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Luminescence Quenching of Tris(2,2'-bipyridine) Ruthenium(II) Complex by Viologens in Anionic Micellar and Polyelectrolyte Solutions: Variation with Alkyl Chain of Viologens

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Luminescence quenching reactions of photoexcited tris(2,2'-bipyridine)ruthenium (II) complex cation, $\text{Ru}(\text{bpy})_3^{2+}$, by dialkylviologens (dimethyl, dioctyl, dibenzyl, methyloctyl, methyl dodecyl, and methylbenzyl) were studied in sodium dodecyl sulfate (SDS), poly(styrenesulfonate) (PSS), and poly(vinylsulfonate) (PVS) solutions. The relative quenching rate varies widely with the microheterogeneous media employed: the highest quenching rate is observed for methyl dodecylviologen in homogeneous aqueous medium, dibenzylviologen in SDS and PVS solutions, and dimethylviologen in PSS solution; the lowest rate is found for dimethylviologen in homogeneous medium and SDS solution, methyl dodecylviologen in PSS and PVS solutions. These results were interpreted in terms of reduction potential of viologens, affinity of $\text{Ru}(\text{bpy})_3^{2+}$ and viologens to the microparticles, and the structures of the viologen-colloid complexes.

Introduction

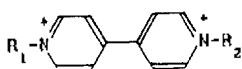
Micelles, polyelectrolytes, and other microheterogeneous systems are increasingly used to control physico-chemical properties and reaction kinetics of substrates.¹ Photosensitized electron-transfer reactions in microheterogeneous media have been an active research area with goal of achieving efficient solar energy conversion systems and, more recently, with emphasis on using the photoredox systems as probes for microheterogeneous environments.^{2,3} Tris(2,2'-bipyridine)ruthenium (II) ($\text{Ru}(\text{bpy})_3^{2+}$)/4,4'-bipyridinium salts (viologens) photoredox couple has been recognized as one of the most promising systems for the former purpose.^{2b,4-6} Much of works have been carried out with dimethylviologen (1,1'-dimethyl-4,4'-bipyridinium). The photoinduced electron-transfer reaction between $\text{Ru}(\text{bpy})_3^{2+}$ and viologens are usually followed by the luminescence quenching of the photosensitizer by the electron acceptors. The presence of anionic micelles and polyelectrolytes remarkably enhances the rate of the quenching reactions.⁷ This was attributed to the condensation of the reacting pair in the potential field of the anionic micelles and polyanions by the coulombic interaction.

Viologens, especially those with long alkyl chain, interact with microphase particles by hydrophobic interaction as well as coulombic force. It was demonstrated that use of dialkylviologens with long alkyl chains results in enhanced quantum yield in $\text{Ru}(\text{II})$ complex photosensitized reduction of the viologens in micelle,⁸ reversed micelle⁹ and water-in-oil mi-

croemulsion,¹⁰ due to the stabilization of the photoproducts against the recombination reaction involving back-electron transfer. Electron spin echo modulation (ESEM) spectroscopy¹¹ and ESR¹² studies on the dialkylviologens in sodium dodecyl sulfate (SDS) micelle and dihexadecyl phosphate (DHP) vesicle revealed that the degree of embedment of viologen in the microphase particles depends on the alkyl chain length of the viologens. This lead to the variation of quenching rate with the alkyl chain of viologens in the microheterogeneous systems.¹³ The reduction potential of viologen varies with alkyl chain,¹⁴ and changes upon the presence of microphase particles such as micelles and vesicles.^{14a,15} Anionic polyelectrolytes interact with $\text{Ru}(\text{II})$ complex cation and viologens and affect the photochemical electron-transfer reaction between them in similar fashion to the anionic micelles.¹⁶ Thus the dependence of the rate of the quenching reaction on the alkyl chains of viologens are also expected in polyelectrolyte solutions.

