

염화마그네슘 존재하의 메틸비올로겐-도데실황산나트륨 용액의 전기화학적 연구

고영춘* · 정근호

*대불대학교 화학환경에너지공학부
전남대학교 화학교육과
(1997. 8. 21 접수)

Electrochemical Studies on the Methylviologen-Sodium Dodecyl Sulfate Solution in the Presence of $MgCl_2$

Young Chun Ko* and Keun Ho Chung

*School of Chemical and Energy/Environmental Engineering, Daebul University,
Youngam-Gun Chonnam 526-890, Korea

Department of Chemistry Education, Chonnam National University, Kwangju 500-757, Korea

(Received August 21, 1997)

요 약 : 100 mM NaCl+27 mM $MgCl_2$ 용액에서, 도데실황산나트륨 (SDS)의 유무에 따른 1.0 mM 메틸비올로겐 (MV^{2+})의 전기화학적 거동을 연구하였다. ΔE_p (산화와 환원 봉우리전위 값의 차이) 대 $-\log[SDS]$ 로 도시한 그림에서 두 선의 교차점을 임계미셀농도 (CMC)로 결정하였다. Mg^{2+} 가 첨가되면, 유리탄소전극에 대한 효과적인 MV^{2+} 의 접근이 가능해지고 미셀형성도 지연되었다.

Abstract: Electrochemical behaviours on 1.0 mM methylviologen (MV^{2+}) in 100 mM NaCl+27 mM $MgCl_2$ solution, without and with sodium dodecyl sulfate (SDS), were studied. The intersection of two lines on ΔE_p (the difference between the anodic, E_{pa} , and the cathodic, E_{pc} , peak potentials) of the first and second redox waves vs. $-\log[SDS]$ plot was determined as a critical micelle concentration (CMC). When Mg^{2+} was added, the effective access of MV^{2+} 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'-bipyridium 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.*^{12,16} and Kaifer *et al.*^{17,18} reported the

electrochemical studies of MV^{2+} -SDS solution in the presence of NaCl. Recently it was reported that divalent cation such as Mg^{2+} 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 MV^{2+} -SDS in 100 mM NaCl+27 mM $MgCl_2$ aqueous solution using cyclic voltammetry (CV). Especially, electrochemical behavior at the concentration of SDS near CMC of MV^{2+} -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 $25 \pm 0.2^\circ\text{C}$. A glassy carbon disk (BAS, MF-2012) with a geometric area of 0.0788 cm² 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 $25 \pm 0.2^\circ\text{C}$.

3. RESULTS AND DISCUSSION

Table 1. Electrochemical data for 1.0 mM MV^{2+} in 100 mM NaCl+27 mM $MgCl_2$ with and without SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate=100 mV/sec

[SDS] (mM)	First redox					Second redox				
	$-E_{pa}$ (mV)	ΔE_p (mV)	$-E_{1/2}$ (mV)	i_{pa} (μA)	i_{pa}/i_{pc}	$-E_{pa}$ (mV)	ΔE_p (mV)	$-E_{1/2}$ (mV)	i_{pa} (μA)	i_{pa}/i_{pc}
0.0	662	54	688	14.8	1.25	1009	35	1026	10.6	2.48
0.5	647	64	679	19.8	1.64	997	64	1028	13.2	1.08
1.0	639	46	662	19.6	1.38	997	68	1030	11.5	0.95
1.5	640	38	659	19.4	1.23	998	67	1032	11.1	0.87
2.0	640	35	658	16.8	0.99	1000	68	1034	9.6	0.84
2.5	636	29	650	15.9	0.91	1004	66	1037	8.9	0.79
3.0	636	30	651	15.2	0.83	1007	67	1041	10.5	0.76
3.5	635	32	651	16.8	0.84	1021	69	1057	12.0	0.81
4.0	635	36	653	17.6	0.87	1021	71	1056	13.3	0.80
5.0	635	39	653	17.8	0.89	1023	73	1060	10.7	0.70
7.0	628	44	649	18.6	1.62	1025	75	1063	8.6	0.66
10.0	613	54	640	10.6	1.35	1037	77	1176	7.6	0.49

