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Electron-Transfer Reactions in SDS Micelles: Reactivity of Pyrene and Tris(2,2′-bipyridyl)ruthenium(II) Excited States Investigated by Time-Resolved Luminescence Quenching

Irina V. Soboleva,[†] Jan van Stam,[‡,§] G. Bhaskar Dutt,[‡,||] Michail G. Kuzmin,*[,†] and Frans C. De Schryver*[,‡]

Department of Chemistry, M. V. Lomonosov Moscow University, 117 234 Moscow, Russia, and Departement Scheikunde, Katholieke Universiteit Leuven, Celestijnenlaan 200F, BE-3001 Heverlee, Belgium

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The effects of micellization on the rate constants and Gibbs energy of electron transfer (ΔG_{et}) are studied by time-resolved luminescence quenching of tris(2,2′-bipyridyl)ruthenium(II) (RUBIPY) and pyrene (PY) by electron acceptors and donors in sodium dodecylsulfate (SDS) micelles. For RUBIPY, which is bound to the SDS micelles and accessible to water, ΔG_{et} is considerably smaller than what is found in organic solutions, though the spectral properties of RUBIPY and the value of diffusion-controlled quenching rate constant are typical for the micellar interior. For this system, dissolution in micelles enables a change of the local reactant concentration and mobility, retaining their higher reactivity in aqueous solution. In contrast, for PY, which is known to be localized in the palisade layer of an SDS micelle, the quenching rate constants coincide well with those found in acetonitrile.

1. Introduction

Chemical reactivity in organized molecular systems is of primary importance for biochemical processes in, e.g., membranes and artificial molecular devices.[1−7] When the nature of the chemical reactions in organized systems is discussed, in particular electron- and proton-transfer reactions, the influence of the local microenvironment on the reactivity, the local concentrations, and the driving force have to be considered. To decrease the complexity of real biochemical systems, micellar solutions are often used as models for compartmentalized systems. Such systems offer the possibility to investigate the effects of the local reactant concentrations in the micellar subphase, as well as of the local microenvironment on the reactivity.

Micellar systems have been extensively studied the past decades, and numerous reviews have appeared.[6−15] Well-characterized surfactants, ionic as well as neutral, are available, and the distribution of dissolved species has been discussed in detail.[16,17] Using a well-characterized micellar system allows one to put the emphasis on other aspects of the system investigated, e.g., the reaction kinetics and the exchange of dissolved species between the micelles. One very common technique for the study of microheterogeneous systems is time-resolved luminescence quenching measurements.[18−22] By the introduction of a luminescent probe and quencher, both the reaction and the exchange rate constant can be determined on a molecular scale.

For the analysis of the luminescence decay data, several models have been developed. A model[23−25] for luminescence deactivation through quenching in micelles that considers the compartmentalization of the dissolved molecules over

* To whom correspondence should be addressed. E-mail addresses: Kuzmin@photo.chem.msu.su; Frans.DeSchryver@Chem.KULeuven.ac.be.

[†] M. V. Lomonosov Moscow University.

[‡] Katholieke Universiteit Leuven.

[§] Present address: Department of Chemistry, Karlstad University, SE-651 88 Karlstad, Sweden.

[||] Present address: Chemistry Division, Bhabha Atomic Research Centre, Trombay, Bombay 400 085, India.

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the micelles, which are viewed as individual entities, is generally used. For the particular case of mobile solutes, extended models, including the exchange of probe and quencher molecules between the micelles, are available.[20,26,27] When the quencher has a very high mobility between the micellar entities, allowing one specific quencher molecule to visit many micelles during the excited-state decay time of the luminescent probe, an alternative model, the pseudophase model, can be applied. Such a situation leads to a very simple monoexponential decay law and considers micellar solutions as two-phase systems, composed of a bulk phase and a micellar pseudophase.[5] It treats the reaction kinetics in these two phases as if they were two separate homogeneous solutions with particular concentrations of dissolved species.