In our laboratory, we have undertaken a series of studies on interactions of dimethylviologen and its reduced cationic radical with SDS,¹⁷ $\text{Ru}(\text{II})$ photosensitizers with anionic surfactants,¹⁸ and on kinetics of the quenching of luminescence from photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ by cationic quenchers including dimethylviologen.¹⁶ In this paper, we report the results of the kinetic studies for electron-transfer quenching reactions of $\text{Ru}(\text{bpy})_3^{2+}$ by various symmetric and asymmetric viologens **1-6** in SDS micellar, and poly(styrenesulfonate) (PSS) and poly(vinylsulfonate) (PVS) polyelectrolyte solutions. We discuss the influence of alkyl chain of the violo-

gens on the quenching rate in terms of the structures of viologen/microphase complexes.



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| 1. R ₁ = CH ₃ | R ₂ = CH ₃ | Dimethylviologen (C ₁ C ₁ V) |
| 2. R ₁ = n-C ₈ H ₁₇ | R ₂ = n-C ₈ H ₁₇ | Dioctylviologen (C ₈ C ₈ V) |
| 3. R ₁ = Benzyl | R ₂ = Benzyl | Dibenzylviologen (BBV) |
| 4. R ₁ = CH ₃ | R ₂ = n-C ₈ H ₁₇ | Methyloctylviologen (C ₁ C ₈ V) |
| 5. R ₁ = CH ₃ | R ₂ = n-C ₁₂ H ₂₅ | Methyldodecylviologen (C ₁ C ₁₂ V) |
| 6. R ₁ = CH ₃ | R ₂ = Benzyl | Methylbenzylviologen (C ₁ BV) |

Experimental

Materials. Ru(bpy)₃(ClO₄)₂ was prepared by reacting RuCl₃ and 2,2'-bipyridine in ethanol in the presence of hydroxylamine, followed by precipitation with aqueous NaClO₄. Dimethylviologen **1** and dioctylviologen **2** were prepared by heating 4,4'-bipyridine (Aldrich) with an excess of methyl iodide and octyl bromide, respectively, in ethanol. For the preparation of the asymmetric viologens **4-6**, N-methyl-4,4'-bipyridinium iodide (MBI) was synthesized by reacting 4,4'-bipyridine, with equimolar amount of methyl iodide in ethanol. After removing ethanol by evaporation, the solid product was washed with benzene to remove unreacted 4,4'-bipyridine and then treated with hot ethanol. The insoluble precipitate, N,N'-dimethyl-4,4'-bipyridinium diiodide, was removed by hot filtration and MBI was recovered upon cooling the filtrate. The asymmetric viologens **4-6** were obtained from reactions of MBI with an excess of the appropriate alkyl halides in ethanol at reflux. After exchanging halide ions (bromide or iodide) for chloride counterion by stirring the aqueous solution of viologens in the presence of AgCl, the solutions were filtered and water was evaporated under reduced pressure. The chloride salts of viologens were recrystallized from ethanol. The proton-NMR spectra of the products were consistent with the structural assignments. Analysis of the chloride counterion by Mohr method showed two moles of chloride ion per formula weight of the viologen. Uv-vis absorption spectra showed maximum at 257 nm with log ε = 4.35 ± 0.02, which agrees well with λ_{max} = 257 nm (log ε = 4.28) for dimethylviologen dichloride.^{17a} Dibenzylviologen dichloride was obtained from Aldrich and used as received.

SDS (Fluka) was recrystallized three times from absolute ethanol after washing with diethyl ether. PSS (Aldrich) and PVS (Polyscience) were purified by precipitation from ethanol.^{16a}

Solutions were prepared with glass-distilled deionized water and contained 0.1 M NaCl. The concentration of Ru(bpy)₃²⁺ was held constant at 1.0 × 10⁻⁵ M. The concentrations of polyelectrolytes were expressed in terms of the concentrations of monomeric units.

Luminescence Measurements and Analysis of Data. Uncorrected luminescence spectra of Ru(bpy)₃²⁺ were recorded with a Hitachi 650-10S fluorescence spectrometer equipped with a thermostatic cell holder at 25 ± 0.1 °C at λ_{ex} = 460 nm. Both the excitation and emission slit widths were adjusted to 5 nm.

