Partition Parameters for Three Redox Forms of Viologen in a Nonionic Micellar Solution

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Synopsis. The partition parameters of 1,1′-dimethyl-4,4′-bipyridinium (**1**), 1-decyl-1′-methyl-4,4′-bipyridinium (**2**), and 1-dodecyl-1′-methyl-4,4′-bipyridinium (**3**) between the micellar and water phases were determined by electrochemical methods. It was shown that $\mathbf{1}^0$, $\mathbf{2}^{+}$, $\mathbf{2}^0$, and $\mathbf{3}^{2+}$ are almost completely solubilized in the micellar phase and that $\mathbf{1}^{2+}$, $\mathbf{1}^{+}$ and $\mathbf{2}^{2+}$ are partitioned into two phases.

In relation to photochemical splitting of water, the reduction of 1,1′-dimethyl-4,4′-bipyridinium (methyl violigen) and its surfactant derivatives with photoexcited sensitizers has been investigated in micellar systems.[1] In order to interpret quantitatively the efficiency and kinetics of this process, we must know partition parameters (K) of the viologens between micellar and water phases, because the reaction rate of micelle-solubilized substance is a function of K for both the reactants and the products.[2,3]

No report, however, has dealt with the change in partition of viologens in redox states of bipyridinium group. The purpose of this paper is to estimate the values of K for divalent, mono-reduced, and fully reduced viologens in a nonionic micellar system by means of electrochemical methods.

The viologen derivatives studied are 1,1′-dimethyl-4,4′-bipyridinium dichloride (**1**), 1-decyl-1′-methyl-4,4′-bipyridinium dibromide (**2**), and 1-dodecyl-1′-methyl-4,4′-bipyridinium dibromide (**3**).

Experimental

3 was prepared by the method described in the literature[4] and identified by elemental analysis and melting point. The synthesis of **2** was similar to that of **3**: Mp 266—267 °C; Found: C, 52.85; H, 6.84; N, 5.73%. Calcd for $C_{21}H_{32}N_2Br_2$: C, 53.52; H, 6.63; N, 5.94%. **1** was used as supplied by Tokyo Kasei Co.

Electrochemical measurements were carried out at 25 °C under a nitrogen atmosphere for test solutions containing 0.1 M (1 M=1 mol dm^{-3}) NaCl as a supporting electrolyte. A glassy-carbon disk electrode and a saturated calomel electrode (SCE) were used respectively as working and reference electrodes in cyclic voltammetry and potential-step chronoamperometry. Controlled potential bulk electrolysis was performed with a Hg working electrode.

The host surfactant used is α-[*p*-(1,1,3,3-tetramethylbutyl)-phenyl]-ω-hydroxypoly(oxyethylene), Triton X-100, (TX-100, Wako Pure Chemicals Co.) and used as supplied. The concentration of TX-100 was kept constant at 0.1 M throughout the experiments. The concentration of **1**, **2**, and **3** in 0.1 M TX-100 micellar solution was ajusted to the condition that one micelle contains not more than one molecule of **1**, **2**, and **3** on average. All of the solutions were prepared with twice-distilled water.

Results and Discussion

Figure 1 shows cyclic voltammograms for solutions of 0.62 mM $\mathbf{1}^{n+}$ (n=2, 1, and 0) containining 0.1 M TX-100 and 0.1 M NaCl. The solutions of $\mathbf{1}^{+}$ and $\mathbf{1}^0$ were prepared by controlled-potential bulk reduction of $\mathbf{1}^{2+}$ at −0.84 and −1.3 V vs. SCE, respectively. The color of the solution of $\mathbf{1}^{+}$ was intense blue, while that of $\mathbf{1}^0$ was brownish yellow.

