

Electrochemical Behavior of Bis(2,2'-Bipyridyl) Copper(II)-Sodium Dodecyl Sulfate Solution in the Presence of MgCl₂

Young Chun Ko and Keun Ho Chung[†]

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

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

(Received Oct. 21, 1996)

염화마그네슘이 있을 때 비스(2,2'-비피리딜)구리(II)-도데실황산나트륨 용액의 전기화학적 거동

고영춘 · 정근호[†]

전남대학교 화학과

[†] 전남대학교 화학교육과

(1996. 10. 21. 접수)

Abstract : Electrochemical behavior of 1.0mM bis(2,2'-bipyridyl)copper(II) ($\text{Cu}(\text{bpy})_2^{2+}$) in 100mM NaCl+27mM MgCl₂ solution with and without sodium dodecyl sulfate(SDS) is investigated. In the presence of SDS, E_{pa} and $E_{1/2}$ of $\text{Cu}(\text{bpy})_2^{2+/1+}$ shifts to the positive direction compared to the SDS free. The intersection of two lines on ΔE_p vs. $-\log[\text{SDS}]$ plot for 1.0mM $\text{Cu}(\text{bpy})_2(\text{NO}_3)_2$ in 100mM NaCl+27mM MgCl₂ solution is a critical micelle concentration(CMC). Reduced form $\text{Cu}(\text{bpy})_2^{1+}$ in the presence of MgCl₂ is more easily associated to dodecyl sulfate anion(DS⁻) than oxidized $\text{Cu}(\text{bpy})_2^{2+}$. As the ionic strength is increased by the addition of multiply charged cations(MgCl₂), the double layer becomes more compact and micelle formation is more difficult.

요약 : 염화마그네슘이 있을 때 비스(2,2'-비피리딜)구리(II) ($\text{Cu}(\text{bpy})_2^{2+}$)-도데실황산나트륨(SDS)의 전기화학적거동이 고찰되었다. SDS가 존재하지 않을 때에 비해 SDS가 있을 때 $\text{Cu}(\text{bpy})_2^{2+/1+}$ 의 E_{pa} 및 $E_{1/2}$ 값은 양의 방향으로 이동된다. 1.0mM $\text{Cu}(\text{bpy})_2^{2+}$ 의 100mM NaCl+27mM MgCl₂ 용액에서, ΔE_p 대 $-\log[\text{SDS}]$ 로 도시되는 두 선의 교차점이 임계미셀농도(CMC)이다. 염화마그네슘이 있을 때, 환원형 $\text{Cu}(\text{bpy})_2^{1+}$ 이 산화형 $\text{Cu}(\text{bpy})_2^{2+}$ 보다 도데실황산이온과 더욱 쉽게 복합한다. 염화마그네슘 첨가에 의해 이온세기가 증가할수록, 이중층이 더욱 좁아지고 미셀형성이 더욱 어렵게 된다.

Key words : bis(2,2'-bipyridyl)copper(II), sodium dodecyl sulfate, critical micelle concentration, microenvironment, ionic strength, double layer, surfactant assembly.

1. Introduction

Micelles are dynamic surfactant assemblies able to combine with ions in terms of hydrophobic and coulombic interactions.¹ Analytical applications in micellar solutions have known a growing interest in recent years. Micellar assemblies have been extensively utilized in order to improve detection limits², permit a efficient separation of ions and organic molecules³, and apply redox processes in biological systems⁴ and a solar energy conversion.¹

Furthermore, although micellar assemblies have been considered as important models for biological molecules⁵, the microenvironments of ions and organic molecules around electrodes have received little attention.^{6,7} Divalent cation such as Mg^{2+} markedly shifts the SDS-dependent activation profiles to a lower concentration range in a biological analysis.⁵ Therefore, in this note, electrochemical behaviors of $(Cu(bpy)_2)^{2+}$ SDS solution in the presence of $MgCl_2$ are investigated using a cyclic voltammetry(CV). The microenvironments around a glassy carbon electrode(GC) resulting from $Cu(bpy)_2^{2+/1+}$ -SDS interaction are rationalized and investigated using the model proposed by A. Jaramillo et al.^{6,7}

2. Experiments

$[Cu(bpy)_2](NO_3)_2$ was prepared according to the previously reported procedures.^{9,10} SDS and NaCl were obtained from Aldrich and used without further purification. Doubly distilled water was used to prepare all solutions. A glassy carbon disk(Bioanalytical Systems, West Lafayette, in USA) with a geometric area of $0.0788cm^2$ was used as a working electrode. It was polished with $0.05\mu m$ γ -alumina/water slurry on a felt surface and then cleaned in ultrasonic chamber for 2min. A saturated calomel electrode(SCE) and a platinum mesh were used as a reference electrode and an auxiliary electrode, respectively. All experiments were performed under a purified nitrogen atmosphere at $25 \pm 0.2^\circ C$.

