

Electrochemistry of Tris(2,2'-bipyridyl)Ruthenium(II)-Sodium Dodecyl Sulfate in 300 mM H₂SO₄ Solution

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Abstract

Electrochemistry of 1.0 mM tris(2,2'-bipyridyl)ruthenium(II) (Ru(bpy)₃²⁺) in 300 mM H₂SO₄ solution with and without sodium dodecyl sulfate (SDS) is studied. In the presence of SDS, E_{pa} of Ru(bpy)₃²⁺ shifts to positive direction compared to the SDS free case. The intersection of two lines on ΔE_p vs. $-\log[\text{SDS}]$ plot is measured as a critical micelle concentration (CMC), which is 3.67 mM SDS.

Key words : tris(2,2'-bipyridyl)ruthenium(II), SDS, CMC

1. Introduction

The application of microbubbles was used at near surfactant concentrations above the CMC.^[1] UV-vis. spectra of methylnaphthalene-2-sulfonate were investigated at different concentration below and above CMC. Indication of premicelle could be showed by the change of the methylnaphthalene-2-sulfonate spectra.^[2] When the concentration of n-dodecylammonium α -glutamate was higher than CMC, heme monomer was released from the hydrophobic cavity of hemoglobin.^[3] Regular theory for binary surfactants revealed negative deviation from ideal behavior at the CMC.^[4] The refractive index increases suddenly at the CMC due to the change caused by adsorption of surfactant molecules onto the surface of the plastic fiber.^[5] And recently a new method to determine CMC was reported by using near-infrared spectroscopic technique.^[6]

As above mentioned, many studies were showed a special characteristics at near concentrations below and above the critical micelle concentration. And so, also in this paper electrochemical behaviors in the vicinity of CMC of SDS-Ru(bpy)₃²⁺ solution are investigated using a electrochemical method. Discussion of SDS-Ru(bpy)₃²⁺ solution is restricted to the regions nearly below and above the CMC. Because the interesting effects is being

discovered at surfactant concentrations below and above the critical micelle concentration.^[7,8] A variation of the microenvironments of SDS-Ru(bpy)₃²⁺ interactions in the vicinity of the CMC is discussed by using the model proposed by Brajter-Toth et al.^[9]

2. Experimental Section

Ru(bpy)₃²⁺, SDS, and H₂SO₄ were obtained from Aldrich, Aldrich, and Wako chemicals, respectively, and used without further purification. Doubly distilled water was used to prepare all solutions. Glassy carbon disk (Bioanalytical Systems, West Lafayette, in USA) with a geometric area of 0.0788 cm² was used as a working electrode. It was polished with 0.05 μ m gamma-alumina/water slurry on a felt surface and then exposed to ultrasonic cleaning about 2 min. A saturated calomel electrode (SCE) and a platinum mesh were used as a reference electrode and an auxiliary electrode, respectively. All electrochemical experiments were performed under a purified nitrogen atmosphere at 25 \pm 0.2°C.

3. Results and Discussion

Cyclic voltammograms of 1.0 mM Ru(bpy)₃²⁺ in 300 mM H₂SO₄ solution with and without SDS are shown in Fig. 1 (a, b, and d) at scan rate=100 mV/sec. Data for the redox waves of Ru(bpy)₃^{2+/3+} are shown with increasing the concentration of SDS in Table 1.

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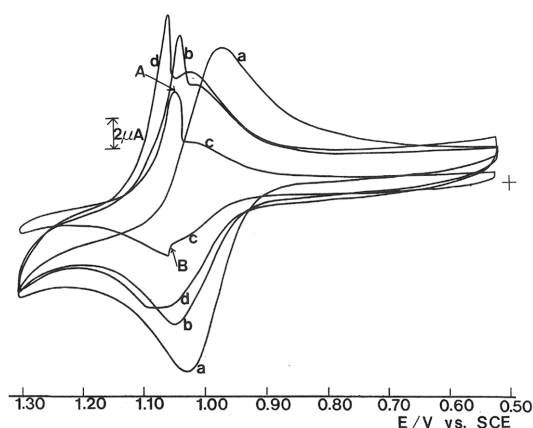
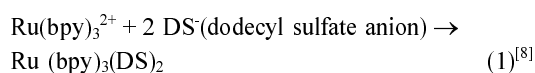


Fig. 1. Cyclic voltammograms of 1.0 mM Ru(bpy)₃²⁺ in 300 mM H₂SO₄ with and without SDS at 25.0±0.2°C. Scan rate=100 mV/s except for [SDS]=5.0 mM (20 mV/s). (a) [SDS]=0 mM ; (b) [SDS]=3.5 mM ; (c) [SDS]=5.0 mM ; (d) [SDS]=7.0 mM.

