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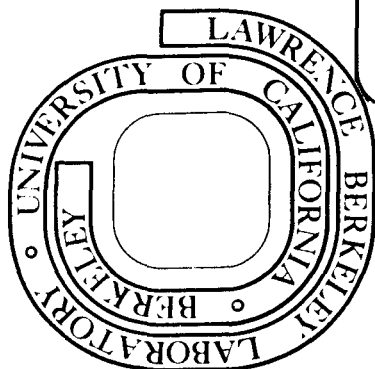
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THE QUENCHING OF RHODAMINE 101 EMISSION IN METHANOL
AND IN COLLOIDAL SUSPENSIONS OF LATEX PARTICLES

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The quenching of rhodamine 101 emission in methanol by triethylamine, N,N-dimethylaniline, diphenylamine and N-methyldiphenylamine was attributed to electron transfer. The values of the rate constants, which range from $10^8 - 10^{10} \text{ M}^{-1}\text{s}^{-1}$, are in agreement with theoretical predictions of electron transfer. A comparison is made between the redox processes in methanol and on the surface of hydrocarbon latex particles suspended in aqueous solution. The association constants for the equilibria of rhodamine 101 and diphenylamine between the latex and bulk solution are 3.0×10^4 and $1.6 \times 10^4 \text{ M}^{-1}$, respectively. The quenching efficiency of diphenylamine containing 17 to 98 ppm latex in solutions / is 22-72 folds higher than that in the methanolic solution. The fluorescence lifetime of rhodamine 101 is 4 ns in methanol. The fluorescence quantum yield in methanol ($\phi_F = 0.99$) and water ($\phi_F = 0.71$) were also determined. The implication of these results to photochemical storage reactions is discussed.

INTRODUCTION

Efficient conversion of light quanta into chemical free energy requires that energy losses of the absorbing system due to luminescence and non-radiative heat production be minimized. In homogeneous solutions, intermolecular electron transfer usually proceeds from the excited triplet state rather than the excited singlet state of a molecule because the lifetime of the latter is short compared with encounter times. Formation of the triplet state, however, entails the loss of the singlet-triplet splitting energy which may be as much as several tens of kcal/mole.¹ In turn, the decrease in excitation energy is associated with a diminution in the oxidizing and reducing power of the state.² The time between excitation and encounter can be an important factor in determining the nature and course of a reaction. By decreasing the distance between donor and acceptor molecules the efficiency of reaction may be markedly affected. In photosynthesis, for example, it is presumed that the proximity of the chlorophyll molecule to the primary acceptor permits the excited singlet state rather than the triplet state of chlorophyll to drive the redox reaction despite the short lifetime of the former state.³

Electron^{2,4} and energy⁵ transfer efficiencies in micellar systems can be greatly enhanced relative to ordinary solution reactions. However, micellar assemblies are in constant dynamic equilibrium which is one of the problems in using them. We are thus trying a more stable system consisting of a cross-linked copolymer of styrene-butadiene acrylic acid. Cellarius and Mauzerall⁶ in modeling the photosynthetic unit observed photosensitized dye reduction via pheophytin adsorbed on neutral polystyrene colloids.

Our current interest in visible light-induced electron-transfer processes has prompted us to examine some rhodamine compounds. The rhodamine dyes

have been extensively studied in relation to their lasing properties and the effect of molecular structure and environment have been discussed.⁷ The redox behavior of the triplet state of several rhodamines has been examined by flash photolysis⁸ and the cation and anion radical of the dyes characterized. The rhodamines have been used as a spectral sensitizer of wide band gap semiconductors⁹; the process involves charge transfer from the excited state of the adsorbed dye to the conduction band of the substrate. Anions such as I^- , SCN^- , Br^- , Cl^- and OH^- can reduce the excited state of rhodamine^{7,10} while Eu^{+3} can oxidize it.¹¹

One of the newest members of this family of dyes is rhodamine 101 about which little photochemistry is known. The internal conversion and intersystem crossing efficiency of this dye are nearly zero in alcohol. In fact, rhodamine 101 has the highest fluorescence quantum yield of all the rhodamines.⁷

This paper describes our effort to utilize the excited singlet state of rhodamine 101 to initiate electron abstractions from triethylamine, N,N-dimethylaniline, diphenylamine and N-methyldiphenylamine. Fluorescence quenching rate constants of the rhodamine-amine systems were measured in methanol and compared with theoretical predictions of Weller^{12,13,14} for electron transfer. A comparison is made between the quenching processes in methanol and those on the surface of anionic polymeric latex particles. Interpretation of the quenching data for the rhodamine-amine latex system requires knowledge of the concentration and location of the rhodamine and the quencher on the latex particles. The results of these measurements and the corresponding interpretations form the nucleus of this paper.

EXPERIMENTAL

Materials. Rhodamine 101 perchlorate (Exciton, laser grade) and diphenylamine (AR grade) were recrystallized from ethanol-water mixtures.

N,N-dimethylaniline, N-methyldiphenylamine and triethylamine were AR grade and used without further purification. The water was freshly redistilled in Pyrex from an alkaline permanganate solution and the methanol was spectral grade. The latex material (Dow Chemical) was composed of a cross-linked copolymer of 57% styrene, 41% butadiene and 2% acrylic acid. Emulsifier and ionic impurities were removed from an aqueous latex suspension by mixed-bed ion exchange consisting of Bio-Rad AG 1X10 and AG 50 WX2 resins. The concentration of latex particles in solution was based on dry weight. A known volume of solution was dried at 60°C in a vacuum oven to a constant weight. Knowing the solution volume, the density of water and the weight of the dried latex, the density of the latex particles was determined to be 1.02 g/cc.

