sorption data, supporting the possibility of the structural differences in the two states.

Acknowledgement. This work was supported by the grant for the Basic Research Institute Program of the Ministry of Education of the Republic of Korea (1988–1989).

References

1. M. Bigby and R. Stern, *J. Am. Acad. Dermatol.* **12,** 866 (1985).
2. R. Stern, *New Engl. J. Med.* **309,** 186 (1983).
3. M. Yoon, H. N. Choi, H. W. Kwon, and K. H. Park, *Bull. Korean Chem. Soc.* **9,** 171 (1988).
4. B. Alis, A. C. Capomacchia, D. Jacson, and S. G. Schulman, *Talenta* **20,** 33 (1973).
5. J. Catalan, F. Toribio and A. U. Acuna, *J. Phys. Chem.* **86,** 303 (1982).
6. S. Nagoka, N. Hirota, M. Sumitani, and K. Yoshihara, *J. Am. Chem. Soc.* **105,** 4220 (1983).
7. M. Swaminathan and S. K. Dogra, *J. Am. Chem. Soc.* **105,** 6233 (1983).
8. A. K. Mishira and S. K. Dogra, *J. Chem. Soc. Perkin Trans. II,* 943 (1984).
9. H. Zinnes, R. A. Comes, F. R. Zuleski, A. N. Caron and J. Shavel Jr., *J. Org. Chem.* **30,** 224 (1985).
10. M. J. Jorgenson and D. R. Hartler, *J. Am. Chem. Soc.* **85,** 878 (1963).
11. G. Yagil, *J. Phys. Chem.* **71,** 1034 (1967).
12. S. G. Schulman, "Fluorescence and Phosphorescence Spectroscopy: Physicochemical Principles and Practice", International Series in Analytical Chemistry (R. Buchler and H. Freiser, ed.), Pergamon Press, Oxford 61 (1977).
13. R. C. Weast ed. "CRC Handbook of Chemistry and Physics" 67th ed., 1986-1987.
14. M. Swamanithan and S. K. Dogra, *J. Chem. Soc. Perkin Trans. II,* 947 (1984).
15. A. U. Acuna, F. Amat-Guerre, J. Catalan and F. Gonzalez-Tables, *J. Phys. Chem.* **84,** 531 (1980).
16. Th. Forster, *Z. Electrochem.* **54,** 531 (1950).
17. M. Krishnamurthy and S. K. Dogra, *Photochem. Photobiol.* **44,** 571 (1986).
18. M. Krishnamurthy and S. K. Dogra, *J. Photochem.* **32,** 235 (1986).

Properties of Sodium Dodecyl Sulfate / Triton X-100 Mixed Micelle

Joon Woo Park*, Myung-Ae Chung, and Kyung Moon Choi

Department of Chemistry, Ewha Womans University, Seoul 120-750. *Received June 20, 1989*

The cmc's of sodium dodecyl sulfate (SDS)/Triton X-100 surfactant mixtures were determined by surface tension measurement at various surfactant compositions. The cmc values were lower than those predicted from ideal mixture. The regular solution theory was applied to calculate the interaction parameter, micellar composition, and the activity coefficients of surfactants in the mixed micelle. The interaction parameter (β) was -2.1. The nonideality arised largely from decreased activity of SDS in the mixed micelle. The mean aggregation numbers ($\bar{n}$) and micropolarity of hydrocarbon region of the mixed micelles were determined by luminescence probe techniques. The total aggregation number ($\bar{n}_{SDS} + \bar{n}_{TX}$) in mixed micelles showed little dependency on the composition of the micelle. The apparent dielectric constant of the hydrocarbon region of the micelle *vs* micellar composition plot showed positive deviation from linearity. Emission and emission quenching of excited tris(2,2'-bipyridine)ruthenium(II) cation, ($Ru(bpy)_3^{2+}$), by methylviologen (MV^{2+}) were also investigated in the mixed micellar solutions. The quenching rate was lowest when the mole fraction of SDS in the surfactant mixtures (α_{SDS}) is about 0.25 and highest at $\alpha_{SDS} = 0.85$. This was explained in terms of combined effects of binding of the cations with the micelle and mobility of the bound cations on the surface of the micelles.

Introduction

The physico-chemical properties of micelle-solubilized or bound substrates are strikingly different from those in homogeneous media. The properties are critically dependent on microenvironment of the substrates in the micellar pseudophase. In view of increasing interest in the chemistry of micellar system,[1] it is desirable to design the micellar systems of particular characteristics. Since homomicellar systems which can be practically used are limited, mixed surfactant systems are required to obtain the desired properties. In fact, surfactants used in practical applications are essentially mixed surfactant systems. In many applications, they exhibit superior properties and are less expensive than single-compound surfactant systems. Therefore, there is increasing interest in understanding the strucutre and properties of mixed micelles.[2-13] However, most of work on mixed surfactant systems are focused on the critical micelle concentration (cmc) and thermodynamics of formation of mixed micelles. Little attention has been paid on the microscopic characteristics of the micelles.

