J. Phys. Chem. **1985**, *89*, 4876–4880

Micellar Effects on the Reductive Electrochemistry of Methylviologen

Angel E. Kaifer and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712 *(Received: April 4, 1985; In Final Form: June 18, 1985)*

The reductive electrochemistry of methylviologen was surveyed in the presence of sodium dodecyl sulfate (SDS), Triton X-100, and cetyltrimethylammonium bromide (CTAB) micelles. The half-wave potentials of the MV^{2+}/MV$^{+\cdot}$ and MV$^{+\cdot}$/MV couples were found to be dependent on the medium composition. The conproportionation constant for the reaction MV^{2+} + MV $\rightleftharpoons$ MV$^{+\cdot}$ decreases in the order SDS micelles > H$_2$O > Triton X-100 micelles > CTAB micelles. Electron spin resonance of these solutions demonstrated that the electron exchange rate between the dication and the cation radical is reduced in the presence of SDS micelles but is unaffected by cationic or nonionic micelles, compared to the micelle-free solution. Absorption spectra showed that the equilibrium constant for dimerization of the cation radical is depressed by the SDS micelles, suggesting that MV$^{+\cdot}$ resides in an essentially nonaqueous environment, such as the micelle hydrocarbon core. Detection of the critical micelle concentration of SDS solutions is possible through the changes observed in the shape of the cyclic voltammograms.

Introduction

Micellar systems have been widely investigated and used in a variety of chemical applications.[1] The nature of the structure of micelles has still not been determined completely[2] probably because of the dynamic nature of these assemblies as opposed to other highly organized lipid bilayer structures, such as vesicles. However, the micellar environment is considered to be a primitive, although simple, model for biological membranes.[3] There have been a few reports in the chemical literature on electrochemistry in micellar solutions.[4–6] Two main lines of research are evident in these works. First, an examination of micellar effects on well-known and reversible redox couples and, second, a search for micellar systems capable of stabilizing reactive intermediates in aqueous solution. Aoyagui and co-workers[4] have described the changes in half-wave potentials for a series of metal complexes upon addition of sodium dodecyl sulfate (SDS) to the solution and interpreted the results in terms of the variations of solvation energy for the oxidized and reduced species in the micellar environment as compared to the isotropic aqueous solution. Saveant et al.[5] have reported a remarkable stabilization of the electrogenerated anion radical of phthalonitrile in the presence of cationic micelles and suggested that the observed 250-fold decrease in the rate of protonation of the anion radical was due to its association with the positively charged micelles. In a later paper, Blount and co-workers[6a] examined the reductive electrochemistry of nitrobenzene in anionic, cationic, and nonionic micelles, and found, in contrast to Saveant's report, that the only medium capable of stabilizing the nitrobenzene anion radical to the point where it became detectable by cyclic voltammetry at 50 mV/s was not the cationic, but rather the anionic micelles. The same authors had previously shown[6b] that the oxidation of 10-methylphenothiazine to the corresponding cation radical is facilitated by anionic micelles.

These results suggest that the influence of micellar aggregates on the electrochemistry of a given substrate cannot be predicted on the basis of simple electrostatic considerations, and that micellar effects are strongly dependent upon the substrate and surfactant structures. We have addressed this problem in this paper in an investigation of micellar effects on the electrochemistry of the methylviologen dication (MV^{2+}). MV^{2+} has been used frequently as an electron acceptor in photochemical energy conversion schemes in which micelles, vesicles, and other organized assemblies play an important role as spacers intended to decrease the rates of detrimental charge recombination reactions.[7] Several authors have reported interactions between MV^{2+} and these spacer structures,[8] which might have implications in the energy conversion processes. Recent reports from this laboratory[9] described the use of MV^{2+} as a probe of the structure of Nafion films and clay layers on electrodes, utilizing electrochemical and ESR methods. Here, we describe the electrochemistry of MV^{2+} in sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB), and Triton X-100 micellar solutions. These micellar systems were chosen as representative of anionic, cationic, and nonionic micelles, respectively.

Experimental Section

(*A*) *Materials*. Methylviologen dichloride hydrate (Aldrich) was recrystallized from methanol and dried at 80 °C in vacuo. SDS, CTAB, and Triton X-100 were obtained from Aldrich and used without further purification. All other reagents were of the best commercial quality available. Triply distilled water was used to prepare all solutions.

(*B*) *Equipment*. Electrochemical experiments were performed with a Princeton Applied Research (PAR) Model 175 universal programmer, a Model 173 potentiostat, and a Model 179 digital coulometer equipped with positive feedback circuitry for IR compensation. Voltammograms were recorded on a Houston Instruments Model 2000 *X–Y* recorder. Diffusion coefficients were measured with a Bioanalytical System (Lafayette, Indiana) BAS-100 electrochemical analyzer. ESR spectra were recorded by using the X-band of a Varian E-9 spectrometer (100-KHz field modulation) equipped with a TE109 dual-sample cavity. Absorption spectra were obtained in a Hewlett-Packard Model 8450A dual-beam spectrophotometer.