Micellar systems also offer convenient model systems for the investigation of the effects of the binding and the local microenvironment on the reactivity. For instance, the effects of the microenvironment on the excited-state acidity of a molecule [28−35] and on the excited-state electron transfer[36−47] has been studied in restricted systems. The difference in shifts of pK_a found for positively charged and uncharged micelles indicates a difference of the interfacial potential between cationic and anionic micelles of about 100 mV.[36] Excited-state proton transfer is generally found to be slower in nonionic and anionic micelles than in homogeneous solution[30−32,36] and of about the same rate in cationic micelles.[32] Moreover, compartmentalization in micelles, leading to a change in the local environment, is known to strongly influence excited-state electron transfer.[41−46,48]

In this contribution, studies on the electron-transfer reactivity in SDS micellar systems are reported. The electron transfer between an excited probe molecule and a quencher molecule was monitored by time-resolved luminescence quenching measurements. Special interest was paid to the limiting case when the mobility of the quencher molecule becomes fast in comparison with the electron-transfer rate. In other words, when the electron transfer is significantly slower than the diffusion rate of the donor and the acceptor, the process will be controlled by reaction kinetics instead of by diffusion.

Two different classes of systems were studied: tris-(2,2′-bipyridyl)ruthenium(II) (RUBIPY) as luminescent probe with electron acceptors as quenchers and pyrene as probe with electron donors or acceptors as quenchers. RUBIPY is supposed to be located close to the SDS micelle−water interface, accessible for water molecules,[6] while pyrene is located in the apolar palisade layer of the micelle but still close to the micelle−water interface.[49]

2. Experimental Details and Data Analysis

Pyrene (PY) and the chloride of tris(2,2′-bipyridyl)ruthenium-(II) (RUBIPY) were used as luminescent probes. PY (Acros) was twice recrystallized from absolute ethanol, while RUBIPY (Aldrich) was used as received. All quenchers were from Aldrich and were recrystallized from ethanol or benzene if not other mentioned.

When PY was employed as probe, the following quenchers were used: 1,2-dicyanobenzene (DCB) (recrystallized from hexane), 4-chlorobenzonitrile (CBN), diethylamine (DEA), and 2-aminopyridine (AP). To quench the emission from RUBIPY, the following compounds were used: toluquinone (TQ) (sublimated three times), 1,3-dinitrobenzene (DNB), 3-nitrobenzaldehyde (NBA), 4-chloronitrobenzene (CNB), 4-fluoronitrobenzene (FNB), 4-nitrotoluene (NT), 4-nitroanisole (NA), and quinaldic acid (QA).

Sodium dodecyl sulfate (SDS) (BDH, specially pure) was used as received. All solvents were of highest purity, and water of Milli-Q quality was used for the aqueous solutions. Stock solutions of probes and quenchers in SDS were sonicated to ensure complete dissolution. The solutions for stationary and time-resolved measurements were prepared by mixing the stock solutions and neat micellar solution to obtain the desired concentrations. The concentrations of the probe and quencher were controlled by absorption measurements. The sample solutions were between 40 and 200 mM with respect to SDS and 1 μM with respect to pyrene or 10 μM with respect to RUBIPY. The quencher concentration was varied to give average occupation numbers between 0.1 and 5. It should be mentioned that the solutions were not deoxygenated; i.e., the luminescence decays were measured in the presence of oxygen dissolved in the solution.

A Specord M-40 spectrophotometer and a Perkin-Elmer LS-50 spectrofluorometer were used for stationary measurements. PY luminescence decays were recorded at 370 nm with a time-correlated single-photon counting instrument, described elsewhere,[50] with $\lambda_{ex} = 320$ nm. RUBIPY luminescence decays were recorded at 600−620 nm by a flash excitation equipment (ORTEC 9352 nanosecond light pulser), with a excitation pulse width of 1 ns. The excitation wavelength was $\lambda_{ex} = 400-420$ nm. All luminescence decays contained 10 000 peak counts, and all measurements were performed at 20 °C. All potentials are given vs SCE.

Luminescence decays were analyzed by a nonlinear least-squares iterative reconvolution method on an IBM RISC 6000 computer. The single and global curve analysis methods used in

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the analysis of the decays have been discussed earlier.[20] The analysis of the simulated decays and the fitting of the dependence of log k_q vs ΔG_{et} were performed within the framework of Microcal ORIGIN.