In this paper, we describe the results of studies on the formation and physico-chemical properties of mixed micelle formed between sodium dodecyl sulfate (SDS) and Triton X-100 (TX-100:polyoxyethylene glycol *p*-isooctyl phenyl ether with about 10 oxyethylene units), which are the most

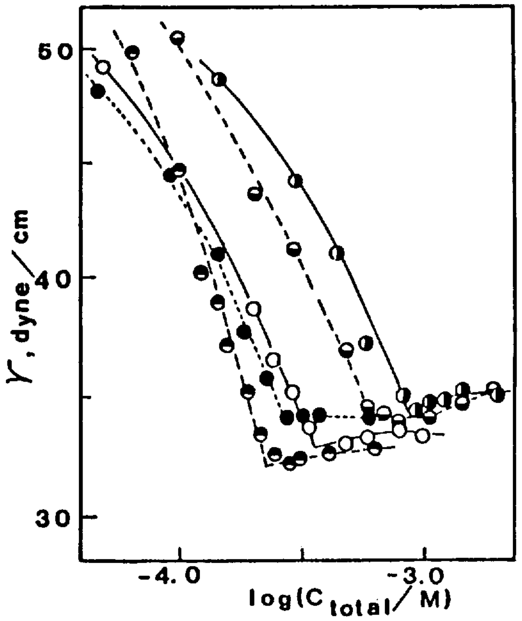

Figure 1. Dependence of surface tension of SDS/TX-100 surfactant mixture solutions on the total concentration of the surfactants at 25 °C: The mole fractions of SDS in the surfactant mixtures are 0.0 (◓), 0.25 (●), 0.50 (○), 0.75 (◒) and 0.85 (◑). The inflection point for pure SDS was observed at [SDS] = 7.59×10^{-3}M (log $C = -2.12$).

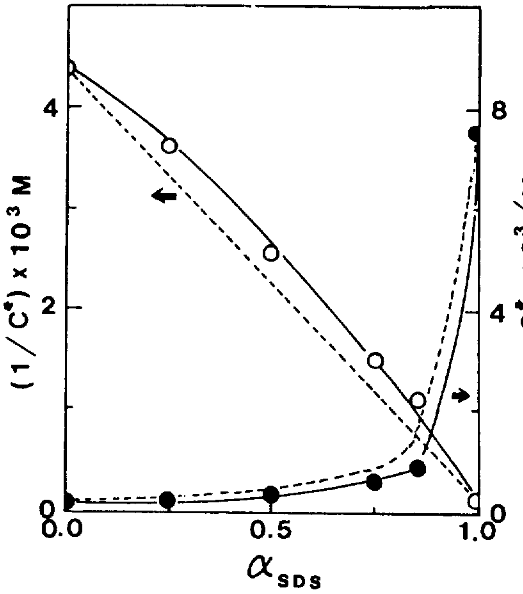

Figure 2. Plots of cmc (C^*:●) and 1/cmr (○) of SDS/TX-100 surfactant mixtures against mole fraction of SDS (α_{SDS}) in the mixtures. Dotted lines are the trends for the ideal mixture.

commonly used anionic and nonionic surfactants, respectively. The dependence of cmc, aggregation number, and micropolarity of the micelles on composition are presented.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS) was obtained from Fluka and purified by three times recrystallization from ethanol after it was washed with ether. TX-100 (Aldrich), 9-methylanthracene (Aldrich), and pyrene (Kanto) were used without further purification. Tris(2,2'-bipyridine)ruthenium(II) diperchlorate, $Ru(bpy)_3^{2+}2ClO_4^-$, and methylviologen dichloride, $MV^{2+}2Cl^-$, were the remainings of a previous study.[14] Glass distilled deionized water was used.

Surface Tension Measurement. A Du Nöuy ring tensionmeter from Fisher with a platinium-iridium ring was used to determine surface tension of solutions. Solutions were allowed to equilibrate until the surface tension readings were stabilized, generally for about 30 min. The temperature was held constant at 25 ± 0.1 °C by circulating constant temperature water through the thermostatted container.