(*C*) *Procedures*. All of the experiments were performed under a purified nitrogen atmosphere. Nitrogen gas was also used to purge all solutions. The electrochemical measurements were carried out in cells of conventional design adapted for Schlenk-line

---

[1] (a) Lindman, B.; Wennerstrom, H. *Top. Curr. Chem.* **1980**, *87*, 1–83. (b) Kalyanasundaram, K. *Chem. Soc. Rev.* **1978**, *7*, 453–472. (c) Mittal, K. L. "Solution Chemistry of Surfactants"; Plenum Press: New York, 1979. (d) Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.

[2] (a) Menger, F. M. *Acc. Chem. Res.* **1979**, *12*, 111–117. (b) Menger, F. M.; Boyer, B. J. *J. Am. Chem. Soc.* **1980**, *102*, 5936–5938.

[3] Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley: New York, 1982; Chapter 2.

[4] (a) Oshawa, Y.; Shimazaki, Y.; Aoyagui, S. *J. Electroanal. Chem.* **1980**, *114*, 235–246. (b) Oshawa, Y.; Aoyagui, S. *J. Electroanal. Chem.* **1982**, *136*, 353–360. (c) Yeh, P.; Kuwana, T. *J. Electrochem. Soc.* **1976**, *123*, 1334–1339.

[5] Meyer, G.; Nadjo, L.; Saveant, J. M. *J. Electroanal. Chem.* **1981**, *119*, 417–419.

[6] (a) McIntire, G. L.; Chiappardi, D. M.; Casselberry, R. L.; Blount, H. N. *J. Phys. Chem.* **1982**, *86*, 2632–2640. (b) McIntire, G. L.; Blount, H. N. *J. Am. Chem. Soc.* **1979**, *101*, 7720–7721.

[7] Reference 3, Chapters 12 and 13.

[8] (a) Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938–1941. (b) Schmehl, R. H.; Whitesell, L. G.; Whitten, D. G. *J. Am. Chem. Soc.* **1981**, *103*, 3761–3764. (c) Lukac, S.; Harbour, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 4248–4250.

[9] (a) Gaudiello, J. G.; Ghosh, P. K. Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 3027. (b) White, J.; Bard, A. J. *J. Electroanal. Chem.*, submitted for publication.

0022-3654/85/2089-4876$01.50/0

TABLE I: Electrochemical Data for Methylviologen in Several Micellar Solutions[a]

medium	first reduction					second reduction					MV^{+} conproportionation const
	$-E_{pc}$	$-E_{pa}$	$-E_{1/2}$	i_{pc}	i_{pa}	$-E_{pc}$	$-E_{pa}$	$-E_{1/2}$	i_{pc}	i_{pa}	
50 mM NaCl	0.72	0.66	0.69	11.8	10.8	1.04	0.99	1.02	10.3		3.8×10^5
50 mM NaCl + 70 mM SDS	0.68	0.61	0.65	4.3	3.5	1.16	1.08	1.12	3.5	2.3	8.8×10^7
50 mM NaCl + 5% (w/v) Triton X-100	0.71	0.65	0.68	11.0	10.0	0.99	0.93	0.96	11.8	9.2	5.4×10^4
50 mM NaCl + 70 mM CTAB	0.72	0.66	0.69	11.5	11.5	0.98	0.92	0.95	11.4	11.3	2.5×10^4

[a] E in volts vs. SCE, i in microamperes.

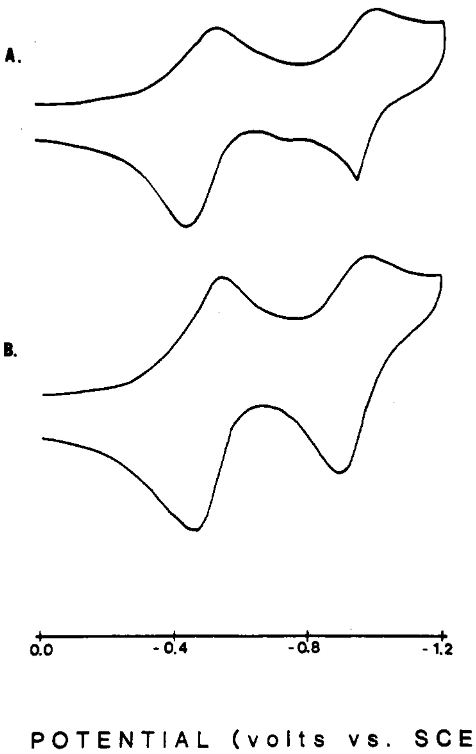


Figure 1. Cyclic voltammogram on glassy carbon of methylviologen in aqueous 50 mM NaCl solution. Sweep rate = 100 mV/s. (A) $[MV^{2+}]$ = 1.0 mM; S = 20 μA. (B) $[MV^{2+}]$ = 0.5 mM; S = 5 μA.

