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Effect of α-Cyclodextrin on the Electrochemistry of (Ferrocenylmethyl)-dodecyldimethylammonium Bromide at a Glassy Carbon Electrode

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Synopsis. The influence of α-cyclodextrin (α-CD) on the electrochemistry of (ferrocenylmethyl)dodecyldimethylammonium bromide (**I**) was studied with a glassy carbon (GC) electrode. α-CD increases the apparent diffusion coefficient of **I**. This unusual effect is explained in terms of disruptive effect of α-CD on **I**'s aggregates. α-CD also influences, to some extent, **I**'s adsorption onto GC electrode when adsorbed from its micromolar aqueous solution.

The electrochemistry of redox active surfactants in aqueous solution has received some attention in the last few years.[1–5] Furthermore, their spontaneous aggregation on the surface of solid electrodes has recently been reported.[6–8]

Cyclodextrins (CDs) are torus shaped cyclic oligosaccharides having a hydrophobic cavity and a hydrophilic exterior. They can function as hosts for hydrophobic moieties of molecules dissolved in aqueous medium.[9] When CDs are added to a surfactant solution, they cause a decrease in the hydrophobicity of the solution. This is due to the inclusion of the hydrophobic alkyl chain of surfactant into the hydrophobic CD cavity.[10,11] Also, the solubility of a few electroreduced surfactants is known to increase by the presence of CD.[12,13]

In this report we show how α-CD influences the electrochemistry of redox active surfactants in aqueous solution. Although the effect of CDs on the behavior of redox inactive chromophore molecules in solution can be evaluated by, for example, UV-visible absorption and induced circular dichroism spectroscopies, that of redox active species can be examined by electrochemical methods, too. It appears not insignificant to show such an example. We chose here a functional surfactant with ferrocene (Fc) moiety, i.e. $FcCH_2N^+(CH_3)_2C_{12}H_{25}Br^-$ (**I**) and studied its properties and behavior in terms of electrochemistry. This molecule aggregates because it contains a long alkyl chain,[6] but is different from often studied viologen surfactants,[7,8] with which attractive interactions between viologen moieties may also cause aggregation.[14] The choice of α-CD, which is composed of six glucose units and has among CDs the smallest hydrophobic cavity with diameters of 0.47—0.52 nm,[9] is to lessen the probability of inclusion of the ferrocene moiety into the cyclodextrin cavity.

Experimental

Materials. **I** was synthesized by the reaction of [(dimethylamino)methyl]ferrocene (Aldrich) with dodecyl bromide (Tokyo Kasei) according to the literature.[1] The product was identified by elementary analysis. Found: C, 60.22; H, 8.70; N, 2.77%. Calcd for $C_{25}H_{42}NFeBr$: C, 60.08; H, 8.62; N, 2.85%. Li_2SO_4 was an extra pure reagent and was used as received. The water used for preparation of electrolyte solutions and sonication of electrodes was purified by a water purifier RO-10C (Tokyo Rikakikai Co., Ltd.).

Equipment and Procedures. Cyclic voltammetry and potential step chronoamperometry were performed using a potentiostat/galvanostat HA-501, an arbitrary function generator HB-105 (both Hokuto Denko), and a 3036 XY recorder (Yokogawa) connected with a water-jacketed three-compartment electrochemical cell at 25 °C. A spiral made of platinum wire served as the counter electrode and a saturated calomel electrode (SCE) as a reference one. As a working electrode a GC (Tokai Carbon GC-20) disc (0.071 cm^2 area) mounted in Teflon was used. It was polished using 0.3 and 0.05 μm β-alumina (Buehler). Each polishing step was followed by rinsing and sonication with water for more than 10 min. Then the electrode was immersed into a nitrogen-saturated solution and electrochemical measurements were performed. Apparent redox potentials (E°_{app}) were determined from cyclic voltammograms as midpotentials of cathodic and anodic peak potentials. Apparent diffusion coefficients (D_{app}) were determined by potential step chronoamperometry[15] by assuming one-electron process. The error of the above parameters was estimated to be 10 mV for E°_{app} and less than 20% for D_{app}.

Circular dichroism spectra were recorded on a JASCO-400X spectropolarimeter connected with a cell having an optical path of 10 mm.

Results and Discussion

The cyclic voltammograms recorded for the 2 mM (1 M=1 mol dm^{-3}) **I** and 0.2 M Li_2SO_4 aqueous solution in the absence and presence of 10 mM α-CD are presented in Fig. 1. It is obvious that **I** adsorbs weakly onto GC as onto Pt electrode.[1] The value of E°_{app} (0.427 V) determined in this particular case as being 0.029 V more positive than the cathodic peak potential, is within the error of experiment, being the same as in the case of Pt electrode.[1]

When the above experiment was performed in the 10 mM α-CD solution, the shape of the anodic peak changed. The 60 mV difference between cathodic and anodic peak potentials and the linear dependence of peak currents on the square root of scan rates in the scan rate range 0.01—0.2 V s^{-1} indicate that this couple is associated with a one-electron process, controlled by mass transport to the electrode.[15] The decrease in the anodic peak current, the shift of E°_{app} by 0.020 V in the anodic direction, and the slight increase in cathodic current in comparison to those determined in the absence of α-CD may be caused by a complexation

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with α-CD and its influence on I's aggregation (see below).