Luminescence quenching data were analyzed by the Stern-Volmer equation (eq. 1).¹⁹

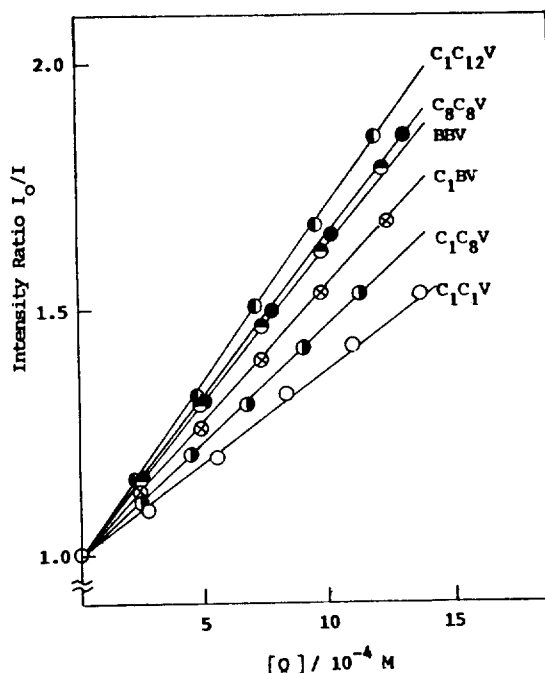


Figure 1. Stern-Volmer plots for luminescence quenching data of Ru(bpy)₃²⁺ by viologens in 0.1 M NaCl aqueous solutions.

$$I_0/I = 1 + K_{sv}(\text{viologen}) \quad (1)$$

where I_0 and I denote the luminescence intensities at a given wavelength in the absence and the presence of the quencher, viologen. K_{sv} is related to luminescence life-time (τ) of the luminescence in the absence of the quencher and the bimolecular rate constant for the quenching reaction (k_q) by $K_{sv} = \tau \times k_q$.¹⁹

Results and Discussion

Quenching in Homogeneous Aqueous Solutions.

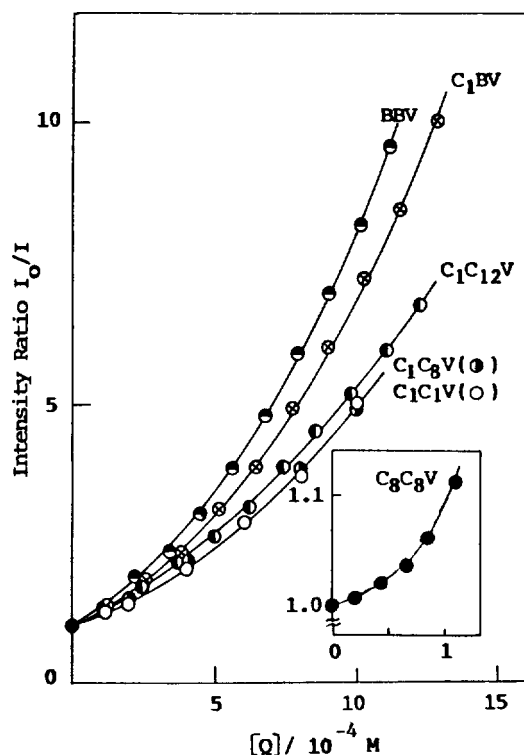
The luminescence spectra of Ru(bpy)₃²⁺ in water displayed a maximum at 600 nm. Addition of viologen to the solutions decreases the emission intensity. Figure 1 shows the plots of emission intensity taken at emission maxima according to the Stern-Volmer equation (1). The data show good linearity within experimental error. K_{sv} values were determined from the slopes of the plots, and then k_q values were evaluated from K_{sv} values using the luminescence life-time of Ru(bpy)₃²⁺ in air saturated aqueous solution at 25 °C. $\tau = 0.4 \mu\text{sec}$.²⁰ The results are summarized in Table 1.

Among viologens investigated, k_q values in homogeneous aqueous phase are C₁C₁V < C₁C₈V < C₁BV < BBV ≤ C₈C₈V < C₁C₁₂V. This order cannot be explained in terms of diffusivity of the viologens. Two possibilities are suggested for the trend. One is the difference in reduction potential of viologens (Table 1). Table 1 shows good correlation between the potential of viologens and k_q , except for C₈C₈V. This accords with Marcus theory which predicts higher reaction rate, for a given electron donor, as the potential of electron acceptor, viologen, is less negative.²¹ The other is contribution of hydrophobicity of viologen to the reaction rate. As a viologen has greater hydrophobic character, it can form more stable encounter complex with Ru(bpy)₃²⁺ by

Table 1. The First Reduction Potentials of Viologens, and the Apparent Stern-Volmer (K_{sv}) and Bimolecular Rate Constants (k_q) for Emission Quenching of Photoexcited $\text{Ru}(\text{bpy})_3^{2+}$ by Viologens at 25 °C^a.