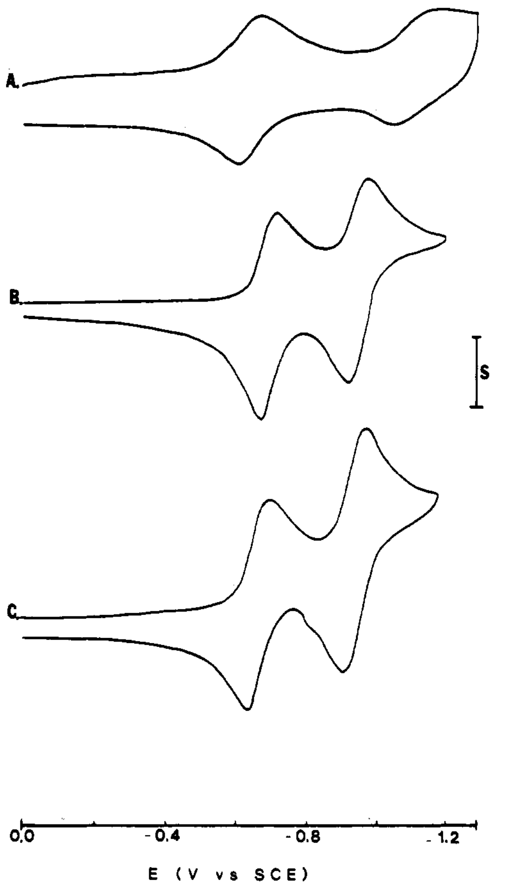


Figure 2. Cyclic voltammogram on glassy carbon of 1.0 mM methylviologen in aqueous 50 mM NaCl solution also containing (A) 70 mM SDS, (B) 70 mM CTAB, and (C) 5%(w/v) Triton X-100. Sweep rate = 100 mV/s. S = 10 μA.

use. Glassy carbon electrodes (BAS, MF2012) were employed as working electrodes for voltammetry. The electrodes were polished with a 0.05-μm alumina/water slurry on a felt surface and sonicated immediately before use. Samples of the methylviologen cation radical were prepared by controlled potential electrolysis on carbon cloth cathodes of solutions containing appropriate concentrations of the parent dication. A platinum mesh was always used as counter electrode. All potentials were recorded against a saturated calomel electrode (SCE).

Results

Cyclic Voltammetry. A cyclic voltammogram of a 1.0 mM solution of MV^{2+} in 0.050 M NaCl was recorded as a control experiment and is shown in Figure 1a. The two couples observed are due to the well-known two-step reduction of methylviologen[10] (eq 1 and 2). This voltammogram shows complications due to

$$MV^{2+} + e^- \rightleftharpoons MV^{+\cdot} \quad (1)$$

$$MV^{+\cdot} + e^- \rightleftharpoons MV \quad (2)$$

adsorption of the neutral form (MV) on the electrode surface. These complications disappear either upon increasing the scan rate or by lowering the MV^{2+} concentration (Figure 1b). Both electrochemical half-reactions are also clearly observable in all three micellar solutions (Figure 2a–c). All of the couples were electrochemically reversible as shown by the value of ΔE_p (the difference between the cathodic, E_{pc}, and the anodic, E_{pa}, peak potentials (see Table I). As expected the reductive electrochemistry of MV^{2+} is essentially unchanged in all three media. There are however noticeable variations in the redox potentials associated with half-reactions 1 and 2 (Table I). For example, in the presence of SDS micelles the first reduction of MV^{2+} shifts to less negative potentials (i.e., is facilitated) while the second reduction, generating MV, is clearly more difficult compared to the same processes in isotropic aqueous solution. In contrast, in both CTAB and Triton X-100 micelles, the second reduction is thermodynamically easier, and the first one remains essentially unaltered as compared to the micelle-free solution. The apparent conproportionation constants (K_{conp}), corresponding to equilibrium 3 can be determined from the redox potentials of couples 1 and

$$MV^{2+} + MV \rightleftharpoons 2MV^{+\cdot} \quad (3)$$

2 by the following equation:[10]

$$K_{conp} = \exp[-F/RT(E_2^{0\prime} - E_1^{0\prime})] \quad (4)$$

The values obtained are given in Table I. Note that K_{conp} is larger in the presence of SDS micelles than in isotropic aqueous solution; this implies that the anionic micelles exert a stabilizing effect on the cation radical $MV^{+\cdot}$ relative to the dicationic and neutral forms. Conversely, in cationic and nonionic micelles K_{conp} is

---

(10) Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49–82.