3. Theory

3.1. Electron-Transfer Reactions in Micellar Systems. Formally, the effect of the microenvironment on the electron-transfer reaction can be discussed in terms of thermodynamics or electrochemical potentials. When one compares an electron-transfer reaction in different media, the Gibbs energy of the reaction and the change of electrochemical potential can be expressed as functions of the solvation energies:

$$\Delta G = \Delta G^0 + \Delta(G_p) - \Delta(\Delta G_r) \tag{1}$$

Here ΔG and ΔG^0 are the changes in the Gibbs energies for the reaction in a given and a standard solvent, respectively, with superscript zero denoting the standard solvent. Similarly, $\Delta(\Delta G_r)$ and $\Delta(\Delta G_p)$ are the differences in the Gibbs energies of the reactants and products, respectively, between the two media, with subscript r denoting the reactants and p the products. Two factors are responsible for these changes: the distribution coefficient ρ of a reactant or product between the two phases and the interfacial potential $\Delta\psi$. The total change in Gibbs energy of transfer of a species j between the two phases can be expressed as

$$\Delta G_j = RT \ln \rho_j + z_j F \Delta\psi \tag{2}$$

with z_j denoting the charge of species j. If the correlation between the rate constant k and the driving force ΔG in a given microenvironment is similar to that in a chosen standard medium, the variation of ΔG can be estimated from the dependence of k on ΔG^0.

In contrast to excited-state proton transfer, of which the rate and equilibrium constants can be measured directly, only the rate constants can be measured for the excited-state electron transfer. Nevertheless, the shift of the equilibrium constant in a given standard solvent can be estimated from the threshold of ΔG^0, at which the rate constant drops substantially. If one assumes a similar dependence of log k on ΔG_r for the media under consideration, estimation of the quenching rate constants for a set of weak electron donors or acceptors from time-resolved luminescence measurements allows the determination of log k as function of ΔG^0. The dependence of the electron-transfer rate constant in micelles on the Gibbs energy was studied earlier for $\Delta G_{et} < -0.2$ eV, where the reaction is diffusion controlled.[51] Only small differences in the quenching rate constant, i.e., by a factor of 4, were found and were attributed to a difference in intramicellar diffusion kinetics.[51−53]

The Gibbs energy change of the forward electron-transfer step can be calculated[54] from the reduction potentials of the acceptor $E_{1/2}(A/A^-)$ and the donor $E_{1/2}(D^+/D)$ and the excited-state energy of the probe E^*:

$$\Delta G^0_{et} = F(E_{1/2}(D/D^+) - E_{1/2}(A^-/A)) - E^* - w_r + w_p \tag{3}$$

Here w_r and w_p are the electrostatic work necessary to bring two reactant or product ions together to a close contact distance, respectively. As all the quenchers used in this study are neutral molecules, w_r is zero. Using acetonitrile as standard solvent, w_p was estimated[55,56] for RUBIPY by calculating ΔG^0_{et} from eq 3 and by the use of the relation

$$w_p = \frac{z_a z_b e^2}{\epsilon d(1 + \beta d(\mu)^{1/2})} \tag{4}$$

where z_a and z_b are the charge of the two product ions, ϵ is the static dielectric constant of the medium, d is the sum of the radii of donor and acceptor, μ is the ionic strength of the medium, and $\beta = 8\pi N_A e/1000\epsilon k_B T$. For RUBIPY in acetonitrile, $z_a = +3$, $z_b = -1$, $\epsilon = 37.5$, and $d = 10.9$ Å, yielding $w_p = -13.4$ kJ/mol. Similarly, for pyrene in acetonitrile, the solvent chosen as standard solvent in this study; $z_a = \pm 1$, $z_b = \pm 1$, and $d = 7$ Å, yielding $w_p = -7$ kJ/mol.

Luminescence quenching experiments yield quenching rate constants that can be used to estimate the activation energy of the electron transfer. In a quasi steady-state situation

$$k_q = \frac{k_{diff}}{1 + k_{-diff}(k_r^{-1} + k_{-r}(k_r k')^{-1})} \tag{5}$$

$$k_r = k_0 \exp[-\Delta G^{\ddagger}/RT] \tag{6}$$

where k_{diff} and k_{-diff} are the forward and backward diffusion rate constants of the encounter complex, respectively, k_r and k_{-r} are the rate constants for the forward and backward electron-transfer reaction, respectively, and k' is the composite decay rate constant of the formed radical ion pair.

The electron-transfer activation energy, $\Delta G^{\ddagger}$, can be expressed by the empirical equation formulated by Rehm and Weller:[54]

$$\Delta G^{\ddagger} = (\Delta G_{et})/2 + [\Delta G_{et}{}^2/4 + (\Delta G^{\ddagger}_0)^2]^{1/2} \tag{7}$$

Here $\Delta G^{\ddagger}_0$ denotes the activation energy of an isoergonic reaction and ΔG_{et} the change in Gibbs free energy of the electron-transfer reaction.