3. Results and discussion

Cyclic voltammograms of $1.0mM Cu(bpy)_2(NO_3)_2$ in $100mM NaCl+27mM MgCl_2$ solution with and without SDS are shown in Fig. 1. Data for the redox waves of $Cu(bpy)_2^{2+/1+}$ are shown with increasing the concentration of SDS in Table 1.

In the absence of SDS, the reduction of $Cu(bpy)_2^{2+}$ to $Cu(bpy)_2^{1+}$ takes place at a cathodic peak poten-

Table 1. Electrochemical Data for $1.0mM Cu(bpy)_2^{2+/1+}$ in $100mM NaCl+27mM MgCl_2$ with and without SDS at $25.0 \pm 0.2^\circ C$. Scan rate= $50mV/s$.

[SDS] (mM)	$-E_{pa}$ (mM)	ΔE_p (mM)	$-E_{1/2}$ (V)	i_{pa} (μA)	i_{pa}/i_{pa}
0.0	126	80	0.166	9.40	0.77
1.0	90	56	0.118	29.70	1.68
1.5	88	51	0.114	33.28	1.71
1.7	105	44	0.127	34.55	1.74
2.0	105	42	0.126	35.80	1.15
2.5	105	40	0.125	33.60	1.24
3.0	105	39	0.124	32.84	1.28
4.0	105	36	0.123	32.45	1.32
5.0	100	63	0.132	18.55	1.55
6.0	86	92	0.132	11.80	1.18
7.0	77	112	0.133	7.65	0.95

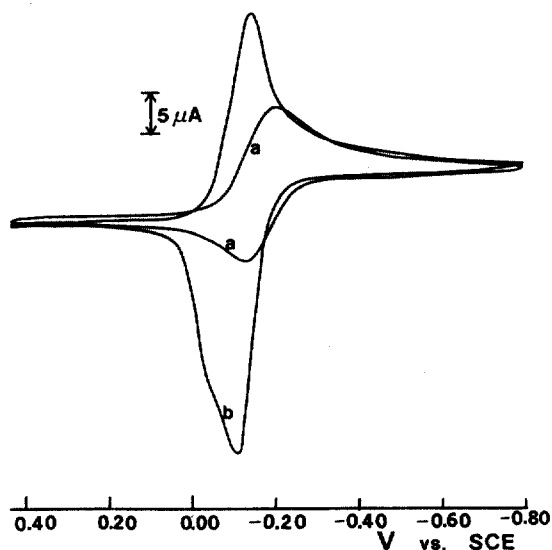


Fig. 1. Cyclic voltammograms of 1.0mM $\text{Cu}(\text{bpy})_2^{2+/1+}$ in 100mM $\text{NaCl}+27\text{mM}$ with and without SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate = 50mV/s . (a) $[\text{SDS}] = 0.0\text{mM}$; (b) $[\text{SDS}] = 4.0\text{mM}$.

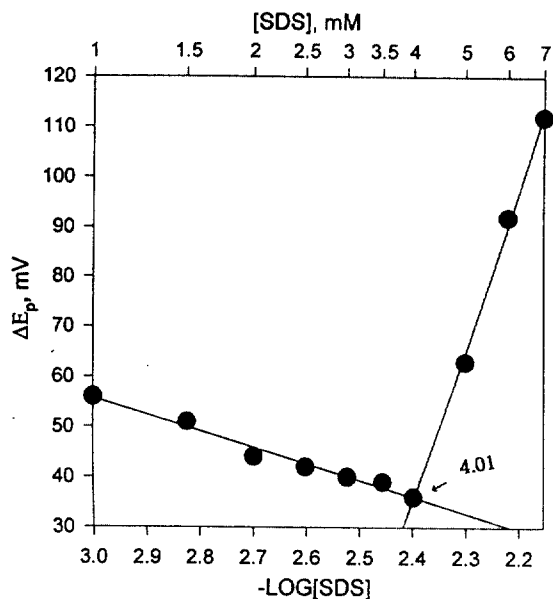


Fig. 2. ΔE_p vs $-\log[\text{SDS}]$ plot for 1.0mM $\text{Cu}(\text{bpy})_2^{2+/1+}$ in 100mM $\text{NaCl}+27\text{mM}$ MgCl_2 .

tial E_{pc} of -206mV and reoxidation of $\text{Cu}(\text{bpy})_2^{1+}$ occurs at -126mV upon scan reversal. The formal potential, $E_{1/2}$ taken as the midpoint of E_{pa} and E_{pc} is -0.166V . In the absence of SDS, from values of ΔE_p and i_{pa}/i_{pc} , the redox couple is electrochemically quasi-reversible.