Medium viologen	$E_{1/2}^b$ (V)	Water		10 mM SDS		8 mM PSS ^c		8 mM PVS ^c	
		K_{sv}	k_q	K_{sv}^e	k_q^e	K_{sv}	k_q	K_{sv}	k_q
$\text{C}_1\text{C}_1\text{V}$	-0.72 ^c	392	0.98	3900	13	18500	26	634	1.6
$\text{C}_8\text{C}_8\text{V}$	-0.71 ^d	637	1.6	(1100)	(3.7)	4700	6.5	912	2.3
BBV	-0.57 ^d	631	1.6	6800	22	9480	13	819	2.1
$\text{C}_1\text{C}_8\text{C}$	-0.69 ^c	465	1.2	4100	13	10390	14	728	1.8
$\text{C}_1\text{C}_{12}\text{V}$	-0.58 ^c	711	1.8	4300	14	1650	2.3	197	0.49
C_1BV		546	1.4	5670	18	9280	13	721	1.8

^aUnits of K_{sv} and k_q are M^{-1} and $10^9 \text{M}^{-1}\text{sec}^{-1}$, respectively. ^bFirst reduction potentials of viologens vs SCE in water. ^cFrom cathodic peak potentials in cyclic voltammograms^{14a} assuming $E_{1/2} = E_{pc} + 0.03 \text{ V}$. ^dFrom ref 14b, ^eApparent values determined at [viologen] = 1.0 mM, except those of $\text{C}_8\text{C}_8\text{V}$ which were taken at $[\text{C}_8\text{C}_8\text{V}] = 0.10 \text{ mM}$. ^fThese values were taken at [viologen] $\rightarrow 0$.^{16a}

**Figure 2.** Stern-Volmer plots of luminescence quenching data of $\text{Ru}(\text{bpy})_3^{2+}$ by viologens in 10 mM SDS and 0.1 M NaCl.

hydrophobic interaction. This results in more efficient electron-transfer and thus the luminescence quenching, which occur in the encounter complex.²² This can explain the high quenching rate by $\text{C}_8\text{C}_8\text{V}$, despite of the similar magnitude of the reduction potential of the compound to $\text{C}_1\text{C}_1\text{V}$.

The possibility of association of $\text{Ru}(\text{bpy})_3^{2+}$ with viologens was suggested for $\text{C}_1\text{C}_1\text{V}$ by Gaines.²⁰ He showed that the Stern-Volmer constant for emission quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by the viologen is greater when it is determined from emission intensity (K_{sv}^f) than the value calculated from life-time measurement (K_{sv}^e), though the former Stern-Volmer plot is linear. From this, the author estimated the association constant K_{sv}^f to be ca. 30 M^{-1} . The association constant for viologen of greater hydrophobic character is expected to be larger. This accords with our results.

Quenching in SDS Micellar Solutions. In air-satu-

rated SDS solution, the luminescence intensity of $\text{Ru}(\text{bpy})_3^{2+}$ is slightly weaker and the emission maximum is red-shifted about 20 nm as compared to the SDS-free solution. Luminescence titration of $\text{Ru}(\text{bpy})_3^{2+}$ with SDS in 0.1 M NaCl show that the changes in the luminescence intensity and emission maximum of $\text{Ru}(\text{bpy})_3^{2+}$ by SDS are leveled off when the concentration of SDS exceeds 2 mM. This indicates that $\text{Ru}(\text{bpy})_3^{2+}$ is completely micellized at $[\text{SDS}] > 2 \text{ mM}$.

