Measurement of Critical Micelle Concentration (CMC) by Cyclic Voltammetry: CMCs for Sodium Dodecyl Sulfate Solution with Compounds Having Pyridine

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Electrochemical behavior of CMC in sodium dodecyl sulfate (SDS)-tris(2,2'-bipyridyl)ruthenium(II) ($Ru(bpy)_3^{2+}$) solution is reported using a cyclic voltammetry (CV). Discussion of SDS-$Ru(bpy)_3^{2+}$ solution is restricted to the regions slightly below and above the CMC.

Kaifer and Bard suggested that detection of the CMC of SDS for methyl viologen is possible through the changes observed in the shape of cyclic voltammograms.[1] This work was originated from doing experiment for enhancement of electrogenerated chemiluminescence intensity in the $Ru(bpy)_3^{2+}$ solution with surfactants. Until recently, most applications of aqueous micelles were restricted to regions extending slightly below and above the CMC.[2-7] Because, the interesting effects are being discovered at surfactant concentrations much below and above the critical point. Although various techniques of electrical conductance, turbidity, osmotic pressure, magnetic resonance, solubilization,[8] light scattering intensity,[9,10] surface tension,[8,11,12] and fluorescence quenching[13] to measure the CMC have been utilized, a determination of the CMC by the CV has been received little attention.[1,14] And so, in this work the method of determining the CMC for compounds having pyridine is explained, and a variation of the microenvironments of SDS-$Ru(bpy)_3^{2+}$ interactions in the vicinity of the CMC is discussed by using the model proposed by Brajter-Toth *et al.*[15,16]

Experimental Section

SDS, $Ru(bpy)_3^{2+}$, and H_2SO_4 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 cm^2 was used as a working electrode. It was polished with 0.05 μm γ-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 ± 0.2 °C.

Results and Discussion

Cyclic voltammograms of 1.0 mM $Ru(bpy)_3^{2+}$ in 100 mM H_2SO_4 solution with and without SDS are shown in Figure 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.

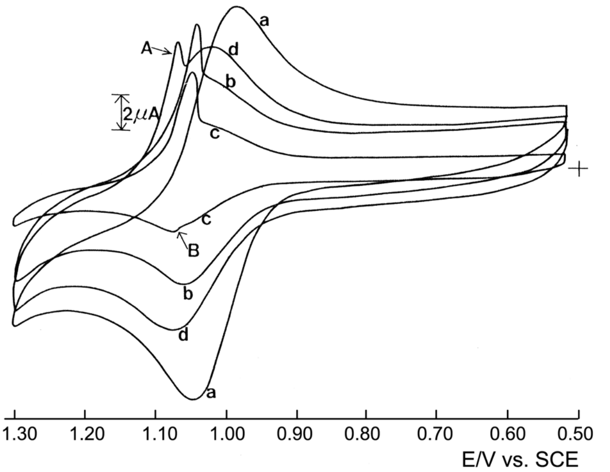

Figure 1. Cyclic voltammograms of 1.0 mM $Ru(bpy)_3^{+2}$ in 100 mM H_2SO_4 with and without SDS at 25.0 ± 0.2 °C. Scan rate = 100 mV/s except for [SDS] = 4.5 mM (20 mV/s). (a) [SDS] = 0 mM; (b) [SDS] = 3.5 mM; (c) [SDS] = 4.5 mM; (d) [SDS] = 7.0 mM.

Table 1. Electrochemical Data for 1.0 mM $Ru(bpy)_3^{+2}$ in 100 mM H_2SO_4 with and without SDS at 25.0 ± 0.2 °C. Scan rate = 100 mV/s

[SDS] (mM)	E_{pa} (mV)	ΔE_p (mV)	$E_{1/2}$ (mV)	i_{pa} (μA)	i_{pa}/i_{pc}
0.0	1047	63	1015	10.96	1.17
1.5	1054	68	1020	5.62	1.35
2.0	1049	54	1022	3.98	1.49
2.5	1043	38	1025	2.80	1.35
3.0	1053	28	1039	3.58	1.19
3.5	1055	30	1040	4.06	1.13
4.0	1060	33	1044	4.68	1.04
4.5	1064	36	1045	5.70	1.00
5.0	1066	39	1047	6.30	0.93
6.0	1075	46	1052	6.18	1.00
7.0	1077	54	1050	6.00	1.09
10.0	1084	72	1048	4.98	1.21

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

$$\mathrm{Ru(bpy)_3}^{2+} + 2\ \mathrm{DS}^- \text{ (dodecyl sulfate anion)} \longrightarrow \mathrm{Ru(bpy)_3(DS)_2} \qquad (1)^{17}$$

At scan rate = 100 mV/sec, those peaks in the region A are appeared approximately in 2.5 mM SDS, reached the maximum in 5.0 mM, and disappeared above 9.0 mM. These in B are perceived as only trace by the eye through moving of the recorder's pen during the experiment. But these are observed outstandingly at scan rate = 20 mV/sec (Figure 1(c)). That is, at scan rate = 20 mV/sec these are appeared about in 3.5 mM SDS and disappeared above 6.0 mM. The separations between that in the region A and this B potentials are 25-35 mV. Judging from this, it seems that the electrode response is related to two-electrons reaction via Eq. (1).