Spectral Techniques. Luminescence spectra were taken with a Hitachi Model 650-10S fluorescence spectrometer. Solutions containing 9-methylanthracene (9-MA) for determination of the aggregation number of the micelles were prepared by a method described in the literature.[15] The concentration of 9-MA was calculated from absorption measurement with Beckman DU-8B UV-VIS spectrophotometer at 388 nm using the molar absorptivity $\varepsilon = 7500$ M^{-1} cm^{-1}.[15] Steady state luminescence quenching data of $Ru(bpy)_3^{2+}$ by 9-MA were used to calculate the mean aggregation numbers of the micelles.[15-17] Excitation wavelength was 450 nm and the emission intensity at peak of the emission spectra, *ca.* 620 nm, was used. Micropolarity of the hydrophobic region of the micelles was followed by the intensity ratio of the third (383 nm) to the first (372 nm) vibronic peak (I_3/I_1) of pyrene.[18-19] Excitation wavelength was 328 nm and the slit widths of excitation and emission light were 2 nm. Details on the treatment of luminescence data for determination of aggregation numbers and micropolarity of the micelles, and electron transfer quenching rate from photoexcited $^*Ru(bpy)_3^{2+}$ to MV^{2+} are described in the Results and Discussion.

Results and Discussion

Cmc and Interaction Parameter of SDS/TX-100 Mixed Micelle. Surface tension(γ) or SDS/TX-100 mixed surfactant solutions at various mole fractions of SDS, $\alpha_{SDS} = \bar{n}_{SDS}/(\bar{n}_{SDS} + \bar{n}_{TX-100})$, in the total surfactant mixtures was measured as a function of the concentration of the total surfactant. The results were presented in Figure 1. The concentration at the inflection point in the γ *vs.* logarithm of surfactant concentration plot corresponds to the critical micelle concentration (cmc) of the surfactant mixture. Dependence of the cmc of the mixed micellization (C^*) on α_{SDS} was shown in Figure 2.

The ideal solution theory on mixed micelle relates C^* of a surfactant mixture to the cmc's of pure component (C_i's) and the mole fractions of the components (α_i's) by[3-4]

$$1/C^* = \sum_{i=1}^{n} \alpha_i/C_i \tag{1}$$

It was found that eq. 1 successfully describes the cmc of surfactant mixture of homologue series.[3] However, large deviation from the ideality was observed in surfactant mixtures with widely different head groups.[6-7] It is evident from Figure 2 that SDS/TX-100 system also deviates from the ideality: the cmc values of the surfactant mixtures are lower than those predicted for ideal mixture.

For the nonideal surfactant mixtures, eq. 1 is modified as

Table 1. Cmc, Mole Fractions (*X*) of Micelles Formed at cmc, and Interaction Parameter (β) of SDS/Triton X-100 Mixed Surfactant[a]

α_{SDS}	$C^* \times 10^3$/M	X_1	X_2	f_1	f_2	β
1.00	7.59	1.00	0.00	1.00	–	–
0.85	0.91	0.29	0.71	0.35	0.84	-2.1
0.75	0.66	0.21	0.79	0.31	0.92	-1.9
0.50	0.39	0.12	0.88	0.21	0.97	-2.0
0.25	0.28	0.07	0.93	0.13	0.99	-2.4
0.00	0.23	0.00	1.00	–	1.00	–

[a] 1 and 2 denote SDS and Triton X-100, respectively.

eq. 2 by considering the activity coefficient of the components (f_i's) in the mixed micelles.

$$1/C^* = \sum_{i=1}^{n} \alpha_i / f_i C_i \tag{2}$$

The regular solution approximation was introduced to treat the nonideality of mixing by assuming that the excess entropy of mixing in zero, and the excess free energy of mixing is due to the enthalpy of mixing.[5,7,12] From the regular solution approximation, the activity coefficients of components of binary mixed micelle (f_1 and f_2) are represented by eqs. 3 and 4.

$$f_1 = \exp \beta (1 - X_1)^2 \tag{3}$$

$$f_2 = \exp \beta X_1^2 \tag{4}$$

where β is the interaction parameter and X_i is the mole fraction of the component *i* in the micelle. The X_1 value is related to α_1, cmc of the mixed surfactant (C^*), and cmc's of pure components (C_1 and C_2) by

$$X_1^2 \ln [\alpha_1 C^* / X_1 C_1] = (1 - X_1)^2 \ln [(1 - \alpha_1) C^* / (1 - X_1) C_2] \tag{5}$$

X_1 can be solved iteratively from this equation by using the predetermined values of α_1, C_1, C_2 and C^*. The interaction parameter β can then be directly calculated from,

$$\beta = \ln [(C^* / C_1 X_1) / (1 - X_1)^2] \tag{6}$$

Then, the calculation of f_1's is straight forward from eqs 3 and 4. Table 1 lists cmc's, X_i's and the interaction parameter of the SDS/TX-100 surfactant mixtures at various mole fraction of SDS.