In the presence of SDS, E_{pa} and $E_{1/2}$ of $\text{Cu}(\text{bpy})_2^{2+/1+}$ shifts to the positive direction compared to the SDS free. ΔE_p shows a special phenomenon as $[\text{SDS}]$ increases. ΔE_p decreases up to 4.0mM $[\text{SDS}]$ and increases gradually from the concentration. In order to see the relation between ΔE_p and a critical micelle concentration (CMC), ΔE_p vs. $-\log[\text{SDS}]$ is plotted for the redox couples in Fig. 2. The intersection of two lines in Fig. 2 is 4.01mM $[\text{SDS}]$, which (relative error = below 3%) is very near CMC measured by tensiometry¹¹ (3.99mM SDS) in Fig. 3.

On the other hand, in the absence of MgCl_2 , the intersection of two lines on $\Delta E_p - \log[\text{SDS}]$ plot for $1.0\text{mM}[\text{Cu}(\text{bpy})_2](\text{NO}_3)_2$ with SDS in 100mM NaCl

solution is 2.89mM SDS (CMC by tensiometry¹¹: 2.88mM SDS; relative error: below 3%). Thus, it must be concluded that the intersection of two lines on $\Delta E_p - \log[\text{SDS}]$ plot is CMC.

As $[\text{SDS}]$ increases up to CMC, the width of the double layer (i.e., distance to the surface) is narrowed by arranging monomers ($(\text{DS}^-)_n$) around the electrode, which speeds up the electron transfer.^{6,7}

Owing to the adsorption of $\text{Cu}(\text{bpy})_2^{1+}$ species to SDS, very large i_{pa} is observed at near CMC (see Table 1). At near above CMC, monomers around the electrode become dynamic to form micelles. Thus, $\text{Cu}(\text{bpy})_2^{1+}$ species adsorbed to SDS is separated, which leads to the decrease of i_{pa} suddenly. As $[\text{SDS}]$ increases above CMC, micelles are formed gradually. The increase of the number of micelle gives rise to the increase of the width of the double layer, which makes the decrease of i_{pa} and the electron transfer velocity (i.e., a increase on ΔE_p).

Tensiometry : Surface tension vs. $-\log[\text{SDS}]$ plot

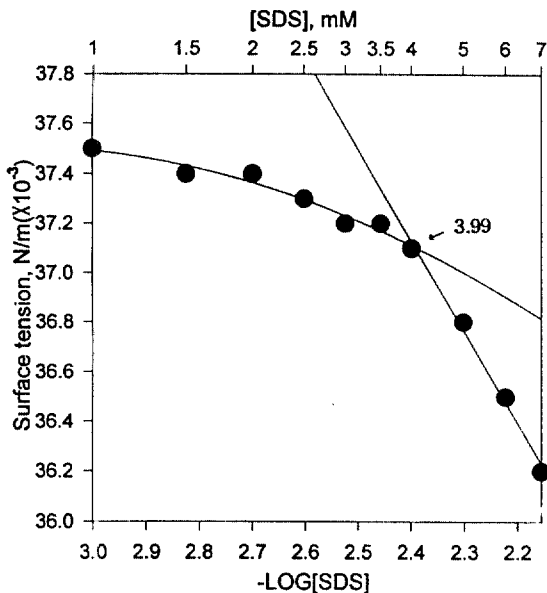


Fig. 3. Surface tension vs. $-\log[\text{SDS}]$ plot for 1mM $[\text{Cu}(\text{bpy})_2](\text{NO}_3)_2$ in 100mM NaCl+27mM MgCl_2 .

for 1mM $[\text{Cu}(\text{bpy})_2](\text{NO}_3)_2$ with SDS in 100mM NaCl+27mM MgCl_2 aqueous solution is shown in the Fig. 3. As $[\text{SDS}]$ increases, the values of surface tension decrease gradually. The intersection of two lines in Fig. 3 is estimated as CMC, 3.99mM SDS. CMC obtained by the tensiometry¹¹ is accordance

with that by CV, 4.01mM $[\text{SDS}]$.

Hydrophobic interaction between Cu complex ion and SDS : The Nernst equation for the reversible le^- redox reactions of the free and associated species can be written as eq. (1) given below.⁵

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

By substituting $E_{1/2}$ in Table 1 to eq (1), the ratios(K_{+1}/K_{+2}) of equilibrium constants for the association of the +1 and +2 ions of Cu complex to DS^- can be obtained. Since K_{+1}/K_{+2} is larger than 1, i_{pa}/i_{pc} is larger than 1. it is concluded that reduced form $\text{Cu}(\text{bpy})_2^{1+}$ in the presence of MgCl_2 is more easily associated to DS^- than oxidized Cu $(\text{bpy})_2^{2+}$. Thus, $\text{Cu}(\text{bpy})_2^{2+/1+}$ with SDS is more affected by hydrophobic interaction than electrostatic interaction.