Unlike the trend in SDS-free solution, the Stern-Volmer plots in SDS solutions (Figure 2) show positive deviation from linearity. This indicates heterogeneity of binding sites in SDS micelle for viologens: surface charge of SDS micelle is neutralized upon binding of $\text{Ru}(\text{bpy})_3^{2+}$, thus the sites remote from $\text{Ru}(\text{bpy})_3^{2+}$ are the preferred binding sites for viologens and binding to the remote sites results in less efficient quenching than the binding to the adjacent sites. Apparent K_{sv} values were calculated at 1.0 mM viologens from eq 1: for $\text{C}_8\text{C}_8\text{V}$, K_{sv} value was estimated at 0.1 mM due to precipitation of the viologen/SDS complex at higher concentration of the viologen. Since the absorbance at the exciting wavelength and the band-width of the luminescence spectra of $\text{Ru}(\text{bpy})_3^{2+}$ do not change appreciably in the presence of SDS, we assume that the ratio of luminescence intensities at peaks, 0.78, is the ratio of excited life-times of $\text{Ru}(\text{bpy})_3^{2+}$. The estimated excited life-time of $\text{Ru}(\text{bpy})_3^{2+}$ is 0.31 μsec in air-saturated 10 mM SDS at 25 °C in the absence of viologens. The apparent bimolecular quenching constants are calculated by dividing the K_{sv} values by 0.31 μsec . The results are included in Table 1.

The quenching rate is in order of $\text{C}_8\text{C}_8\text{V} \ll \text{C}_1\text{C}_1\text{V} \leq \text{C}_1\text{C}_8\text{V} \leq \text{C}_1\text{C}_{12}\text{V} < \text{C}_1\text{BV} < \text{BBV}$. The low quenching rate for $\text{C}_8\text{C}_8\text{V}$ can be understood by embedment of alkyl chains of the viologen in the hydrocarbon region of SDS micelle, which reduces the mobility of the viologen on the micelle surface. The more conclusive data from this argument can be found in the work of Miyashita *et al.*¹³ who showed monotonic decrease in quenching rate constant of $\text{Ru}(\text{phen})_3^{2+}$ and $\text{Ru}(\text{dpphen})_3^{2+}$ by symmetric dialkylviologens as the alkyl groups vary from methyl to hexyl. It is interesting to note that the asymmetric viologens $\text{C}_1\text{C}_8\text{V}$ and $\text{C}_1\text{C}_{12}\text{V}$ show similar quenching constant to that for $\text{C}_1\text{C}_1\text{V}$, despite of the presence of long alkyl chains. It is thought that only the long alkyl chains of these viologens are inserted into SDS micelle placing the bipyridinium ring per-

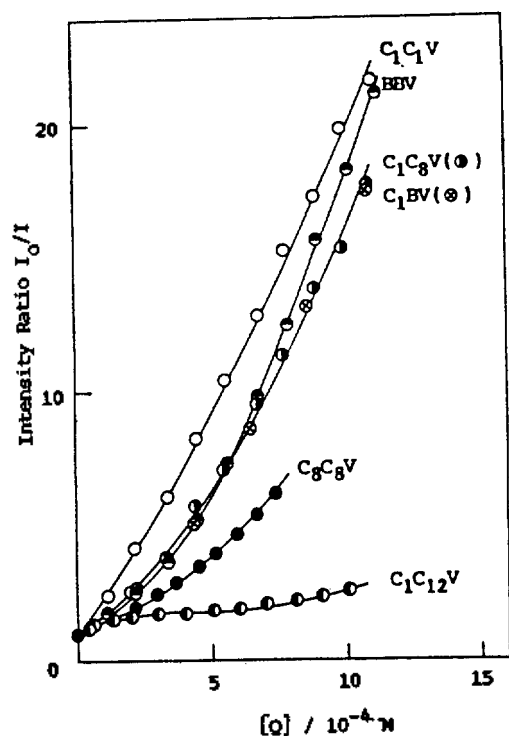


Figure 3. Stern-Volmer plots of luminescence quenching data of $\text{Ru}(\text{bpy})_3^{2+}$ by viologens in 8.0 mM PSS and 0.1 M NaCl.

