Electrochemistry of bis(1,10-phenanthroline)copper(II)-sodium dodecyl sulfate solution in the presence of MgCl₂

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염화마그네슘 존재 하의 비스(1,10-페난트롤린)
구리(II)-도데실황산나트륨 용액의 전기화학

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Abstract: Electrochemistry of 1.0 mM bis(1,10-phenanthroline)copper(II) (Cu(ph)$_2^{2+}$) in 100 mM NaCl solution including 27 mM MgCl₂ with and without sodium dodecyl sulfate (SDS) is studied. In the presence of SDS, E_{pa} and $E_{1/2}$ of Cu(ph)$_2^{2+}$ by adding Mg^{2+} shifts to a positive direction compared to the SDS free. The intersection of two lines on ΔE_p vs -log[SDS] plot is determined as a critical micelle concentration (CMC). When Mg^{2+} is added, it seems that the double layer became more compact. And the formation of micelles is retarded.

요 약: 염화마그네슘 존재하의 비스(1,10-페난트롤린)구리(II) (Cu(ph)$_2^{2+}$)-도데실황산나트륨(SDS)의 전기화학적 거동들이 고찰되었다. Mg^{2+}의 첨가에 의한 SDS의 용액에서 Cu(ph)$_2^{2+}$의 E_{pa}와 $E_{1/2}$ 값은 양의 값으로 이동했다. 1.0 mM Cu(ph)$_2^{2+}$의 27 mM MgCl₂을 포함한 100 mM NaCl 용액에서, ΔE_p 대 -log[SDS]로 도시한 그림에서 두 선의 교차점을 임계미셀농도로 결정하였다 (순환 전압전류법에 의해 3.48 mM SDS; 표면 장력법에 의해 3.34 mM SDS). Cu(ph)$_2^{2+}$의 용액에 Mg^{2+}가 첨가되었을 때 유리탄소전극에서의 이중층의 거리가 감소했고 미셀형성이 지연되었다.

Key words : bis(1,10-phenanthroline)copper(II), sodium dodecyl sulfate, critical micelle concentration, ionic strength, double layer

1. Introduction

Bis(1,10-phenanthroline)copper(II) acted as effective electron-transfer mediators in solar cells[1] and enhanced the electrocatalytic activity to electron transfer for O₂ reduction.[2] But the resulting electron self-exchange rate constant of Cu(ph)$_2^{2+}$ is slower than bis(2,9-dimethy-1,10-phenanthroline)copper(II) because of

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the smaller structural change between the copper(II) and copper(I) complex due to the distorted tetragonal geometry.[1] Nevertheless, it seems that the addition of anionic surfactant SDS in the complex can be more speed up electron transfer velocity in the regions below and above a critical micelle concentration. Also, applications of surfactants have been extensively utilized in order to improve solubility,[3] evaluate mimic binding micellar models for biological membranes,[4] capture images of atomic force microscopy,[5] characterize the structure of molecules by fluorescence spectroscopy.[6] And divalent cation such as Mg^{2+} noticeably shifts the SDS-dependent activation profiles to a lower concentration range in a analysis.[7,8]

In this paper, thus, electrochemical behaviors of $Cu(ph)_2^{2+}$-SDS solution in the presence of $MgCl_2$ are investigated in terms of the model[9] proposed by Brajter-Toth *et al.*

2. Experiments

Bis(1,10-phenanthroline)copper(II) bromide was prepared according to the previously reported procedures.[10,11] SDS, NaCl, and $MgCl_2$ were obtained from Aldrich and used without further purification. Doubly distilled water was used to prepare all solutions. Surface tension measurement[12,13] was carried out using CSC-Du Noüy (CAT. No. 70535) tensiometer. 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 gamma-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) 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±0.1°C.

3. Results and Discussion

Cyclic voltammograms of 1.0 mM $Cu(ph)_2^{2+}$ in 100 mM NaCl solution including 27 mM $MgCl_2$, without and with SDS are shown in *Fig.* 1. Data for
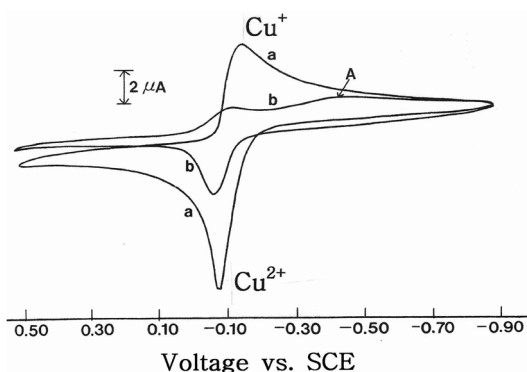
Fig. 1. Cyclic voltammograms of 1.0 mM $Cu(ph)_2^{2+}$ in 100 mM NaCl including 27 mM $MgCl_2$ with and without SDS at 25.0±0.1°C. Scan rate=50 mV/s. (a) [SDS]=0 mM; (b) [SDS]=3.0 mM.

