

Voltammetric Study of Anionic Surfactant-Modified Glassy Carbon Electrode for Bis(2,2'-Bipyridyl)Copper(II) in 200 mM NaBr

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Abstract

When a hydrophobic and hydrophilic environments of bis(2,2'-bipyridyl) copper(II) ($\text{Cu}(\text{bpy})_2^{2+}$) are produced in the presence of anionic surfactant sodium dodecyl sulfate (SDS), cyclic voltammetry is used to investigate the microscopic environments which occurs at the glassy carbon electrode. In order to see the relation between ΔE_p and a critical micelle concentration (CMC), ΔE_p vs. $-\text{Log}[\text{SDS}]$ for the redox couples are plotted. The concentration at the intersection of two lines is 2.57 mM SDS, and this concentration can be determined as the CMC (relative error: below 0.03%; 2.63 mM SDS by surface tensiometry).

Key words: Bis(2,2'-Bipyridyl)Copper(II), SDS Modified Glassy Carbon Electrode, Cyclic Voltammetry, Double Layer

1. Introduction

Several workers have been used different modified electrodes made by using various surfactants. And these electrodes have been utilized significantly to enhance selectivity in the fields of qualitative and quantitative analysis for a specific materials.

Zhu, Cao, and Cao used cetyltrimethylammonium bromide to modify a carbon paste electrode for determination of bisphenol A^[1]. Serpi, Voulgaropoulos, and Grousi adsorbed dodecyltrimethylammonium bromide and tetradecyltrimethylammonium bromide to modify a carbon paste electrode with multiwalled carbon nanotubes for examining the oxidation of guanine residues on the dsDNA molecule^[2]. And Ma, Chao, and Wang used sodium dodecyl sulphate to modify a glassy carbon electrode with graphene for the determination of Sudan i in food samples^[3]. Vishwanath et al used sodium dodecyl sulphate to modify a carbon paste electrode with Li_2ZrO_3 nanoparticles for determination of dopamine at pH 7.2 phosphate buffer solution^[4]. Meng et al used sodium dodecyl sulfate to modify a pyrolytic graphite electrode with graphene for determination of 5-

methylcytosine^[5]. Zhang *et al.* used sodium dodecyl benzene sulfonate to modify a carbon paste electrode with cysteic acid for determination of ofloxacin and gatifloxacin^[6]. Shankar et al used sodium dodecyl benzene sulfate to modify a carbon paste electrode for determination of dopamine, uric acid, and ascorbic acid^[7]. And Ko, Kim and Chung used SDS to modify a glassy carbon electrode (GCE) for determination of iron(III)^[8].

As above mentioned papers, different modified electrodes made by using various surfactants have been used for qualitative and quantitative analysis of many materials. Therefore, in this paper, microenvironments of electrochemical behaviors in each concentration of SDS solution containing 1.0 mM bis(2,2'-bipyridyl)copper(II) are studied by cyclic voltammetry (CV) in 200 mM NaBr. Also this study will be helped to survey microenvironments of electrochemical behaviors of copper metal complex in vicinity of CMC.

2. Experimental Section

SDS and NaBr were purchased from Sigma-Aldrich, and used without further purification. Bis(2,2'-bipyridyl)copper(II) was made as already reported method^[9]. Doubly distilled water was used in this experiment. Each the glassy carbon disk, saturated calomel electrode, platinum mesh was used as working, reference, and auxiliary electrode just like Ko^[9]. All experimental

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conditions were performed under exactly the same $25 \pm 0.2^\circ\text{C}$ as Ko. SDS modified glassy carbon electrode (GCE) was made easily by electrolyzing glassy carbon disk in each concentration of SDS solution containing 1.0 mM bis(2,2'-bipyridyl)copper(II) in 200 mM NaBr. After electrochemical activation by cyclic voltammetry, the activated SDS modified GCE was used to investigate the copper(II) complex below and above the CMC in 200 mM NaBr.

3. Results and Discussion

Cyclic voltammograms of 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr solution with and without SDS are shown in Fig. 1(a and b) at scan rate = 50 mV/sec. Data for the redox waves of $\text{Cu}(\text{bpy})_2^{2+}$ are shown with increasing the concentration of SDS in Table 1.

In the absence of SDS, the reduction of $\text{Cu}(\text{bpy})_2^{2+}$ to $\text{Cu}(\text{bpy})_2^+$ occurs at a cathodic peak potential E_{pc} of -179 mV and reoxidation of $\text{Cu}(\text{bpy})_2^+$ takes place at -127 mV on scan reversal. The formal potential, $E_{1/2}$ obtained as the midpoint of E_{pa} and E_{pc} is -0.153 V. In the absence of SDS, from each value 66 mV and 0.92 of ΔE_p and i_{pa}/i_{pc} , the electrode reaction of the redox couple is electrochemically quasi-reversible. Judging from these, it seems that the naked electrode response is related to 0.89-electron reaction.

