The TS(3a) (1,3-(C, N, O)-H shift) is similar to the TS in the 1, 3-(O, C)-H shift of vinyl alcohol,[1b] but here again large antibonding interaction between the rearranging H atom and p_y lone pair of the central N atom tends to increase barrier height. On the other hand, the position of the TS is consistent with the Hammond postulate as it was found for the 1, 3-(C, O)-H shift.[1b] In the TS(3a) the OH bond length is considerably long since the enol form is more stable than the keto form.

The relative energy barriers for various 1,3-H shifts studied in this work are presented in Figure 1.

In this system, the reaction pathway via two 1,2-H shifts involving an intermediate, (III), is more favorable than the corresponding 1,3-H shift as it was found to be the case for nitrous acid. The energy profiles for various 1,2-H shifts are presented in Figure 2.

In conclusion, our MINDO/3 results predict the relative reactivity of the three systems studied to be 1,2-(O, N, O)-H $<$ 1,2-(C, N, O)-H $<$ 1,3-(C, N, C)-H, which is exactly the opposite to that found for corresponding systems with central carbon atom.

Acknowledgements. We are grateful to the Ministry of Education and the Korea Research Center for Theoretical Physics and Chemistry for support of this work.

References

(1) (a) I. Lee, J. K. Cho, and B-S. Lee, *J. Comput. Chem.*, in press; (b) J. K. Cho, I. Lee, H. K. Oh and I. H. Cho, Submitted for Publication in *J. Korean Chem. Soc.*

(2) (a) R. C. Bingham, M. J. S. Dewar, and D. M. Lo, *J. Amer. Chem. Soc.*, 97, 1285 (1975); (b) M. L. Olson and J. F. Chiang, QCPE, 10, 309 (1976).

(3) (a) I. Lee, *Bull. Korean Chem. Soc.*, **1**, 4 (1980); (b) L. R. Larson, N. D. Epiotis, and F. Bernardi, *J. Amer. Chem. Soc.*, **100**, 5713 (1978); (c) L. Radom, W. J. Hehre, and J. A. Pople, *ibid*, **94**, 2371 (1972); (d) L. Radom, W. J. Hehre and J. A. Pople, *ibid.*, **93**, 289 (1971).

(4) P. D. Adeney, W. J. Bouma, L. Radom and W. R. Rodwell *ibid.*, **102**, 4069 (1980).

(5) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(6) (a) T. J Zielinski, D. L. Breen, and Rein, *ibid.*, **100**, 6266 (1978); (b) G. Klopman, P. Andreozzi, A. J. Hopfinger, O. Kikuchi, and M. J. S. Dewar, *ibid.*, **100**, 6267 (1978).

Association of Methyl Viologen and Its Cationic Radical with Sodium Dodecyl Sulfate

Joon Woo Park† **and Hye-L. Nam**

Department of Chemistry, College of Natural Sciences, Ewha Womans University, Seoul 120, Korea

(*Received April 130, 1984*)

The polarographic and conductometric studies of methyl viologen (MV^{++}) solutions with varying concentration of sodium dodecyl sulfate (SDS) showed strong association of MV^{++} and its cationic radical, MV^{+}., with SDS below the critical micelle concentration. The stoichiometries of these associations were found to be their electric charge ratios. Both electrostatic and hydrophobic interactions were found to contribute to the associations. The formation constant of $MV^{+}.DS^{-}$ in 0.1M NaCl was 7×10^{3}M. The MV^{++}-SDS association was observed to be cooperative leading to formation of large aggregates. In the presence of MV^{++}, the micellization of SDS was formation of SDS homo-micelle without direct involvement of MV^{++}.

Introduction

The chemistry of N,N′-dimethyl-4,4′-bipyridinium (methyl viologen: MV^{++}) has been subjects of intense studies because of the intrinsic interest of the chemistry and the promise in use of the viologen and related compounds in solar energy conversion and electrochromic displays, and as a herbicide and a probe for various biological systems.[1,2] Most of interesting properties of methyl viologen arise from strong electron affinity of MV^{++}, and stability of violet-colored cationic radical, MV^{+}. The radical can be formed via chemical, electrochemical or photosensitized reduction of MV^{++}. Chemical properties of MV^{+}, as well as MV^{++} play critical roles in many applications of MV^{++}, and the properties strongly depend on the nature of the system employed.

To enhance desirable characteristics of MV^{++} and to provide biologically mimetic environment for MV^{++}, microheterogeneous systems were extensively utilized: these include the use of amphiphilic viologens[3-6], amphiphilic electron donors[3,7-9], surfactant vesicles[10-13], and micelles[3,7,8,14-20]. The effects of these systems on the reduction potentials of viologens[14], the stability of charge transfer complexes between viologens and electron donors[15,16], and the efficiency of the electron transfer process from excited photosensitizers to viologens leading to the formation of viologen radical ions[4,9,19,20] have been well recognized. These effects were mainly attributed to the interaction of viologens and electron donors with charged micelles or vesicles. However, the nature of this interaction is not known in detail.

