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The Solubilization Site of Methylferrocene in Cationic Micelles

Katsuyoshi Hoshino, Tetsuo Saji, Yasuhiko Ohsawa, and Shigeru Aoyagui*
Department of Chemical Engineering, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

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Synopsis. The voltammetry of methylferrocene (MeFC) in a dodecyltrimethylammonium bromide micellar solution leads to the conclusion that most MeFC molecules reside in the micelle phase. They are located within the hydrophobic core where water cannot reach, judging from our finding that oxygen decomposes MeFC in the presence of water, but otherwise does not.

The most important function of aqueous micelles is to solubilize water-insoluble substances. A number of investigations have been devoted to determining the partition of such substances between the water phase and the micelle phase. Further interest has been taken in the problem of the location of the solubilizate in the micelle, *i.e.*, either the hydrophobic site in the micelle core or the hydrophilic site near the head group.[1)]

This paper will deal with the solubilization site of methylferrocene (MeFC) in cationic micelles of dodecyltrimethylammonium bromide (DTMAB). In an earlier paper dealing with the cyclic voltammetry and potentiometry of ferrocene (FC) in nonionic micellar solutions, Yeh and Kuwana suggested that the environment of FC in the micelles was quite similar to that in the hydrophobic liquid membrane, but they gave no direct evidence for it.[2)] Unfortunately, the generally applicable method of site determination, which is based on the different absorption maximum frequencies (λ_{max}) of the solubilizate in polar and nonpolar media, cannot be used in our case, because the λ_{max} values of MeFC in both media are very close to each other and MeFC is only poorly soluble in water. Instead, we make use of our finding that oxygen decomposes MeFC in the presence of water, but does not do so in its absence. Though this is a kind of the probe technique which has been extensively used for studying the microenvironment of the micelle, the chemical reactions of the guest substances have rarely been used for this purpose, except for quenching reactions[1)] and chemical equilibria.[3—6)] The redox potential of the $MeFC^{+/0}$ couple in DTMAB micellar solution is also measured to determine the partition of MeFC between the micelle phase and the water phase.

Table 1. Solubility and partition parameter (K_R) of ferrocene (FC), methylferrocene (MeFC) and buthylferrocene (n-BuFC) in 0.2 M Li_2SO_4 with and without 0.1 M dodecyltrimethylammonium bromide at 25 °C

Complex	$[C_W]_{sat}$[a)]/mM	$[C]_{sat}$[b)]/mM	10^2K_R[c)]
FC[d)]	0.035	1.35	2.7
MeFC	0.15	11.1	1.4
n-BuFC	0.14	8.32	1.7

a, b) Solubility of complex (C) in a) water and b) a micellar solution respectively. c) Ratio of the concentration of the complex in the water phase to that in the micelle phase. d) Data in Ref. 8.

Experimental

MeFC was prepared by the literature method.[7)] The molar absorptivity values of MeFC at 250 nm, $1.8\times10^3\ M^{-1}\ cm^{-1}$ ($1\ M=1\ mol\ dm^{-3}$) in the water phase and $4.0\times10^3\ M^{-1}\ cm^{-1}$ in the micelle phase, were determined by the method described in a previous paper.[8)] The other experimental procedures used in this work were also described in that paper.

Results and Discussion

According to our previous paper,[8)] we can determine the partition parameter, K_R *i.e.*, the ratio of the concentration in moles of MeFC in water to that in micelles, per liter of the micellar solution, under the specific conditions of $MeFC^+$ residing only in the water phase. To see if these conditions are fulfilled, the observed value for the reversible half-wave potential of the $MeFC^{+/0}$ in the micellar solution ($E^r{}_{1/2}$) was compared with the value calculated by using the following equation:[8)]

$$E^r_{1/2}=E^0_W+(RT/F)\ln(1+K_R)/K_R-(RT/F)\ln(D_0/D_R)^{1/2}, \quad (1)$$

with:

$$D_R=(D_{RM}+K_RD_{RW})/(1+K_R) \quad (2)$$

and:

$$K_R=[MeFC_W]/[MeFC_M]=[MeFC_W]_{sat}/([MeFC]_{sat}-[MeFC_W]_{sat}). \quad (3)$$

The abbreviations used are the same as have been described in a previous paper.[8)]

Tables 1 and 2 summarize, respectively, the results of the spectroscopic determination of the solubility and

Table 2. Voltammetric data of methylferrocene (MeFC) and methylferrocenium ($MeFC^+$) in 0.2 M Li_2SO_4 with and without 0.1 M dodecyltrimethylammonium bromide (DTMAB) at 25 °C[a)]

Complex	DTMAB/M	D_R[b)]/cm² s⁻¹	D_0[c)]/cm² s⁻¹	$E^r{}_{1/2}$[d)]/V	$E^r{}_{1/2w}$[e)]/V
MeFC	0.1	0.82×10^{-6}	—	0.185	—
$MeFC^+$	0.1	—	7.1×10^{-6}	0.185	—
MeFC	0	—	—	—	0.114

a) All the voltammograms are diffusion-controlled, as is indicated by the linear plot of the peak current *vs.* the square root of the potential-scan rate. b, c) Apparent diffusion coefficients of b) $MeFC^+$ in a micellar solution respectively. d, e) Reversible halfwave potentials of the $MeFC^{+/0}$ redox system in d) a micellar solution and e) water respectively. The latter value was estimated from the peak potential in the reduction of $MeFC^+$ plus 0.029 V.

