

## Voltammetric Study of Surfactant-Modified Carbon Electrode: $\text{Ru}(\text{ph})_3^{2+}$ in Sodium Dodecyl Sulfate Solution

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**Abstract** : Cyclic voltammetric method is used to survey microscopic environments which take place at the surfactant-modified carbon electrode when the hydrophobic and hydrophilic environments of  $\text{Ru}(\text{ph})_3^{2+}$  (tris 1,10-phenanthroline ruthenium(II) chloride) is created by the addition of anionic surfactant, sodium dodecyl sulfate (SDS). Critical micelle concentration (CMC) of SDS in  $\text{Ru}(\text{ph})_3^{2+}$  measured by cyclic voltammetry (CV) is in agreement with that by surface tensiometry. Influence of the concentration of supporting electrolyte at surfactant-modified carbon electrode is investigated.

**Keywords** : Tris 1,10-phenanthroline ruthenium(II) chloride, Sodium dodecyl sulfate, Surfactant-modified carbon electrode, Critical micelle concentration, Cyclic voltammetry, Hydrophobic and hydrophilic environments, Surface tensiometry.

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### 1. Introduction

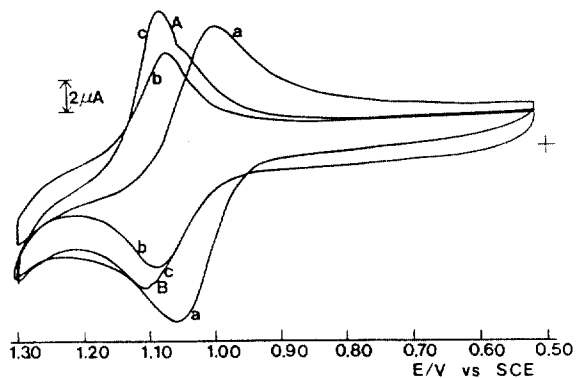
CV in the system of micelle has been used to determine a formal potential[1]. Reagents in micelle are used as mediators and the standard solutions of the titration in the process of biological electron transfer[2]. Armstrong and Hery examined usefulness of adding surfactant in chromatography and demonstrated that the surfactant which interacts with the solute in

mobile phase due to the hydrophobic properties provides hydrophobic site[3]. The major benefit of using micelle in mobile phase is to speed up the elution of compounds without changing the composition in stationary phase[4]. Since hydrophilic and hydrophobic compounds dissolved is localized due to microscopic heterogeneity, the local concentration and reaction kinetics increase[5,6]. Interaction

between the properties of the solvation of surfactant and the hydrophobicity is an important factor significantly influencing structural properties of polymer[7]. The adsorbed surfactant changes the double layer structure, the velocity of electrons transfer, and the formal potential of electroactive species[8,9]. As mentioned above, surfactant is recently studied in various fields. In this paper, we survey microscopic environments which take place in the electrode, i.e., surfactant-modified carbon electrode, response when the hydrophobic and hydrophilic environments of metal complexes is created by the addition of anionic surfactant SDS. Furthermore, this paper compares CMC of SDS in  $\text{Ru}(\text{ph})_3^{2+}$  as the concentration of supporting electrolyte is changed, which is measured by CV with CMC by surface tensiometry.

## 2. Experimental

$\text{Ru}(\text{ph})_3^{2+}$ , SDS and  $\text{H}_2\text{SO}_4$  were obtained from Aldrich and used without further purification, respectively. Doubly distilled water was used to prepare all solutions. Surface tension measurement was carried out using CSC-Du Noüy(CAT. No. 70535) tensiometer. CV was performed with potentiostat constructed in our laboratory and described elsewhere[10,11]. Glassy carbon disk(Bioanalytical Systems, West Lafayette, in USA) with a geometric area of  $0.0788 \text{ cm}^2$  was used as a working electrode. It was polished with  $0.05 \mu\text{m}$   $\gamma$  alumina/water slurry on a felt surface and then subjected to ultrasonic cleaning about 2 min. A saturated carmel electrode(SCE), prepared according to Sawyer[10], was used in all experiments as a reference electrode. Platinum mesh was used as auxiliary electrode. All experiments were performed under a purified nitrogen atmosphere, and were carried out at  $25 \pm 0.2 \text{ }^\circ\text{C}$ .