In recent papers,[16,17] the association of MV^{++} with SDS below the critical micelle concentration of the surfactant were suggested. The presence of the submicellar association can lead to alternative explanation of so-called 'micellar effects' on MV^{++}, and many desirable properties of MV^{++} can be obtained below CMC of the surfactant. In this report, we present results of polarographic and conductometric studies on the MV^{++}-SDS system performed to explore the detailed nature of the interaction between MV^{++}, as well as MV^{+}, and SDS.

Experimental

Methyl viologen dichloride was prepared by reacting 4, 4'-bipyridine and methyl iodide in ethanol, followed by substitution of I^- into Cl^- as described elsewhere.[16] SDS was obtained from Kanto Chemical Co. and recrystallized from ethanol three times. Other chemicals were extra pure grade and used as received. All solutions were prepared with deionized distilled water.

Polarograms were taken from a Solea-Tacussel PRG 5 pulse polarograph using water jacketed sample container at 25°C under nitrogen atmosphere. A glass capillary of 60-80μm diameter was used as dropping mercury electrode, of which dropping time was controlled to 0.1 sec. Saturated calomel electrode (SCE) and Pt electrode were used as reference and auxiliary electrodes, respectively. Diffusion currents (i_d) were measured from DC polarograms taken at scan rate of 4mV/sec. Half-wave potentials ($E_{\frac{1}{2}}$) were obtained from differential polarograms recorded at scan rate of 2mV/sec with pulse height of 20mV. Solutions for polarographic measurements contained 0.1M NaCl and 0.004 % Triton X-100 as supporting electrolyte and maxima suppressor, respectively.

Condutivity measurements were performed at 25±0.1°C employing a Conductivity Bridge Model RC 150. UV spectra were taken from a Beckman DU-8B UV-VIS spectrophotometer at 25±0.1°C.

Results and Discussion

The normal DC polarograms of MV^{++} exhibited two well-separated reduction waves as shown in Figure 1. In the absence of SDS, i_d's of both steps were nearly same, and the nernstian plots of both waves according to Eq. 1 yielded good straight lines with slope of 59mV, *i. e.*, $n=1$ (Figure not shown).

$$E=E_{\frac{1}{2}}+\frac{0.059(V)}{n}\log((i_d-i)/i) \qquad (1)$$

$E_{\frac{1}{2}}$ values of first and second waves were −0.705 and −1.04V *vs*. SCE, respectively. These results indicate that both reduction steps are reversible and one-electron processes, and agree well with previous reports.[21-23]

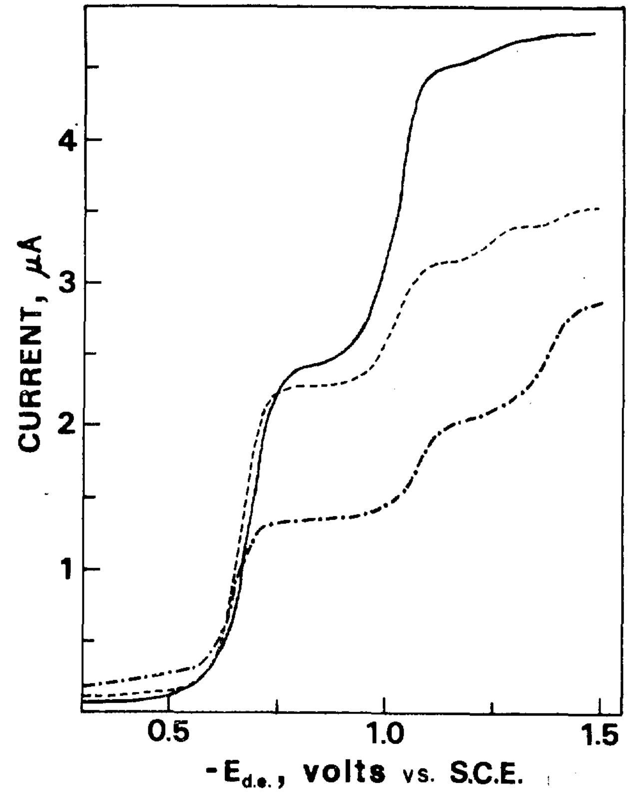

Figure 1. Variations of DC polarograms of 1×10^{-3} M MV^{++} in 0.1M NaCl at 25°C. SDS concentrations are 1×10^{-4}(——), 1.75×10^{-3}(- - - -), and $1.37\times10^{-2}M$(-·-·-·).