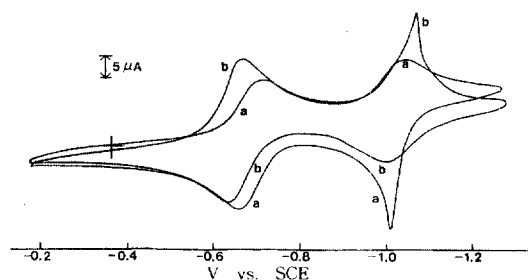


Fig. 1. Cyclic voltammograms for 1.0 mM MV^{2+} in 100 mM NaCl+27 mM $MgCl_2$ without (a) and with (b) 2.5 mM SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate=100 mV/sec.

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^{2+} and $MV^{0/+}$ are shown with increasing the concentration of SDS in Table 1.

In the absence of SDS, two successive reduction waves of MV^{2+} to MV^0 take place at -714 ($MV^{2+} \rightarrow MV^+$) and -1043 mV ($MV^+ \rightarrow MV^0$) vs. SCE. In the backward scan, two successive reoxidation waves of MV^0 to MV^{2+} occur at -1009 ($MV^0 \rightarrow MV^+$) and -662 mV ($MV^+ \rightarrow MV^{2+}$). Each formal potential $E_{1/2}$ taken as the midpoint of E_{pa} and E_{pc} is -688 and -1026 mV. From values of ΔE_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

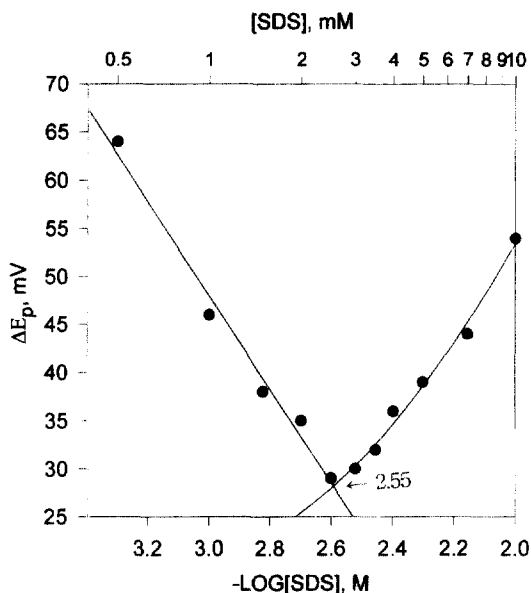


Fig. 2. ΔE_p vs. $-\log[\text{SDS}]$ plot for 1.0 mM $\text{MV}^{\cdot+2+}$ in 100 mM NaCl+27 mM MgCl_2 .

$\rightarrow \text{MV}^{\cdot+}$) at -1009 mV as shown in Fig. 1(a) presents a sharp spike. This is due to the adsorption of MV^0 onto the GC in absence of SDS as reported by Kaifer and Bard.¹⁷

In the presence of SDS, E_{pa} and $E_{1/2}$ for $\text{MV}^{\cdot+2+}$ shift to the positive direction compared to the SDS free. ΔE_p shows a special phenomenon as [SDS] increases. It decreases up to 2.5 mM SDS and increases above the concentration. In order to see the relation between ΔE_p and CMC,²³ ΔE_p vs. $-\log[\text{SDS}]$ for the redox couples were plotted in Fig. 2. The concentration of SDS at the intersection of two lines in the Fig. 2 is 2.55 mM, and this concentration can be determined as CMC, which is near the CMC (2.52 mM SDS) measured by tensiometry (relative error: below 1%). In the same procedure, for $\text{MV}^{0/+}$ CMC can be determined as 2.78 mM. As [SDS] increases up to CMC, the width of the double layer (i.e., distance to the GC surface) is narrowed by arranging dodecyl sulfate anionic monomers ($(\text{DS}^-)_n$) around the electrode, which speeds up the electron transfer. As [SDS] increases above CMC, micelles are formed gradually. The increase in the number of micelles causes the width of the double layer to increase, which makes the electron