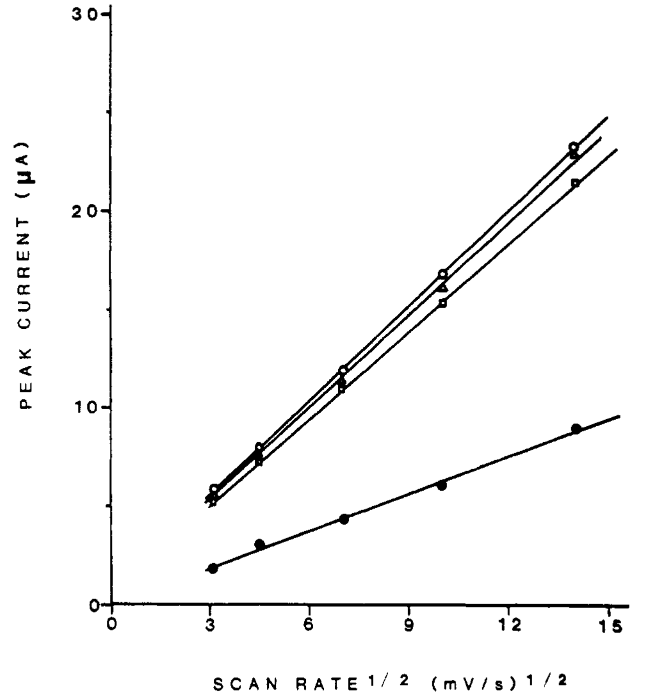


Figure 3. Scan rate dependence of the cathodic peak current for the first reduction of 1.0 mM MV^{2+} solutions also containing (○) 50 mM NaCl, (●) 50 mM NaCl + 70 mM SDS, (□) 50 mM NaCl + 5% Triton X-100, and (△) 50 mM NaCl + 70 mM CTAB.

smaller than in 0.050 M NaCl. This trend seems to indicate that electrostatic interactions are important in the stability of $MV^{+\cdot}$.

Diffusion Coefficients. The peak currents (i_p) corresponding to the first reduction of MV^{2+} in all the solutions investigated were diffusion controlled for scan rates (v) ranging from 10 to 200 mV/s, as verified by the constancy of $i_p/v^{1/2}$ (see Figure 3). The slope of the i_p vs. $v^{1/2}$ line corresponding to the SDS solution is significantly smaller than those corresponding to the remaining media. Moreover, the cyclic voltammogram of a 1.0 mM solution of MV^{2+} containing SDS micelles shows a remarkable depression of all the peak currents as compared to those in the other media under study. These observations can only be explained by changes in the diffusion coefficients (D_0's) of the electroactive species. To find accurate D_0 values, chronocoulometry was used. The projected area of the glassy carbon electrode was determined by chronocoulometric oxidation of ferrocyanide ($D_0 = 6.50 \times 10^{-6}$ cm^2/s in 0.10 M KCl),[11] and was found to be 0.0788 cm^2. This value was subsequently used to determine the apparent D_0 values of MV^{2+} in the absence and in the presence of SDS micelles. Linear Q vs. $t^{1/2}$ (Cottrell) plots with zero intercepts, indicative of uncomplicated electrochemical behavior, were obtained in both cases. In the absence of SDS, D_0 was 6.56×10^{-6} cm^2/s, while a value of 9.48×10^{-7} cm^2/s was obtained in the presence of 70 mM SDS. The nearly 7-fold decrease of the D_0 value upon SDS addition accounts very well for the observed depression in the i_p's of the cyclic voltammograms. The magnitude of the decrease in D_0 also agrees very well with previously reported D_0 reductions of other species due to association with micellar assemblies.[4a,6a] In principle, the formation of a substrate–micelle aggregate is expected to increase the effective radius of the substrate by a factor of about 4 (the SDS micellar radius is in the order of 25 Å,[11] while the radius of MV^{2+} along the principal symmetry axis is about 6 Å); this would explain the observed changes in the diffusion coefficients.

No chronocoulometric determination of D_0 values was performed in the presence of either CTAB or Triton X-100 micelles, since the CV peak currents were nearly identical in both cases with those observed in 0.050 M NaCl.

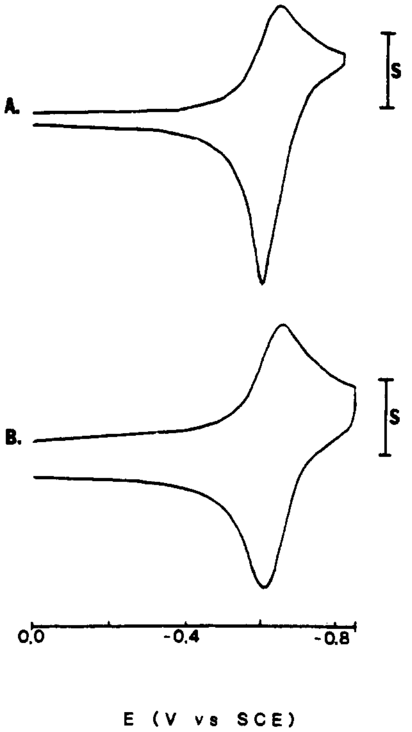


Figure 4. Cyclic voltammogram on glassy carbon of 1.0 mM methylviologen in aqueous 50 mM NaCl solution also conataining (A) 1.0 mM SDS, and (B) 3.0 mM SDS. Sweep rate = 100 mV/s. S = 10 μA.