*Fig. 1.* Cyclic voltammogram of 1.0 mM  $\text{Ru}(\text{ph})_3^{2+}$  in 100 mM  $\text{H}_2\text{SO}_4$  with and without SDS at  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ . Scan rate=100 mV/s. (a)  $[\text{SDS}]=0.0 \text{ mM}$ ; (b)  $[\text{SDS}]=3.5 \text{ mM}$ ; (c)  $[\text{SDS}]=5.0 \text{ mM}$ .

## 3. Results and discussion

Cyclic voltammograms of 1.0 mM  $\text{Ru}(\text{ph})_3^{2+}$  in 100 mM  $\text{H}_2\text{SO}_4$  aqueous solution without and with SDS are shown in *Fig. 1*. Voltammetric results are given in *Table I*, in which data for the wave of the redox are shown with increasing concentration of SDS.

*Table I.* Electrochemical Data for 1.0 mM  $\text{Ru}(\text{ph})_3^{2+}$  in 100 mM  $\text{H}_2\text{SO}_4$  with and without SDS at  $25.0 \pm 0.2 \text{ }^\circ\text{C}$ . Scan rate=100 mV/s.

[SDS]/ mM	$E_{pa}/$ mV	$\Delta E_p/$ mV	$E_{1/2}/$ V	$i_{pa}/$ $\mu\text{A}$	$i_{pa}/i_{pc}$
0.0	1058	62	1.027	9.32	1.22
1.5	1066	67	1.033	5.80	1.95
2.0	1075	51	1.050	5.10	2.52
2.5	1078	36	1.060	2.85	2.59
3.0	1078	27	1.065	2.02	1.96
3.5	1087	16	1.079	5.40	1.10
4.0	1084	39	1.065	6.56	1.41
4.5	1099	49	1.075	6.58	1.30
5.0	1105	54	1.078	6.62	1.26

6.0	1107	60	1.077	5.42	1.48
7.0	1107	61	1.077	5.34	1.56
10.0	1100	66	1.067	5.24	1.62

In the absence of SDS, the reduction of Ru(ph)<sub>3</sub><sup>+3</sup> to Ru(ph)<sub>3</sub><sup>+2</sup> takes place at a cathodic peak potential, E<sub>pc</sub>, of 996 mV vs SCE and reoxidation of Ru(ph)<sub>3</sub><sup>+2</sup> occurs upon scan reversal, at 1058 mV. The formal potential, E<sub>1/2</sub>, taken as the average of E<sub>pa</sub> and E<sub>pc</sub>, is 1.027 V. Judging from the values of ΔE<sub>p</sub>, i<sub>pa</sub>/i<sub>pc</sub>(Table I, Fig. 1(a)) and the plot of anodic peak current vs scan rate<sup>1/2</sup>(ν<sup>1/2</sup>)(Fig. 3), the redox couples are reversible, 1e<sup>-</sup> process.

E<sub>pa</sub> of Ru(ph)<sub>3</sub><sup>+3/+2</sup> in the presence of SDS shifts in positive direction compared to that in the absence of SDS. Also, E<sub>1/2</sub> shifts in positive direction. On the other hand, ΔE<sub>p</sub>