Table 1. Electrochemical Data for 1.0 mM $Cu(ph)_2^{2+}$ in 100 mM NaCl including 27 mM $MgCl_2$ with and without SDS at 25.0±0.1°C. Scan rate=50 mV/s.

[SDS] (mM)	$-E_{pa}$/ mV	ΔE_p/ mV	$-E_{1/2}$ (V)	i_{pa} (μA)	i_{pa}/i_{pc}
0	75	75	0.113	9.70	1.71
1.0	66	109	0.121	5.92	2.21
1.5	53	97	0.102	6.50	3.49
2.0	60	70	0.095	5.98	4.21
2.5	66	56	0.094	4.60	2.30
3.0	70	46	0.094	3.46	2.31
3.5	71	37	0.090	3.70	1.14
4.0	62	57	0.091	6.58	0.98
4.5	60	65	0.093	8.62	0.89
5.0	60	73	0.097	10.20	0.90
6.0	63	60	0.099	8.28	1.49
7.0	72	58	0.101	8.52	1.69

the redox waves of $Cu(ph)_2^{2+}$ are shown with increasing the concentration of SDS in *Table* 1.

In the absence of SDS, the reduction of $Cu(ph)_2^{2+}$ to $Cu(ph)_2^+$ occurs at a cathodic peak potential E_{pc} of -150 mV and reoxidation of $Cu(ph)_2^+$ takes place at -75 mV on scan reversal. The formal potential, $E_{1/2}$ obtained as the midpoint of E_{pc} and E_{pa} is -0.113 V. 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 $Cu(ph)_2^{2+}$ by adding Mg^{2+} shifts to a positive direction compared to the SDS free (except 1.0 mM SDS). ΔE_p decreases up to 3.0 mM SDS with increasing the concentration
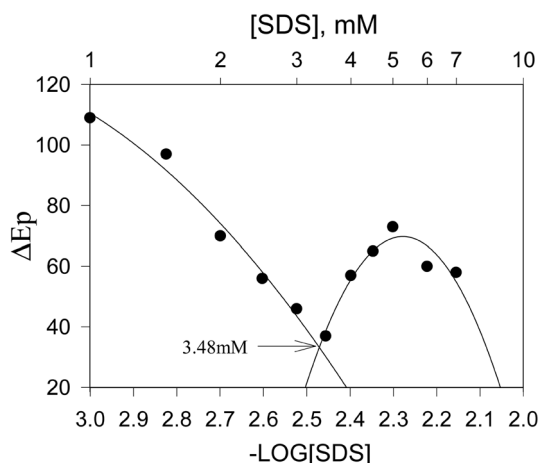
Fig. 2. ΔE_p vs. [SDS] plot for 1.0 mM Cu(ph)$_2^{2+}$ in 100 mM NaCl including 27 mM MgCl$_2$.

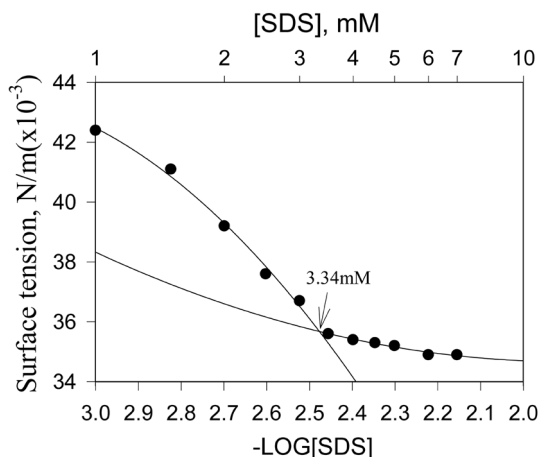*Fig.* 3. Surface tension vs. [SDS] plot for 1.0 mM Cu(ph)$_2^{2+}$ in 100 mM NaCl including 27 mM MgCl$_2$.

of SDS. And this value increases to 5.0 mM SDS gradually and after that decreases (*Fig.* 2). In other to see the relation between ΔE_p and a critical micelle concentration (CMC), ΔE_p vs -log[SDS] is plotted for the redox couples in *Fig.* 2. The intersection of two lines is 3.48 mM [SDS], which (relative error=below 4.2 %) is very near CMC measured by surface tensiometry (3.34 mM SDS) in *Fig.* 3.