At the concentration of the rhodamine employed in methanol no aggregation takes place as indicated by the lack of deviation from Beer's law. The solutions used in fluorescence quenching studies were not deoxygenated since preliminary results indicated no difference between the emission intensity of argon and air-saturated dye solutions. The absence of the oxygen quenching effect is consistent with the short lifetime of rhodamine 101 and the concentration of oxygen in an air-saturated solution ($\leq 10^{-3}$ M). Errors derived from self-absorption were insignificant at the concentration of dye employed. No photochemical deterioration of the rhodamine in quencher-free solution was observed spectrophotometrically during the course of the experiments. All fluorescence quenching measurements were carried out at 22°C.

Absorption Spectra. Absorption spectra were obtained using 0.5, 1.0 and 10.0 cm path length quartz cuvettes on a Cary 118 spectrophotometer.

Fluorescence Spectra and Quantum Yields. Fluorescence spectra for kinetic experiments were recorded on a Hitachi Perkin-Elmer MPF-2A spectrofluorimeter equipped with a red sensitive Hamamatsu R136 photomultiplier tube. Quantum yield measurements were determined on a Perkin-Elmer MPF-3L spectrofluorimeter with a corrected spectrum attachment. Excitation and

emission bandpasses of 4 nm were employed for all measurements. The quantum yields were determined relative to rhodamine 6G in ethylene glycol ($\phi_F = 0.96$).¹⁵ The standard and sample solutions were made up to have equal absorbances (<0.03) at their respective excitation and emission wavelengths (534 nm for rhodamine 6G, 567 nm and 570 nm for rhodamine 101 in methanol and water, respectively). A quadratic correction for refractive index differences¹⁶ was applied to the results. A relative error of 10% is estimated for the quantum yield determination.

Fluorescence Lifetime Measurement. The fluorescence lifetime of rhodamine 101 was measured using time-correlated single-photon counting having sub-nanosecond time resolution.¹⁷ The rhodamine solution was excited at 550 nm and the emission at 590 nm was monitored at right angles to the irradiation direction by a red sensitive RCA 8852 photomultiplier. The emission decay curve was exponential.

RESULTS AND DISCUSSION

Considerations of Absorption and Emission Properties of Rhodamine 101.

The first excited singlet state of rhodamine 101 is 2.1 eV above the ground state in methanol as the onset of the first singlet-singlet absorption band is ca 593 nm (Figure 1). In the more polar water, the main absorption band is about 8 nm red shifted and the singlet excitation energy is reduced to 2.06 eV. Rhodamine 101 has a large extinction coefficient (Figure 1) in the visible region which is consistent with a strongly allowed $\pi\pi^*$ state transition. As with most of the rhodamines,⁷ the fluorescence spectrum of the dye bears a mirror-image relation to the long wavelength absorption band.

The rate constants of rhodamine 101 for intersystem crossing k_{ISC} and internal conversion k_{IC} are much lower than that for radiative decay k_F as the fluorescence quantum yield ϕ_F is 0.99 in methanol and 0.71 in water.

$$\phi_F = \frac{k_F}{k_F + k_{ISC} + k_{IC}} \quad (1)$$

The former value is in agreement with reports in the literature,^{7,15} while the latter has not been measured previously.

Fluorescence Quenching in Methanol. Rhodamine 101 was excited with 550 nm light and the intensity of its fluorescence was monitored at 587 nm for methanolic solution containing various aromatic and aliphatic amines. At the concentration of dye ($<10^{-5}$ M) employed, rhodamine is mainly unprotonated as can be seen in Table 1 by comparing the position of its absorption maximum in acidic and basic methanol with that in which no acid or base was added. At the excitation wavelength only the rhodamine absorbs.

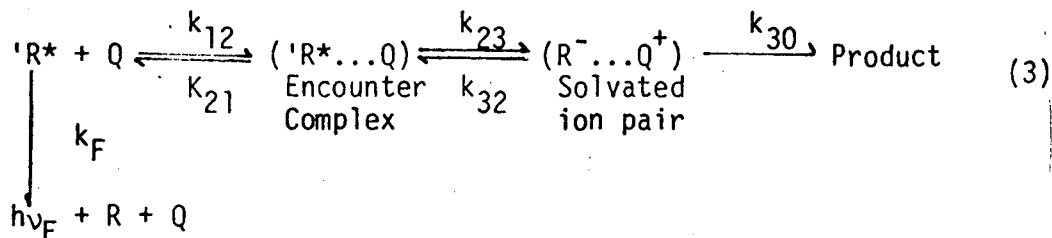
The Stern-Volmer constant (τk_Q) was calculated using

$$\tau k_Q = \left[\frac{F_0}{F} - 1 \right] / [Q] \quad (2)$$

where $[Q]$ is the concentration of the quencher, (k_Q) the quenching constant of the excited singlet state, and F_0 and F are the fluorescence intensities in the absence and presence of the quencher (Figures 2 and 3). In methanol the lifetime (τ) is 4.0 ± 0.1 ns, which is consistent with the lifetimes of other rhodamines in methanol and ethanol.¹⁸

The fluorescence quenching rate constants k_Q range from 10^8 to 10^{10} $M^{-1}s^{-1}$ (Table 2); the quenching constants of the arylamines are diffusion controlled. Since the energy of the excited singlet state of rhodamine is 2.1 eV above the ground state whereas the excitation energy of the amines are larger than 3.5 eV, the quenching of the dye fluorescence is not due to dipole-dipole energy transfer.