pendicular to the micellar surface.^{11,13} This could result in higher surface diffusivity for the viologens than the symmetric viologens such as $\text{C}_8\text{C}_8\text{V}$ which bear two long alkyl chains and thus both of the alkyl chains are buried in micelle placing the bipyridinium ring parallel to the Stern-layer.¹³ Of course it is expected that $\text{C}_1\text{C}_{12}\text{V}$ has lower mobility in micellar phase than $\text{C}_1\text{C}_8\text{V}$. However it seems that the effect of mobility on quenching rate is roughly compensated by the effect of reduction potential revealed in SDS-free solutions. In relation to this, it is worth to mention that the reduction potentials of methylalkylviologens in L- α -phosphatidylcholine (PC) vesicle are close to the values taken in homogeneous aqueous solutions.^{14a}

BBV and C_1BV exhibit higher quenching rate for $\text{Ru}(\text{bpy})_3^{2+}$ than the viologens with long alkyl chain in SDS, micellar solutions. Upon the presence of SDS the quenching rates are enhanced about 13-fold, which is the same as that observed for $\text{C}_1\text{C}_1\text{V}$. This implies that the mobilities of $\text{C}_1\text{C}_1\text{V}$, C_1BV and BBV in SDS micellar phase are not much different from each other. Since benzyl group is bulky and not flexible with respect to the bipyridinium ring, insertion of the group deeply into the micelle is not feasible. Based on these arguments, we propose that the three viologens are loosely bound on the surface of SDS micelle.

Quenching in PSS Solutions. The luminescence intensity of $\text{Ru}(\text{bpy})_3^{2+}$ in aqueous medium increases 1.8 times with concomitant 3 nm red-shift of the emission maximum upon addition of PSS.^{16a} The excited state life-time in PSS solution without added quencher is expected to be 1.8 times of that in PSS-free solution, $\tau_{\text{PSS}} = 0.4 \times 1.8 \mu\text{sec} = 0.72 \mu\text{sec}$. The association constant of $\text{Ru}(\text{bpy})_3^{2+}$ with PSS in 0.1 M NaCl is reported to be $6 \times 10^4 \text{M}^{-1}$.^{16a} This value implies virtually complete binding of the complex cation on 8

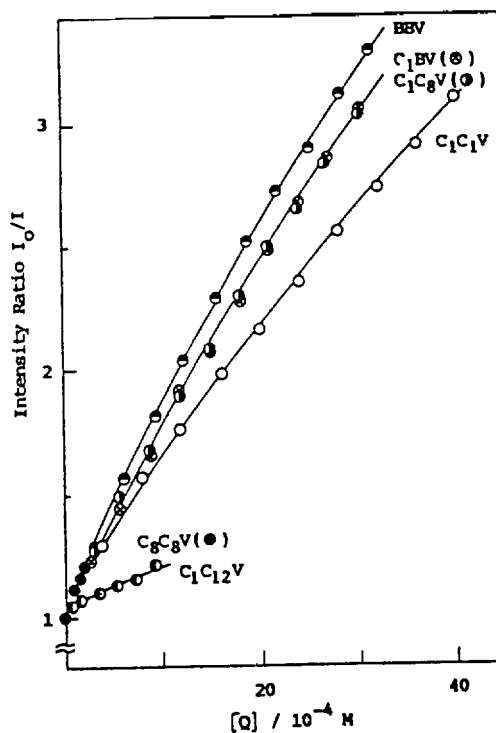


Figure 4. Stern-Volmer plots of luminescence quenching data of $\text{Ru}(\text{bpy})_3^{2+}$ by viologens in 8.0 mM PVS and 0.1 M NaCl.

mM PSS employed in this study.

Except $\text{C}_1\text{C}_1\text{V}$, the viologens form precipitate with 8 mM PSS, typically, when the concentration of viologens exceeds 1 mM. This allows the quenching study in 8 mM PSS only at viologen concentration below 1 mM. The quenching data are shown in Figure 3. As in the preceding section, we calculated the apparent K_{sv} and k_q values for the quenching reactions and the results are included in Table 1.