The addition of SDS resulted in marked changes in i_d and $E_{\frac{1}{2}}$ values of both reduction steps. However, the concentration range of SDS at which i_d and $E_{\frac{1}{2}}$ change was considerably different between two steps. When concentration of SDS is lower than 10^{-3} M, i_d of the second reduction wave appearing near −1.0V ($(i_d)_2$) decreases with increasing concentration of SDS, while that of the first step ($(i_d)_1$) remains virtually unchanged. The decrease in $(i_d)_2$ was accompanied by shift of $E_{\frac{1}{2}}$ of the first step ($(E_{\frac{1}{2}})_1$) to less negative values. The decrase in $(i_d)_1$ and shift of $E_{\frac{1}{2}}$ of the second step ($(E_{\frac{1}{2}})_2$) to more negative values were observed at higher concentration of SDS. Typical polarograms displaying effects of SDS are shown in Figure 1. The variation of i_d and $E_{\frac{1}{2}}$ values with the concentration of SDS are plotted in Figure 2 and 3, respectively.

The increased bulk viscosity of MV^{++} solutions at high SDS concentration can cause decrease in i_d of MV^{++}. However, the viscosity of MV^{++} solution increased only 6 % when concentration of SDS was increased from 1×10^{-4} to 1.5×10^{-2} M. This would result in only 3 % decrease in i_d, which is far less than amounts observed in this experiment. Thus, our observations can be attributed to interaction of MV^{++} and MV^{+} with SDS.

The difference in the concentration range of SDS at which $(i_d)_1$ and $(i_d)_2$ decrease as shown in Figure 2 indicates that MV^{++} and MV^{+} associate with SDS at different concentration range. The decrease in $(i_d)_2$ with increasing concentration of SDS, while $(i_d)_1$ remains virtually constant, up to [SDS] $=10^{-3}$ M can be interpreted that only MV^{+} associates with SDS in the condition. The association of MV^{++} with SDS appears at higher SDS concentration as can be judged from variation of $(i_d)_1$. These associations are reflected in changes of $E_{\frac{1}{2}}$'s as shown in Figure 3. Thus when [SDS] is lower

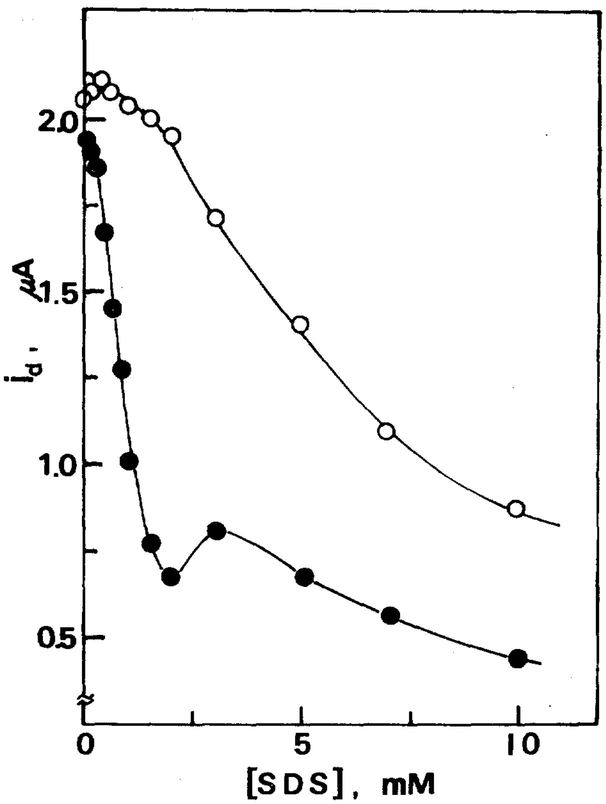

Figure 2. Diffusion currents vs [SDS] plots for 1×10^{-3} *M* MV^{++} at 25 °C: first reduction step(○); second reduction step(●).

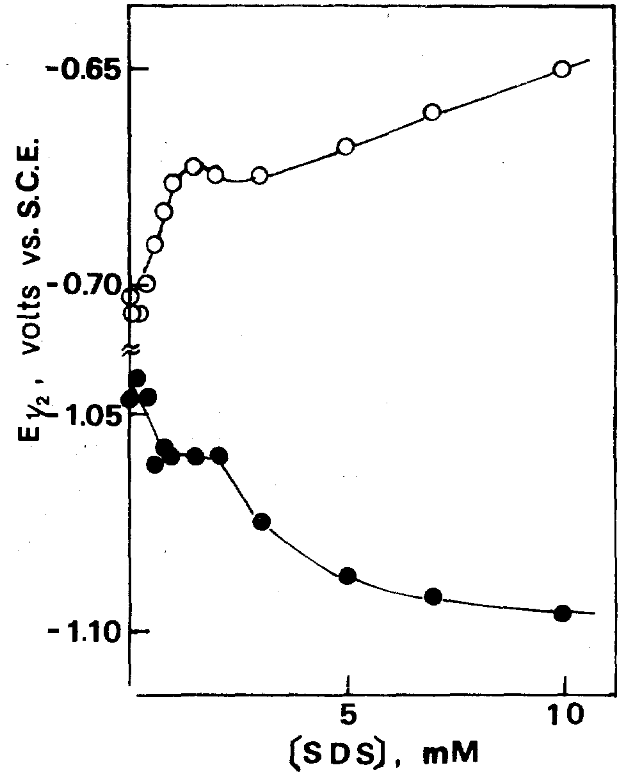

Figure 3. Variations of half-wave potentials of MV^{++} with [SDS]: first reduction step(○); second reduction step(●).