On the basis of arguments given below we propose that the quenching mechanism involves a sequence of steps resulting in the electron transfer from the quencher amine (Q) to rhodamine 101 (R) according to the scheme:



The encounter complex formation between the rhodamine excited singlet state and the quencher is followed by the actual charge transfer, producing an ion pair in the solvent cage which either separates into free ions or gives the ground or triplet state of rhodamine and the ground state of the amine. Excitation of the triplet states of the amines cannot occur since their triplet states are at least 1 eV higher in energy than the excited singlet state of rhodamine 101. This model was formulated by Rehm and Weller^{12,13} to account for the fluorescence quenching of a number of polynuclear aromatic hydrocarbons by a wide assortment of electron donors including arylamines. More recently, the mechanism has been applied successfully to several organic dye triplet systems.¹⁹

A kinetic analysis¹³ of the reaction scheme has shown that the rate constant of the excited singlet state quenching k_Q is correlated with the free energy change ΔG_{23} of the electron transfer according to

$$k_Q = \frac{k_{12}}{1 + \frac{k_{12}}{k_{30}} \left[\exp\left(\frac{\Delta G_{23}^\ddagger}{RT}\right) + \exp\left(\frac{\Delta G_{23}}{RT}\right) \right]} \quad (4)$$

It was shown¹³ that $k_{12}/k_{30} \approx 0.25$ and that the diffusion-controlled rate constant $k_{12} = 2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. The charge transfer is assumed to occur by an outer-sphere mechanism and requires that the activation free energy ΔG_{23}^\ddagger is a monotonic function of ΔG_{23} .

$$\Delta G_{23}^{\ddagger} = \frac{\Delta G_{23}}{2} + \left[\left(\frac{\Delta G_{23}}{2} \right)^2 + \left(\Delta G_{23}^{\ddagger}(0) \right)^2 \right]^{1/2} \quad (5)$$

where $\Delta G_{23}^{\ddagger}(0)$ is the activation free energy at $\Delta G_{23} = 0$. When $\Delta G_{23}^{\ddagger}(0)$ is 2.4 kcal/mole, Eq (7) is found to agree closely with the experimental rate constants.^{12,13} In terms of the electron-transfer theory of Marcus,¹⁹ however, ΔG_{23}^{\ddagger} is a quadratic function of ΔG_{23} . Except for large negative values of ΔG_{23} (> -16 kcal/mole) both relations yield similar results.¹³

As close agreement between the experimental and calculated rate constants has been used as evidence for electron transfer, we intend to use Equations 4 and 5 to assess our results.

The free energy change ΔG_{23} , involved in the actual charge-transfer process can be determined using¹³

$$\Delta G_{23} = E(Q^+/Q) - E('R^*/R^-) + e^2/\epsilon a \quad (6)$$

where the first two terms are redox potentials and the third is the Coulomb energy released in bringing the ions to within the encounter distance, a . The reduction potential of the excited singlet state of rhodamine 101, $E('R^*/R^-)$ may be estimated from the redox potential of the ground state of the dye and its singlet excitation energy ($E_s = 2.09$ eV)

$$E('R^*/R^-) = E(R/R^-) + E_s \quad (7)$$

To a good approximation, the reduction potential of rhodamine 101 should be the same as that of rhodamine B which has been reported²¹ to be -0.75 V (vs NHE) in alkaline aqueous solution. Thus, $E('R^*/R^-)$ is 1.34 V. This calculation assumes that the excited singlet and ground states have about the same entropy and geometrical configurations¹⁴. The redox potentials of the amines $E(Q^+/Q)$ are half-wave potentials measured polarographically and these are listed in Table 2.

The Coulomb term $e^2/\epsilon a$ is calculated with knowledge of the dielectric constant of the solvent (methanol: $\epsilon \approx 32.6$) and the encounter distance $a = 7\text{\AA}$.¹³ Table 2 summarizes the calculation of the free energy change ΔG_{23} and allows the comparison of the experimental and calculated rate constants. The values of the experimentally determined rate parameters are in close agreement with the predicted ones. Furthermore, it can be seen that at small negative ΔG_{23} values, the rate constants are nearly diffusion controlled. When the free energy becomes positive, the rate constant shows a marked drop off. Whether or not there is an additional fall off in rate constants at large negative ΔG_{23} as predicted by the Marcus theory,²⁰ cannot be ascertained from the range of ΔG_{23} used in this investigation.