In the absence of SDS (Figure 1(a) and Table 1), the oxidation of $\mathrm{Ru(bpy)_3}^{2+}$ to $\mathrm{Ru(bpy)_3}^{3+}$ takes place at E_{pa} of 1047 mV *vs*. SCE and rereduction of $\mathrm{Ru(bpy)_3}^{3+}$ occurs at 984 mV upon scan reversal. The formal potential $E_{1/2}$ taken as the average of E_{pa} and E_{pc} is 1015 mV. From values of the separation between the anodic and the cathodic peak potentials (ΔE_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 $\mathrm{Ru(bpy)_3}^{2+}$ shifts to positive direction compared to the SDS free case except 2.5 mM SDS. But at 2.5 mM SDS, it seems that shifting of E_{pa} to negative direction is due to dynamic environment by forming monomers to micelles. Also, ΔE_p shows a special phenomenon as [SDS] increases. It decreases up to 3.0 mM SDS and increases above the concentration.

In order to see the relation between ΔE_p and a CMC, $\Delta \mathrm{E_p}$ *vs*. –log[SDS] for the redox couples were plotted in Figure 2. The concentration at the intersection of two lines in Figure 2 is 3.04 mM, and this concentration can be determined as the CMC, which (relative error: below 1.5%) is very near a CMC measured by surface tensiometry (3.00 mM SDS, Figure 3).

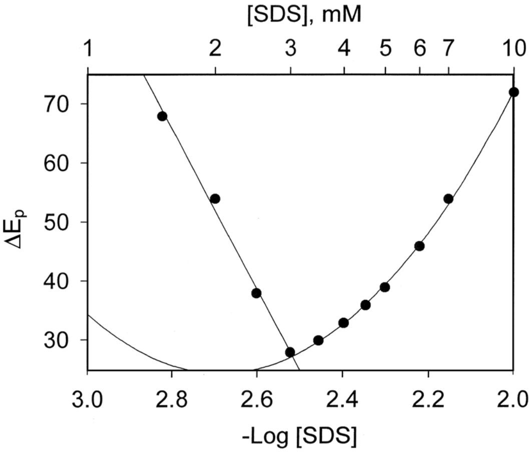

Figure 2. E_p *vs*. -log[SDS] plot for 1.0 mM $\mathrm{Ru(bpy)_3}^{2+}$ in 100 mM $\mathrm{H_2SO_4}$.

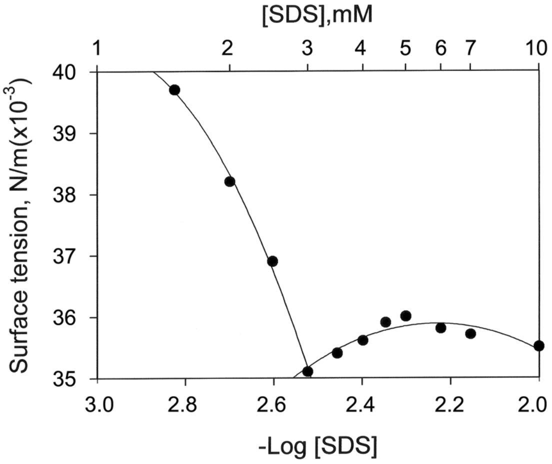

Figure 3. Surface tension *vs*. -log[SDS] plot for 1.0 mM $\mathrm{Ru(bpy)_3}^{2+}$ in 100 mM $\mathrm{H_2SO_4}$.

As mentioned above, the CMC for SDS solution of $\mathrm{Ru(bpy)_3}^{2+}$ exits in the vicinity of a minimal value of ΔE_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 ($(\mathrm{DS}^-)_n$) around the electrode, which speeds up the electron transfer.[13,14] As [SDS] increases above the CMC, micelles are formed gradually.[18] 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).[15,16]

i_{pa} decreases up to 2.5 mM SDS because of the increase of the electrode surface screening with the increasing in the number of monomers, but increases at 3.0-5.0 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 [SDS] is reached at 6 mM, i_{pa} decreases due to the decrease in the number of $\mathrm{Ru(bpy)_3}^{2+}$ species per

Table 2. CMCs (by CV) of SDS-each tris(2,2'-bipyridyl)ruthenium (II), tris(2,2'-bipyridyl)iron(II), tris(1,10-phenanthroline)iron(II), bis(2,2'-bipyridyl)copper(II), methylviologen dichloride hydrate, and bis(di-2-bipyridylamine)copper(II)

Complex Supporting electrolyte	CMC (mM SDS)
Tris(2,2'-bipyridyl)ruthenium(II) 100 mM $\mathrm{H_2SO_4}$	3.04
Tris(2,2'-bipyridyl)iron(II) 50 mM $\mathrm{H_2SO_4}$	3.38[14]
Tris(1,10-phenanthroline)iron(II) 100 mM $\mathrm{H_2SO_4}$	2.47[14]
Bis(2,2'-bipyridyl)copper(II) 100 mM NaCl	2.88[19]
Methylviologen dichloride hydrate 100 mM NaCl	2.55[20]
Bis(di-2-bipyridylamine)copper(II) 100 mM NaCl	4.00[21]

micelles.[18]

The CMCs of compounds having pyridine-SDS are listed in Table 2. In addition, in the presence of the other anionic surfactant sodium dodecyl benzene sulfite (SBS), CMC of 1.0 mM tris(1,10-phenanthroline)iron(II) was measured by CV (4.00 mM SBS).[22] But the addition of both cationic (hexadecyltrimethylammonium bromide) and nonionic (triton X-100; igepal DM-970) surfactants instead of SDS and SBS causes no significant shift in the cyclic voltammetric peak potentials for compounds having pyridine mentioned in Table 2. This invariance of peak potential indicates the absence of interactions between the compound having pyridine and surfactant in each of cationic and nonionic micellar systems.

In the presence of anionic surfactant, therefore, it should be given as a conclusion that CMC of compounds having pyridine can be measured by the intersection of two lines on the ΔE_p *vs*. -log[anionic surfactant].

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