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ELECTROLYTE EFFECTS ON THE ELECTROCHEMICAL ACTIVITY OF MICELLE-SOLUBILIZED SUBSTANCE

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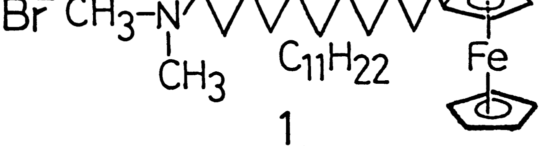
The cyclic voltammetry of a cationic surfactant with ferrocenyl moiety (Fc) in an anionic micellar solution leads to the conclusion that Fc incorporated in the micelle is electrochemically inactive in the absence of electrolytes and active in the presence of electrolytes.

Micellar solutions are often employed in solubilizing water-insoluble species and frequently used to accelerate (or retard) desired chemical reactions.[1-3] Recently, electrochemistry of a micelle-solubilized substance has been reported by many authors.[4-8] Ohsawa et al.[4] and Grätzel et al.[6] have revealed that the electrochemical behavior of some micelle-solubilized substances could be reasonably interpreted by assuming that electroactive species incorporated in micelles are electrochemically inactive. However, the evidence of this assumption has not been given by any authors. This letter is the first report to deal with the electrolyte effects on the electroactivity of a substance incorporated in a micelle and enhancement of the electrode reaction in the presence of electrolytes. The reactivity of functional groups in a micelle is of general importance because the obtained results can be widely applicable to colloidal and biological systems.

The preparation of (11-ferrocenyl)undecyltrimethylammonium bromide (**1**) was reported in our previous paper.[9]



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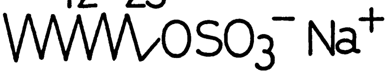

SDS

Electrochemical measurements were carried out at 25 °C, by using the test solutions containing 0.1 M (1 M = 1 mol dm^{-3}) sodium dodecylsulfate (SDS) and electrolyte. A glassy carbon disk electrode from BAS and a platinum wire electrode were fitted in the main compartment of a usual two-compartment electrolysis cell as the working and the counter electrodes, respectively, and in the auxiliary compartment was a NaCl-agar bridge which led to a saturated calomel electrode (SCE) because K^+ from SCE formed precipitate with SDS. SDS was purified by the usual method.$^{1)}$ The concentration of SDS was kept constant at 0.1 M. The concentration of **1** in a micellar solution was ajusted so that a micelle will not contain more than one molecule of **1** on average. The concentration of micelles, [c], was estimated by using the data of cmc$^{10)}$ and aggregation number (N)$^{11)}$ in the presence of electrolyte.

$$[c] = (0.1 - \mathrm{cmc})/N$$

The diffusion coefficients of the SDS micelles, D, were determined by the method described in the literature.$^{4)}$

The cyclic voltammogram of 0.45 mM **1** (1 mM = 1 mmol dm^{-3}) in 0.1 M SDS showed one oxidation step with a half-wave potential ($E_{1/2}$) of +0.17 V vs. SCE. This value is close to that of ferrocene in water, +0.16 V vs. SCE.$^{4a)}$ The value of $E_{1/2}$ depended little on the kind of electrolyte, the concentration of electrolytes, and a sweep rate. Figure 1 shows the plot of the oxidation peak current, i_{pa}, vs. the square root of the sweep rate, $v^{1/2}$. A linearity of the plot indicates that the electrode reaction of **1** is diffusion-controlled, which means that the electroactive species is the micelle-solubilized **1** in the bulk of the solution.

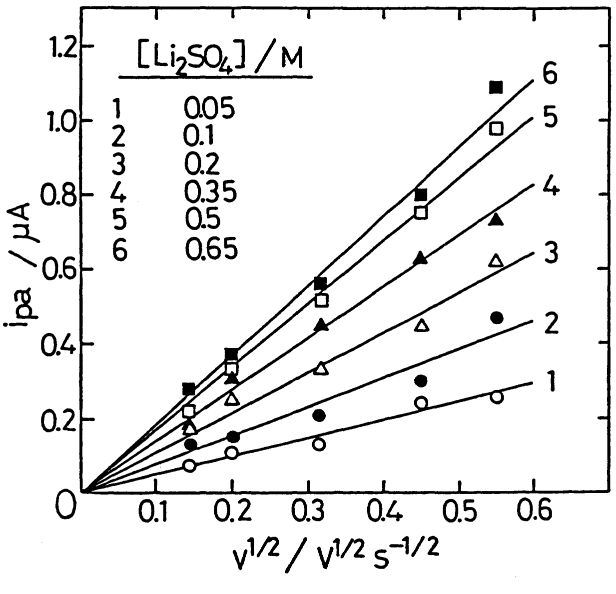

Fig. 1. The plot of the oxidation peak current, i_{pa}, of **1** vs. the square root of a sweep rate, $v^{1/2}$, at 25 °C for $[Li_2SO_4]$ = (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.35, (5) 0.5, and (6) 0.65 M.