In the meanwhile, in the absence of MgCl$_2$, the intersection of two lines on ΔE_p vs -log[SDS] plot for 1.0 mM Cu(ph)$_2^{2+}$ with SDS in 100 mM NaCl solution is 3.03 mM SDS (2.99 mM SDS; relative error : below 2 %).[14]

Thus, it can be concluded that the intersection of two lines on ΔE_p vs -log[SDS] plot is CMC.

As [SDS] increases to CMC, the width of the double layer in terms of ΔE_p is narrowed by arranging monomers (dodecyl sulfate anions : (DS$^-$)$_n$) around the electrode, which speeds up the electron transfer.[9] Nevertheless, it seems that the anodic current of Cu(ph)$_2^+$ decreases due to decomposition of Cu(ph)$_2$SO$_4$. As [SDS] increases up to 5.0 mM SDS at near above CMC, monomers around the electrode become dynamic to form micelles, which leads to the increases of ΔE_p and anodic peak current. More, as [SDS] increases, micelles is formed gradually, which makes the decreases of ΔE_p and anodic peak current because of more compact of the double layer-width and the increase of the electrode surface screening, respectively, with the increasing in the number of micelles.

3.1. Effect of multivalent cations on the redox reaction of Cu(ph)$_2^{2+}$

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

Comparing *Table* 1 with *Table* 2 in the presence of SDS, when MgCl$_2$ is added, the decrease of i_{pa} and decrease of ΔE_p are observed for Cu(ph)$_2^{2+}$.

At glassy carbon electrode, the addition of MgCl$_2$

Table 2. Electrochemical Data for 1.0 mM Cu(ph)$_2^{2+}$ in 100 mM NaCl with and without SDS at 25.0±0.1°C.[14] Scan rate=50 mV/s.

[SDS] (mM)	-E$_{pa}$/ mV	ΔE_p/ mV	-E$_{1/2}$ (V)	i_{pa} (μA)	i_{pa}/i_{pc}
0	49	83	0.091	18.12	1.47
1.0	55	149	0.130	14.16	3.01
1.5	57	120	0.117	12.88	3.10
2.0	60	100	0.110	13.56	2.83
2.5	67	80	0.107	14.21	1.93
3.0	78	68	0.112	14.96	1.13
3.5	63	70	0.098	17.94	1.41
4.0	68	72	0.104	20.44	1.48
5.0	74	72	0.110	19.90	1.58
6.0	75	71	0.111	15.42	1.75
7.0	105	68	0.139	5.06	1.51

*CMC : 3.03 mM SDS(CV), 2.99 mM SDS(tensiometry)[14]

results in the decrease of ΔE_p for $Cu(ph)_2^{2+}$ (except 7.0 mM SDS). Nevertheless, the increase of ionic strength by adding $MgCl_2$ brings the decrease of i_{pa} (decreasing the surface concentration of $Cu(ph)_2^{2+}$) due to decomposition of $Cu(ph)_2^{2+}$. Peak of A in the vicinity of -400 mV appeared when SDS was added (see *Fig.* 1(b), which is considered to be peak formed owing to the electrode response (via eq. (2)) of SDS with Cu^{2+} derived by the decomposition (by means of eq. (1)) of $Cu(ph)_2^{2+}$.

$$Cu(ph)_2^{2+} \rightarrow Cu^{2+} + 2ph \qquad (1)$$
$$Cu^{2+}\text{-}(DS^-)_n + e^- \rightleftharpoons Cu^+\text{-}(DS^-)_n \qquad (2)$$
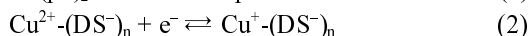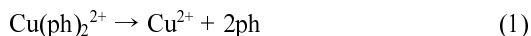
A blank test, the electrode response (via eq. (2)) of SDS with $CuSO_4$, shows the same peaks.

Thus, this is concluded that, as the ionic strength is increased by adding multiply charged cations ($MgCl_2$), the double layer becomes more compact and the surface concentration of $Cu(ph)_2^+$ decreases.