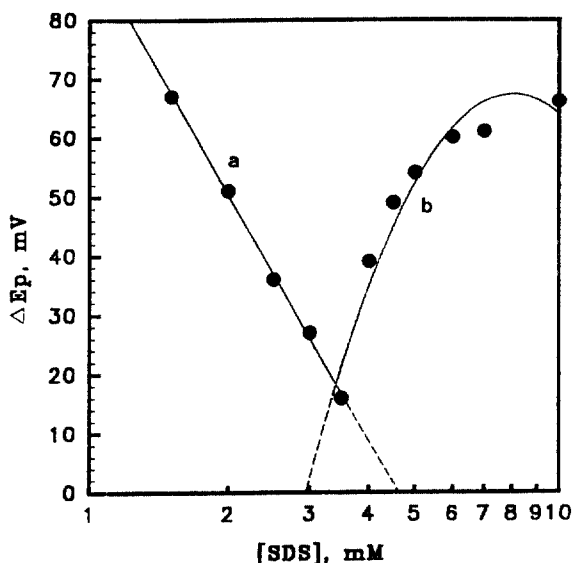


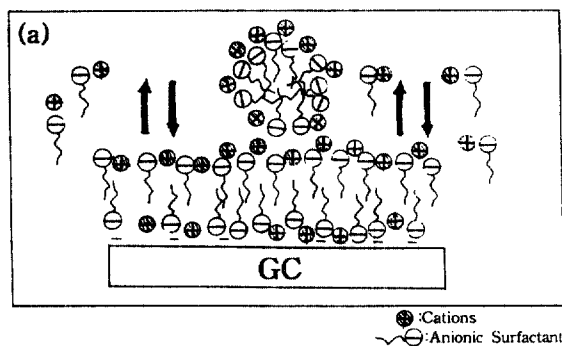
Fig. 2. ΔE<sub>p</sub> vs [SDS] plot for 1.0 mM Ru(ph)<sub>3</sub><sup>+2</sup> in 100 mM H<sub>2</sub>SO<sub>4</sub>.

shows a special phenomenon as the concentration of SDS increases gradually. That is, in the presence of SDS ΔE<sub>p</sub> decreases to 3.5

mM SDS and thereafter increases gradually to 10.0 mM. With this in mind, in order to obtain CMC we plotted ΔE<sub>p</sub> vs the concentration of SDS, for the redox couples in Fig. 2. We can draw two lines(a and b) in the figure and estimated the intersection of two lines as CMC, 3.41 mM SDS. CMC(3.41 mM SDS) found by CV is in agreement with CMC(3.46 mM) measured by the surface tensiometry in Fig. 4. In this paper, we determined CMC as ΔE<sub>p</sub> vs [SDS] plot by CV(Table I, Fig. 2).

As mentioned above, as the concentration of SDS increases(in Fig. 2) the slope of ΔE<sub>p</sub>-[SDS] plot linearly decrease up to CMC(a), but it curvilinearly increases above that(b). We presume that the addition of surfactant changes the structure of the double layer. This may be because the monomers at the concentration up to CMC form the double layer by arranging linearly around the electrode, but the micelles at above that form globally.

SDS provides hydrophobic and hydrophilic environments for the response of Ru(ph)<sub>3</sub><sup>+3/+2</sup>. Ru(ph)<sub>3</sub><sup>+3/+2</sup> interacts not only with ionic head groups of (R)<sub>12</sub>OSO<sub>3</sub>Na, SDS, owing to electrostatic coulomb's force but also with the



Scheme 1. Bilayer model of surfactant assembly at glassy carbon electrode[8].

hydrocarbon chain of that due to hydrophobic properties. The slope of the ΔE<sub>p</sub>-[SDS] plot up

to CMC linearly decreases with increasing concentration of SDS (Fig. 2). This may be because as shown in Scheme I [8], as the concentration of SDS increases up to CMC, the distance of the double layer (i.e., distance to the surface) is more narrowed by arranging monomers,  $(DS^-)_n$ , around the electrode which speeds up the electrons transfer [8,9]. But it may also be that screening of the electrode surface by arranging monomers can reduce a response for  $Ru(ph)_3^{+2}$  species. The response can reduce  $i_{pa}$  as concentration of SDS increases up to CMC (Table I). As the more the concentration of SDS increases above CMC, the distance of the double layer by the formation of micelle is more broadened, so it shows slower electron transfer. Also, since above CMC micelle is formed gradually, monomers around the electrode become dynamic to form micelle. Thus,  $i_{pa}$  of  $Ru(ph)_3^{+2}$  species is more increased (Table I). After that, due to screening of the electrode surface by arranging micelle,  $i_{pa}$  is decreased and  $\Delta E_p$  increased.

At 25 °C the peak current of reversible systems is [12,13]

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

The current will be in amperes when A is in  $cm^2$ ,  $D_0$  is in  $cm^2/s$ ,  $\nu$  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  $Ru(ph)_3^{2+}$  in 0.0 M SDS, 3.0 mM SDS, and 5.0 mM SDS:  $1.07 \times 10^{-5}$   $cm^2/s$ ,  $5.95 \times 10^{-8}$ , and  $4.05 \times 10^{-6}$ , respectively). The results of the apparent diffusion coefficient reflect the change in  $i_{pa}$  depending on the variation in [SDS] (Table I and Fig. 3). In absence of SDS the plot of  $i_{pa}$  vs  $\nu^{1/2}$  is both linear and relatively passes through origin.  $\Delta E_p$  is 62 mV. Thus, we can say  $Ru(ph)_3^{+3/+2}$  is a reversible and diffusion