In the presence of SDS for SDS modified GCE, E_{pa} and $E_{1/2}$ of $\text{Cu}(\text{bpy})_2^{2+}$ species shifts to a positive direction compared to the SDS free. ΔE_p decreases up to

2.5 mM SDS with increasing the concentration of SDS. And after that, this value increases to 7.0 mM SDS gradually (Table 1, Fig. 2).

On one hand in the absence of SDS (Fig. 1(a), peak of A in near -350 mV came out, which is considered to be peak formed owing to an oxidation reaction at the electrode for Cu^+ species derived by force of a negative scan of equation (1). At the blank test, the electrode response for a positive scan in reduced species of Cu^{2+} in 200 mM NaBr shows the same peak.



To see the relation between ΔE_p and a critical micelle concentration (CMC)^[9], ΔE_p vs. $-\log[\text{SDS}]$ are plotted for the redox couples of $\text{Cu}(\text{bpy})_2^{2+}$ in Fig. 2. The intersection of two lines is 2.57 mM [SDS], which (relative error=below 0.03 %) is very near CMC measured by surface tensiometry (2.63 mM SDS) in Fig. 3. That is, observing Table 1 for SDS modified GCE, the width of the double layer in terms of ΔE_p is narrowed by arranging dodecyl sulfate anions ($(\text{DS}^-)_n$) around the electrode as [SDS] increases to CMC. This fact presents that SDS modified GCE can improve the electron transfer rate. Distance of the double layer narrowed speeds up the electrons transfer^[9]. It seems that the associative power of $\text{Cu}(\text{bpy})_2^+$ species to DS^- is strong considerably. And so, very large anodic peak currents of $\text{Cu}(\text{bpy})_2^+$ are observed up to 4.0 mM SDS of near concentration above CMC. In the above concentration of SDS, just in

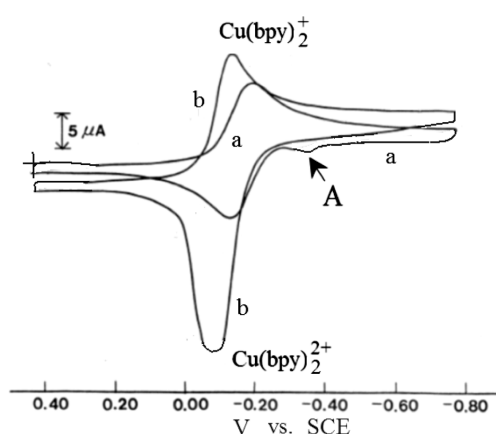


Fig. 1. Cyclic voltammograms of 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr with and without SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate = 50 mV/s. (a) [SDS] = 0 mM; (b) [SDS] = 2.0 mM.

Table 1. Electrochemical Data for 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr with and without SDS at $25.0 \pm 0.2^\circ\text{C}$. Scan rate = 50 mV/s

[SDS] (mM)	$-E_{pa}$ (mV)	ΔE_p (mV)	$-E_{1/2}$ (mV)	i_{pa} μA	i_{pa}/i_{pc}
0	127	66	0.153	8.99	0.92
1.0	98	72	0.145	24.35	1.78
1.5	96	68	0.105	24.32	1.65
2.0	94	67	0.113	24.49	1.56
2.3	92	64	0.116	24.32	1.52
2.5	92	63	0.128	23.58	1.42
3.0	95	68	0.130	23.42	1.38
4.0	102	75	0.142	23.16	1.24
5.0	100	79	0.142	7.32	0.73
6.0	96	82	0.135	5.46	0.72
7.0	92	89	0.129	4.37	0.70

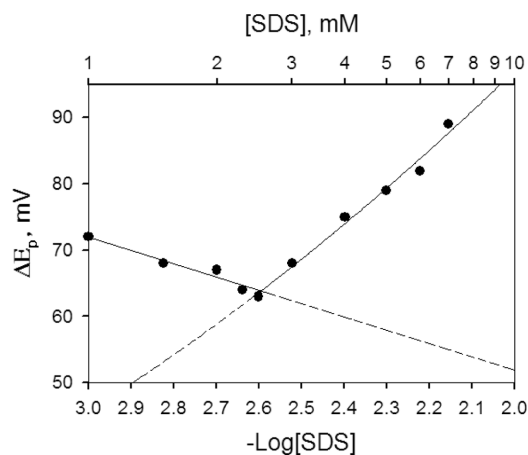


Fig. 2. ΔE_p vs. $-\log[\text{SDS}]$ plot for 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr.