than 10^{-3} *M*, the reaction processes can be written as follows;

$$MV^{++} \underset{-1e}{\overset{+1e}{\rightleftharpoons}} MV^{\dagger} \qquad (2)$$

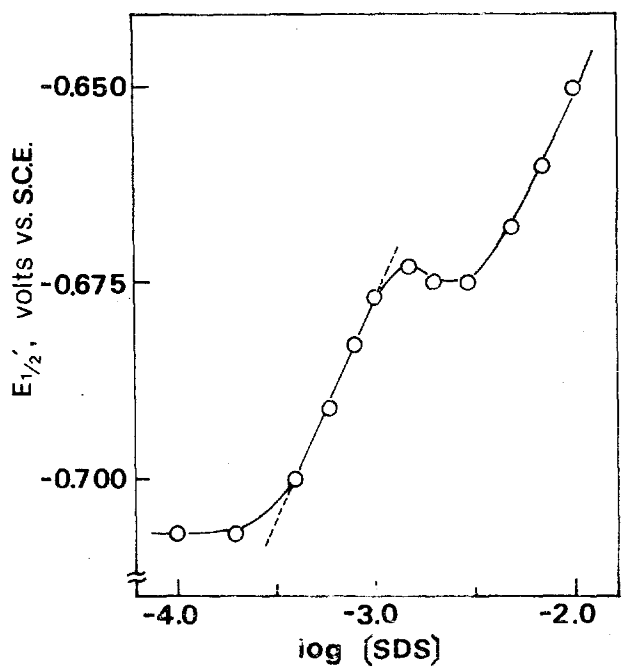

Figure 4. Plot of the half-wave potentials of the first reduction step of MV^{++} against log[SDS] accor ding to Eq. 4. [MV^{++}] is 1 m*M*.

$$MV^{\dagger} + p\,DS^- \rightleftharpoons MV^{\dagger}(DS^-)_p \qquad (3)$$

where DS^- and p denote dodecyl sulfate anion and stoichiometry of association, respectively. If $MV^{\dagger}(DS^-)_p$ is in equilibrium with $MV^{\dagger}$, and DS^- and MV^{++} does not associate with DS^-, half-wave potential of the first redution step of MV^{++} at 25°C ($E_{\frac{1}{2}}'$) should vary with SDS concentration following Eq. 4.[24,25]

$$E_{\frac{1}{2}}' = E_{\frac{1}{2}} + 0.059\log K + 0.059(p)\log[\mathrm{SDS}] \qquad (4)$$

In this equation, SDS is assumed to be completely dissociated. The plot of $E_{\frac{1}{2}}'$ vs log[SDS]would Yield straight line, and equilibrium constant (K) and p of the reaction 3 can be obtained from slope and intercept of the plot. Figure 4 shows the plot of our experimental data assuming [SDS] is total concentration of SDS in solutions. Good linearity between $E_{\frac{1}{2}}'$ and log [SDS] is evident in the range of $-3.4\sim-3.0$ of log [SDS]. The slope of this linear portion was 63mV, which is close enough to the value of 59mV for $p=1$. Thus, one can soundly conclude that each $MV^{\dagger}$ associates with one DS^-. The intercept of the linear region extrapolated to log [SDS]=0 was -580mV giving K value of 7×10^3 M from $E_{\frac{1}{2}}$ value, -705mV, which is $(E_{\frac{1}{2}})_1$ of MV^{++} in the absence of SDS.

Since the critical micelle concentration (CMC) of SDS in 0.1*M* NaCl is 1.4×10^{-3} *M*,[26] it can be concluded that $MV^{\dagger}$ associates with DS^- in monomeric state rather than micelle. Deviation from linearity in Figure 4 when log [SDS] is less than -3.5 can be attributed to nonequilibrium between $MV^{\dagger}$ and DS^- in the condition. Deviation at log $[\mathrm{SDS}] \gtrsim -3$ seems to araise from interaction between MV^{++} and SDS, which leads to change in electrochemical process of Eq. 2 and decrease in free SDS concentration.