The Stern-Volmer plots (Figure 3) also show positive deviation from linearity as in SDS solutions (Figure 2) reflecting heterogeneity of binding sites with respect to the affinity for viologens. However a few noticeable differences are found between quenchings in SDS and PSS solutions. The enhancement of the quenching rate upon the presence of PSS ($k_{q,\text{PSS}}/k_{q,\text{water}}$) is 1.3 for $\text{C}_1\text{C}_{12}\text{V}$, 4 for $\text{C}_8\text{C}_8\text{V}$, 8 for BBV, 9 for C_1BV , 12 for $\text{C}_1\text{C}_8\text{V}$, and 29 for $\text{C}_1\text{C}_1\text{V}$. This shows close parallelism between the degree of suppression of the quenching by a viologen in PSS solutions and the hydrophobic character of the viologen. Amphiphilic molecules bind to PSS by electrostatic and hydrophobic interactions, and the bound amphiphiles aggregate to form micelle-like clusters in the polymer domain.²³ Such association with PSS is also expected for hydrophobic viologens. Because of positive charge and bulkiness of $\text{Ru}(\text{bpy})_3^{2+}$, the complex cation cannot be intimate enough to allow the electron-transfer to the viologen in the clusters. This can explain why the more hydrophobic viologen, which forms the cluster more effectively, is less effective quencher for $\text{Ru}(\text{bpy})_3^{2+}$ in PSS solutions.

Quenching in PVS Solutions. Unlike in PSS solution, the luminescence spectrum of $\text{Ru}(\text{bpy})_3^{2+}$ is not significantly altered by the presence of PVS. In Figure 4, we present the Stern-Volmer plots for quenching in PVS solutions. The K_{sv}

and k_q values extrapolated to $[\text{viologen}] = 0 \text{ mM}$ were calculated and the results are summarized in Table 1.

In contrast to the trend in SDS and PSS solutions, the Stern-Volmer plots for data taken in PVS solutions show negative deviation from linearity. Also quenching is much less efficient in PVS solution than the other two microheterogeneous solutions. Compared to the rate in homogeneous aqueous solution, the presence of PVS drops the quenching rate to $1/3$ for $C_{12}V$ and increases it less than 2 times for the other viologens. The large difference between PSS and PVS in the effects for the quenching rate is also found for Cu^{2+} : PSS in 0.1 M NaCl enhances the k_q over 20 times, whereas PVS in the same salt solution increases the rate less than 4 times.^{16a} Contrast to this, Meisel and co-workers showed that the rates of quenching of $\text{Ru}(\text{bpy})_3^{2+}$ by Cu^{2+} and Fe^{3+} increase as high as 1000 fold when PVS is added to salt-free solutions.²⁴ Therefore, we can soundly attribute the small enhancement in quenching rate by PVS observed in this study to the presence of 0.1 M NaCl.

The interaction between PVS and $\text{Ru}(\text{bpy})_3^{2+}$ or viologens is mainly electrostatic. The high ionic strength of the medium suppresses the electrostatic interaction. Thus the concentrating effect of PVS for reactants, hence the enhancement in reaction rate, is small in 0.1 M NaCl. In fact, our quenching data suggest most of $\text{Ru}(\text{bpy})_3^{2+}$ cations are free, not bound to PVS, in 0.1 M NaCl. On the other hand, PSS bears the hydrophobic phenyl groups which interact with the ligands of $\text{Ru}(\text{bpy})_3^{2+}$ through hydrophobic or $\pi-\pi$ interaction. This localizes the complex cations on the domain of PSS resulting in the spectral change and large enhancement of emission quenching.

The inhibition of the quenching reaction between $\text{Ru}(\text{bpy})_3^{2+}$ and $C_{12}V$ by PVS can then be explained as follows. Because of the presence of long alkyl chain, $C_{12}V$ forms micelle-like aggregates on PVS. The aggregates are wrapped up with polymer chain. Thus $\text{Ru}(\text{bpy})_3^{2+}$ ions, which reside mainly in bulk phase, are not accessible to the viologen.

Conclusions

Comparison of the rates of electron-transfer quenching between $\text{Ru}(\text{bpy})_3^{2+}$ and viologens in homogeneous aqueous phase, SDS, PSS, and PVS solutions leads to the following conclusions.

(1) In homogeneous aqueous medium, the quenching rate is governed by the first reduction potentials and hydrophobicity of viologens. The hydrophobic viologens form more stable encounter complex with $\text{Ru}(\text{bpy})_3^{2+}$ and thus show faster quenching rate.