The average value of the interaction parameter for SDS/TX-100 system was -2.1. This value is less negative than the value of -3.4 obtained for the mixed micelle of SDS and decaethylene glycol-*n*-nonylphenyl ether, C_9PhE_{10}, another nonionic surfactant having similar structure with TX-100.[20] This indicates that the interaction between SDS and TX-100 is weaker than the interaction between SDS and C_9PhE_{10}. The presence of branched alkyl chain, isootyl, in TX-100 instead of linear chain, *n*-nonyl, in C_9PhE_{10} might be responsible for the weaker interaction in the former surfactant, through looser packing with *n*-dodecyl chain of SDS in the hydrocarbon core of the mixed micelle.

Table 1 shows that the composition of the mixed micelle formed between SDS and TX-100 at cmc is richer in TX-100 than the composition in the bulk media. Table 1 also shows that the non-ideality in SDS/TX-100 arises mainly from the decreased activity coefficient of SDS in the mixed micellar phases. This can be attributed to reduced electrostatic repulsion between dodecyl sulfate anions in the mixed micelle, compared to SDS homomicelle.

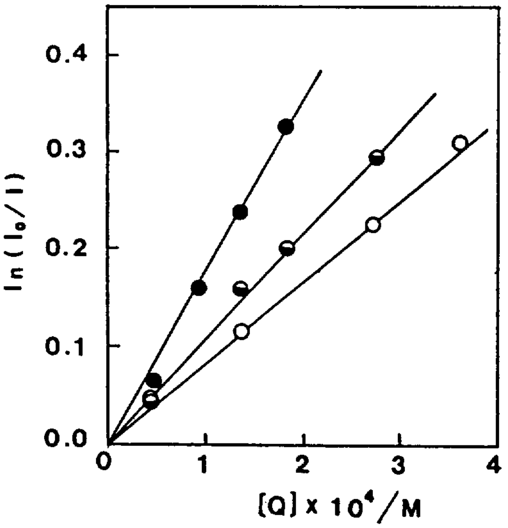

Figure 3. Plots of emission quenching data of $Ru(bpy)_3^{2+}$ by 9-methylanthracene (*Q*) in SDS/TX-100 mixed surfactant (α_{SDS} = 0.50) solutions according to eq. 7. The SDS concentrations in the surfactant mixtures are 20 (●), 30 (◒) and 40 mM (○).

Aggregation Numbers of SDS / TX – 100 Mixed Micelles. The mean aggregation numbers of sufactant molecules in SDS/TX-100 micelles were determined from the study of steady state luminescence quenching of $Ru(bpy)_3^{2+}$ by 9-MA. For the luminephore and quencher pair, Turro and Yekta[16] related the ratio of emission intensities (I/I_0) of $Ru(bpy)_3^{2+}$ in the presence and in the absence of the quencher Q to the concentration of micelle, [M], by a very simple expression:

$$I/I_0 = \exp \{-[Q]/[M]\} \tag{7}$$

where the concentration of micelle [M] is related to the total concentration of a surfactant ([S]), mean aggregation number ($\bar{n}$) of the micelle, and the concentration of free surfactant monomer by eq. 8.

$$[M] = \frac{[S] - [\text{free monomer}]}{\bar{n}} \tag{8}$$

The plot of $\ln(I_0/I)$ against [Q] yields a straight line and slope of the plot corresponds to 1/[M]. The Plot of [M] *vs.* [S] allows determination of $\bar{n}$ from eq. 8. This method was successfully applied for determination of $\bar{n}$ of SDS homomicelle.[15-17]

Figure 3 shows plots of luminescence quenching data of $Ru(bpy)_3^{2+}$ by 9-MA in solutions of SDS/TX-100 surfactant mixtures of α_{SDS}=0.5 at 20, 30 and 40mM SDS according to eq. 7. The good linearity in the plots indicates validity of eq. 7 for SDS/TX-100 mixed surfactant system. The same plot was made at other mole fractions of SDS, α_{SDS} = 1.0, 0.85 and 0.75. The results were summarized in Table 2. For the SDS/TX-100 mixtures of α_{SDS} lower than 0.5, we could not perform similar experiment due to interference from the fluorescence of TX-100 and incomplete binding of $Ru(bpy)_3^{2+}$ with the micelle: complete binding of the lumin-