Comparing Figure 2 and 3, the close correlation between variations of $(E_{\frac{1}{2}})_1$ and $(i_d)_2$ with [SDS] can be found. This result suggests that MV^+DS^- is not reduced near $-1.0V$, where MV^+ is reduced in the absence of SDS. In fact, we observed another polarographic wave near $-1.3V$ when SDS is present. The diffusion current of this new wave increased as $(i_d)_2$ decreased with increasing [SDS] (see Figure 1). Therefore, we can assume that $E_{\frac{1}{2}}$ of MV^+DS^- is about -1.3 V vs SCE.

The temporary increase of $(i_d)_2$ in Figure 2 and decrease of $(E_{\frac{1}{2}})_1$ in Figure 3 as [SDS] increases near $[SDS]=2\times10^{-3}$ M are of particular interest. These temporal behaviors of $(i_d)_2$ and $(E_{\frac{1}{2}})_1$ coincide with the sharp decrease of $(i_d)_1$, which reflects decrease in diffusivity of MV^{++}. The cooperative association of MV^{++} with SDS forming large aggregate could explain the observation. The aggregate formation would deplete free SDS leading to partial dissociation of MV^+DS^-, which manifests itself in increase in $(i_d)_2$ and decrease in $(E_{\frac{1}{2}})_1$. Even though the concentration of SDS at which MV^{++} associates with SDS cooperatively is close to CMC of SDS in the condition, formation of SDS micelle without cooperative interaction between MV^{++} and SDS could not explain our observation: formation of SDS homo-micelle would not decrease free SDS concentration below CMC, thus the increase in $(i_d)_2$ as [SDS] increases is not expected.

Further supporting evidences of cooperative association of MV^{++} with SDS were revealed in conductivity measurement of MV^{++} solutions with increasing [SDS]. The conductance vs [SDS] relationships at different concentration of MV^{++} are plotted in Figure 5. In the absence of MV^{++}, the plot exhibits two linear portions with a sharp break at 8×10^{-3} M SDS, which points to CMC of the surfactant.[26] When $[SDS]\lesssim10^{-3}$ M, slopes of conductance vs [SDS] plots were observed to be virtually same regardless of the presence of MV^{++}. This implies that there is no appreciable interaction between MV^{++} and SDS in this SDS concentration range. However, as [SDS] is further increasing, conductance vs [SDS] plots for solutions containing MV^{++} displayed a large curvature, linear portion, a break in linearity, and then another linear portion as [SDS] increases. The curvature appearing near 1×10^{-3} *M* SDS must be interpreted as cooperative association of MV^{++} with SDS. This conclusion is in good agreement with that drawn from polarographic studies. This finding also confirm earlier suggestions of interaction between MV^{++} and SDS at submicellar levels of SDS from charge transfer complexing,[16] pulse radiolysis,[17a] and fluorescence quenching[17b] studies of MV^{++}.

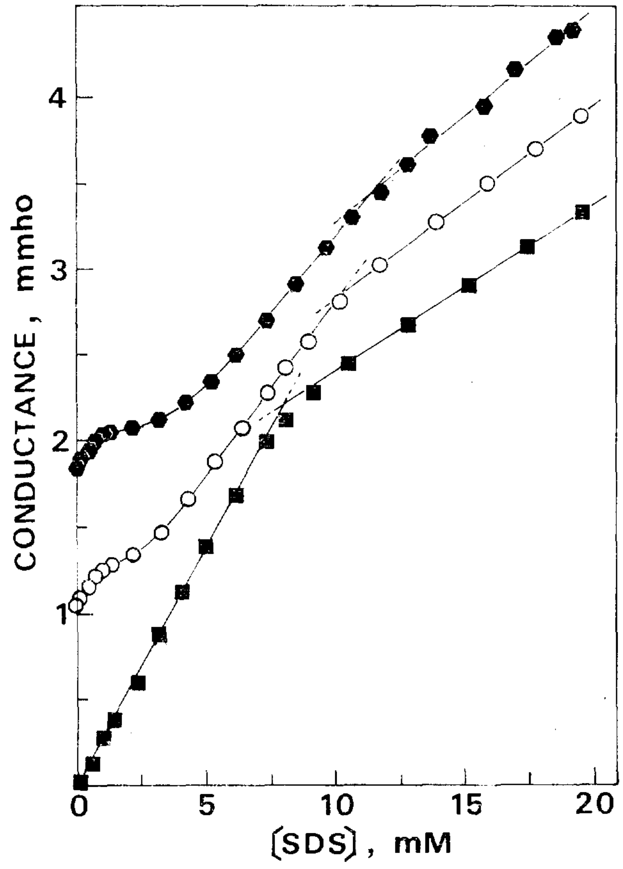

Figure 5. The conductance as a function of [SDS] at 25°C. $[MV^{++}]$ are 2×10^{-3} (●), 1×10^{-3} (○), and 0 *M* (■).