It should also be noted in Table 2 that the quenching constant of diphenylamine is slightly higher than the calculated rate constant. At high concentrations of diphenylamine, the absorbance of rhodamine 101 deviates from Beer's law and the Stern-Volmer plot becomes nonlinear (Figure 3). The main absorption band of rhodamine 101 diminishes and shifts to lower energy as the concentration of the quencher is increased. By the maximum concentration of diphenylamine, the main absorption band is decreased by 6% and is shifted 2-3 nm to the red with respect to the quencher-free dye solution. Also at this same concentration of the amine, no change in the position and spectral distribution of the fluorescence was observed. In contrast, the Stern-Volmer plot for N-methyldiphenylamine is linear. Taking these observations into consideration, the nonlinearity is attributed to aggregate formation between rhodamine 101 and diphenylamine. Evidence for the existence of dimers of rhodamine B and rhodamine 110 in ethanol has been reported.²⁵ In these cases, the aggregates were believed to have a head-to-tail configuration (COOH...NH₂ links) as indicated by a red shifted J band. A similar explanation seems to be appropriate to diphenylamine and rhodamine 101 in methanol. Interaction between the carboxyl group of the dye and the hydrogen of the

secondary amine would leave the rhodamine chromophore basically unperturbed and give the ground state complex spectral properties similar to the uncomplexed dye molecule.

In view of the short lifetime of the excited singlet state of rhodamine 101, it is informative to estimate the mean diffusion length, $d = \sqrt{2D\tau}$. Taking the diffusion coefficient $D = 10^{-5} \text{ cm}^2/\text{sec}$ and the fluorescence lifetime $\tau = 4 \text{ ns}$, d is ca. 30 \AA . Thus, because of the short lifetime of the excited singlet state, the quencher must be in proximity to the dye at the time of excitation in order for reaction to take place. Close association of the donor and acceptor molecules can be facilitated by the use of colloidal latex particles.

Physical Properties of the Latex Particles. Figure 4 shows an electron micrograph of the latex particles. The size distribution is rather narrow; each particle is spherical having an average diameter of $1400 \pm 100 \text{ \AA}$. The carboxyl groups of the latex are available for acid-base titration and there are $0.27 \text{ meq CO}_2^-/\text{g}$ of latex which corresponds to each group occupying a surface area of 25 \AA^2 . Although 25 \AA^2 is a reasonable surface area for a carboxyl group, quite conceivably some of the carboxyl groups are located inside the microsphere but are still accessible to hydrophilic reactants.²⁶ The pK_a of the acid groups is 6.1 which is similar to that of the carboxyl group of the dye, 6.2. The acidity of the aqueous solutions was adjusted to pH 7 so that the surface groups were ionized and the latex was negatively charged.

Distribution of Rhodamine 101 and Diphenylamine Between the Latex and Aqueous Phases. Absorption changes of a wide variety of aromatic molecules as a function of solvent polarity have been used extensively in order to determine the position of the solubilize in micelles.²⁷ A similarity

between the absorption spectrum in micellar solution and polar solvent is generally interpreted to imply that the solubilize is in a polar environment of the micelle. Conversely, resemblance of the spectrum in the micellar solution to that in an apolar solvent is presumed to indicate that the molecule resides in a lipid-like environment. Because of their hydrophobic nature, rhodamine 101 and diphenylamine are expected to partition between the latex microphase and the aqueous phase. The strong solvent dependence of the position of the absorption maximum of rhodamine 101 has been used to infer its solubilization site in latex solution. Table I shows that the positions of the absorption and emission maxima of the dye-latex system correlates with those in water rather than the positions of the less polar methanolic solution suggesting that rhodamine 101 is situated near the aqueous part of the latex environment. Similar spectral evidence locates diphenylamine at the latex-water interface which is consistent with nmr²⁸ and absorption²⁹ studies of dimethylaniline in ionic micellar solution.

The adsorption process can be considered as an equilibrium between the molecules in the aqueous phase, A_f , vacant adsorption sites, S_f , on the latex particles and bound molecules, A_b .



It was desirable for the interpretation of the fluorescence quenching data discussed below to know the fractions of rhodamine 101 and diphenylamine adsorbed on the latex material. Assessment of the relative concentrations of latex-bound and unbound molecules was made by difference measurements of the absorbance of several rhodamine-diphenylamine-latex solutions before and after removal of the latex. Separation of the bound and free molecules by dialysis and membrane filtration (Amicon UM 20) proved ineffective because of the tendency of the reactants, possibly through their amino groups, to

adhere to the filtering material. Some improvement in the method of separation and reproducibility involved centrifugation of the system in glass tubes which had been prerinsed with the solution to reduce adsorption of the molecules on the vessel walls. Tables 3 and 4 show the results of these measurements. From the tables, it can be determined that approximately 11,000 dye molecules are associated with each 1400 Å diameter latex particle corresponding to each rhodamine occupying a surface area of 560 Å². A similar number of diphenylamine molecules, 17000, are associated with each latex particle. Because of the difficulty of correcting for both the spectral contribution of rhodamine 101 to the ultraviolet absorption band of diphenylamine and light scattering due to residual latex particles, the data for diphenylamine in Table 4 were obtained in the absence of rhodamine 101.