Table 1. Electrochemical Data for 1.0 mM Ru(bpy)₃²⁺ in 300 mM H₂SO₄ with and without SDS at 25.0±0.2°C. Scan rate=100 mV/s

[SDS] (mM)	<i>E</i> _{pa} (mV)	Δ <i>E</i> _p (mV)	<i>E</i> _{1/2} (mV)	<i>i</i> _{pa} (μA)	<i>i</i> _{pa} / <i>i</i> _{pc}
0.0	1028	60	998	11.50	1.23
1.5	1032	58	1003	6.18	1.32
2.0	1033	51	1008	5.70	1.35
2.5	1036	46	1013	5.40	1.51
3.0	1047	41	1027	5.23	1.49
3.5	1050	38	1031	7.60	1.28
4.0	1053	39	1034	8.50	1.24
4.5	1054	40	1034	8.64	1.25
5.0	1060	42	1039	8.78	1.22
6.0	1070	46	1047	7.94	1.12
7.0	1074	54	1047	6.10	1.01
10.0	1077	60	1047	5.16	1.23

In the absence of SDS (Fig. 1(a)), the sharp peaks in the region A and the peaks in B are not shown. But in the presence of SDS (Fig. 1(b-d)), maybe, it seems that those in the region A and these in B are appeared due to Eq. (1) as in 300 mM H₂SO₄:



At scan rate=100 mV/sec, those peaks in the region A are appeared approximately in 3.5 mM SDS, reached the maximum in 4.5 mM, and disappeared above 6.0 mM. These in B are observed outstandingly at scan rate=20 mV/sec (Fig. 1(c)). That is, at scan rate=20 mV/sec these are appeared in 4.5 mM SDS and disappeared above 6.0 mM. The separations between that in the region A and this B potentials are 20–40 mV. Judging from this, it seems that the electrode response is related to roughly two-electrons reaction via Eq. (1).

In the absence of SDS (Fig. 1(a) and Table 1), the oxidation of Ru(bpy)₃²⁺ to Ru(bpy)₃³⁺ takes place at *E*_{pa} of 1028 mV vs. SCE and reduction of Ru(bpy)₃³⁺ occurs at 968 mV upon scan reversal. The formal potential *E*_{1/2} taken as the average of *E*_{pa} and *E*_{pc} is 998 mV. From values of the separation between the anodic and the cathodic peak potentials (Δ*E*_p), and the anodic (*i*_{pa})/the cathodic peak current (*i*_{pc}), it can be considered that the redox couple is electrochemically reversible.

In the presence of SDS, *E*_{pa} of Ru(bpy)₃²⁺ shifts to positive direction compared to the SDS free case. Δ*E*_p shows a special phenomenon as [SDS] increases. It decreases up to 3.5 mM SDS and increases above the concentration.

In order to see a CMC,^[7-9] Δ*E*_p vs. -log[SDS] for the redox couples is plotted in Fig. 2. The concentration at the intersection of two lines in Fig. 2 is 3.67 mM, and this concentration is determined as the CMC, which is very near a CMC measured by surface tensiometry (3.38 mM SDS).

As mentioned above, the CMC for SDS solution of Ru(bpy)₃²⁺ exists in the vicinity of a minimal value of *E*_p. As [SDS] increases up to the CMC, the width of the double layer (i.e., distance to the glassy carbon electrode surface) is narrowed by arranging dodecyl sulfate anionic monomers ((DS)_n) around the electrode, which speeds up the electron transfer.^[7-9] As [SDS] increases above the CMC (3.67 mM SDS), micelles are formed gradually. The increase in the number of micelles makes the electron transfer slower (i.e. a increase on Δ*E*_p).^[7-9]

*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 3.5–5.0 mM SDS range (see Table 1). This is due to the decrease of the electrode surface screening, because monomers around the electrode become dynamic to form micelles.^[7,8] When [SDS] is reached at 6.0 mM, *i*_{pa}

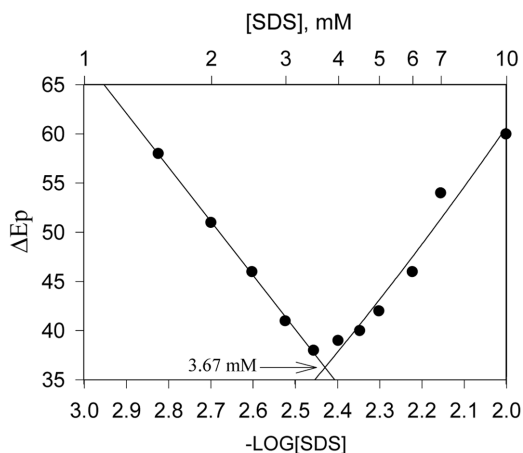


Fig. 2. ΔE_p vs. $-\log[\text{SDS}]$ plot for 1.0 mM $\text{Ru}(\text{bpy})_3^{2+}$ in 300 mM H_2SO_4 .