Effect of multivalent cations on $\text{Cu}(\text{bpy})_2^{2+/1+}$: In the absence of MgCl_2 , data for the redox reaction of 1.0mM $\text{Cu}(\text{bpy})_2^{2+}$ in 100mM NaCl solution are shown with increasing $[\text{SDS}]$ in Table 2.

Comparing Table 1 with Table 2 in the presence of SDS, when MgCl_2 is added, the increase of i_{pa} and the decrease of ΔE_p are observed for $\text{Cu}(\text{bpy})_2^{2+/1+}$.

Table 2. Electrochemical Data for 1.0mM $\text{Cu}(\text{bpy})_2^{2+/1+}$ 100mM NaCl with and without SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate=50mV/s.

[SDS] (mM)	$-E_{pa}$ (mV)	ΔE_p (mV)	$-E_{1/2}$ (V)	i_{pa} (μA)	i_{pa}/i_{pc}
0.0	115	68	0.149	9.28	1.01
1.0	98	110	0.153	17.32	1.60
1.5	95	82	0.136	18.64	1.87
2.0	89	66	0.122	26.38	1.75
2.5	100	62	0.131	24.94	1.69
3.0	113	53	0.140	22.44	1.63
3.5	112	69	0.147	7.72	0.83
4.0	100	87	0.144	6.26	0.71
5.0	93	89	0.138	5.78	0.75
6.0	90	95	0.138	4.98	0.78
7.0	88	94	0.135	4.48	0.81

* CMC : 2.89mM SDS(CV), 2.88mM SDS(tensiometry)¹²

At GC, the addition of MgCl_2 results in the decrease of ΔE_p for $\text{Cu}(\text{bpy})_2^{2+/1+}$ except 7.0mM SDS, i.e., the decrease of a distance to the surface. The surface concentration of $\text{Cu}(\text{bpy})_2^{2+/1+}$ as measured by i_{pa} is affected by the addition of MgCl_2 . The increase of ionic strength by the addition of MgCl_2 brings the increase of i_{pa} (increasing the surface concentration of $\text{Cu}(\text{bpy})_2^{1+}$) and the decrease of ΔE_p (decreasing the distance to the surface). Thus, this is concluded that, as the ionic strength is increased by the addition of multiply charged cations (MgCl_2), the double layer becomes more compact, which demonstrates better surface access to GC for $\text{Cu}(\text{bpy})_2^{2+/1+}$ and results in the increase of the electrode reaction rate measured by the increase of the current.

Surfactant assembly at GC in the presence of Mg^{2+} :

A significant improvement in response of i_{pa} and ΔE_p for $\text{Cu}(\text{bpy})_2^{2+/1+}$ is observed in the presence of Mg^{2+} . Mg^{2+} is screening the negative charges of surfactant on GC surface and retarding the formation of micelle. Thus, as ionic strength increases by the addition of 27mM MgCl_2 CMC of SDS for 1mM $[\text{Cu}(\text{bpy})_2](\text{NO}_3)_2$ in 100mM NaCl solution increases from 2.88mM to 4.01mM SDS. It can be concluded that micelle formation is more difficult

as ionic strength increases by the addition of MgCl_2 .

References

1. J. H. Fendler, "Membrane Mimetic Chemistry," Academic press: New York, 1982.
2. C. Moulin and et al., *J. Colloid Interface Sci.*, **157**, 411-417(1993).
3. P. Reller and et al., *J. Colloid Interface Sci.*, **163**, 81-86(1994).
4. M. Calvin, *Acc. Chem. Res.*, **11**, 369-379(1978).
5. A. E. Kaifer and A. J. Bard *J. Phys. Chem.*, **89**, 4876-4880(1985).
6. A. Jaramillo, A. Marino, and A. B. -Toth, *Anal. Chem.*, **65**, 3441-3446(1993).
7. A. Marino and A. B. -Toth, *Anal. Chem.*, **65**, 370-374(1993).
8. S. Yamada, K. Hojo, H. Yoshimura, and K. Ishikawa, *J. of Biochem.*, **117**, 1162-1169(1995)
9. L. S. Parbhmirashi, G. N. Natu, and J. K. Khoje, *J. Therm. Anal.*, **35**, 1097-1101(1989).
10. M. Kabesova, J. Pirskej, and M. D. -Jurco, *M. J. Therm. Anal.*, **34**, 1349-1353(1988).
11. B. Lindman and H. Wennerström, *Top. Curr. Chem.*, **87**, 1-83(1980).
12. Y. C. Ko, and J. Y. Kim. submitted in *J. of Suncheon National Uni.*, 1996.