To compare ΔG_{et} and $\Delta G^{\ddagger}_0$ for electron-transfer reactions in different media, eq 9 can be rewritten

$$\Delta G^{\ddagger} = (\Delta G^0_{et} + \delta)/2 + [(\Delta G^0_{et} + \delta)^2/4 + (\Delta G^{\ddagger}_0)^2]^{1/2} \tag{8}$$

with ΔG^0_{et}, the Gibbs free energy of electron transfer in the standard solvent (acetonitrile). δ is the shift in a given medium relative to the standard solvent; i.e., $\Delta G_{et} = \Delta G^0_{et} + \delta$.

Combing eqs 5−8 yields an expression for the quenching rate constant dependence on the electron-transfer activation energy:

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$$k_q = k_{diff}/\{b1 + b\{\exp[(\langle\Delta G^0_{et} + \delta\rangle/2 + \{\langle\Delta G^0_{et} + \delta\rangle^2/4 + \langle\Delta G^{\ddagger}_0\rangle^2|^{1/2})/RT] + c\exp[\langle\Delta G^0_{et} + \delta\rangle/RT]\}\} \quad (9)$$

where $b = k_{-diff}/k^0$ and $c = k_{-diff}/k'$. If $\Delta G^0_{et} + \delta \ll -\Delta G^{\ddagger}_0$, the electron transfer is diffusion controlled and $k_q \approx k_{diff}$, while if $\Delta G^0_{et} + \delta \gg \Delta G^{\ddagger}_0$, the electron transfer is controlled by the reactivity of the reactants, i.e., by $\Delta G^{\ddagger}$, and $k_q \approx k_r k_{diff}/k_{-diff}$.

Hence, from eq 9, the variables δ and $\Delta G^{\ddagger}_0$ can be obtained from the experimental data, if b and c are known. For PY, $b = c = 0.25$,[54] while, from the studies of Kitamura et al.,[55−57] b can be set equal to 0.01 and c to 10 for RUBIPY/electron acceptors, whereas, for RUBIPY/electron donors, $b = c = 0.01$. These values were used in the fittings of eq 9 to the SDS data as well as to the data from homogeneous solutions. If $k_{-r} \ll k'$, i.e., for endergonic electron transfer, the term $k_{-r}/(k_r k')$ vanishes and $k_q \approx k_{diff}/(1+k_{-diff}/k_r)$.

To estimate k_{diff} for SDS micelles, the maximum value of k_q, obtained for quenchers with $\Delta G^0_{et} < -0.2$ eV, was used. From $k_{diff} = 3 \times 10^8$ M^{-1} s^{-1} and the relation $k_{diff} = 8RT/3000\eta$, the intramicellar SDS viscosity was calculated to be $\eta_{SDS} = 20$ cP. Values on the local translational viscosity in SDS micelles have been reported and are of the same order.[17,58]

3.2. Kinetics of Luminescence Quenching in Micelles with a Stationary Probe and a Mobile Quencher. Infelta[23,25] and Tachiya[24] developed a model for the quantitative description of the kinetics of the quenching of an excited probe in micellar solutions, assuming Poisson distribution of probe and quencher molecules over the micelles and the possibility of quencher migration between the micelles. This model, which has been extensively used[52,59−68] and elaborated on,[19,20,26,27] can, for the case of a stationary probe and a quencher which is allowed to migrate between the micelles via the bulk, be given as

$$F_t = F_0 \exp[-A_2 t - A_3(1 - \exp(-A_4 t))] \quad (10)$$

where F_0 is the luminescence intensity at time $t = 0$ and the parameters $A_2 - A_4$ are given by

$$A_2 = k_0 + \langle n\rangle k_{out} k_{qm}/A_4 \quad (11)$$

$$A_3 = \langle n\rangle k^2_{qm}/{A_4}^2 \quad (12)$$

$$A_4 = k_{out} + k_{qm} \quad (13)$$

k_0 is the composite decay rate constant of the probe in the absence of any quenchers, k_{qm} the first-order rate constant for quenching by one quencher molecule in a micelle, k_{out} the first-order rate constant for one quencher to exit from a micelle to the bulk, and $\langle n\rangle$ the average number of quencher molecules per micelle. For the case of simplicity, it is assumed that the only mechanism for quencher migration is via the bulk; i.e., hopping due to a fusion−fission mechanism is neglected. This assumption is valid for ionic surfactant micelles at low concentrations.