Included in Tables 3 and 4 are the equilibrium constants (K) for the association of rhodamine and diphenylamine to the latex using the Langmuir adsorption isotherm³⁰

$$K = \frac{1}{C} \frac{[A]_b}{[A]_m - [A]_b} \quad (9)$$

where $[A]_b$ is the concentration of molecules adsorbed to the latex particles, $[A]_m$ is the maximum concentration of molecules adsorbed and C is the aqueous concentration of adsorbing species at the latex-aqueous interface. The maximum concentration of adsorbed molecules is obtained assuming a molecular monolayer. An examination of a model of rhodamine 101 indicates that 100 Å² would be a reasonable approximation of the area occupied by the adsorbed dye molecule. With this number and the area of a 1400 Å diameter sphere, the maximum number of surface sites on a latex particle is calculated to be 6.14×10^4 so that $[A]_m = (6.14 \times 10^4) [\text{latex}]$ where the concentration of latex refers to moles of particles per liter of solution. Using an area of

60 \AA^2 derived from the molar volume, the maximum concentration of diphenylamine molecules on each microsphere is, on the average, (1.03×10^5) [latex].

Thus the association constants of rhodamine 101 and diphenylamine in the latex system are $3.0 \pm 0.7 \times 10^4$ and $1.6 \pm 0.6 \times 10^4 \text{ M}^{-1}$, respectively.

The magnitudes of the binding constants fall within the range of those found normally in micellar systems ($K \approx 10^3 - 10^6 \text{ M}^{-1}$) for molecules of comparable structure³¹ and indicate strong association.

In the determination of the binding constants several approximations were made. Because of irregularities in the surface, the estimate of the surface area is expected to be a lower limit; however, in the case of $2327 \pm 86 \text{ \AA}^2$ carboxylated latex particles, Connor and Ottewill³² found the area based on size distribution to be ca. 20% higher than that determined by krypton adsorption. Also, the orientation, position and interaction of the adsorbates should affect the maximum possible number of molecules in the surface. Other interactions may involve the hydrophobic and hydrophilic surface sites, although spectral evidence presented previously indicates rhodamine 101 and diphenylamine are in similar polar environments.

Fluorescence Quenching in Latex Solution. Figure 5 shows the effect of latex on the fluorescence quenching of ca 10^{-5} M rhodamine 101 by diphenylamine. As the concentration of latex is increased from 17 to 98 ppm, the extent and rate of quenching are enhanced. The observed increase of quenching efficiency with increase in [latex] must be explained by an increase in the number of molecules removed from solution bulk and adsorbed onto the latex particles. The quenching efficiency will continue to increase as long as there are sufficient dye and quencher molecules in solution to occupy the available sites on the latex. Ultimately, it is expected that the quenching efficiency will drop off with an increase in latex concentration as the available sites largely exceed the number of dye and quencher molecules in the system. Because of the low solubility of diphenylamine in aqueous

solution, ca 1.2×10^{-4} M, and the scattering problem associated with higher latex concentrations, we were unable to explore this facet of the kinetics in the present system, although such a quenching effect has been observed in micellar chemistry³³ and in polyelectrolyte systems.³⁴ In normal homogeneous kinetics this type of quenching behavior does not occur.

The nonlinearity of the Stern-Volmer plots for the latex system is presumed to be a consequence of the equilibrium situation described in Equation 11. As the concentration of diphenylamine is increased, the amount of adsorption on the latex increases and the more important become the quenching processes occurring on the latex relative to those in solution bulk. A similar explanation has been given by Thomas and coworkers²⁹ to account for the nonlinear fluorescence quenching of pyrene by dimethylaniline in micellar solution. Accordingly, Figure 5 shows that the slopes of the quenching curves for the latex system approach the homogeneous case in methanol at low diphenylamine concentrations. Despite the low total concentrations of diphenylamine ($0.0 - 1.2 \times 10^{-4}$ M) and the latex particles (17-98 ppm), Figure 5 reveals a 22-72 fold enhancement of the quenching process over that occurring in methanol. The quenching of rhodamine 101 emission at higher diphenylamine concentrations in latex solution is clearly associated with the colloidal particles. This is particularly remarkable as at least ca 70% of the total concentration of reactants are in homogeneous bulk solution as can be determined from the adsorption data in Tables 3 and 4. If only the local quenching on the latex is considered, the quenching rate should be several orders of magnitude higher than that in methanol.

From the data in Tables 3 and 4, it can be estimated that the average distance between molecules is about 15 Å which is comparable to the dimensions of the molecules. Thus, taking into consideration this distance and the

evidence for J-aggregates in methanol discussed above, it is likely that these structures play a role in the arrangement of the molecules on the latex surface and hence in the quenching processes. At this distance the probability for the transfer of charge between the excited state of rhodamine and diphenylamine would be very high. Also since the triplet excited state of the rhodamines have been observed to reduce its ground state,⁸ the analogous reaction involving the excited singlet state must also be considered as possible at these distances on the surface. Such singlet-singlet electron-transfer reactions occur on a time scale between 10^{-9} - 10^{-12} seconds and require fast techniques to observe them. Confirmation of the proposal that charge transfer rather than collisional energy transfer is mainly responsible for the quenching of rhodamine 101 emission must await additional experimental evidence.

Final Remarks. Our results suggest that despite its short lifetime, the excited singlet state of a molecule can be utilized efficiently to promote electron transfer on the surface of a colloid. These findings are relevant to photochemical storage reactions in which light acts as an electron pump to drive endothermic chemical reactions. Relative to the triplet state, the excited singlet state will carry a larger fraction of the light quantum into the redox reaction and the ΔG of the process will consequently be more negative. The latex surface serves to bring the electron donor and acceptor into proximity and to enhance bimolecular interactions. The close arrangement of molecules on the latex surface is reminiscent of the close packing of chlorophyll in chloroplast. As in photosynthesis, it may be possible in heterogeneous systems to suppress the thermodynamically favorable back electron transfer between states of common multiplicity.