(2) Both $\text{Ru}(\text{bpy})_3^{2+}$ and viologens are completely micellized to SDS micelles. The quenching in SDS is largely controlled by the surface mobility of viologens, which is governed by the degree of embedment of alkyl chains in the micelle. Benzyl group of methylbenzylviologen or dibenzylviologen is not buried in the micelle.

(3) $\text{Ru}(\text{bpy})_3^{2+}$ is totally bound to 8 mM PSS. The quenching in PSS solution decreases as the viologen is more hydrophobic. The viologens with long alkyl chain form clusters on PSS and the electron-transfer from $\text{Ru}(\text{bpy})_3^{2+}$ to the viologens in the clusters is not efficient.

(4) The presence of PVS in 0.1 M NaCl decreases or only slightly enhances the quenching rate. This is due to the weak affinity of $\text{Ru}(\text{bpy})_3^{2+}$ to PVS and formation of clusters of viologens with long alkyl chain on PVS domain.

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On the Transition between Stable Steady States in a Model of Biochemical System with Positive Feedback

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The transition from one stable steady state branch to another stable steady state branch in a simple metabolic system with positive feedback is discussed with the aid of the bimodal Gaussian probability distribution method. Fluctuations lead to transitions from one stable steady state branch to the other, so that the bimodal Gaussian evolves to a new distribution. We also obtain the fractional occupancies in the two stable steady states in terms of a parameter characterizing conditions of the system.

Introduction

Biochemical reactions with feedback mechanisms may show the interesting phenomena of multiple steady states, such as hysteresis due to transition among the branches of steady states and oscillation.¹⁻³ The multiple steady states which result from the use of homogeneous macroscopic equations have been observed in a variety of systems, especially in superconductor, in van der Waals gases, and etc.⁴ Many authors have studied the existence of multiple steady states and hysteresis in chemical and biochemical systems.^{2,5,7,8} These behaviors are exhibited due to nonlinearity of the kinetic equation involved. There exist simple kinetic models consisted of many dimensional ordinary differential equations for the concentrations of the metabolites in a biochemical system.^{3,7} Even though they are simplified, they are at least comparable with the experimental results qualitatively.

The purpose of the present paper is to investigate the transition between branches of stable steady states of a biochemically reacting system which is controlled by a positive feedback mechanism.⁷⁻¹⁰ At first, we obtained the steady state values from the deterministic equations which describe the instability for a biochemical reaction model with positive feedback. With the aid of the Fokker-Planck equation corresponding to the Langevin equation which describes fluctuations from the steady state due to the random forces (diffusion),^{5,6} we obtain the bimodal Gaussian distribution in the region of multiple steady states. The bimodal Gaussian distribution should evolve to a new distribution by fluctuations. Thus, in order to discuss transitions between stable steady states due to fluctuations we obtain the fractions which describes a new Gaussian distribution at stable steady

states in terms of the parameter which characterizes conditions of the system.

Theory

A kinetic equation for a model of metabolic control circuit with positive feedback is given as^{1,7}

$$\frac{d}{dt}X_1 = f(X_n, u) - k_1 X_1 \quad (2.1)$$

$$\frac{d}{dt}X_j = X_{j-1} - k_j X_j, \quad (2 \leq j \leq n)$$

where X_j and k_j are the dimensionless concentration and the rate constant of the j -th component, respectively, and

$$f(X_n, u) = \frac{u + X_n^p}{1 + X_n^p} \quad (2.2)$$

Here, p is the cooperativity of the positive feedback system and u is the controllable parameter depending on temperature and concentrations and etc.

Under the steady state approximation, the steady state value, X_n^0 , is the solution of the following equation:

$$f(X_n^0, u) - \varphi X_n^0 = 0, \quad (2.3)$$

with $\varphi = \prod_{i=1}^n k_i$. The steady state value X_n^0 is discontinuous at the marginal stability point u_r . As the parameter u is slowly increased, the system reaches a marginal stability point. Further increase in the parameter causes the system to change to another stable branch. As the parameter is decreased, the system evolves to another marginal stability