transfer slower (i.e., a increase on ΔE_p).²³

In the first couple ($\text{MV}^{\cdot+2+}$), 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 electrode 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 $\text{MV}^{\cdot+}$ per micelles.²³ In the second redox couple ($\text{MV}^{0/+}$), 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 $[\text{SDS}] \leq 0.7$ mM. In absence of MgCl_2 (only, in presence of 100 mM NaCl), this peak showed only a trace when $[\text{SDS}] \leq 1.0$ mM. The oxidation peak A might be ascribable to the electron reaction of aged film as noticed by Park *et al.*¹² This peak current was increased as the scan rate (at 20~200 mV/sec range) decreases.

3.1. Interaction between both $\text{MV}^{\cdot+2+}$ and $\text{MV}^{0/+}$ ions, and SDS

The Nernst equation for the reversible $1e^-$ redox reaction of free and associated (or adsorbed) species can be written as

$$E_a^{0'} - E_f^{0'} = 0.059 \log (K_+/K_{2+}) \quad (1)$$

$$E_a^{0'} - E_f^{0'} = 0.059 \log (K_0/K_+) \quad (2)$$

Here, $E_a^{0'}$ and $E_f^{0'}$ are the formal potentials of the +2/+1 (or +1/0) couple of the methylviologen in free and associated forms, respectively. K_+ , K_{2+} , and K_0 are the corresponding association constants for +1, +2, and 0 ions of methylviologen to DS^- . By sub-

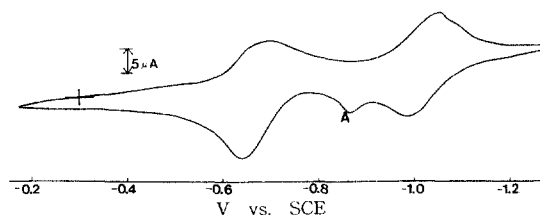


Fig. 3. Cyclic voltammogram for 1.0 mM MV^{2+} in 100 mM NaCl+27 mM MgCl_2 with 0.5 mM SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate=100 mV/sec.

stituting $E_{1/2}$ in Table 1 to either Eq. (1) or (2), the ratios (each K_+/K_{2+} and K_0/K_+) of equilibrium constants for the association of methylviologen ions can be obtained. K_+/K_{2+} 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_0/K_+ 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 $MV^{\cdot+}$) and the decrease of ΔE_p (decreasing the distance to the surface) are observed. In the presence of SDS, MV^{+2+} kinetics are slow (large ΔE_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 ΔE_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 $MV^{\cdot+}$ on GC surface decreases as divalent cations are added. When the concentration of SDS is reached at 5.0 mM, the decrease of ΔE_p is preserved and the increase of i_{pa} (higher surface concentration of $MV^{\cdot+}$) is observed. These confirm more effective $MV^{\cdot+}$ 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 $MV^{\cdot+}$) and the decrease of ΔE_p (decreasing the distance to the surface) are observed. In the presence of SDS, although $MV^{0/+}$ kinetics become fast (small ΔE_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 ΔE_p and the decrease of i_{pc} (lowering surface concentration of $MV^{\cdot+}$) are observed. Thus, when divalent cations is added, the amount of $MV^{\cdot+}$ on GC surface decreases at 0~3.5 mM SDS range. When the concentration of SDS is 4.0 mM, the decrease of ΔE_p