Breaks in linearity, at 10×10^{-3} *M* SDS for 1×10^{-3} *M* MV^{++} and 12×10^{-3} *M* SDS for 2×10^{-3} M MV^{++}, can be attributed to micellization of SDS. In polarographic measurements presented in previous sections, this micellization was not noticeable because of low CMC of SDS under high concentration of NaCl. The apparent CMC of SDS appears to increase with $[MV^{++}]$ by twice of $[MV^{++}]$ *i.e.*, $[CMC]_{app}=[CMC]_{[MV^{++}]=0}+2\times[MV^{++}]$, suggesting that each MV^{++} associates with two DS^-, i.e., in their charge ratio. This result also implies that $MV^{++}-2DS^-$ association is completed before micellization of excess SDS, and MV^{++} does not *directly* involve in the micellization.

The cooperativeness in MV^{++} $-$SDS association and the large decrease in $(i_d)_1$ of MV^{++} with [SDS] indicate that the association leads to formation of large aggregates, $(MV^{++}(DS^-)_2)_{agg}$. The aggregate formation would be favored energetically, because of hydrophobicity of $MV^{++}(DS^-)_2$. Since no noticeable precipitaion was observed visually as well as in UV measurement, the aggregates are believed to behave as colloidal particles, and have micelle-like structure. Formations of $MV^{++}(DS^-)_2$ aggregates and SDS homomicelle do not rule out the possibility of dissolution of the aggregate by SDS micelles and subsequent association of MV^{++} with micelle as suggested for intermicellar exchange of MV^{++}.[8] However, such redistribution of MV^{++} would not give any appreciable conductance change: the conductance of a micellar solution is mainly arised from free ions, and those incorporated into micelle contribute little to the conductance. On the other hand, the redistribution of MV^{++} would cause change of mean diffusivity of MV^{++}, and thus $(i_d)_1$. The decrease in $(i_d)_1$ over wide concentration range of SDS above CMC (Figure 2) may reflect the process.

The polarographic behavior of MV^{++} was also investigated in a non-ionic surfactant, Triton X-100, and in a cationic surfactant, CTAB. Over wide concentration range of the surfactants, reduction waves of both reduction steps were not affected significantly by the presence of the surfactants. Only CTAB caused the first reduction wave to appear at slightly more negative potential, but i_d of the wave was not changed with [CTAB] : this can be attributed to blocking effect of CTAB due to adsorption of the surfactant on mercury drops.[27] Therefore, the association of MV^{++} and $MV^{\dot{+}}$ with SDS can be accounted to the anionic character of the surfactant. This view is supported by stoichiometries of the association.

Besides the electrostatic interaction, the hydrophobic effect seems also to contribute to the association of MV^{++} and $MV^{\dot{+}}$ with SDS in great extent. This view is supported by the closeness of SDS concentration at which MV^{++} associates cooperatively with SDS in polarographic and conductometric studies, despite of large difference in the concenration of NaCl, *i.e.*, 0.1 *M vs.* 0 *M*. The large value of formation constant of $MV^{\dot{+}}DS^-$ in 0.1 M NaCl also supports the idea. The hydrophobic nature of MV^{++} $-$SDS association was manifested in microenvironment of MV^{++} at high SDS concentration in UV spectra (Figure 6). In water, UV spectrum of MV^{++} displayed a peak at 257nm with molar absorptivity of 19,000 $cm^{-1}M^{-1}$, whereas in $1\times10^{-2}\,M$ SDS the peak was at 260nm with molar absorptivity of 18,000 $cm^{-1}M^{-1}$. These changes are similar to those observed by Watanabe and Honda[28], changing the solvent for MV^{++} from H_2O to CH_3OH, C_2H_5OH, or CH_3CN. This implies that the association of MV^{++} with SDS provides slightly hydrophobic environment to the dication.

So far, we demonstrated that MV^{++} and $MV^{\dot{+}}$ associate strongly with DS^- in their charge ratios at submicellar levels of SDS. Both electrostatic and hydrophobic interactions were shown to contribute to the association. Since the association results in uncharged species, the electrostatic interaction does not involve even when charged electron donors interact with MV^{++} or $MV^{\dot{+}}$ in their associated forms.