From time-resolved luminescence quenching measurements in micellar systems, the first-order quenching rate constant k_{qm} is determined. This constant refers to the quenching rate of *one* quencher molecule in a micelle. If the micellar volume, V_m, is known, the second-order constant k_q can be calculated from k_{qm}: $k_q = k_{qm} V_m N_A$. For SDS micelles, a volume of 20 nm^3 is assumed, corresponding to a micellar radius of 16−17 Å.[69]

If the migration of quencher molecules is very fast compared to the quenching rate constant, i.e., $k_{out} \gg k_{qm}$, the model presented in eqs 10−13 will take a simpler form. The parameters A_2−A_4 will under these circumstances approximately be given as

$$A_2 = k_0 + \langle n\rangle k_{qm} \quad (14)$$

$$A_3 = \langle n\rangle k^2_{qm}/k^2_{out} \quad (15)$$

$$A_4 = k_{out} \quad (16)$$

and eq 10 takes the form of a monoexponential decay function

$$F_t = F_0 \exp(-t/\tau) \quad (17)$$

with $\tau = (k_0 + \langle n\rangle k_{qm})^{-1}$. Under such conditions, a different approach can be used to describe the reaction kinetics, the so-called pseudophase model.[5,46] In this model, the micelles are considered to form one homogeneous pseudophase. The reactants are assumed to be distributed over the micellar pseudophase and the bulk phase, this distribution being described by their distribution coefficients, i.e., their equilibrium distribution. It is supposed that the equilibrium distribution is reached faster than the reaction rate. The pseudophase model postulates that the reaction kinetics in the micellar pseudophase is similar to that in a homogeneous solution. The only difference is that the local, pseudophase, reactant concentrations should be used instead of the total concentrations. In this way, τ can directly yield the second-order quenching rate constant k_q:

$$\tau = (k_0 + k_q Q_m)^{-1} \quad (18)$$

Here Q_m is the local molar concentration of the quencher in the micellar pseudophase,

$$Q_m = Q_t\{\rho^{-1} + V_s N_A S_m\} = \langle n\rangle/(\langle a\rangle V_s N_A) \quad (19)$$

Q_t is the total quencher concentration in the solution, V_s the volume of a surfactant molecule, and $\langle a\rangle$ the average number of surfactant molecules per micelle. The distribution coefficient, ρ, for the distribution of the quencher between the micellar pseudophase and the bulk phase, is defined as the ratio of the equilibrium concentrations of

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Table 1. Parameters Obtained for Luminescence Quenching of PY and RUBIPY in SDS Micelles by Various Electron Acceptors and Donors[a]

N	chromophore	quencher	τ_0, ns	ΔG^0_{et}, eV	$10^{-6}\ k_{qm}$, s^{-1}	$10^{-7} k_q$, $M^{-1}\ s^{-1}$	ρ
	pyrene		178				
1		DCB		−0.81	18	8	50
						22[b]	100
2		CBN		−0.09	2.3	2.8	100
3		DEA		0.02	0.54	0.65	≈1
4		AP		0.03	0.97	1.2	50
	RUBIPY		420				
5		TQ		−0.57	12	14	30
6		DNB		0	5.4	6.5	160
7		NBA		0.21	3.7	4.5	40
8		CNB		0.25	3.0	3.6	540
9		FNB		0.32	1.6	1.9	30
10		NT		0.40	1.3	1.6	50
11		NA		0.46	1.3	1.6	400
12		QA		0.89	0.40	0.48	100

[a] k_q was calculated from the experimentally estimated k_{qm} values and the SDS micellar volume. [b] Determined by the pseudophase model.

the quencher in the both phases:

$$\rho = Q_m/Q_b \tag{20}$$

Q_m is the pseudophase concentration, and Q_b, the concentration in the bulk. The concentration of surfactant participating in the forming of the micelles, S_m, is given by

$$S_m = S_t - cmc \tag{21}$$

S_t and cmc denote the total molar surfactant concentration and critical micelle concentration, respectively.