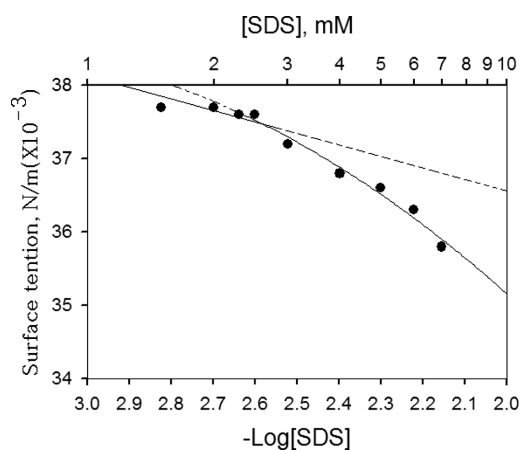


Fig. 3. Surface tension vs. $-\log[\text{SDS}]$ plot for 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr.

more than 5.0 mM SDS, most of monomers $(\text{DS}^-)_n$ around the glassy carbon electrode become dynamic to form micelles. Therefore it seems that $\text{Cu}(\text{bpy})^+$ species associated to DS^- are almost separated, which leads to the decrease of anodic peak currents of $\text{Cu}(\text{bpy})^+$. As more many micelles are formed, the width of the double layer become wider and the screening of the electrode surface increase, which give rise to the decrease of electron transfer velocity and anodic peak current.

At 25°C the peak current of reversible systems is^[10]

$$i_p = (2.69 \times 10^5) n^3 C_0 D^{1/2} v^{1/2} \quad (2)$$

The current will be in amperes when A is in cm^2 , D

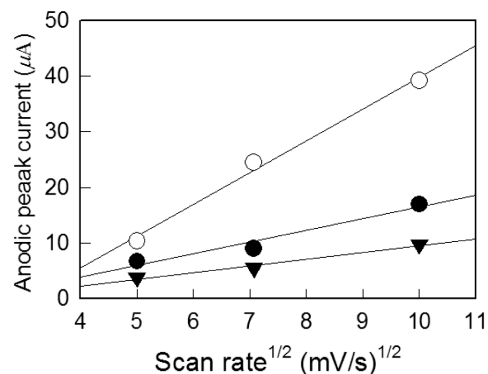


Fig. 4. Scan rate dependence of the anodic peak current for 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr without and with SDS. (●) [SDS] = 0 mM; (▼) [SDS] = 2.0 mM; (○) [SDS] = 6.0 mM.

is in cm^2/s , is in volts/s, and C_0 is bulk concentration in moles/ cm^3 . On the basis of equation (2), a apparent diffusion coefficient is evaluated by the slope of i_{pa} vs $v^{1/2}$, which is $0.849 \times 10^{-7} \text{ cm}^2/\text{s}$, $0.661 \times 10^{-6} \text{ cm}^2/\text{s}$, $0.539 \times 10^{-7} \text{ cm}^2/\text{s}$ for 1.0 mM $\text{Cu}(\text{bpy})_2^{2+}$ in 200 mM NaBr without SDS and with 2.0 mM, 6.0 mM SDS, respectively (Fig. 4). The results of the apparent diffusion coefficient reflect the variation in anodic peak current depending on change in the concentration of SDS. Therefore, it is concluded the apparent diffusion coefficient could be controlled by change in the concentration of anionic surfactants, SDS.

4. Conclusion

In the absence of SDS, the reduction of $\text{Cu}(\text{bpy})_2^{2+}$ to $\text{Cu}(\text{bpy})^+$ occurs at a cathodic peak potential E_{pc} of -179 mV and reoxidation of $\text{Cu}(\text{bpy})^+$ takes place at -127 mV on scan reversal. The formal potential, $E_{1/2}$ obtained as the midpoint of E_{pa} and E_{pc} is -0.153 V. In the presence of SDS for SDS modified GCE, E_{pa} and $E_{1/2}$ of $\text{Cu}(\text{bpy})_2^{2+}$ species shifts to a positive direction compared to the SDS free. ΔE_p decreases up to 2.5 mM SDS with increasing the concentration of SDS. And after that, this value increases to 7.0 mM SDS gradually. To see the relation between ΔE_p and a critical micelle concentration (CMC), ΔE_p vs. $-\log[\text{SDS}]$ are plotted for the redox couples of $\text{Cu}(\text{bpy})_2^{2+}$. The intersection of those two lines is 2.57 mM [SDS], which (relative error=below 0.03%) is very near CMC measured by surface tensiometry (2.63 mM SDS). As many micelles

are formed, the width of the double layer become wider and the screening of the electrode surface increase, which give rise to the decrease of electron transfer velocity and anodic peak current. And it is concluded the apparent diffusion coefficient could be controlled by change in the concentration of anionic surfactants, SDS.

Acknowledgments

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