3.2. Interaction between Cu complex ion and SDS

The Nernst equation for the reversible $1e^-$ redox reactions of the free and associated species can be written as eq. (3) given below.

$$E_a^{0'}\text{-}E_f^{0'}=0.059 \log(K_+/K_{2+}) \qquad (3)$$

By substituting $E_{1/2}$ in *Table* 1 or *Table* 2 to eq. (3), the ratios(K_+/K_{2+}) of equilibrium constants for the association of +1 and +2 ions of Cu complex to DS^- can be obtained. In the presence of Mg^{2+} (*Table* 1), since K_+/K_{2+} is larger than 1 (except 1 mM SDS), a reduced form $Cu(ph)_2^+$ is more easily associated to DS^- than an oxidized form $Cu(ph)_2^{2+}$. But in the absence of Mg^{2+} (*Table* 2), since K_+/K_{2+} is smaller than 1, the oxidized form $Cu(ph)_2^{2+}$ is more easily associated to DS^- than the reduced form $Cu(ph)_2^+$.

Thus, in the presence of Mg^{2+}, it can be concluded that $Cu(ph)_2^{2+}$ with SDS is more affected by hydrophobic interaction than electrostatic interaction. But in the absence of Mg^{2+}, $Cu(ph)_2^{2+}$ with SDS is more affected by electrostatic interaction than hydrophobic interaction.

3.3. Surfactant assembly at glassy carbon electrode in the presence of Mg^{2+}

A meaningful improvement in response of ΔE_p is observed in the presence of Mg^{2+}. Mg^{2+} is screening the negative charges of SDS on glassy carbon electrode and retarding the formation of micelle. As ionic strength increases by the addition of 27 mM $MgCl_2$, CMC of SDS for 1 mM $[Cu(ph)_2]Br_2$ in 100 mM NaCl solution increases from 3.03 mM to 3.48 mM SDS. It can be concluded that micelle formation is more difficult as ionic strength increases by the addition of $MgCl_2$.

4. Conclusions

Results obtained this paper show that in presence of SDS, E_{pa} and $E_{1/2}$ of $Cu(ph)_2^{2+}$ by adding Mg^{2+} shifts to a positive direction compared to the SDS free. At glassy carbon electrode, the addition of $MgCl_2$ results in the decrease of ΔE_p for $Cu(ph)_2^{2+}$. Nevertheless, the increase of ionic strength by adding $MgCl_2$ brings the decrease of i_{pa} due to decomposition of $Cu(ph)_2^{2+}$.

In the presence of Mg^{2+}, it can be concluded that $Cu(ph)_2^{2+/+}$ with SDS is more affected by hydrophobic interaction than electrostatic interaction. But in the absence of Mg^{2+}, $Cu(ph)_2^{2+/+}$ with SDS is more affected by electrostatic interaction than hydrophobic interaction.

Mg^{2+} is screening the negative charges of SDS on glassy carbon electrode and retarding the formation of micelle. Thus, it is concluded that micelle formation is more difficult as ionic strength increases by the addition of $MgCl_2$.

Acknowledgment

References

1. S. Hattori, Y. Wada, S. Yanagida and S. Fukuzumi, *J.*

Am. Chem. Soc., **127**, 9648-9654 (2005).

2. S.-J. Liy, C. -H. Huang and C.-C. Chang, *Mat. Chem. and Phy.*, **82**, 551-556 (2003).

3. C. Wang, E. Wyn-Jones, J. Sidhu and K. C. Tam, *Langmuir*, **23**, 1635-1639 (2007).

4. D. Mitra, I. Chakraborty, S. C. Bhattacharya and S. P. Moulik, *Langmuir*, **23**, 3049-3061 (2007).

5. M. S. Bakshi, A. Kaura, J. D. Miller and V. K. Paruchuri, *J. Coll. Interf. Sci.*, **278**, 472-477 (2004).

6. G. Caminati, N. J. Turro and D. A. Tomalia, *J. Am. Chem. Soc.*, **112**, 8515-8522 (1990).

7. S. Yamada, K. Hojo, H. Yoshimura, and K. Ishikawa, *J. of Biochem.*, **117**, 1162-1169 (1995).

8. Y. C. Ko and K. H. Chung, *Anal. Sci. & Tech.*, **11**, 151-155 (1998).

9. A. Jaramillo, A. Marino and A. Brajter-Toth, *Anal. Chem.* **65**, 3441-3446 (1993).

10. C.-W. Lee and F. C. Anson, *Inorg. Chem.* **23**, 837-844 (1984).

11. C. -W. Lee and F. C. Anson, *J. Phys. Chem.* **87**, 3360-3362 (1983).

12. B. Lindman and H. Wennerstrm, *Top. Curr. Chem.*, **87**, 1-83 (1980).

13. Y. C. Ko, J. Ree and K. H. Chung, *Bull. Korean. Chem. Soc.*, **18**, 113-116 (1997).

14. Y. C. Ko, *J. of Dabul University*, **4**, 545-551 (1998).