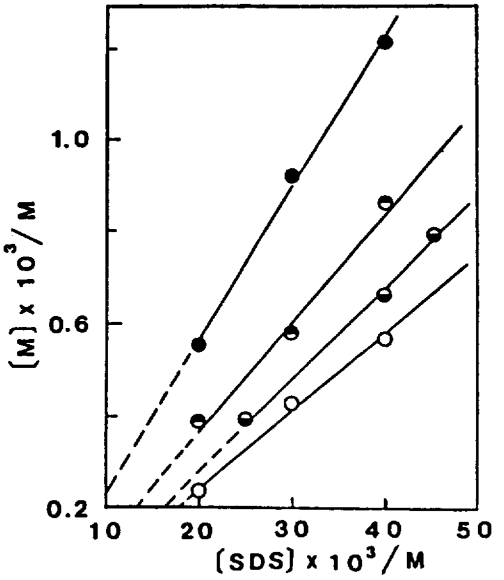

Figure 4. Plots of the concentrations of micelles obtained from plots as shwon in Figure 3 against the concentration of SDS according to eq. 8. The α_{SDS} values are 0.50 (●), 0.75 (◓) 0.85 (◒), and 1.0 (○).

ephore and the quencher is a prior assumption for eq. 7.[16]

The plots of [M] against total concentration of SDS in the solutions were shown in Figure 4. The mean aggregation number of SDS($\bar{n}_{SDS}$) in the micelle and free concentration of SDS were calculated from the plots. The results were included in Table 2. The mean aggregation number of SDS homomicelle, 62, is in accordance with the reported values of 63 from membrane osmometry[21] and 62 from light scattering studies[22] of the surfactant. Since the mole fraction of TX-100 in SDS/TX-100 mixed micellar pseudophase is much greater than the mole fraction in bulk water phase, the concentration of free TX-100 is nearly zero.[17,23] This argument is supported by the high concentration of free SDS monomer (Table 2), compared to the cmc of the surfactant mixtures (Table 1). Therefore, the aggregation number of TX-100 in the micelle can be given by simply deviding the concentration of TX-100 with [M].

$$\bar{n}_{TX} = [TX-100]/[M] \tag{9}$$

The calculated $\bar{n}_{TX}$'s and mole fraction of SDS in the mixed micelle (X_{SDS}) were also listed in Table 2. Table 2 clearly shows that as the mole fraction of SDS decreases, the number of SDS molecule per micelle ($\bar{n}_{SDS}$) also decreases while that of TX-100 increases. However, the total number of surfactant molecule per micelle remains virtually constant at 60-65.

Polarity of Hydrophobic Region of SDS/TX-100 Mixed Micelle. The I_1/I_3 ratio of pyrene fluorescence is known to be an excellent index of the effective polarity of the probe environment.[24] A linear relationship between I_1/I_3 and dielectric constant (ε) of the media was obtained for a series of solvents.[20]

$$\varepsilon = (I_1/I_3 - 1.25)\,86.2 + 20 \tag{10}$$

We obtained fluorescence spectra of 1.0×10^{-7}M pyrene in 40 mM SDS solutions containing various amount of TX-100. The I_1/I_3 ratios were determined from the spectra and the effective dielectric constants of microenvironment of pyrene probe were calculated from eq. 10. The results were presented in Figure 5 as a function of mole fraction of SDS in the micelle. The aparent dielectric constant of pure SDS micelle, $\varepsilon = 10.5$, is much smaller than the value (25-50) obtained with probes bearing polar groups, which bind on the micelle-water interface and indicate micropolarity at the interface.[25] Since pyrene is a highly hydrophobic molecule, it peretrates deeply into the hydrophobic region of the micerlle. Thus the dielectric constant estimated by pyrene probe can be regarded as the polarity of hydrophobic region of the micelle.

The solid lines in Figure 5 is the calculated value assuming the additivity relationship.[20]

$$\varepsilon_{mix} = \varepsilon_{SDS} X_{SDS} + \varepsilon_{TX-100}(1 - X_{SDS}) \tag{11}$$

The actual values of ε of the micelle show large positive deviations from eq. 11. This results can be taken as an indication of looser packing of the hydrocarbon chains in the mixed micelle, compared to the average packing in the pure surfactant micelles.