The concentration dependences ($0.2 \leqq [\mathbf{I}] \leqq 4$ mM) of D_{app} and $E^\circ{}_{app}$ of **I** in the 10 mM α-CD and 0.2 M Li_2SO_4 aqueous solution are shown in Fig. 2. The D_{app} decreases slightly with the increase in [**I**] but it is larger than that in the absence of α-CD, except in the 0.2 mM **I** solution (compare also with Fig. 2 in Ref. 1). This behavior is opposite to that generally observed.[16] It has been shown that D_{app} is lower when molecules of redox probe aggregate than when aggregation does not occur.[1] Therefore, the effect of α-CD on the D_{app} of **I** may be caused by its disruptive effect on I's micelles (the twofold increase in critical micelle concentration (cmc) of tetraalkylammonium surfactants in the presence of CD has been explained similarly[10,11]).

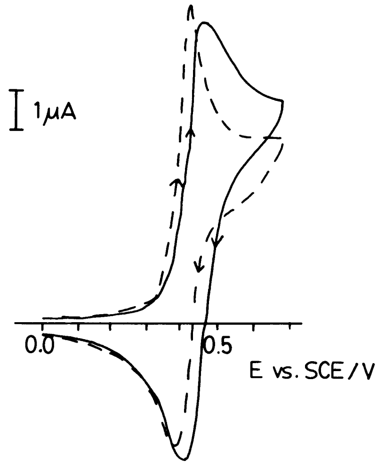

Fig. 1. The cyclic voltammograms recorded in 2 mM solution of **I** in 0.2 M Li_2SO_4 aqueous solution at GC electrode with scan rate 0.1 V s^{-1} (broken line). The same with 10 mM α-CD (solid line).

The D_{app} value estimated at the maximum concentration of **I** in the presence of α-CD is about 20% higher than that estimated in the absence of α-CD.[1] This may be due to the higher value of cmc as well as the smaller molecular weight of micelles in the presence of α-CD (the cmc values of **I** in the 0.2 M Li_2SO_4 in the absence and presence of α-CD are estimated to be, at 25 °C, ca. 0.5 mM[1] and ca. 2 mM (from Fig. 2), respectively). The D_{app} value estimated for the 0.2 mM solution of **I** is smaller than that estimated in the absence of α-CD. At this concentration **I** does not form aggregates[1] and this decrement in D_{app} may be ascribed only to CD complex formation.[16] The dependence of $E^\circ{}_{app}$ on [**I**] is similar to that evaluated in the absence of α-CD,[1] but $E^\circ{}_{app}$ is slightly shifted in the anodic direction. The anodic shift of $E^\circ{}_{app}$ in the 0.2 mM solution of **I** may indicate a stronger complexation of the reduced form of **I** by α-CD. At higher concentrations of **I**, the concentration dependence of $E^\circ{}_{app}$ may be caused by both aggregation and complexation.

Circular dichroism is induced when a chromophore is trapped in the cavity of CDs.[17] Accordingly, the lack of circular dichroism signals in the range of 200—500 nm in the 0.5 mM **I** and 10 mM α-CD solution indicates that the ferrocene chromophore is not included into the α-CD cavity.

The influence of CD on the surface aggregation of redox surfactants in solution has recently been mentioned.[8] Therefore, we performed a similar experiment with **I**. The cyclic voltammograms recorded at $[\mathbf{I}]/\mu\mathrm{M}=30$ in the 0.2 M Li_2SO_4 solution are presented in Fig. 3A. The linear dependence of anodic and cathodic peak currents (after subtraction of the current recorded in the electrolyte solution) on scan rate in the range 0.01—0.2 V s^{-1} indicates that **I** adsorbs onto the GC electrode from this solution. The $E^\circ{}_{app}$ value (+0.49 V) of the $\mathbf{I}^{0/+1}$ couple is shifted in the anodic direction by 0.13 V relative to that determined