Cyclic Voltammetry at Varying Concentrations of SDS. Since the above results indicate a strong influence of SDS micelles on the electrochemistry of MV^{2+}, we investigated these effects as a function of the SDS concentration, with the aim of clarifying the nature of the interactions involved. The shape of the cyclic voltammogram for a 1.0 mM MV^{2+}/1.0mM SDS/50 mM NaCl solution is shown in Figure 4a. The shape of the anodic peak clearly suggests that adsorption of $MV^{+\cdot}$ on the electrode surface occurs, and yields, on oxidation, the large parabolic anodic peak.[13] The same electrochemical behavior was observed, even when the concentration of SDS was either doubled or decreased below the 1.0 mM level. These experiments indicate that the minimum level of anionic surfactant required for this behavior is in the range 0.1–0.5 mM, while the upper limit is about 2.0 mM. Since this behavior is not found in the absence of SDS, deposition of the cation radical onto the electrode surface is triggered by adsorption of SDS. This phenomenon is not due to a precipitation reaction, since after mixing equal volumes of a 2.0 mM $MV^{+\cdot}$ and 2.0 mM SDS solutions no precipitate formation was observed after more than 12 h. However, at 3.0 mM SDS, the peak corresponding to $MV^{+\cdot}$ oxidation becomes essentially diffusion controlled, as shown in Figure 4b. At 4.0 mM SDS the voltammogram closely ressembles that shown in Figure 2a, which corresponded to a much larger concentration of surfactant (70 mM).

The elimination of the adsorption–desorption pattern for $MV^{+\cdot}$ above the 3.0 mM SDS level is clearly related to the appearance of micelles in the solution. Micellar assemblies seem to prevent the adsorption of $MV^{+\cdot}$ onto the electrode surface because it is now associated with the SDS micelles. Thus, below the critical micelle concentration (cmc), adsorption of a monolayer of dodecyl sulfate anions is possible, and electrogenerated $MV^{+\cdot}$ is held on the surface. Above the cmc, micelles are formed and the $MV^{+\cdot}$ is solubilized. The cmc of SDS in the presence of 50 mM NaCl was recently reported[14] to be 2.25 mM, as obtained by staircase–tensammetric titration. In good agreement, our voltammograms reveal a remarkable change of CV behavior between 2.0 and 3.0 mM SDS. To the best of our knowledge this is the

---

[11] Stackelberg, M.; Pilgram, M.; Toome, V. *Z. Electrochem.* **1953**, *57*, 342.

[12] Mazer, N. A.; Benedek, G. B.; Carey, M. C. *J. Phys. Chem.* **1976**, *80*, 1075–1084.

[13] Wopschall, R. H.; Shain, I. *Anal. Chem.* **1967**, *39*, 1514.

[14] Britz, D.; Mortensen, J. *J. Electroanal. Chem.* **1981**, *127*, 231–240.

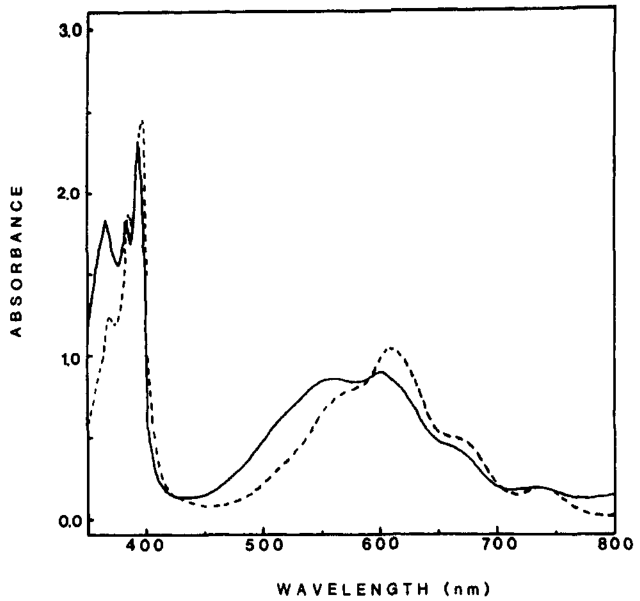


Figure 5. Absorption spectra of reduced 1.0 mM MV^{2+} in aqueous 50 mM NaCl solution (solid line), and with 70mM SDS added (dotted line). Optical pathway = 0.1 cm.

first time that the cmc has been estimated by cyclic voltammetry.