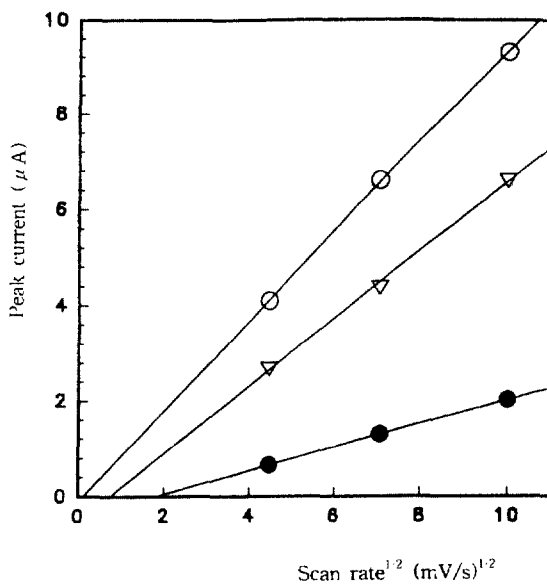
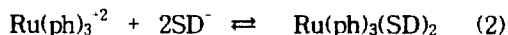


Fig. 3 Scan rate dependence of the anodic peak current for 1.0 mM  $Ru(ph)_3^{+2}$  in 100 mM  $H_2SO_4$  with and without SDS. (○) [SDS]=0.0 mM; (●) [SDS]=3.0 mM; (▷) [SDS]=5.0 mM.

controlled.

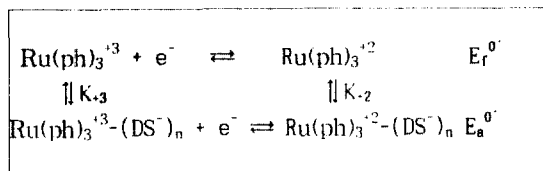
As shown Fig. 1(c), the waves of adsorption (A and B) which is relatively 30–40 mV (i.e., two electrons process) seem to be mechanism by eqn. (2).



These waves appear approximately in 3.5 mM SDS and disappear in above 6.0 mM.

$E_{1/2}$  can be used to measure the ratios of associating constant which shows +3 or +2 ions associated to dodecyl sulfate anion,  $DS^-$ . In a system in which both the oxidized form  $Ru(ph)_3^{+3}$  and reduced  $Ru(ph)_3^{+2}$  associate with  $DS^-$  in solution, Scheme II can be applied [14]: Here,  $Ru(ph)_3^{+3/+2}-(DS^-)_n$  denotes a  $Ru(ph)_3^{+3/+2}$  species associated to  $DS^-$ .  $E_t^{0'}$  and  $E_a^{0'}$  are the formal potentials of the +3/+2 couple, in the free

Scheme II



and associated forms, respectively. K<sub>.3</sub> and K<sub>.2</sub> are the corresponding associating constants for the +3 and +2 ions to DS<sup>-</sup>, respectively. Considering the Nernst equations for the reversible redox reactions of the free and associated species and the corresponding equilibrium constants for associating of each oxidation state to DS<sup>-</sup>, we can obtain, for a 1e<sup>-</sup> redox process

$$E_a^{0'} - E_r^{0'} = 0.059 \log(K_{.2} / K_{.3}) \quad (3)$$

By substituting formal potentials in Table I for eqn.(3), we can obtain the ratios of equilibrium constants for associating of the +2 and +3 ions to DS<sup>-</sup> which are listed in Table II. As

Table II. Ratios of the Association Constants for the Ru(ph)<sub>3</sub><sup>2+</sup> and Ru(ph)<sub>3</sub><sup>3+</sup> Species to DS<sup>-</sup> in 100 mM H<sub>2</sub>SO<sub>4</sub>.