decreases due to the decrease in the number of $\text{Ru}(\text{bpy})_3^{2+}$ species per micelles.^[7,8]

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

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

The current will be in amperes when A is in cm^2 , D⁰ is in cm^2/s , ν is in volts/s, and C^0 is the bulk concentration in moles/ cm^3 . On the basis of eqn. (1), a apparent diffusion coefficient is evaluated by the slope of i_{pa} vs. $\nu^{1/2}$ (1.0 mM in 0 mM SDS, 2.5 mM SDS, and 5.0 mM SDS: $1.42 \times 10^{-5} \text{ cm}^2/\text{s}$, $1.77 \times 10^{-6} \text{ cm}^2/\text{s}$, and $3.18 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively). The results of the apparent diffusion coefficient reflect the change in i_{pa} depending on variation in [SDS] (Table 1 and Fig. 3). In absence of SDS the plot of i_{pa} vs. $\nu^{1/2}$ is both relatively passes through origin and linear. ΔE_p is 60 mV. Thus, it can be concluded is a diffusion controlled and a reversible reaction.

Effect of supporting electrolyte on the redox reaction of $\text{Ru}(\text{bpy})_2^{2+}$: In the absence of SDS, data for the redox reaction of 1.0 mM $\text{Ru}(\text{bpy})_2^{2+}$ in 100 mM H_2SO_4 solution are shown by Ko^[8]. The formal potential of $\text{Ru}(\text{bpy})_2^{2+}$ in 100 mM H_2SO_4 is 1015 mV, whereas in 300 mM H_2SO_4 is 998 mV. Thus this shows that in the absence of SDS the more increased the concentration of electrolyte is, the more unstable $\text{Ru}(\text{bpy})_2^{2+}$ is. Comparing Table 1 with Ko's data^[8] in the presence of SDS,

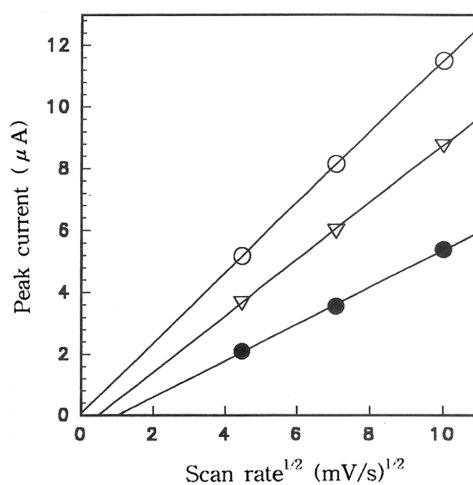


Fig. 3. Scan rate dependence of the anodic peak current for 1.0 mM $\text{Ru}(\text{bpy})_3^{2+}$ in 300 mM H_2SO_4 with and without SDS. (○) [SDS]=0 mM; (●) [SDS]=2.5 mM; (△) [SDS]=5.0 mM.

when the concentration of electrolyte is increased, the increase of i_{pa} and decrease of ΔE_p are observed for $\text{Ru}(\text{bpy})_3^{2+}$. But at near CMC or above near CMC, the increase on the concentration of electrolyte causes the width of double layer to increase (*i.e.* a increase on ΔE_p) due to increase of hydrophobic environment on $\text{Ru}(\text{bpy})_3^{2+}$. Increase of ΔE_p means increasing the distance to the electrode surface. As the concentration of supporting electrolyte increases to 300 mM H_2SO_4 instead of 100 mM, CMC of SDS for 1mM $\text{Ru}(\text{bpy})_3^{2+}$ increases from 3.04 mM to 3.67 mM SDS. It should be concluded that micelle formation is more difficult as the concentration of supporting electrolyte increases by sulfuric acid.

Interaction between Ru complex ion and SDS :

The Nernst equation for the reversible $1e^-$ redox reactions of the free and associated species can be written as eq. (2) given below.^[7]

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

By substituting $E_{1/2}$ in Table 1 to eq. (2), the ratios ($K_{2+/3+}$) of equilibrium constants for the association of +2 and +3 ions of Ru complex to DS^- can be obtained. In the presence of SDS (Table 1), since $K_{2+/3+}$ is larger than 1, a reduced form $\text{Ru}(\text{bpy})^{+2}$ is more easily associated to DS^- than an oxidized form $\text{Ru}(\text{bpy})^{3+}$. Thus,

in the presence of SDS, it should be concluded that Ru(bpy)₃^{3+/2+} with SDS is more affected by hydrophobic interaction than electrostatic interaction.

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