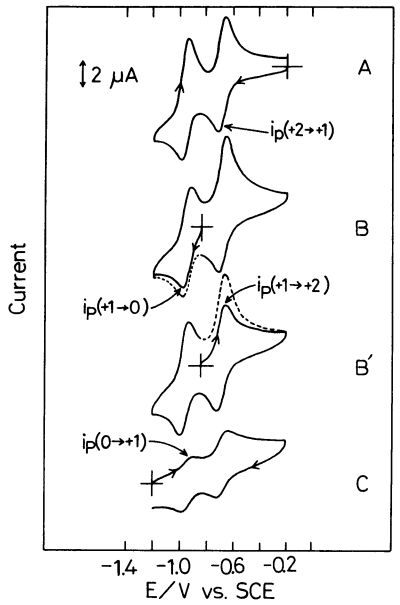

Fig. 1. Cyclic voltammograms for (A) a solution of 0.62 mM $\mathbf{1}^{2+}$, (B) and (B′) a solution of 0.62 mM $\mathbf{1}^{+}$, and (C) a solution of 0.62 mM $\mathbf{1}^0$ containing 0.1 M TX-100 and 0.1 M NaCl at 25 °C. Sweep rate: 12 mV s^{-1}. Working electrode area: 0.071 cm^2.

The first and the second reduction steps seem to be reversible one-electron processes judging from the value of peak separation, i.e., the difference between cathodic and anodic peak potentials.[5] The half-wave potentials were −0.69 and −0.96 V vs. SCE for the first and the second reduction steps, respectively. These values agreed well with those described in the literature.[6] The peak current for the first reduction step of $\mathbf{1}^{2+}$, $i_p(+2\rightarrow+1)$, in Fig. 1A is nearly equal to that for the first reduction step of $\mathbf{1}^{+}$, $i_p(+1\rightarrow0)$, in Fig. 1B and that for the first oxidation step of $\mathbf{1}^{+}$, $i_p(+1\rightarrow+2)$, in Fig. 1B′. On the other hand, the peak current for the first oxidation step of $\mathbf{1}^0$, $i_p(0\rightarrow+1)$, in Fig. 1C is much smaller than $i_p(+2\rightarrow+1)$, $i_p(+1\rightarrow0)$, and $i_p(+1\rightarrow+2)$.

Table 1 shows the apparent diffusion coefficients (D_{app}) for $\mathbf{1}^{2+}$, $\mathbf{1}^{+}$, and $\mathbf{1}^0$ in a solution containing 0.1 M TX-100 and 0.1 M NaCl. D_{app} was determined from inclination of the current vs. (time)$^{-1/2}$ plot in potential-step chrono-amperometry.[5]

According to the electrochemistry of micelle-solubilized substances,[3,7] D_{app} for the solubilizate (S) partitioning into micellar and aqueous phases gives the partition parameter (K) defined as the ratio of concentration of S in aqueous phase, [S]$_w$, to that in

Table 1. Apparent Diffusion Coefficient (D_{app}), Partition Parameter (K), and Mole Fraction in the Micellar Phase (x) of **1**, **2**, and **3** in 0.1 M NaCl with and without 0.1 M TX-100 at 25 °C

Solubilizate	Surfactant	$D_{app}\times10^6$ / $cm^2\,s^{-1}$	K	x
$\mathbf{1}^{2+}$	—	14	—	—
$\mathbf{1}^{2+}$	0.1 M TX-100	7.4	1.0	0.50
$\mathbf{1}^{+}$	0.1 M TX-100	7.4	1.0	0.50
$\mathbf{1}^{0}$	0.1 M TX-100	0.73	0.01	0.99
$\mathbf{2}^{2+}$	—	8.0	—	—
$\mathbf{2}^{2+}$	0.1 M TX-100	3.1	0.50	0.67
$\mathbf{2}^{+}$	0.1 M TX-100	1.4	0.11	0.90
$\mathbf{2}^{0}$	0.1 M TX-100	0.71	0.01	0.99
$\mathbf{3}^{2+}$	—	8.0	—	—
$\mathbf{3}^{2+}$	0.1 M TX-100	0.87	0.03	0.97

micellar phase, $[S]_M$:

$$D_{app} = ([S]_W D_W + [S]_M D_M)/([S]_W + [S]_M), \quad (1)$$

$$K = [S]_W/[S]_M = (D_{app} - D_M)/(D_W - D_{app}), \quad (2)$$

where D_M is the diffusion coefficient of micelles and D_W, the diffusion coefficient of the monomeric S measured in an aqueous solution without micelle. These equations are based on the assumption that the solubilization equilibrium of S is established in the diffusion process of S toward the electrode.