Luminescence Quenching of Ru(bpy)$_3^{2+}$ by MV^{2+} in SDS/TX-100 Mixed Micellar Solutions. The electron

Table 2. Mean Aggregation Number of SDS/Triton X-100 Mixed Micelle at 25 °C

α_{SDS}	[SDS]/mM	[TX]/mM	[M]/mM	[Free SDS]/mM	$\bar{n}_{SDS}$	$\bar{n}_{TX}$[a]	X_{SDS}
1.0	20.0	0.0	0.24	5.1	62	0.0	1.0
	30.0	0.0	0.43			0.0	1.0
	40.0	0.0	0.57			0.0	1.0
0.85	25.0	4.4	0.39	5.0	52	11.4	0.82
	40.0	7.1	0.66			10.4	0.83
	45.5	8.0	0.80			10.2	0.83
0.75	20.0	6.7	0.40	3.7	43	17.6	0.71
	30.0	10.0	0.58			16.3	0.72
	40.0	13.3	0.86			15.7	0.73
0.50	20.0	20.0	0.55	3.0	30	35.4	0.46
	30.0	30.0	0.92			34.7	0.46
	40.0	40.0	1.22			32.5	0.48

[a] All of Triton X-100 was assumed to be associated with the micelle.

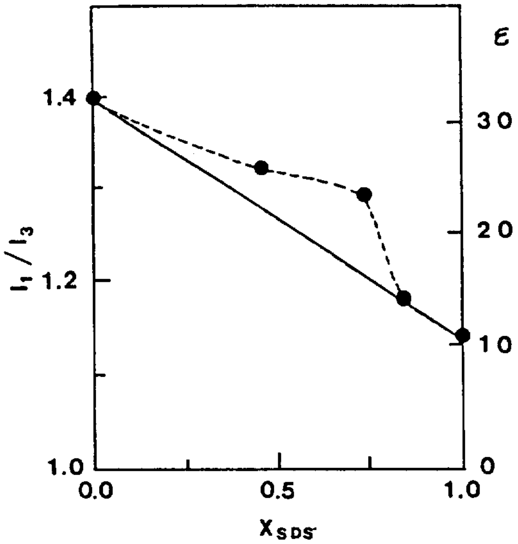

Figure 5. Dependence of the emission intensity ratio of pyrene fluorescence (I_1/I_3) and the calculated effective dielectric constant of hydrocarbon core of SDS/TX-100 mixed micelle on the mole fraction of SDS in the micelle.

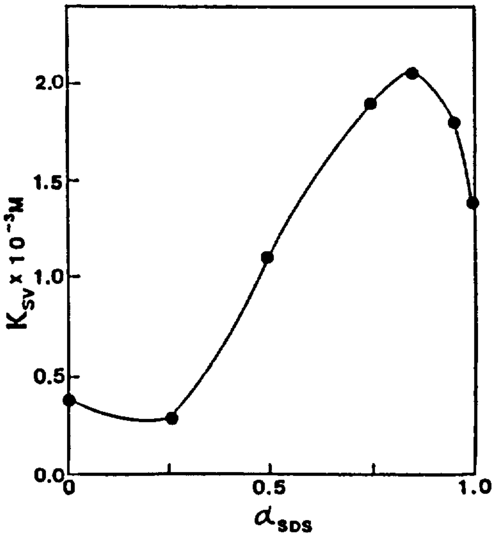

Figure 6. Variation of the apparent Stern-Volmer constant for emission quenching of $Ru(bpy)_3^{2+}$ by MV^{2+} with mole fraction of SDS in the SDS/TX-100 surfactant mixtures at 25 °C. The total surfactant concentration was 20 mM. Solutions contained 0.1 M NaCl.

transfer quenching of photoexcited $Ru(bpy)_3^{2+}$ by MV^{2+} has been a subject of intense studies from the possibility of using the system in solar energy conversion into the stored chemical energy.[26] The quenching rate increases remarkably in the presence of anionic surfactants, presumably due to condensation of the reacting cations on the anionic micellar surfaces by coulombic interaction. We have measured luminescence intensity of $Ru(bpy)_3^{2+}$, excited at 450 nm, in the solutions of SDS/TX-100 surfactant mixture solutions (total surfactant concentration was 20 mM). The ratio of emission intensities (I_o/I) in the absence (I_o) and in the presence (I) of MV^{2+}, and emission maxima of the emission spectra were summarized in Table 3.

The emission behavior of $Ru(bpy)_3^{2+}$ in pure TX-100 solution ($\alpha_{SDS} = 0$) did not differ significantly from that in surfactant free solution. This agrees well with a report by Dressick *et al.*[27] and indicates that the complex cation does not bind on TX-100 homomicelle, presumably due to the absence of electrostatic attraction between the cation and nonionic TX-100. The hydrophobic interaction between $Ru(bpy)_3^{2+}$ and TX-100 may not be large enough to ensure significant binding, though Ru(II) complexes with greater hydrophobic character bind with TX-100 micelle by hydrophobic effect.[27]

In SDS/TX-100 mixed surfactant solutions, red-shift of emission peak of $Ru(bpy)_3^{2+}$, as compared to that in surfactant free solution, was observed. This reveals binding of the cation with the mixed micelle. The extent of red-shift was greater as the mole fraction of SDS in the surfactant mixture increased. The smaller change in TX-100 rich (*e.g.* $\alpha_{SDS} = 0.25$) mixed micelle might be dut to incomplete binding of $Ru(bpy)_3^{2+}$ with the micelle at total surfactant concentration of 20 mM.