The latex system offers some advantages over simple micellar solutions. Polymeric latex particles are static structures unlike micellar assemblies

which are in constant dynamic equilibrium. Also, electron donating and accepting systems can be covalently coupled to the latex material³⁵ which offer possibilities to manipulate different parameters in electron transfer processes.

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REFERENCES

1. J.A. Barltrop and J.D. Coyle, Excited States in Organic Chemistry, John Wiley and Sons, London, (1975) p. 53.
2. A.J. Frank, M. Grätzel, A. Henglein and E. Janata, Intern. J. Chem. Kinetics, 7, 817 (1976); A.J. Frank, M. Grätzel, A. Henglein and E. Janata, Ber. Bunsenges. physik Chem. 79, 475 (1975).
3. S.S. Brody and E. Rabinowitch, Science, 125 555 (1957); O.D. Dimitrievsky, V.L. Ermolaev, A.N. Terenin, Dokl. Akad. Nauk SSSR 114, 751 (1957).
4. S.A. Alkaitis, G. Beck and M. Grätzel, J. Am. Chem. Soc. 97, 5724 (1975); M. Grätzel, John J. Kozak, and J.K. Thomas, J. Chem. Phys., 62, 1632 (1975).
5. J.R. Escabi-Perez, F. Nome, and J.H. Fendler, J. Am. Chem. Soc., 99, 7749 (1977); U. Lachish, M. Ottolenghi, and J. Rabani, J. Am. Chem. Soc., 99, 8062 (1977).
6. R.A. Cellarius and D. Mauzerall, Biochem. Biophys. Acta, 112, 235 (1966).
7. K.H. Drexhage, J. Research 80A, 421 (1976); K.H. Drexhage in "Topics in Applied Physics", F.P. Schäfer, ed., Springer-Verlag Berlin, Heidelberg, Vol. 1 (1973).
8. V.E. Korobov, V.V. Subin and A.K. Chibisov, Chem. Phys. Lett. 45, 498 (1977).
9. M.T. Spitler and M. Calvin, J. Chem. Phys. 67, 5193 (1977).
10. U. Krüger and R. Memming, Ber. Bunsenges. physik Chem., 78, 679 (1974).
11. T.A. Shakhverdov, Opt. Spectrosc. 29, 166 (1970).
12. D. Rehm and A. Weller, Israel J. Chem. 8, 259 (1970).
13. D. Rehm and A. Weller, Ber. Bunsenges Physik. Chem., 73, 834 (1969).
14. H. Leonhardt and A. Weller, Ber. Bunsenges Phys. Chem., 67, 791 (1963).
15. R.E. Schwerzel and N.E. Klosterman, Paper presented at The 12th Informal Conference on Photochemistry, N.B.S., Washington, D.C., June 1976.

16. J.N. Demas and G.A. Crosby, *J. Phys. Chem.*, 75, 991 (1971).
17. B.L. Leskovar, C.C. Lo, P.R. Hartig, and K. Sauer, *Rev. Sci. Instrum.*, 47, 1113 (1976); P.R. Hartig, K. Sauer, C.C. Lo, and B. Leskovar, *Rev. Sci. Instrum.*, 47 1122 (1976).
18. K.A. Selanger, J. Falnes, and T. Sikeland, *J. Phys. Chem.* 81, 1960 (1977); A.K. Chibisov, H.A. Kezle, L.V. Levshin, and R.D. Slavnova, *JCS Chem. Comm.*, 1292 (1972); I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York (1971).
19. E. Vogelmann, S. Schreiner, W. Rauscher, and H.E.A. Kramer, *Z. Physik. Chem. Neue Folge*, 101, 321 (1976).
20. R.A. Marcus, *J. Chem. Phys.*, 43, 679 (1965).
21. T. Tani and S. Kikuda, Report of the Institute of Industrial Science, The University of Tokyo, 1968.
22. J.W. Loveland and G.R. Dimeler, *Anal. Chem.*, 33, 1196 (1961).
23. E.T. Seo, R.F. Nelson, J.M. Fritsch, L.S. Marcoux, D.W. Leedy, and R.N. Adams, *J. Am. Chem. Soc.*, 88, 3498 (1966).
24. V. Dvořák, I. Němec and J. Zýka, *Microchem. J.*, 12, 99 (1967).
25. M.M. Wong and Z.A. Schelly, *J. Phys. Chem.*, 78, 1891 (1974).
26. A. Rembaum, S.P.S. Yen, E. Cheong, S. Wallace, R.S. Molday, I.L. Gordon, and W.J. Dryer, *Macromolecules*, 9, 328 (1976).
27. J.H. Fendler, E.J. Fendler, G.A. Infante, P.S. Shih, and L.K. Patterson, *J. Am. Chem. Soc.*, 97, 89 (1975); S.J. Rehfeld, *J. Phys. Chem.*, 75, 3905 (1971); S.J. Rehfeld, *J. Phys. Chem.*, 74, 117 (1970); M. Donbrow and C.T. Rhodes, *J. Pharm. Pharmacol.*, 18, 424 (1966).
28. J.C. Eriksson and G. Gillberg, *Acta Chem. Scand.*, 20, 2019 (1966).
29. B. Katušin-Ražem, M. Wong, and J.K. Thomas, *J. Am. Chem. Soc.* 100, 1679 (1978).