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

[SDS] (mM)	First redox					Second redox				
	$-E_{pa}$ (mV)	ΔE_p (mV)	$-E_{1/2}$ (mV)	i_{pa} (μA)	i_{pa}/i_{pc}	$-E_{pa}$ (mV)	ΔE_p (mV)	$-E_{1/2}$ (mV)	i_{pa} (μA)	i_{pa}/i_{pc}
0.0	663	56	691	17.3	1.69	1003	41	1024	13.3	3.21
0.5	638	50	663	21.6	1.62	995	91	1041	13.8	0.74
1.0	636	43	657	21.7	1.24	990	81	1030	13.3	0.66
1.5	634	37	653	20.2	1.14	995	76	1033	13.1	0.65
2.0	651	32	667	20.4	1.08	1012	43	1033	14.2	0.64
2.5	645	39	665	19.7	1.16	1010	50	1035	14.7	0.54
3.0	643	43	664	19.9	1.19	1011	55	1038	14.9	0.54
3.5	640	46	663	24.5	1.77	1021	64	1047	12.2	0.54
4.0	620	51	646	20.5	2.09	1025	75	1062	6.7	0.57
5.0	612	55	639	12.6	1.37	1030	80	1070	5.9	0.59
7.0	612	57	640	10.4	1.29	1040	85	1083	5.2	0.62
10.0	628	59	657	6.2	1.09	1060	88	1104	3.5	0.63

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

and the increase of i_{pc} (higher surface concentration of $MV^{\cdot+}$) are observed. This indicates also closer access to GC surface for $MV^{0/+}$ 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

1. L. Michaelis and E. S. Hill, *J. Gen. Physiol.*, **16**, 859 (1933).
2. Y. Nishimura, H. Sakuragi and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **65**, 2887 (1992).
3. I. Willner, Y. Eichen, A. J. Frank and M. A. Fox, *J. Phys. Chem.*, **97**, 7264 (1993).
4. T. Yonezawa and N. Toshima, *J. Mole. Cata.*, **83**, 167 (1993).
5. J. Hirota and I. Okura, *J. Phys. Chem.*, **97**, 6867 (1993).
6. O. Horvath and J. H. Fendler, *J. Phys. Chem.*, **96**, 9591 (1992).
7. Y. Ueno, K. Yamada, T. Yokota, K. Ikeda, N. Takamiya and M. Kaneko, *Electrochim. Acta*, **38**, 129 (1993).
8. J. R. Schoonover, G. F. Strouse, P. Y. Chen, W. D. Bates and T. J. Meyer, *Inorg. Chem.*, **32**, 2618 (1993).
9. T. Nagamura, *Mole. Cryst. Liq. Cryst.*, **224**, 75 (1993).
10. N. Leventis and Y. C. Chung, *J. Mat. Chem.*, **3**, 833 (1993).
11. T. Saika, T. Iyoda and T. Shimidzu, *Bull. Chem. Soc. Jpn.*, **66**, 2054 (1993).
12. J. W. Park, S. H. Ko and J.-Y. Park, *Bull. Korean Chem. Soc.*, **13**, 259 (1992).
13. E. S. Brigham, P. T. Snowden, Y. I. Kim and T. E. Mallouk, *J. Phys. Chem.*, **97**, 8650 (1993).
14. K. K. Park, W. K. Joung and S. Y. Choi, *Bull. Korean Chem. Soc.*, **14**, 461 (1993).
15. G. J. Yao, T. Onikubo and M. Kaneko, *Electrochim. Acta*, **38**, 1093 (1993).
16. J. W. Park and Y. H. Paik, *J. Phys. Chem.*, **91**, 2005 (1987).
17. A. E. Kaifer and A. J. Bard, *J. Phys. Chem.*, **89**, 4876 (1985).
18. A. E. Kaifer and A. J. Bard, *J. Phys. Chem.*, **91**, 2006 (1987).
19. S. Yamada, K. Hojo, H. Yoshimura and K. Ishikawa, *J. Biochem.*, **117**, 1162 (1995).
20. A. Jaramillo, A. Marino and A. B. -Toth, *Anal. Chem.*, **65**, 3441 (1993).
21. A. Marino and A. B. -Toth, *Anal. Chem.*, **65**, 370 (1993).
22. B. Lindman and H. Wennerström, *Top. Curr. Chem.*, **87**, 1 (1980).
23. Y. C. Ko, J. Ree and K. H. Chung, *Bull. Korean Chem. Soc.*, **18**, 113 (1997).