THE JOURNAL OF
PHYSICAL CHEMISTRY

# Effects of sodium dodecyl sulfate at concentrations near the critical micelle concentration on the first cyclic voltammetric wave of methylviologen

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*J. Phys. Chem.*, **1987**, 91 (7), 2006-2007 • DOI: 10.1021/j100291a066

Journal of Physical Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

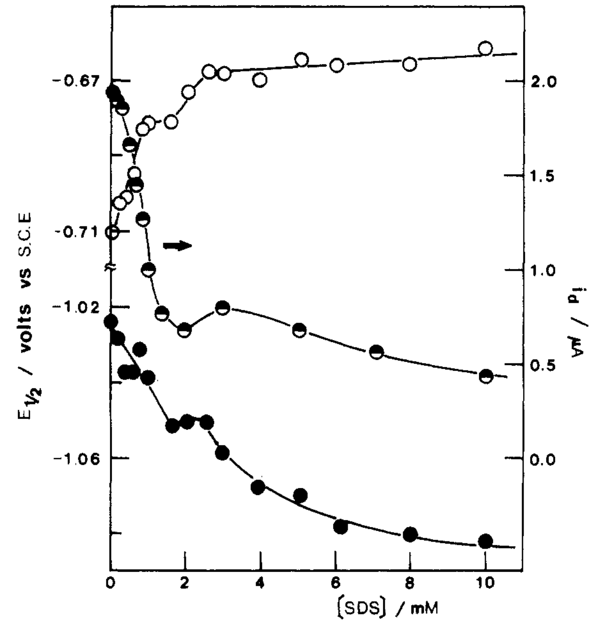

**Figure 1.** Variations of half-wave potentials corresponding to $MV^{2+}/MV^{\cdot+}$ (○) and $MV^{\cdot+}/MV$ (●) couples with [SDS] in aqueous 0.1 M NaCl solutions at 25 °C. These data were taken from cyclic voltammograms and are essentially the same as those from polarograms in ref 2. (◒) are diffusion currents of the normal second reduction wave of $MV^{2+}$ taken from ref 2.

polarographic studies on the same systems. However, the explanation on the nature of the interactions of $MV^{2+}$ and its reduced cationic radical, $MV^{\cdot+}$, with sodium dodecyl sulfate (SDS) near or below the critical micelle concentration (cmc) of the surfactant is considerably different from ours. We would like to present some comments on this, based on the results of our publication[2] and other experimental results.

One major contention is on the interaction of $MV^{\cdot+}$ radical with dodecyl sulfate anion ($DS^-$). Kaifer and Bard attributed large parabolic anodic peaks for the oxidation of $MV^{\cdot+}$ to $MV^{2+}$ in the cyclic voltammogram when [SDS] is 0.1–2 mM to the deposition of the cation radical on the glassy carbon electrode surface, triggered by SDS. Essentially the same cyclic voltammograms were observed in this laboratory by using a platinum electrode as well as a glassy carbon electrode on the $MV^{2+}$–SDS system. However, in agreement with results of our polarographic study,[2] a close examination of the cyclic voltammograms revealed that the half-wave potentials of the $MV^{2+}/MV^{\cdot+}$ and $MV^{\cdot+}/MV$ couples are highly dependent on the concentration of SDS, as shown in Figure 1, regardless of the electrodes used. This indicates that the variation of $E_{1/2}$ and the pattern of cyclic voltammograms with [SDS] do not arise from deposition of $MV^{\cdot+}$ onto the electrode surface as Kaifer and Bard explained,[1] but from interaction of $MV^{2+}$ and its reduced cationic radical ($MV^{\cdot+}$) with SDS. The changes in half-wave potentials were accompanied by a large decrease in the diffusion current ($i_d$) of the normal second reduction of $MV^{2+}$ (see Figure 1).[3] However, the $i_d$ of the first reduction was virtually unaffected by the presence of SDS, up to ca. 2 mM SDS in 0.1 M NaCl solutions. These observations clearly suggest association of the reduced $MV^{\cdot+}$ with dodecyl sulfate anion, while there is no appreciable interaction between $MV^{2+}$ and SDS, when [SDS] < 2 mM. The coupled reactions can be written as follows:

$$MV^{2+} + e^- = MV^{\cdot+} \qquad (1)$$

$$MV^{\cdot+} + pDS^- = MV^{\cdot+}(DS^-)_p \qquad (2)$$

In this case, it is expected that the half-wave potential corresponding to the first reduction (eq 1) varies linearly with log [SDS] with a slope of 59($p$) mV.[4] Indeed, the plot yielded good linearity with a slope of 63 mV, in the SDS concentration range of 0.2–1 mM.[2] This implies that the stoichiometric ratio of the association, $p$, is 1. The lower limit of [SDS], 0.2 mM, for the linearity can be attributed to the requirement of minimum concentration of SDS for the linearity.[5] The upper limit is due to the cooperative association of $MV^{2+}$ with SDS discussed below. The association constant was estimated to be $7 \times 10^3$ $M^{-1}$ from the plot.