30. S. McLaughlin in Current Topics in Membranes and Transport, F. Bonner and A. Kleinzeller, eds., Academic Press, New York (1977).
31. J.H. Fendler and E.J. Fendler, Catalysis in Micellar and Macromolecular System, Academic Press, New York (1975), Chapter 4.
32. P. Conner and R.H. Ottewill, *J. Colloid Interface Sci.*, 37, 647 (1971).
33. G.S. Singhal, E. Rabinowitch, J. Hevesi, and U. Srinivasan, *Photochem. Photobiol.* 11, 531 (1970).
34. D. Meisels, J. Rabani, D. Meyerstein, and M.S. Matheson, *J. Phys. Chem.*, 82, 985 (1978); D. Meisels and M.S. Matheson, *J. Am. Chem. Soc.*, 90, 6577 (1978).
35. A.J. Frank, unpublished results.

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Table 1. Rhodamine 101. Wavelength position of the main absorption and emission bands in various solvents.

Solvent	Absorption λ_{\max} (nm)	Emission λ_{\max} (nm)
Methanol	567	588
Methanol (0.1 M KOH)	567	588
Methanol (10^{-2} M HCl)	575	595
Water	575	596
Water (0.1 M KOH)	575	596
Water (10^{-2} M HCl)	579	600
Latex	576	596
Latex (0.1 M KOH)	576	596
Latex (10^{-2} M HCl)	579	600

Table 2. Fluorescence quenching rate constants, oxidation potentials, and ΔG -values in methanol

Quencher	$E(Q^+/Q)^a$ (V)	ΔG_{23} (kcal/mole)	calc $k_Q \times 10^{-9}$ ($M^{-1}s^{-1}$)	exptl $k_Q \times 10^{-9}$ ($M^{-1}s^{-1}$)
Triethylamine	1.39 ²²	2.61	0.075	0.068
N-methyldiphenylamine	1.08 ²³	-4.54	8.2	10.2
Diphenylamine	1.07 ²⁴	-4.77	8.4	12.5
N,N-dimethylaniline	0.95 ²³	-7.54	11.0	11.4

^aPolarographic half-wave reduction potentials (V vs NHE) for $Q^+ + e \rightarrow Q$ in acetonitrile.

Table 3. Adsorption characteristics of 7.82×10^{-6} M rhodamine 101 (R) in the presence of 2.14×10^{-5} M diphenylamine (DPA) as a function of latex concentration

Latex concentration $\times 10^{11}$ M	Adsorbed R concentration $\times 10^7$	Nonadsorbed R concentration $\times 10^7$	Number of R molecules per latex particle	Association constant ^a M^{-1}
2	2.35	75.9	11750	3.11×10^4
4	4.93	73.3	12325	3.41×10^4
6	4.93	73.3	8217	2.09×10^4
8	9.62	68.6	<u>12025</u>	<u>3.53×10^4</u>
			11000 ± 2000	$3.0 \pm 0.7 \times 10^4$

^aSee discussion of Equation 9 in text.

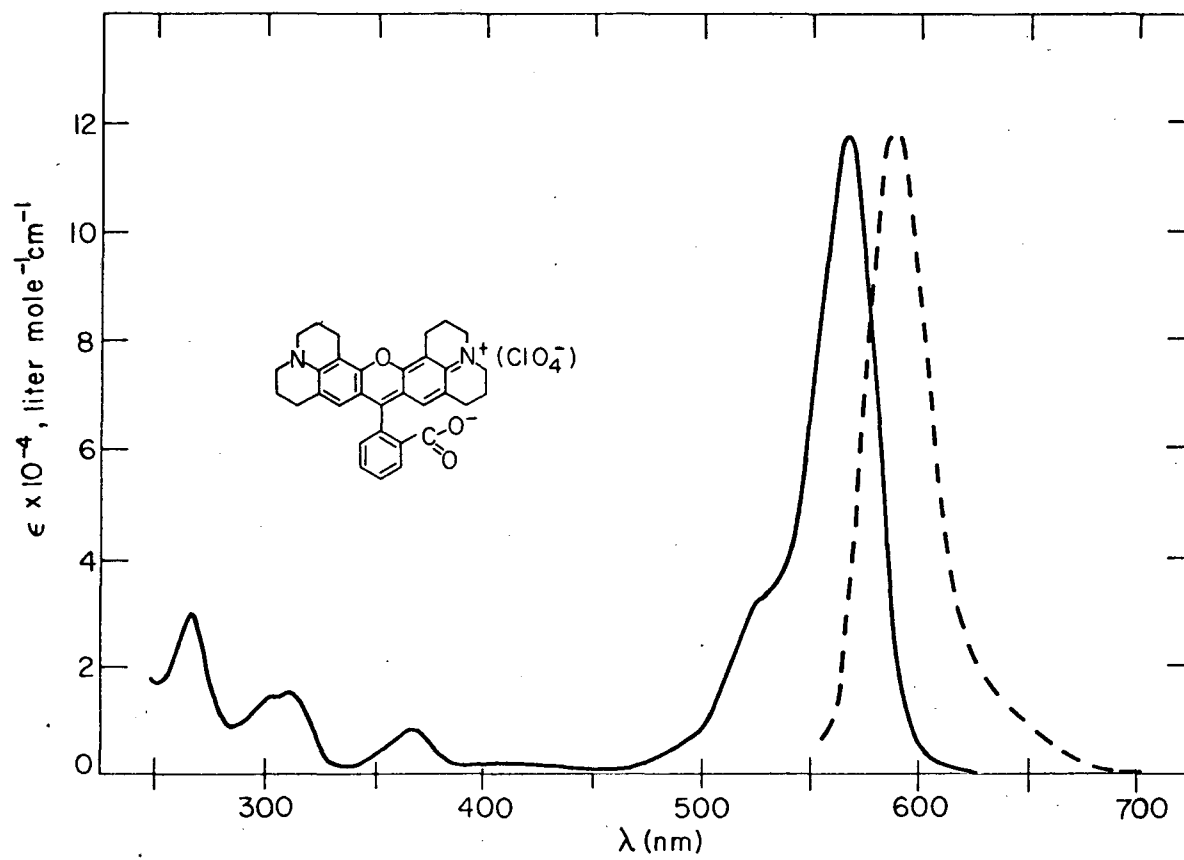
Table 4. Adsorption characteristics of 1.4×10^{-5} M diphenylamine (DPA) as a function of latex concentration