The emission quenching data by a quencher Q are usually analyzed by Stern-Volmer equation.

$$I_o/I = 1 + K_{sv}[Q] \tag{12}$$

We have plotted the emission quenching data (Table 3) of $Ru(bpy)_3^{2+}$ by MV^{2+} according to eq. 12 (graphs are not shown). The plots of data taken in micellar solutions showed positive deviation from the linearity.[28] This can be ascribed to the increased surface mobility[29] of micelle bound $Ru(bpy)_3^{2+}$ and MV^{2+} as negative surface charge of the anionic mixed micelle is compensated by MV^{2+} cation. We have calculated the apparent K_{sv} values at $[MV^{2+}] = 1.0$ mM.

Table 3. Emission Maxima and Emission Quenching of $Ru(bpy)_3^{2+}$ by MV^{2+} in 20 mM SDS/Triton X-100 Mixed Surfactant Solutions Containing 0.1 M NaCl at 25 °C

	Surfactant Solutions							Water
α_{SDS}	0.0	0.25	0.50	0.75	0.85	0.95	1.0	
λ_{max}/nm	600	608	618	619	620	620	620	600
$[MV^{2+}]$/mM				I_o/I				
0.0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.5	1.18	1.13	1.56	1.84	1.90	1.76	1.47	1.21
1.0	1.40	1.30	2.10	2.90	3.06	2.80	2.38	1.42
1.5	1.57	1.41	2.61	3.89	4.28	4.10	3.30	1.62
2.0	1.79	1.57	4.70	5.04	5.55	5.54	4.42	1.83

The results were plotted as a function of α_{SDS} in Figure 6.

The K_{sv} value in TX-100 solution was 400 M^{-1}. This value agrees reasonably well with the value obtained in surfactant free solution, 420 M^{-1}, within the experimental error range. This indicates that the presence of TX-100 homomicelle does not influence the bimolecular quenching reaction between $^*Ru(bpy)_3^{2+}$ and MV^{2+}. This suggests that MV^{2+} as well as $Ru(bpy)_3^{2+}$ does not bind with the TX-100 micelle. When α_{SDS}=0.25, the K_{sv} value was smaller than that in water, despite of significant binding of $Ru(bpy)_3^{2+}$ with the micelle as revealed by the spectral shift of the complex cation. It seems that the surface charge density of SDS/TX-100 micelle at α_{SDS}=0.25 is not large enough for MV^{2+} to bind on the micelle to any significant extent in the experimental condition of 0.1M NaCl. Thus $Ru(bpy)_3^{2+}$ is localized mainly in the micellar pseudophase and MV^{2+} remains in bulk aqueous phase leading to less efficient electron transfer quenching reaction between the cations.

As the mole fraction of SDS in the micelle increases, the quenching rate also increases reflecting more efficient binding of MV^{2+} on the micelle due to electrostatic interaction. Interestingly, the K_{sv} value was highest when α_{SDS} was about 0.85. This cannot be explained if one considers only local concentrations of the reacting cations in the micellar pseudophase: if this is held, one can expect steady increase of K_{sv} with α_{SDS} or levelling off of the quenching constant beyond certain α_{SDS} at which both $Ru(bpy)_3^{2+}$ and MV^{2+} are completely micellized. The other factor to be considered in micellar effect on the quenching reaction is diffusion constants of the cations on the micellar surface.[29] The observation of the maximum in K_{sv} *vs.* α_{SDS} plot at $\alpha_{SDS} = 0.85$ suggests that the surface diffusion constants of the cations are greater at $\alpha_{SDS} = 0.85$ than that at higher α_{SDS} value. It appears that the surface mobility of anionic micelle *bound* cations is greater with less surface charge density of the micelle since they are less firmly bound. This is in a line with explanation of the after-mentioned positive deviation in Stern-Volmer plots in the micellar solutions. The observation of the miximum in K_{sv} *vs.* α_{SDS} can be ascribed to the combined effects of micellar binding and surface diffusion constant depending on the composition of micelles.

Acknowledgements. This work was supported by Korea Science and Engineering Foundation (871-0303-033-2) and Basic Research Institute Program of the Ministry of Education of the Republic of Korea.