The other contention is the cooperative association of $MV^{\cdot+}$ with SDS. Figure 1 shows an abrupt increase in the diffusion current of the normal second reduction at about [SDS] = 2 mM. We also observed a slight decrease in $E_{1/2}$ of the first reduction as [SDS] is increased to about 2 mM. These results suggested a cooperative association of $MV^{2+}$ with SDS: the temporal increase in $i_d$ of the normal second reduction reflects the decreased concentration of $DS^-$, which arises from depletion of free $DS^-$ due to the association. The formation of SDS micelle and solubilization of $MV^{\cdot+}$ in the micelle proposed by Kaifer and Bard[1] cannot explain this observation as well as the dependence of $E_{1/2}$ on [SDS].

A clearer evidence of the cooperative association of $MV^{2+}$ with SDS was revealed in the conductometric titrations of $MV^{2+}$ solutions with SDS in the absence of added salt.[2] When [SDS] < 1 mM, the slope of conductance vs. [SDS] plots was observed to be virtually constant, regardless of the presence of $MV^{2+}$. However, large curvatures in the plots were exhibited near [SDS] = 1 mM, which is far below the cmc of the surfactant, 8 mM.[6] This curvature can be taken as evidence of the cooperative premicellar association of $MV^{2+}$ with SDS. The similar premicellar association of $MV^{2+}$ with SDS was also revealed in charge-transfer complexing,[7] pulse radiolysis,[8] and fluorescence quenching[9] studies which involved $MV^{2+}$ in SDS solutions of low concentration. Therefore, the claim of detection of cmc of SDS made by Kaifer and Bard[1] under the assumption that neither $MV^{2+}$ nor $MV^{\cdot+}$ interacts with SDS below the cmc of the surfactant should be seriously reconsidered.

*Acknowledgment.* This work was supported, in part, by the Korea Science and Engineering Foundation. Y.H.P. is a recipient of fellowship from KOSEF.

**Registry No.** SDS, 151-21-3; $MV^{2+}$, 4685-14-7; $MV^{\cdot+}$, 25239-55-8.

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[3] Besides the normal second reduction wave ($MV^{\cdot+}/MV$) near −1.0 V vs. SCE, we observed another reduction wave near −1.3 V in the polarograms of $MV^{2+}$ taken in the presence of SDS. This new wave increased as the normal second reduction wave decreased by the addition of SDS. We assigned this as the reduction wave of $MV^{\cdot+}$–$DS^-$.[2]

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(5) The linearity between $E_{1/2}$ and log [SDS] is a semiempirical relationship under the condition $[MV^{\cdot+}DS^-] \ll$ [SDS]. Since $MV^{\cdot+}$ is generated during electrochemical measurements, the concentration of $MV^{\cdot+}DS^-$ is expected to be much lower than that of $MV^{2+}$(1 mM), satisfying the linearity condition above SDS concentrations of 0.2 mM.

(6) We also observed a break in the conductance vs. [SDS] plot at about [SDS] = (8 + $[MV^{2+}] \times 2$) mM. This was interpreted as an indication that $MV^{2+}$–SDS association is completed before micellization of excess SDS, and $MV^{2+}$ is not *directly* involved in the formation of SDS homomicelle.

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*Received: January 14, 1986; In Final Form: July 9, 1986*

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## Effects of Sodium Dodecyl Sulfate at Concentrations near the Critical Micelle Concentration on the First Cyclic Voltammetric Wave of Methylviologen

*Sir:* In the course of our investigation on the effects of anionic, cationic, and nonionic micelles on the reductive electrochemistry of methylviologen,[1] we noticed remarkable changes in the shape

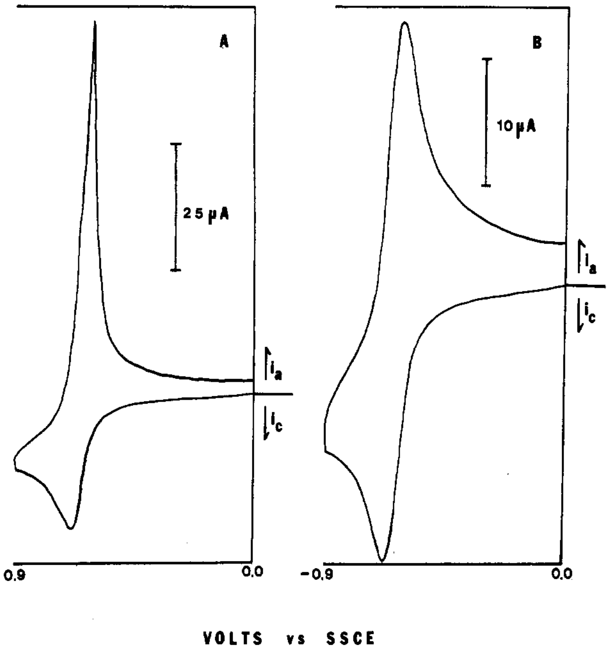

**Figure 1.** Cyclic voltammograms at a glassy carbon electrode of 1.0 mM methylviologen in aqueous 50 mM NaCl solution containing (A) 6 mM SdecS and (B) 12 mM SdecS (scan rate 100 mV/s).