Absorption Spectra. There is a great deal of evidence for some form of autoassociation of the methylviologen cation radical.[15] For example, dimerization has been demonstrated in aqueous solutions by UV–vis spectroscopy.[16] To explore the extent of dimerization in our systems and to assess the effects, if any, of the different micellar environments on the dimerization equilibium, eq 5, absorption spectra were examined. The absorption spectrum

$$2MV^{+\cdot} \rightleftharpoons (MV^{+\cdot})_2 \qquad (5)$$

of a 1.0 mM MV^{2+} solution, exhaustively reduced at –0.8 V vs. SCE, is given in Figure 5. The presence of CTAB or Triton X-100 micelles does not alter the spectral features, which correspond predominantly to the monomer.[16] The presence of some dimer can be deduced from the peak at 562 nm; the magnitude of this peak is consistent with the reported value of 380 M^{-1} for the dimerization constant;[16] i.e., at a total $MV^{+\cdot}$ concentration of 1.0 mM, the monomer and dimer concentrations should be 0.66 and 0.16 mM, respectively. In contrast to this, the absorption spectrum in the presence of SDS micelles (Figure 5) does not show a defined peak near 560 nm, indicating that the dimer concentration in this solution is greatly decreased. This spectrum closely corresponds to those reported for $MV^{+\cdot}$ in nonaqueous solvents where dimerization is substantially depressed.[16b] We conclude that the cation radical exists predominately in the monomeric form, in SDS solutions, where the dimerization equilibrium constant is decreased. The presence of other surfactant micelles in the solution does not affect the dimerization equilibrium, at least not in a detectable way.

ESR Experiments. The ESR spectrum of a 70 mM SDS solution containing 1 mM $MV^{+\cdot}$, prepared by exhaustive electrochemical reduction of a 1 mM MV^{2+} solution, is shown in Figure 6a. The spectrum is similar to those previously reported in the absence of micelles in aqueous solution[9a] or in nonaqueous solvents.[16,17] The hyperfine structure is due mainly to the coupling of the unpaired electron with two equivalent nitrogen nuclei and six equivalent hydrogen nuclei. The tumbling of the cation radical does not slow down noticeably in the presence of SDS micelles, perhaps as a result of the dynamic nature of micellar aggregates. However, the hyperfine structure of the ESR spectrum of $MV^{+\cdot}$ is known to be extremely sensitive to the presence of unreduced MV^{2+} in solution. This is attributed to the electron exchange reaction in eq 6. In isotropic aqueous solution the ESR spectrum

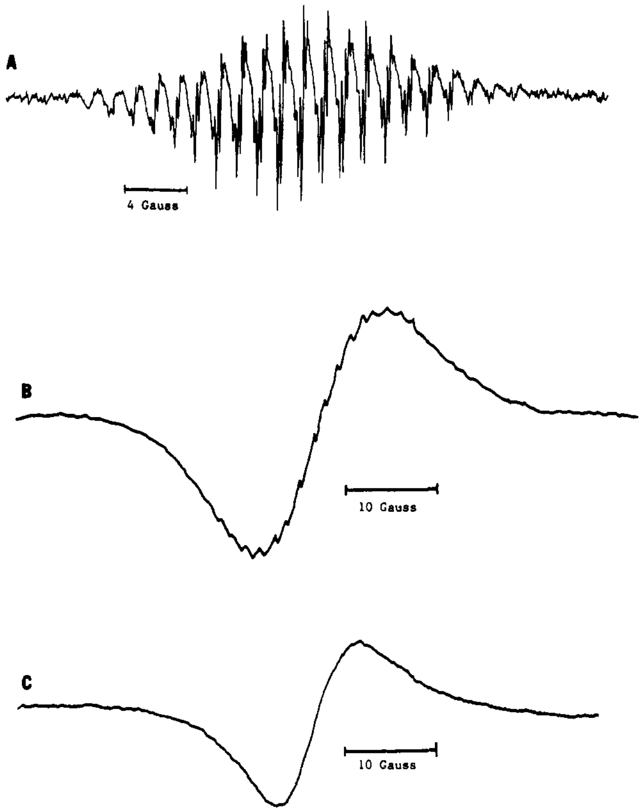


Figure 6. ESR spectra of reduced MV^{2+} in aqueous 50 mM NaCl. (A) 1.0 mM reduced MV^{2+} in the presence of 70 mM SDS, (B) 1.0 mM reduced MV^{2+} in the presence of 0.1 M MV^{2+} and 70 mM SDS, and (C) 1.0 mM reduced MV^{2+} in the presence of 0.1 M MV^{2+} and 70 mM CTAB. Modulation amplitude ≤ 0.1 G, microwave power ≤ 5 mW.