References

1. For recent monographs, (a) J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems,* Academic Press, New York, 1975. (b) J. H. Fendler, *Membrane Mimetic Chemistry,* Wiley, New York, 1982 (c) J. K. Thomas, *The Chemistry of Excitation of Interfaces,* ACS, Washington DC 1984, Monograph 181. (d) K. Kalyanasundaram, *Photochemistry in Microheterogeneous System,* Academic Press, New York, 1987.
2. *"Phenomena in Mixed Surfactant Systems",* J.F. Scamehorn Ed., ACS, Washington DC, 1986, Monograph 311.
3. J. H. Clint, *J. Chem. Soc. Faraday Trans. I,* **71,** 1327 (1975).
4. (a) C. Tanford, *"The hydrophobic: Formation of Micelles and Biological Membranes",* 2nd. Ed, Wiley Interscience, New York, 1979, Chapter 9; (b) H. Lange and K. H. Beck, *Kollid Z. U-Z. Polymer.,* **251,** 424 (1979).
5. D. N. Rubingh, in "Solution Chemistry of Surfactant", K. L. Mittal Ed: Plenum Press., Vol. I, 1979, pp. 337-354.
6. P. Mukerjee and Y. S. Yang, *J. Phys. Chem.,* **80,** 1388 (1976).
7. P. M. Holland and D. N. Rubingh, *J. Phys. Chem.,* **87,** 1984 (1983).
8. D. G. Hall and T. J. Price, *J. Chem. Soc. Faraday Trans. I.* **80,** 1193 (1984).
9. R. F. Kamrath and E. I. Franses, *J. Phys. Chem.,* **88,** 1642 (1984).
10. I. W. Osborne-Lee, *J. Colloid Interface Sci.,* **108,** 60 (1985).
11. C. M. Nguyen, J. F. Rathman and J. F. Scamehorn, *J. Colloid Interface Sci.,* **112,** 438 (1986).
12. P. M. Holland, *Adv. Colloid Interface Sci.,* **26,** 111 (1985).
13. M. J. Rosen and D. S. Murphy, *J. Colloid Interface Sci.,* **110,** 224 (1986).
14. J. W. Park and Y. H. Paik, *Bull. Korean. Chem. Soc.,* **7,** 137 (1986).
15. M. Almgrem and J.-E. Löfroth, *J. Colloid Interface Sci.,* **81,** 486 (1984).
16. N. J. Turro and A. Yekta, *J. Am. Chem. Soc.,* **100,** 3951 (1978).
17. M. Almgren and S. Swarup, *J. Phys. Chem.,* **86,** 4212 (1982).
18. M. T. Flanagan and S. Ainsworth, *Biochim. Biophys. Acta.,* **168,** 16 (1968).
19. H. J. Pownall and L. C. Smith, *J. Am. Chem. Soc.,* **95,** 3136 (1973).
20. J. J. Turro, P.-L. Kuo, P. Somasundaran and K. Wang. *J. Phys. Chem.,* **90,** 288 (1986).
21. H. Coll, *J. Phys. Chem.,* **74,** 520 (1970).
22. K. Granath, *Acta. Chem. Scand.,* **7,** 297 (1953).
23. M. Almgren and S. Swarup, *J. Phys. Chem.,* **87,** 876 (1987).
24. (a) K. Kalyanasundaram and J. K. Thomas, *J. Am. Chem. Soc.,* **99,** 2039 (1979); (b) D. Dong and M. A. Winnik, *Photochem. Photobiol,* **35,** 17 (1982); (c) P. G. Lians, J. Lang, C. Strazielle and R. Zana, *J. Phys. Chem.,* **86,** 1019 (1982); (d) B. Elsa and J. C. Scaiano, *J. Am. Chem. Soc.,* **106,** 6274 (1984).
25. p. 44 of Ref. 1c.
26. (a) D. G. Whitten, *Acc. Chem. Res.,* **13,** 83 (1980); (b) pp. 492-505 of Ref. 1b; (c) E. A. Seddon and K. R. Seddon, *"The Chemistry of Ruthenium,"* Elesvier, New York, 1984, pp. 1173-1260.
27. W. J. Dressick, B. L. Hauenstein, Jr., T. B. Gilbert, J. N. Demas and B. A. DeGraff, *J. Phys. Chem.,* **88,** 337 (1984).
28. At high concentration of the quencher, the Stern-Volmer plot shows downward curve after passing maximum. This is due to competition between the reacting cations for common and finite binding sites on micelle.
29. T. Miyashita and T. Murakata, *J. Phys. Chem.,* **87,** 4529 (1983).