Equations 18−21 provide a possibility to determine the bimolecular quenching rate constant, k_q, and the distribution coefficient from measurements of the luminescence decay times at various quencher and surfactant concentrations. It should be stressed that the pseudophase model can be used for the determination of the quenching rate constant only if the luminescence decay is monoexponential in the presence of a quencher.

4. Results and Discussion

4.1. RUBIPY and Pyrene Luminescence Decay. In the absence of quenchers, the luminescence decays of PY and RUBIPY were monoexponential for all SDS solutions. The RUBIPY decay times in different SDS solutions varied in the range of 380−420 ns, but in every set of experiments, samples with identical τ_0 were used. The estimated values of k_q were independent of the value of τ_0. The PY decay time was about 180 ns in all sets.

The values of the quenching rate constant k_q depend on Table 1, which confirms that the quenching in these systems follows the electron-transfer mechanism. This has also been reported for the quenching of RUBIPY in acetonitrile by various electron donors and acceptors.[55−57,70,71]

The luminescence decays, in the presence of quenchers, of RUBIPY or PY in SDS micelles were analyzed to yield the data presented in Table 1. Representative luminescence decays of PY in SDS micelles in the presence of quenchers are given in Figure 1.

For RUBIPY in the presence of weak quenchers (NBA, NT, FNB, and QA), the luminescence decay was monoexponential or did not deviate much from monoexponentiality at low quencher concentrations, i.e., $k_q \ll k_{out}$. For these sets, the first-order (k_{qm}) and the bimolecular (k_q) quenching rate constants were determined by eqs 12−15 and 24 and 25, respectively. Quenching the RUBIPY luminescence by the strong acceptors DNB and CNB, however, yielded multiexponential decays even at low quencher concentrations, and the quenching rate constants, as determined by eqs 12−15, indicate a diffusion-controlled electron-transfer reaction.

For the quenching of the PY luminescence, only one quencher, i.e., the very week electron donor DEA, yielded

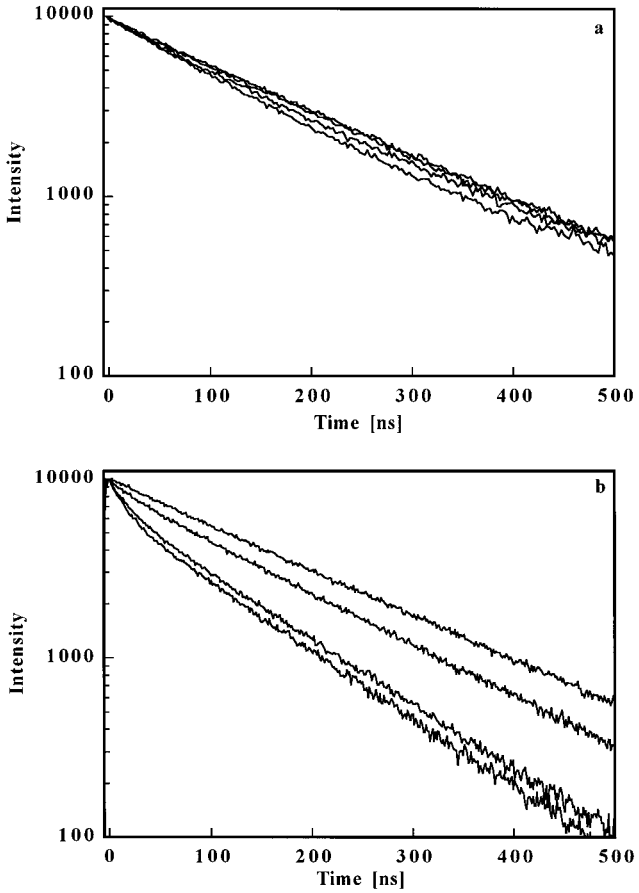

Figure 1. Luminescence decay curves for the quenching of PY in SDS micelles at various concentrations of a quencher. (a) DEA as quencher. The quencher concentration is, from the top decay curve to the bottom, 0, 19.2, 57.6, and 96.0 mM, respectively. The SDS concentration was 48 mM.(b) DCB as quencher. The quencher concentration is, from the top decay curve to the bottom, 0, 0.27, 0.83, and 0.96 mM, respectively. The SDS concentration was 40 mM.