$$S + \text{micelle} \rightleftarrows S(\text{in micelles}), \quad (3)$$

This assumption is valid for $\mathbf{1}^{n+}$ (n=2, 1, and 0), $\mathbf{2}^{n+}$ (n=2, 1, and 0), and $\mathbf{3}^{2+}$ because the electrode reactions were diffusion-controlled, i.e., the current vs. $(\text{time})^{-1/2}$ plots in potential-step chronoamperometry gave straight lines.[8] D_M for TX-100 micelle in the presence of 0.1 M NaCl was 6.5×10^{-7} $cm^2\,s^{-1}$ determined by the method described in the literature.[3] D_W for $\mathbf{1}^{2+}$ in 0.1 M NaCl aqueous solution was 1.4×10^{-5} $cm^2\,s^{-1}$. The values of K for $\mathbf{1}^{2+}$, $\mathbf{1}^{+}$, and $\mathbf{1}^{0}$ were determined by Eq. 2 on the assumption that the values of D_W for $\mathbf{1}^{+}$ and $\mathbf{1}^{0}$ are equal to D_W for $\mathbf{1}^{2+}$ (Table 1). Table 1 also lists the mole fraction (x) of $\mathbf{1}^{n+}$ (n=2, 1, and 0) solubilized in the micellar phase, which can be derived from the respective K value.

$$x = [\mathbf{1}^{n+}]_M/([\mathbf{1}^{n+}]_M + [\mathbf{1}^{n+}]_W),$$

$\mathbf{1}^{2+}$ and $\mathbf{1}^{+}$ are partitioned equally into two phases, and $\mathbf{1}^{0}$ is almost completely solubilized in the micellar phase.

Figure 2 shows cyclic voltammograms for solutions of 0.62 mM $\mathbf{2}^{n+}$ (n=2, 1, and 0) containing 0.1 M TX-100 and 0.1 M NaCl. At a relatively slow sweep rate, both the first and the second reduction steps were electrochemically reversible one-electron steps. The half-wave potentials were −0.56 and −0.84 V vs. SCE for the first and the second reduction steps, respectively.

The peak current is in order of $i_p(+2\rightarrow+1) > i_p(+1\rightarrow0) = i_p(+1\rightarrow+2) > i_p(0\rightarrow+1)$, suggesting that the value of D_{app} is in order of $\mathbf{2}^{2+} > \mathbf{2}^{+} > \mathbf{2}^{0}$. The values of D_{app}, K, and x for $\mathbf{2}^{2+}$, $\mathbf{2}^{+}$, and $\mathbf{2}^{0}$ determined by potential-step chronoamperometry are listed in Table 1. K and x show that the proportion of the solutes in the micellar phase is in order of $\mathbf{2}^{2+} < \mathbf{2}^{+} < \mathbf{2}^{0}$, and that $\mathbf{2}^{+}$ is more hydrophobic than $\mathbf{2}^{2+}$. This result is different from the case of methyl viologen.

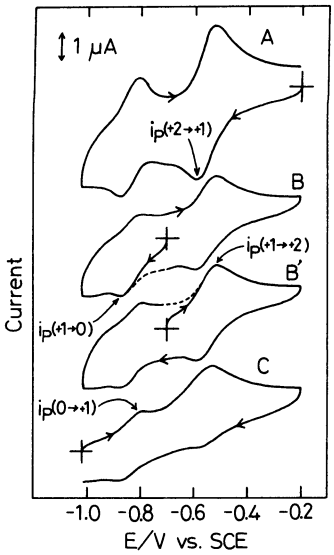

Fig. 2. Cyclic voltammograms for (A) a solution of 0.62 mM $\mathbf{2}^{2+}$, (B) and (B') a solution of 0.62 mM $\mathbf{2}^{+}$, and (C) a solution of 0.62 mM $\mathbf{2}^{0}$ containing 0.1 M TX-100 and 0.1 M NaCl at 25 °C. Sweep rate: 12 mV s^{-1}. Working electrode area: 0.071 cm^2.

D_{app}, K, and x for $\mathbf{3}^{2+}$ are also shown in Table 1. The values of x mean that $\mathbf{3}^{2+}$ is completely solubilized in the micellar phase irrespective of its highly hydrophilic character of bipyridinium group. D_{app} values for $\mathbf{3}^{+}$ and $\mathbf{3}^{0}$ were not obtained, because their electrochemical behavior was complicated due to the adsorption on electrode surface.

The results described in this paper and particularly the suggestion of hydrophobic nature of viologen derivatives with different redox states will be useful for designing a redox system with viologen and for predicting reaction mechanism of chemical conversion of light energy.

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