of the cyclic voltammograms at concentrations near the cmc of the anionic surfactant used (sodium dodecyl sulfate, or SDS). Our interpretation of these specific results is now questioned by Park and Paik (PP),[2] who present evidence for the premicellar association of the cation radical of methylviologen ($MV^{\bullet +}$) with the monomeric dodecyl sulfate anion. While we did not address the question of premicellar association of $MV^{\bullet +}$ with $DS^-$, such an association is not inconsistent with our results and our interpretation concerning the effect of SDS concentration on adsorption of $MV^{\bullet +}$.

Our cyclic voltammogram at glassy carbon showed that the first reduction of methylviologen in the presence of SDS concentrations ranging from 0.2 to 2.0 mM exhibits a sharp anodic peak on scan reversal (see Figure 4 in ref 1). The shape of this peak clearly indicates the weak adsorption of the product of the electron-transfer process at the electrode surface. This agrees with the analysis of Wopschall and Shain[3] on the effects of adsorption on the shape of current–potential curves in linear and cyclic potential scan techniques, where enhanced currents and symmetry on the anodic scan arise from the accumulation of electrochemical product on the electrode surface. Therefore, in this SDS concentration range, the cation radical clearly is weakly adsorbed on the electrode surface after its electrogeneration from the freely diffusing dication. Since surfactant ions or molecules are known to adsorb at solid–liquid interfaces,[4] the obvious conclusion is that adsorbed $DS^-$ ions hold the $MV^{\bullet +}$ species near the electrode surface. Notice that there is an implicit admission of the interaction between these two species in this statement. PP's results actually reinforce our conclusion by providing evidence for such an interaction.

When the concentration of SDS is increased above 2.0 mM, the anodic peak loses sharpness and the usual shape (controlled by diffusion) gradually reappears. Again, this can only be taken as evidence for the elimination of the conditions leading to the adsorption of the cation radical. In our experiments we utilize 50 mM NaCl as the supporting electrolyte. The cmc of SDS at this level of NaCl has been reported to be 2.25 mM.[5] It is then very likely that the onset of micelle formation or premicellar aggregates is responsible for the disappearance of the $MV^{\bullet +}$ adsorption pattern. Indeed, surfactant solutions at concentrations near the cmc are very complex systems in which premicellar aggregates can play an important role. The presence of 1.0 mM $MV^{2+}$ might also alter the aggregation properties of $DS^-$ ions at these concentrations. However, the concentration range where the $MV^{\bullet +}$ adsorption is eliminated strongly suggests that micelles (and perhaps premicellar aggregates) are involved in the solubilization of the cation radical.

In summary, we believe that our results clearly demonstrate the adsorption of $MV^{\bullet +}$ in the 0.2–2 mM SDS concentration range, with the adsorption effects disappearing at higher SDS concentrations. In fact, recent experiments with methylviologen and sodium decyl sulfate (SdecS) show similar effects[6] (Figure 1). PP base their objections[2] on their finding of association between $MV^{\bullet +}$ and $DS^-$. We do not dispute this interaction at all but fail to see how it can explain the adsorption effects observed below the cmc and the return to diffusion control above the cmc (a finding not addressed by PP). The interaction of one of the redox forms involved in an electron-transfer process with another solution component may certainly shift the potential of the redox couple, but the sharp anodic peaks observed in our work are undoubtedly caused by the weak adsorption of the cation radical. In addition, PP also report a cooperative $MV^{2+}$–$DS^-$ interaction which seems to be of no concern in the interpretation of our results, because they acknowledge that it is not appreciable when [SDS] $< 2$ mM. We must also point out that their experiments were performed in 0.1 M NaCl solutions which makes the cmc of the surfactant slightly lower (1.49 mM) from that found under our experimental conditions (2.25 mM) where the salt concentration was 0.05 M.

*Acknowledgment.* This research was supported by the National Science Foundation (Grant CHE-8402135) and the University of Miami Research Council.

**Registry No.** SDS, 151-21-3; C, 7440-44-0; $DS^-$, 557-47-1; NaCl, 7647-14-5; $MV^{\bullet +}DS^-$, 106762-34-9; MV, 1910-42-5.

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*Received: August 8, 1986*

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## Comment on Size Measurement of SERS-Relevant Silver Colloid Particles by Photon Correlation Spectroscopy

*Sir:* A theoretical understanding of the surface-enhanced Raman scattering (SERS) effect—observed with colloidal silver solutions—requires knowledge of the colloidal particle size. In a number of papers this size has been derived from light absorption studies of colloidal silver solutions[1–4] or from transmission electron microscopy studies of the colloidal particle residue after evaporation of the solvent.[1,3,5–7]

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