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Table 2. Shifts (δ) of ΔG_{et}, Relative to the Standard Acetonitrile Solution (ΔG^0_{et}), Activation Energies for the Isoergonic Reaction ($\Delta G^{\ddagger}_0$), and Diffusion Rate Constants (k_{diff}) for Excited-state Electron Transfer Reactions in Various Media

reaction	medium	δ, eV	$\Delta G^{\ddagger}_0$, eV	log k_{diff}
PY/donors and acceptors	acetonitrile	-0.18 ± 0.02	0.20 ± 0.02	10.2
PY/donors and acceptors	SDS micelles	-0.10 ± 0.10	0.14 ± 0.06	8.5
RUBIPY/acceptors	acetonitrile	-0.13 ± 0.03	0.19 ± 0.01	10.2
RUBIPY/electron donors	acetonitrile	0.07 ± 0.01	0.18 ± 0.04	10.2
RUBIPY/acceptors	ethanol	-0.34 ± 0.04	0.25 ± 0.02	9.6
RUBIPY/acceptors	H_2O	-1.25 ± 0.02	0.24 ± 0.01	9.6
RUBIPY/acceptors	SDS micelles	-1.25	0.39 ± 0.01	8.5

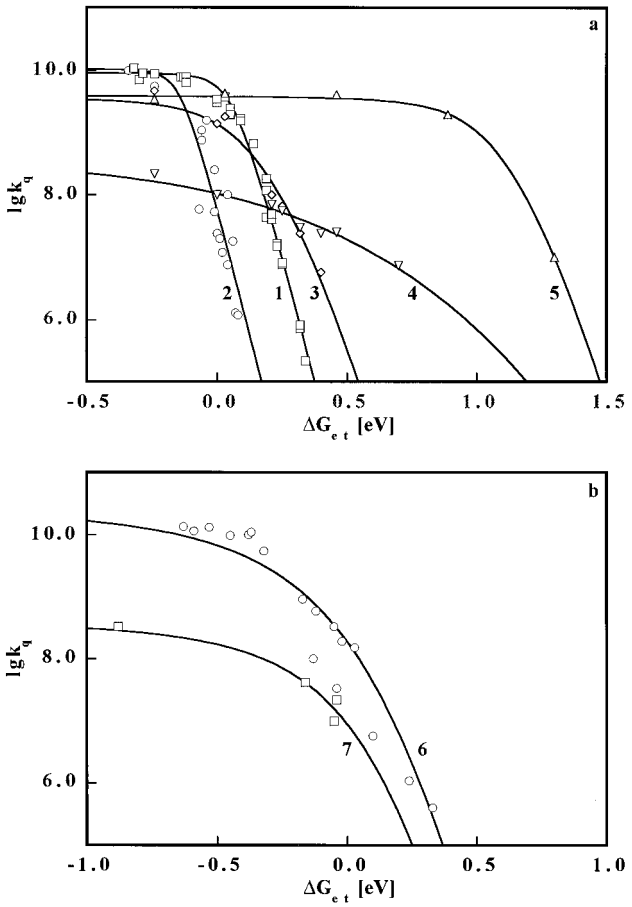

Figure 2. Dependence of the quenching rate constants k_q on Gibbs energy of electron transfer (ΔG^0_{et}), calculated by eq 9. The curves are the result of the fitting of eq 9 to the data. (a) Quenching of RUBIPY: by acceptors (1, □) and by donors (2 , ○) in acetonitrile;[56,70] by acceptors in ethanol (3, ◇), In water (4,▽), and in SDS micelles (5, △). Quenching of PY: by electron donors and acceptors in acetonitrile (6, ○)[79] and in SDS micelles (7, □).

monoexponential decays over a broad range of concentration, Figure 1a, and eqs 24 and 25 were used to determine k_q. Other quenchers, e.g., the strong electron acceptor DCB ($\Delta G^0_{et} = -0.8$ eV), yielded multiexponential decays regardless of the quencher concentration, Figure 1b, and eqs 12−15 were used to calculate k_{qm}.