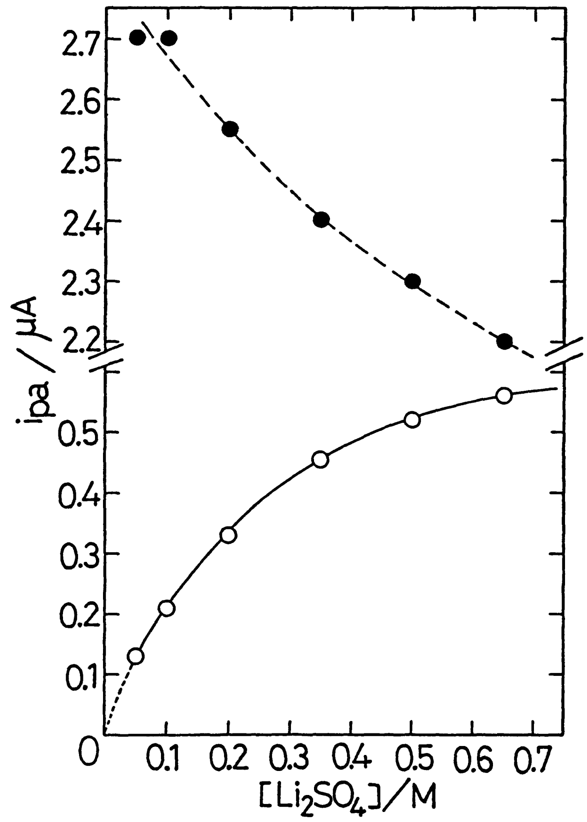

Fig. 2. The dependence of the peak current (i_{pa}) for the oxidation of 0.45 mM **1** on the concentration of Li_2SO_4, $[Li_2SO_4]$, at 25 °C. Solid line: experimental value. Dotted line: calculated value. Sweep rate: 100 mV s^{-1}. Working electrode area: 0.071 cm^2.

The solid line in Fig. 2 shows the plot of i_{pa} vs. the concentration of Li_2SO_4, $[Li_2SO_4]$. The value of i_{pa} increased with increasing concentration of Li_2SO_4. The value of i_{pa} extrapolated to the intercept was close to 0 μA, indicating that **1** solubilized in the SDS micelle may not be elctroactive in the absence of Li_2SO_4. The dotted line in Fig. 2 shows i_{pa} calculated by assuming that all of **1** in the micelle is oxidizable at an electrode, and by using the value of D. In general, the addition of electrolytes increases the size of ionic micelles, i.e., reduces the value of D;[12)] hence the calculated value of i_{pa} decreases with increasing concentration of Li_2SO_4. The ratio of the experimental i_{pa} to the calculated one increased from 4.8% ($[Li_2SO_4]$ = 0.05 M) to 25% ($[Li_2SO_4]$ = 0.65 M).

To see if the enhancement of i_{pa} depends on the kind of electrolytes, the effect of some lithium or sodium salts on i_{pa} was investigated. Figure 3 shows the plot of i_{pa} vs. the concentration of various salts, [added salt]. As in the case of Li_2SO_4, all the salts used enhanced the value of i_{pa} and the extrapolated intercepts of i_{pa}'s were nearly equal to 0 μA independently of the kind of added salts. These findings show that **1** in the SDS micelle is electroactive only in the presence of electrolytes.

The electrode reaction of **1** in the hydrophobic site of micelles[5c)] has to satisfy the electroneutrality condition. In other words, an anion has to reside in the vicinity of Fc moiety in order to neutralize the Fc^+ moiety generated. The addition of electrolytes may increase the fraction of anions residing in the vicinity of Fc moiety, and hence more Fc moiety will be oxidizable. Less hydrophilic anion like BF_4^- may penetrate into the hydrophobic site more easily than hydrophilic anion like SO_4^{2-}, hence more Fc moiety will be also oxidizable.

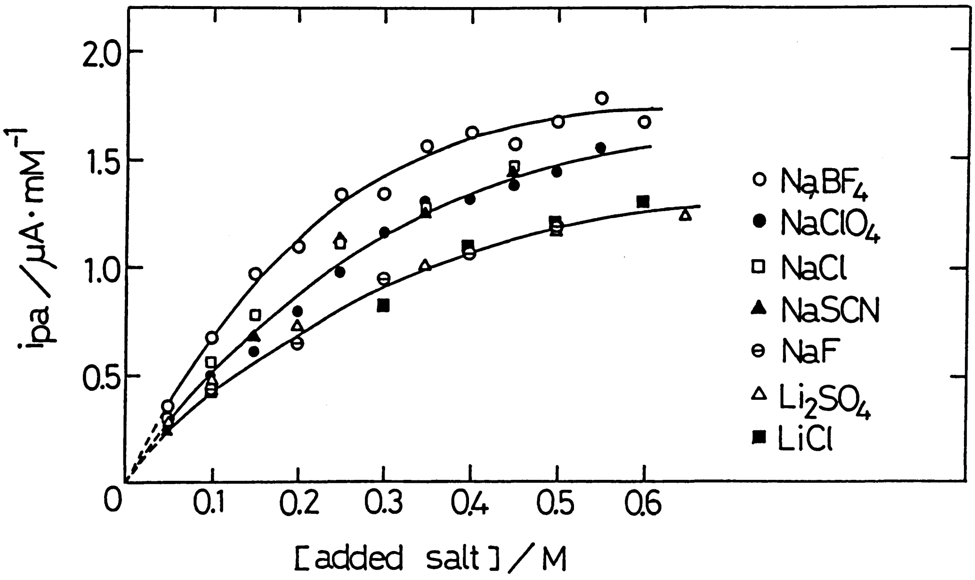

Fig. 3. Salt effects on the oxidation peak current per 1 mM of **1** solubilized in 0.1 M SDS, i_{pa}, at 25 °C. Sweep rate: 100 mV s^{-1}. Working electrode area: 0.071 cm^2. (○) $NaBF_4$; (●) $NaClO_4$; (□) NaCl; (▲) NaSCN; (⊖) NaF; (△) Li_2SO_4; (■) LiCl.

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