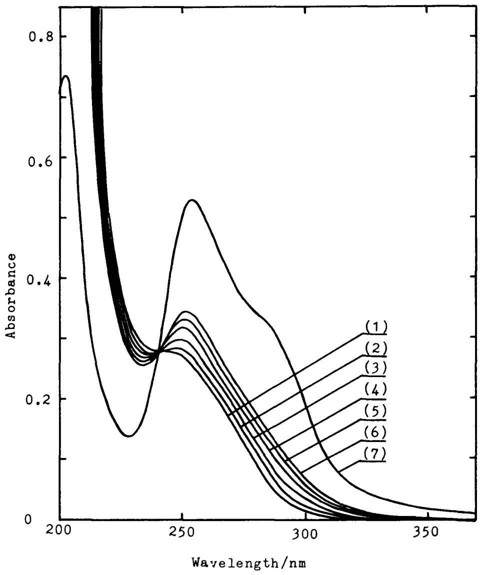

Fig. 1. UV absorption spectra of methylferrocene saturated in aqueous 0.2 M Li_2SO_4 at 25 °C recorded at time t after oxygen introduction into the solution: t=(1) 0, (2) 40, (3) 87, (4) 150, (5) 203, (6) 258 min, and (7) 7 d.

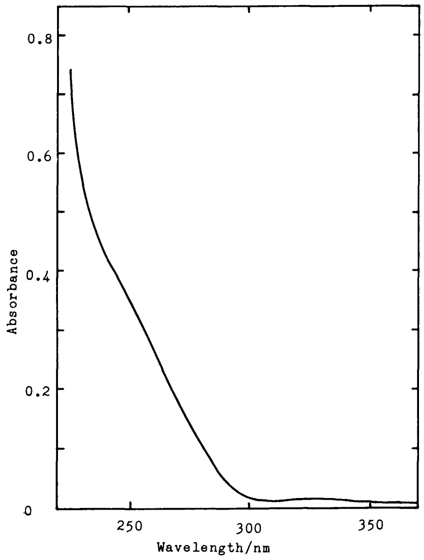

Fig. 2. UV absorption spectrum of 0.088 mM methylferrocene in an aqueous solution of 0.2 M Li_2SO_4 and 0.1 M dodecyltrimethylammonium bromide.

the voltammetric determination of the diffusion coefficient and the reversible half-wave potential. Table 1 also lists the data for FC and butylferrocene (n-BuFC). The $(E^{\mathrm{r}}_{1/2\mathrm{w}})$, value for the redox couple $\mathrm{MeFC}^{+/0}$ calculated from Eqs. 1 and 3 with these data was 0.186 V *vs.* SCE. It is in excellent agreement with the experimental value of 0.185 V. Consequently, Eq. 1 applies to this redox system; hence, it can be concluded that the MeFC^{+} ions are located only in the water phase and that most of the MeFC molecules reside in the micelle phase, as is indicated by the small K_{R} value of 1.4×10^{-2}.

Figure 1 shows the absorption spectra of a saturated solution of MeFC (0.15 mM) in 0.2 M Li_2SO_4, which were recorded (1) before and (2—7) after the introduction of oxygen gas into the solution. In the absence of oxygen, the 1 spectrum was kept unchanged for more than a day, but in its presence a new peak appeared at about 250 nm and grew linearly in height with the time, while the peak at 200 nm got lower. The isosbestic point at 240 nm indicates that this reaction gives only one product. The reaction scheme of the oxidation of MeFC will be discussed in a separate paper. Contrary to aqueous solutions, the spectra of MeFC in nonaqueous solvents, such as hexane, ethanol, and acetonitrile, were kept unchanged for more than 100 d in the presence of oxygen. These findings show that MeFC reacts with oxygen only in the coexistence of water.

Figure 2 shows an absorption spectrum of MeFC in a micellar solution. According to the above voltammetric results, the spectroactive species is the MeFC located in and/or on the micelle. The fact that the shape of this spectrum did not change for more than 4 h after introducing oxygen gas into the solution strongly suggests that the microenvironment of the solubilized MeFC molecules is highly hydrophobic for the following reasons: the decomposition of MeFC requires both water and oxygen; the solubilities of ferrocene and oxygen are higher in aliphatic solvents than in water; we have evidence for oxygen residing in micelles.[9] Considering the NMR experimental finding of Menger *et al.* that water molecules can penetrate into the micelle core as far as seven carbon atoms away from the head group,[10] we can conclude that the MeFC molecules reside deep in the interior of the micelle core where water molecules cannot reach. However, another finding of the same authors, that the CH≡ group substituted for the terminal methyl protons of DTMA^{+} is located in a **wet** environment[11], seems incompatible with our findings, if no specific conformation of this surfactant molecule is assumed.

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