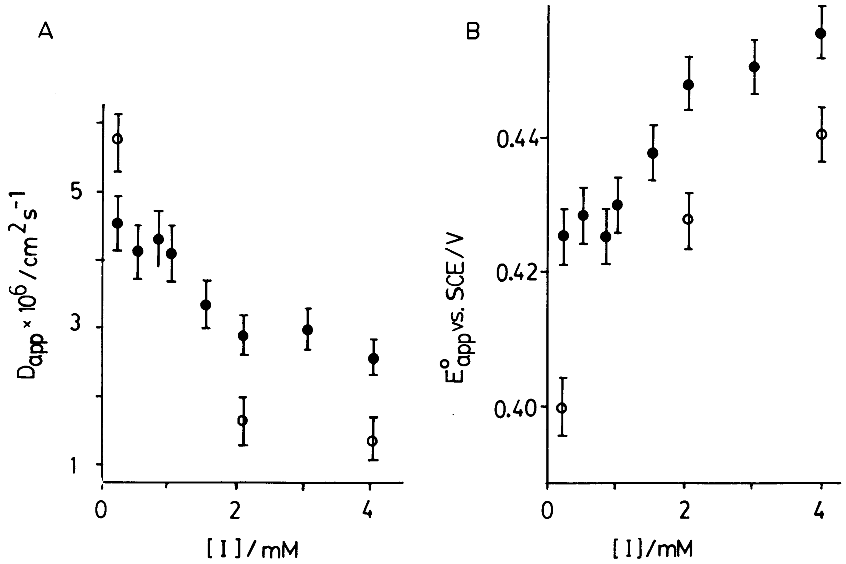

Fig. 2. The dependence of (A) D_{app} of **I** and (B) E°_{app} of $\mathbf{I}^{0/+1}$ couple on [**I**] in aqueous 0.2 M Li_2SO_4 (○). The same with 10 mM α-CD (●).

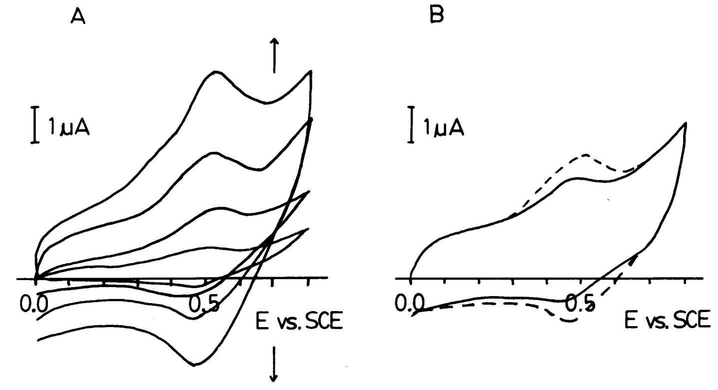

Fig. 3. The cyclic voltammograms recorded at GC electrode in 0.2 M Li_2SO_4 solution containing 30 µM of **I** (A) with scan rates 0.025, 0.05, 0.1, and 0.2 V s^{-1}, and (B) with the scan rate 0.1 V s^{-1} in the absence (broken line) and presence (solid line) of 0.5 mM α-CD.

for ferrocenyltrimethylammonium cation (0.36 V vs. SCE[18]). This indicates that, of the two redox forms, the oxidized one is more weakly bonded to the electrode. This may be caused by stronger repulsive interactions among head groups in the oxidized species of **I**. The differences between the anodic and cathodic peak potentials are equal to 0.04—0.06 V and their half widths (though difficult to estimate) are larger by more than 0.07 V than the theoretical value (0.091 V[19]). This indicates that the layer cannot be regarded as tightly packed, although the area per molecule (about 50 nm^2) is similar to that reported for the monolayer of (ferrocenylmethyl)octadecyldimethylammonium cations deposited on Au electrode by the Langmuir–Blodgett technique.[20]

When the experiments described above were performed in the 0.5 mM α-CD solution, i.e. at [α-CD]/[**I**]=17 (Fig. 3B), both the anodic and cathodic peak currents decreased by ca. 50%, and when [α-CD] was increased to ca. 10 mM ([α-CD]/[**I**]=ca. 3333), the two peaks disappeared. This behavior is different from that of viologen surfactant where 10-fold excess of α-CD was enough to prevent the surface aggregation onto Au electrode.[8] The formation constant of alkyl chain surfactant–α-CD complexes are about 10^3 dm^3 mol^{-1},[10,11] and it does not depend on the length of alkyl chain of surfactants when the chain contains more than 10 carbon atoms.[11] Therefore, it seems reasonable to assume a similar formation constant for **I**–α-CD complexes. If so, in the above experiments more than 90% of **I**'s molecules are considered to be complexed with α-CD. In spite of such a high degree of complexation, the decrease of adsorption is slight compared with other systems.[8] This may indicate the presence of some attractive interactions between **I** and hydrophilic GC surface. The lock of circular dichroism signals suggests no inclusion of ferrocenyl moiety. Accordingly, if some interaction exists between the electrode surface and **I**, **I**'s ferrocenyl group would be participating in the interaction.

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