} - E_{a}^{\prime \prime} = 0.059 \log (K_{a}K_{a}) \]  \hspace{1cm} (2)

Here, \( E_{a}^{\prime} \) and \( E_{a}^{\prime \prime} \) are the formal potentials of the +
2/+1 (or +1/0) couple of the methylviologen in free and
associated forms, respectively. \( K_{a} \), \( K_{a} \), and \( K_{a} \)
are the corresponding association constants for +1,
+2, and 0 ions of methylviologen to DS\textsuperscript{-}. By sub-

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stituting $E_{1/2}$ in Table 1 to either Eq. (1) or (2), the ratios (each $K_s/K_{2s}$, and $K_o/K_s$) of equilibrium constants for the association of methylviologen ions can be obtained. $K_s/K_{2s}$ is larger than 1, and $i_{pa}/i_{pc}$ is larger than 1 (except 2.0~5.0 mM SDS range due to either the increase of the electrode surface screening by monomers or micelles dynamics). It can be explained that reduced form MV$^{\cdot-}$ in the first redox couple is more easily either associated or adsorbed to dodecyl sulfate anion than oxidized MV$^{2+}$. On the other hand, $K_o/K_s$ is smaller than 1 and $i_{pa}/i_{pc}$ is smaller than 1. It also can be explained that MV$^{0/+}$ in the presence of SDS is more affected by electrostatic interaction than hydrophobic interaction.

3.2. Effect of divalent cations on MV$^{2+}$

In the absence of MgCl$_2$ (divalent cations), data for the redox reaction of 1.0 mM MV$^{2+}$ in 100 mM NaCl solution are shown with increasing [SDS] in Table 2.

When MgCl$_2$ is added for MV$^{+/-2+}$ (comparing Table 1 and 2), in the absence of SDS, the decrease of $i_{pa}$ (lowering surface concentration of MV$^{+}$) and the decrease of $\Delta E_p$ (decreasing the distance to the surface) are observed. In the presence of SDS, MV$^{+/-2+}$ kinetics are slow (large $\Delta E_p$) up to 2.0 mM SDS and $i_{pa}$ is somewhat small. These are due to the electrode surface screening in terms of the adsorption of divalent cations. At 2.5~4.0 mM SDS range, although $\Delta E_p$ decreases, a little decrease of $i_{pa}$ is observed. This shows that divalent cations compete with each other for GC surface groups. Accordingly, at 0~4.0 mM SDS range, the amount of MV$^{0/+}$ on GC surface decreases as divalent cations are added. When the concentration of SDS is reached at 5.0 mM, the decrease of $\Delta E_p$ is preserved and the increase of $i_{pa}$ (higering surface concentration of MV$^{+}$) is observed. These confirm more effective MV$^{+}$ access to GC surface.

When MgCl$_2$ is added for MV$^{0/+}$ (comparing Table 1 and 2), in the absence of SDS, the decrease of $i_{pc}$ (lowering surface concentration of MV$^{+}$) and the decrease of $\Delta E_p$ (decreasing the distance to the surface) are observed. In the presence of SDS, although MV$^{0/+}$ kinetics become fast (small $\Delta E_p$) up to 1.5 mM SDS, $i_{pc}$ doesn't show a significant change. This shows that divalent cations compete with each other for GC surface groups. At 2.0~3.5 mM SDS range, the increase of $\Delta E_p$ and the decrease of $i_{pc}$ (lowering surface concentration of MV$^{+}$) are observed. Thus, when divalent cations is added, the amount of MV$^{+}$ on GC surface decreases at 0~3.5 mM SDS range. When the concentration of SDS is 4.0 mM, the decrease of $\Delta E_p$

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**Table 2. Electrochemical Data for 1.0 mM MV$^{2+}$ in 100 mM NaCl with and without SDS at 25.0±0.2°C. Scan rate=100 mV/sec**

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* CMC (2.08 mM SDS (1st redox), 2.10 mM SDS (2nd redox) by CV; 1.98 mM SDS by tensiometry.

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and the increase of $i_{pe}$ (highering surface concentration of MV$^{n+}$) are observed. This indicates also closer access to GC surface for $MV^{n+}$. due to effective charge screening by Mg$^{2+}$.

### 3.3. Surfactant assembly at GC in the presence of Mg$^{2+}$

As ionic strength increases by the addition of 27 mM MgCl$_2$, CMC of SDS for 1.0 mM $MV^{2+}$ in 100 mM NaCl solution was increased from 2.08 mM to 2.55 mM SDS (first redox). This means, as ionic strength increases by the addition of MgCl$_2$, the formation of micelles is retarded.

**REFERENCES**