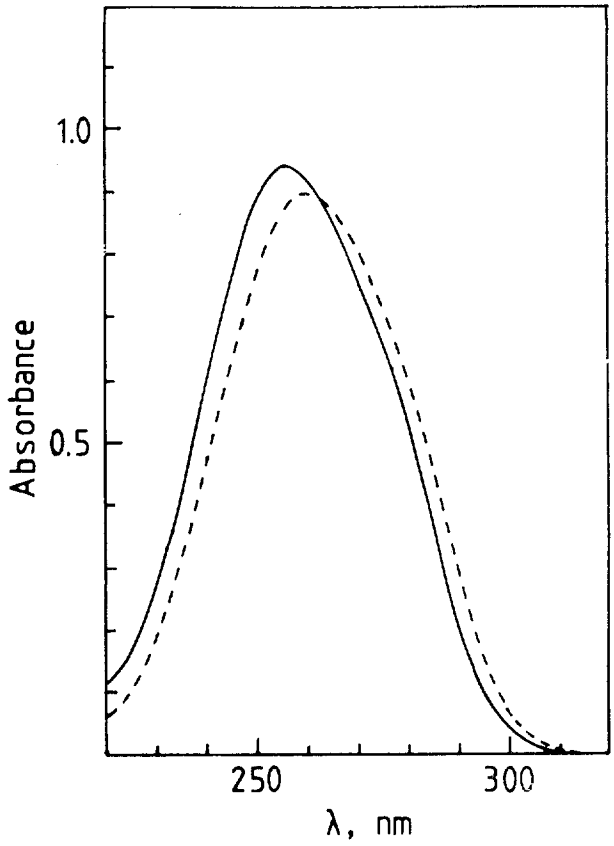

Figure 6. Absorption spectra of 5×10^{-4} M MV^{++} in the absence (——) and presence of $1\times10^{-2}\,M$ SDS (- - - -).

This can explain the reported strong enhancement of charge transfer complexing between MV^{++} and indole derivatives,[16] and efficient $Ru(bpy)_3{}^{2+}$ fluorescence quenching by MV^{++} at low concentration of SDS. From this nature, the use of low concentration of a surfactant may have advantage over conventional micellar systems of high surfactant concentration in many applications of MV^{++}. The formation of electrochemically stable $MV^{\dot{+}}DS^-$ without decreasing diffusivity of MV^{++} in low [SDS] can be utilized in the efficient electrochemical formation of $MV^{\dot{+}}$ without complicating further reduction of $MV^{\dot{+}}$. This property can resolve the limitation of viologens in using them in electrochromic displays.[29]

Acknowledgement. We gratefully acknowledge the financial support of Korea Science and Enginereing Foundation for this work.

References

(1) For recent reviews on the chemistry and applications of methyl viologen and related comdounds, see: (a) T. J. Meyer. *Acc.Chem. Res.*, **11**, 94 (1978); (b) D. G. Whitten, *Acc. Chem. Res.*, **13**, 82 (1980); (c) J. W. Park and H. –L.Nam, *Prog. Chem. Chem. Ind.*, **24**, 248 (1984).
(2) L. A. Summers, "The Bipyridinium Herbicides," Academic Press, New York, 1980.
(3) Y. Tsutsui, K. Takuma, T. Nishijima and T. Matsuo, *Chem. Lett.*, 617 (1979).
(4) P.–A. Brugger and M. Grätzel, *J. Amer. Chem. Soc.*, **102**, 2461 (1980).
(5) K. Takuma, K. Sakamoto, T. Nagamura and T. Matsuo, *J. Phys. Chem.* **85**, 619 (1981).
(6) P.–A. Brugger, P. P. Infelta, A. M. Braun and M. Grätzel, *J. Amer. Chem. Soc.*, **103**, 320 (1981).
(7) K. Kalyanasundaram, *J. Chem. Soc. Chem. Commun.*, 628 (1978).
(8) R. H. Schmehl and D. G. Whitten, *J. Amer. Chem. Soc.*, **102**, 1938 (1980).
(9) R. H. Schmehl, L. G. Whitesell and D. G. Whitten, *J. Amer. Chem. Soc.*, **103**, 3761 (1981).
(10) M. S. Tunuli and J. H. Fendler, *J. Amer. Chem. Soc.*, **103**, 2507 (1981).
(11) L. Y–C. Lee, J. K. Hurst, M. Politi, K. Kurihara and J. H. Fendler, *J. Amer. Chem. Soc.*, **105**, 370 (1983).
(12) S. Lukac and J. R. Harbour, *J. Amer. Chem. Soc.*, **105**, 4248 (1983).
(13) M. S. Tunuli and J. H. Fendler, *ACS Adv. Chem. Ser.*, **177**, 53 (1982).
(14) Y. Ohsawa, S. Shimazaki and A. Aoyagui, *J. Electroanal. Chem.*, **114**, 235 (1980).
(15) F. M. Martens and J. M. Verhoeven, *J. Phys. Chem.*, **85**, 1773 (1981).
(16) J. W. Park and S.–J. Kim, *Bull. Kor. Chem. Soc.*, **5**, 121 (1984).
(17) (a) M. A. J. Rodgers, D. C. Foyt and Z. Simek, *Radiat.*

Res., **75**, 296 (1978); (b) M. A. J. Rodgers and J. C. Becker, *J. Phys. Chem.*, **84**, 2762 (1980).

(18) J. P. Otruba and D. G. Whitten, *J. Amer. Chem. Soc.*, **105**, 6503 (1983) and references therein.