$$MV^{+\cdot} + MV^{2+} \rightleftharpoons MV^{2+} + MV^{+\cdot} \qquad (6)$$

of a 1 mM $MV^{+\cdot}$ solution that contains 0.1 M MV^{2+} consists of only a single broad and featureless line due to the rapidity of the electron exchange process.[9a] When the same experiment was performed in the presence of SDS at the 70 mM concentration level, the ESR spectrum still showed some hyperfine structure superimposed to a broad line (Figure 6b). This result suggests that the SDS micelles slow down the rate of the electron exchange process. The same experiment, performed with cationic CTAB or nonionic Triton X-100 micelles at the same concentration levels, yields an ESR spectrum without any hyperfine structure, i.e., indistinguishable from that recorded in the absence of surfactants (Figure 6c).

Discussion

In a surfactant solution the concentration of micelles, [M], for a given total concentration of surfactant, C_s, is given by eq 7, where

$$[M] = (C_s - \mathrm{cmc})/N \qquad (7)$$

cmc represents the critical micelle concentration and N is the aggregation number. It is well-known that both the aggregation number and cmc are affected by the addition of electrolytes to the surfactant solution. However, the level of supporting electrolyte (50 mM) used in this work was sufficiently low as to not change significantly the aggregation number of the surfactants.[12] Thus, if we assume that the addition of 1.0 mM $MVCl_2$ does not affect the aggregation properties of the surfactant solution, the effective micelle concentration can be estimated from the cmc. In the case of SDS micelles, using a cmc of 2.25 mM[14] and an aggregation number of 60[12], we calculate a micelle concentration

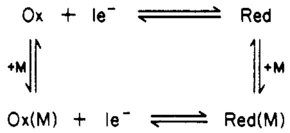
---

(15) Bard, A. J.; Ledwith, A.; Shine, H. J. *Adv. Phys. Org. Chem.* **1976**, *13*, 155.

(16) (a) Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *86*, 5524–5527. (b) Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617–2619.

(17) (a) Johnson, C. S.; Gutowski, H. S. *J. Chem. Phys.* **1963**, *39*, 58. (b) Guerin-Ouler, D.; Nicollin, C. *Mol. Phys.* **1977**, *34*, 161.

SCHEME I



of 1.1 mM for a surfactant concentration of 70 mM. In the case of either CTAB or Triton X-100 micelles similar micelle concentrations are estimated on the basis of existing cmc and aggregation number data.[7] Therefore, the concentration of micellar aggregates is about the same as that of methylviologen under our experimental conditions.

The electrochemical evidence presented here indicates the association between $MV^{+}\cdot$ and SDS micelles. That the conproportionation constant reaches a maximum value (see Table I) in the presence of SDS clearly supports this affirmation. Other reports had previously established that $MV^{+}\cdot$ also interacts with SDS micelles.[8] Indeed, this interaction is consistent with the observed seven fold decrease in the MV^{2+} diffusion coefficient upon addition of SDS to the isotropic aqueous solution. For a redox couple in which the oxidized and reduced forms interact with micellar aggregates Scheme I applies. Equation 8 may then be used to relate the formal potentials of the redox couples and the association of the oxidized and reduced species with the micellar aggregates

$$E_M{}^{0\prime} - E^{0\prime} = RT/F \ln (K_R/K_O) \qquad (8)$$

where $E^{0\prime}$ and $E_M{}^{0\prime}$ represent the formal potentials of the redox couple in the absence and in the presence of micelles, and K_R and K_O stand for the association constants of the reduced and oxidized species, respectively, with the micelles. From the reported value for the association constant between MV^{2+} and SDS micelles, 868,[8b] and the data in Table I, a value of 4100 is derived from eq 8 for K_R, the association constant of $MV^{+}\cdot$ and SDS micelles. The potentials in Table I are half-wave potentials and the error introduced in this calculation is larger than usual, because the presence of micelles gives rise to significant differences in the diffusion coefficients of the electroactive species involved. However, the error margin for this figure is estimated to be $\leq 10\%$, and clearly SDS micelles associate more strongly with $MV^{+}\cdot$ than with MV^{2+}.