4.2. Effects of Micellization on the Electron-Transfer Rate Constants. The quenching rate constants k_q for a set of weak electron donors or acceptors were used to calculate $\Delta G^{\ddagger}_0$ and the shift δ of ΔG_{et} for excited-state electron transfer in SDS micelles relative to the standard solvent, acetonitrile, Figure 2. The data were evaluated by the use of eq 11, and the results are compiled in Table 2. The shift δ depends mainly on the values of ΔG^0_{et} when k_q starts to drop. Close to the diffusion limit, at high values of k_q, and for strong quenchers, k_{diff} is almost insensitive to ΔG_{et}. The estimates of $\Delta G^{\ddagger}_0$ are in good agreement with literature data, e.g., 0.26 eV for RUBIPY in acetonitrile,[55] 0.22−0.25 eV for RUBIPY in H_2O,[72] and 0.56 eV for PY in SDS micelles.[53]

For electron transfer reactions of RUBIPY and PY in homogeneous solutions, electrochemical data are known. For RUBIPY, the redox potentials of both reactants are substantially different in aqueous and organic (including protic) solvents. The experimental oxidation potential of RUBIPY decreases from 1.29 V in acetonitrile[70] to 1.0 V in water between pH 2 and 7 [73] and to 0.84 V in high ionic strength aqueous solution.[72] As the reduction potentials for the quenchers used in this study increases by 0.65−0.92 V when going from acetonitrile to water,[74] ΔG_{et} decreases significantly when shifting from an organic solvent to water. This decrease yields a large positive shift (ca. 1 eV) of log k_q vs ΔG^0_{et} in aqueous solutions as compared to organic solvents. The comparison of the quenching of RUBIPY by electron acceptors, i.e., quinones and nitroaromatic compounds, in SDS micelles and in homogeneous solutions[48,75,76] shows that the values of ΔG_{et} in SDS micelles are close to those in water. The emission spectrum of RUBIPY in SDS micelles, however, is notably shifted ($\lambda_{max} = 628$ nm) relative to that in water or in polar organic solvents ($\lambda_{max} = 608-610$ nm). The value of the diffusion rate constant k_{diff} is typical for what is found in micelles and 1 order of magnitude lower than that in water. It has been shown, by the magnitude of the D_2O/H_2O isotope effect on the excited-state lifetime, that only about 30% of the RUBIPY surface is accessible to water molecules when RUBIPY is dissolved in an SDS solution.[77] Others also report data supporting the RUBIPY to be embedded in the SDS corona region.[78,79] Despite the localization of the probe in the corona and the quenchers inside the micelle, the value of the electron-transfer driving force (ΔG_{et}) is typical for what is found in aqueous solutions. This indicates a considerable reorganization of the local environment during the electron-transfer reaction, a reorganization leading to the large observed change of ΔG_{et}.

For PY, no remarkable difference between the values of k_q in SDS micelles and in acetonitrile was found, in contrast to RUBIPY. The reactivity of PY in organic and aqueous solutions cannot be compared, however, since

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the solubility of PY in water is too low. Hence, one cannot conclude whether the difference between PY and RUBIPY is caused by their different localization in the micelles or by the absence of a "water effect" on the reactivity of PY. Investigation of other aromatic probes with a higher water solubility, e.g., naphthalene, could be a promising way to study the effect of micellization on the reactivity of hydrophobic probes.

5. Conclusions

Time-resolved luminescence quenching measurements have been employed to investigate the effect of solubilization in SDS micelles on the excited-state electron-transfer reactivity for two luminescence probes, RUBIPY and PY, using weak electron donors and acceptors as luminescence quenchers. Excited-state electron transfer in micelles is controlled by the diffusion of the reactants inside the micelle and their local micellar concentration. RUBIPY has a much higher oxidation potential in aqueous solutions relative to organic solvents, and its excited-state electron-transfer reactions are about 1 eV more exergonic in aqueous solutions as compared to acetonitrile.

The luminescence spectra and electron-transfer kinetics prove that RUBIPY and PY are both dissolved in the SDS host micelles. A comparison of the dependence of log k_q on ΔG^0_{et} in SDS micelles, in acetonitrile solutions, and in aqueous solutions demonstrates a considerable difference between RUBIPY and PY. For RUBIPY in SDS micelles, the rate constants and energetics of the electron transfer correspond to an aqueous solution rather than to organic media. For PY in SDS micelles, though, the rate constants and energetics coincide with what is found in organic media. Due to the low aqueous solubility of PY, no data are available for water as solvent.

The substantial difference between the data on the localization of RUBIPY in SDS micelles and its kinetic properties indicates that a significant reorganization of the local microenvironment occurs during the electron-transfer process. This reorganization might affect the rates of hydration and dissociation of the formed radical ion pair. In this way, solubilization in micelles provides means to change the local concentration of the reactants without affecting their effective redox potentials.

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