[SDS] / mM	K <sub>.2</sub> /K <sub>.3</sub>
1.5	1.26
2.0	2.45
2.5	3.63
3.0	4.41
3.5	7.61
4.0	4.41
4.5	6.51
5.0	7.32
6.0	7.04
7.0	7.04
10.0	4.76

shown in Table II, E<sub>1,2</sub> of Ru(ph)<sub>3</sub><sup>+3/+2</sup> shifts in positive direction in the presence of DS<sup>-</sup> rather than in the absence of it. The results also shows that reduced form Ru(ph)<sub>3</sub><sup>+2</sup> is more easily associated to DS<sup>-</sup> than oxidized Ru(bpy)<sub>2</sub><sup>+3</sup> because K<sub>.2</sub>/K<sub>.3</sub> is larger than 1. In the presence of DS<sup>-</sup> i<sub>pa</sub>/i<sub>pc</sub> is larger than 1. The results above mentioned indicate that Ru(ph)<sub>3</sub><sup>+3/+2</sup> in the presence of SDS is more affected by hydrophobic interactions than by electrostatic.

**Tensiometry** Values of surface tension for 1.0 mM Ru(ph)<sub>3</sub><sup>+2</sup> in 100 mM H<sub>2</sub>SO<sub>4</sub> in the absence or presence of SDS are showed in Table III. The plot of surface tension vs [SDS] is showed in the Fig. 4. Value of surface tension decreases significantly when SDS is added rather than SDS does not exist. With the increase of [SDS], value of surface tension

Table III. Values of Surface Tension for 1.0 mM Ru(ph)<sub>3</sub><sup>2+</sup> in 100 mM H<sub>2</sub>SO<sub>4</sub> with and without SDS at 25.0 ± 0.2 °C.

[SDS] / mM	Surface tension/ N/m (× 10 <sup>-3</sup> )
0.0	66.0
1.5	40.8
2.0	39.1
2.5	38.1
3.0	35.7
3.5	35.8
4.0	35.8
4.5	35.6
5.0	35.6
6.0	35.4
7.0	35.5
10.0	35.2

decrease gradually. As shown in Fig. 4 we can

estimate the intersection of two lines(a and b) as CMC. 3.46 mM SDS(3.41 mM SDS by CV).

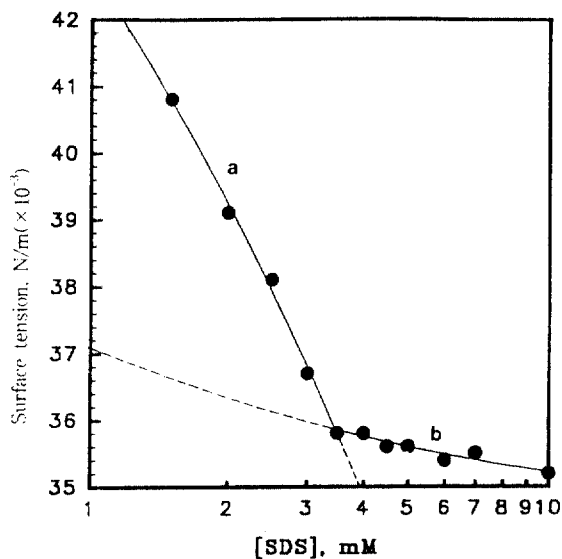


Fig. 4. Surface tension vs [SDS] plot for 1.0 mM  $\text{Ru}(\text{ph})_3^{3+2}$  in 100 mM  $\text{H}_2\text{SO}_4$ .

**Influence of the concentration of supporting electrolyte** In the absence of SDS the formal potential of  $\text{Ru}(\text{ph})_3^{3+2}$  in 100 mM  $\text{H}_2\text{SO}_4$  is 1.027 V, whereas in 300 mM  $\text{H}_2\text{SO}_4$  is 1.013 V. Thus, this shows that in the absence of SDS the more increased the concentration of electrolyte is, the more unstable  $\text{Ru}(\text{ph})_3^{3+2}$  is. As the concentration of supporting electrolyte is more increased, CMC of SDS in  $\text{Ru}(\text{ph})_3^{3+2}$  increases (In 100 mM  $\text{H}_2\text{SO}_4$ , CV: 3.41 mM SDS; surface tensiometry: 3.46. In 300 mM  $\text{H}_2\text{SO}_4$ , CV: 4.06 mM SDS; surface tensiometry: 4.20). This may be that in SDS solution of  $\text{Ru}(\text{ph})_3^{3+2}$  the more increased the concentration of electrolyte is, the more

increased charge repulsion between ionic head groups is, the more decreased both hydrophobic repulsion between hydrocarbon chain and water, and interaction of van der Waals's force between alkyl chains are.

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