That this is the case is clearly supported by the ESR experiments. The ESR spectrum of a 1.0 mM solution of the cation radical is unaltered by the presence of micelles at similar concentration levels, even in the case of the anionic SDS micelles where $MV^{+}\cdot$ is strongly associated with the micelles. This can probably be attributed to the highly dynamic nature of micellar aggregates so that they do not slow down, to an appreciable extent, the tumbling rate of the paramagnetic cation. Even when associated to much more rigid assemblies, such as dihexadecyl phosphate vesicles[8c] or a polymeric Nafion matrix,[9a] $MV^{+}\cdot$ shows an ESR spectrum with only a small amount of broadening. The association with SDS micelles is clearly evident in the ESR spectra of solutions containing 1.0 mM $MV^{+}\cdot$ and 0.1 M MV^{2+}. Under these conditions the electron exchange rate between the paramagnetic cation and the diamagnetic dication (in 100-fold excess) is so large that no hyperfine structure is detected in isotropic aqueous solution. The presence of CTAB or Triton X-100 micelles does not change these spectral features. However, SDS micelles at the 1.0–1.1 mM level (near 70 mM of total SDS concentration) allow the observation of an ESR spectrum with some hyperfine structure. Simple equilibrium calculations, with the association constants given above, show that, under these experimental conditions (total micelle concentration 1.1mM), 5% of the micelles are associated with $MV^{+}\cdot$, 94% are associated with MV^{2+}, and 1% are "free" micelles. In other words, approximately 95% of the cation radicals would remain unassociated in the bulk solution and undergo fast electron exchange with the neighboring dications, while the remaining 5% would be micellized and be relatively shielded from the dications. This fraction of cation radicals would thus be responsible for the residual hyperfine structure observed under these experimental conditions. A recent report from this laboratory[9a] has shown that $MV^{+}\cdot$ incorporated into a polymeric Nafion film in the presence of excess MV^{2+} displays ESR spectra without any loss of hyperfine structure. Therefore, the perfluorosulfonate polymer decreases the electron exchange rate corresponding to eq 6. The effect of SDS micelles is similar, although probably of smaller magnitude because of the differences in number and spatial distribution of binding sites between both systems.

Dimerization of the cation radical is always a complication to be considered in the chemistry of alkylviologens. However, the absorption spectra of all the methylviologen solutions used in this work showed evidence for the predominance of the monomeric form. This is the expected result, since the $MV^{+}\cdot$ concentration was always relatively small, preventing extensive dimer formation. The presence of CTAB or Triton X-100 micelles does not shift the dimerization equilibrium on a detectable extent. However, in SDS micellar solutions the dimer concentration was found to be extremely small, almost undetectable at the 1.0 mM $MV^{+}\cdot$ level. This is reminiscent of the situation in nonaqueous solvents in which the dimerization of the alkylviologen cation radicals is much less favored than in aqueous media.[16b] These facts suggest that the average environment of the methylviologen cation radical in SDS micellar solutions is predominantly water-free. In principle, this indicates that the micelle core will be the residence site, but it is well-known that, in spite of its hydrophobic nature, it is not impermeable to water molecules.[2] However, recent work points toward a relatively closed and well-defined structure for SDS micelles.[18] Thus, an alternative would be to recognize that the $MV^{+}\cdot$ can penetrate the micellar surface and associate with the hydrocarbon core via hydrophobic interactions.

Conclusions

Significant micellar effects are observed on the reductive electrochemistry of methylviologen. The stability toward disproportionation of the methylviologen cation radical decreases in the order SDS micelles > H_2O > Triton X-100 micelles > CTAB micelles. Although this might be interpreted in terms of electrostatic interactions, with the anionic micelles giving rise to the largest stabilization of the cation radical, the observed stronger association of $MV^{+}\cdot$ compared to MV^{2+} suggests that other factors are also important. For example, $MV^{+}\cdot$ shows a more pronounced hydrophobic character, so that hydrophobic interactions are postulated to play an important role in the interaction between the cation radical and the micelle. Thus, the dication might interact with the micelle ionic head groups (essentially as a counterion) while the cation radical, due to its increased hydrophobic nature, can penetrate farther to the micellar hydrocarbon core. This conclusion is supported by the decrease of the equilibium constant for dimerization of $MV^{+}\cdot$ as well as the decrease in the rate of electron transfer between the dication and monocation in the presence of SDS micelles, as determined by ESR. These effects were not observed in CTAB or Triton X-100 micellar solutions.

Since the relative stabilities of redox species and the rate of electron transfer among them are crucial to the design of artificial photosynthetic schemes, electrochemical techniques might be useful in assessing the effects that membrane-like structures exert on these parameters.

Acknowledgment. A.K. thanks the MARC program (N.I.H.) for a postdoctoral fellowship. This research was supported by a grant from the National Science Foundation (CHE-8402135).

Registry No. MV^{2+}, 4685-14-7; $MV^{+}\cdot$, 25239-55-8; MV, 25128-26-1; SDS, 151-21-3; CTAB, 57-09-0; NaCl, 7647-14-5; C, 7440-44-0; Triton X-100, 9002-93-1.

---

(18) (a) Szajdzinska-Pietek, E.; Maldonado, R.; Kevan, L.; Jones, R. R. M.; Coleman, M. *J. Am. Chem. Soc.* **1985**, *107*, 784–788. (b) Szajdzinska-Pietek, E.; Maldonado, R.; Kevan, L.; Jones, R. R. M. *J. Am. Chem. Soc.* **1984**, *106*, 4675.