(19) T. K. Foreman, W. M. Sobol and D. G. Whitten, *J. Amer. Chem. Soc.*, **103**, 5333 (1981).

(20) T. Miyashita, T. Murakata and M. Matsuda, *J.Phys. Chem.*, **87**, 4529 (1983).

(21) L. Michaelis and E. S. Hill, *J. Amer. Chem. Soc.*, **55**, 1481 (1933).

(22) R. M. Elofson and R. L. Edsberg, *Can. J. Chem.*, **35**, 646 (1957).

(23) M. Mohammad, R. Iqbal, A. Y. Khan, M. Bhattl, K. Zahir and R. Jahan, *J. Phys. Chem.*, **85**, 2816 (1981).

(24) A. J. Bard and L. R. Faulkner, *"Electrochemical Methods,"* John-Wiley, New York, p. 34-37. 1980,

(25) G. L. McIntire and H. N. Blount, *J. Amer. Chem. Soc.*, **101**, 7720 (1979).

(26) M. F. Emerson and A. Holtzer, *J. Phys. Chem.*, **71**, 1898 (1967).

(27) N. Shinozuka and S. Hayano, *"Solution Chemistry of Surfactants,"* Vol. 2, K. L. Mittal Ed., New York, Pleunm Press, p. 599-623, 1979.

(28) T. Watanabe and K. Honda, *J. Phys. Chem.*, **86**, 2617 (1982).

(29) K. Belinko, *Appl. Phys. Lett.*, **29**, 363 (1976).

Convenient Syntheses of Carboxylic Esters and Thiol Esters Using Acid Chlorides and Zinc Chloride

Sunggak Kim†, Won Jae Lee and Jae In Lee

Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea.

(*Received May 16, 1984*)

Reaction of acid chlorides with primary alcohols, secondary alcohols, and aryl alcohols in the presence of a catalytic amount of zinc chloride gave the corresponding esters in high yields, whereas the reaction with tertiary alcohols failed to give the esters due to the fast solvolytic reactions of tertiary alcohols with hydrogen chloride generated from the reaction. The use of molecular sieves as a scavenger for hydrogen chloride was found to be moderately effective in the reaction of mesitoyl chloride with tertiary alcohols. Reaction of acid chlorides with thiols in the presence of zinc chloride in acetonitrile proceeded cleanly, yielding the corresponding thiol esters in high yields.

The combination of an organic acid chloride or an organic acid anhydride and a Lewis acid is very useful and well-known reagent in synthetic organic chemistry and has enjoyed its role as a source of an acylium ion in cleavage of acyclic and cyclic ethers since 1901.[1,2] Besides the cleavage of ethers, these types of reagents have been recently utilized in the sysnthesis of β,γ-unsaturated ketones[3] and aroyl azides.[4] Furthermore, the reaction of acid chlorides in the presence of zinc chloride with aldehydes and ketones has been reported.[5] However, the reaction of acid chlorides in the presence of Lewis acid with alohols or thiols has been largely ignored by organic chemists, although syntheses of relatively sterically hindered carboxylic esters from acid chlorides with alcohols in the presence of silver cyanide[6] or acetic anhydride with t-butyl alcohol in the presece of zinc chloride[7] have been reported.

In connection with our continuous study directed toward development of new synthetic methods by use of transition metal salts,[8] we had occasion to study the reaction of pivaloyl chloride with a highly hindered mesitol in the presence of 0.5 equiv of cupric bromide in acetonitrle at room temperature. The reaction proceeded smoothly, yielding 92 % of mesityl pivate in 3 h, whereas the reaction in the absence of cupric bromide did not occur to an observable extent.

Since this initial discovery we have examined a number of reactions to optimize the reaction condition by using an equimolar mixture of pivaloyl chloride and mesitol as a model study. The relative effectiveness of various metal salts was examined in acetonitrile at room temperature and is indicated in Table 1. Although zinc chloride and silver tetrafluoroborate were the most effective among various metal salts employed, zinc chloride was the reagent of the choice in view of the ready availability and the cheapness of zinc chloride. Furthermore, the esterification was complete within 10 min in the presence of 0.1 equiv of zinc chloride, indicating that zinc chloride effectively catalyzes the reaction of acid chloride with alcohols. Cupric bromide and aluminum chloride were also effective but less effective than zinc chloride. Other metal salts such as cupric cyanide, cuprous iodide, and nickel bromide did not give good results, even after stirring at room temperature for 24 h. Cupric acetate was totally ineffective and mesitol was recorded unchanged.

Although a number of useful and reliable methods for the preparation of carboxylic esters have been reported,[9] there are only several methods available in the literature for the preparation of sterically hindered esters.[6,10] The results obtained here indicate that the present procedure is very useful for the preparation of sterically hindered esters. Thus, we have studied the reaction with structurally different acids and alcohols to determine the scope and limitations