Latex concentration $\times 10^{11}$ M	Adsorbed DPA concentration $\times 10^7$ M	Nonadsorbed DPA concentration $\times 10^7$ M	Number of DPA molecules per latex particle	Association constant ^a M^{-1}
2	4.4	136	2200	2.00×10^4
4	6.92	133	17300	1.52×10^4
6	5.84	134	9300	0.78×10^4
10	19.3	121	<u>19300</u>	<u>1.90×10^4</u>
			17000 ± 5000	$1.6 \pm 6 \times 10^4$

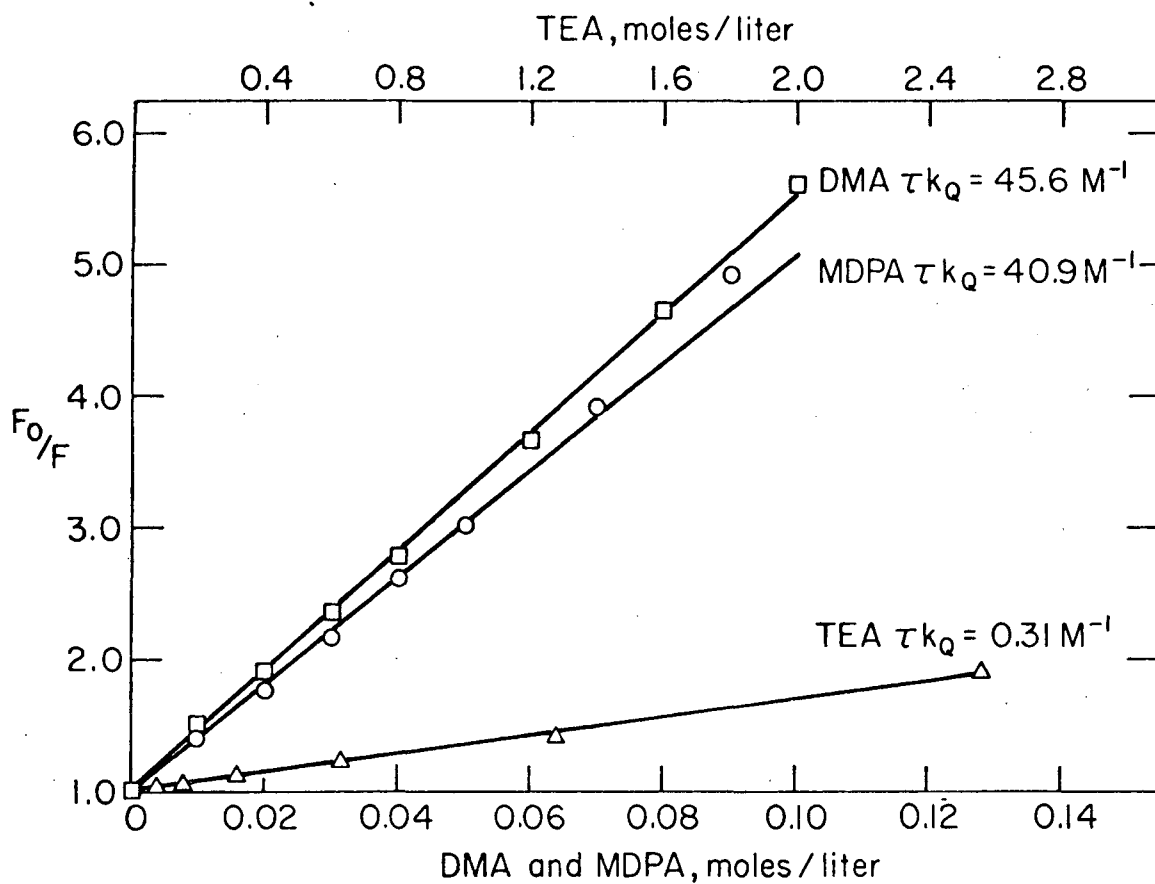
^aSee discussion of Equation 9 in text

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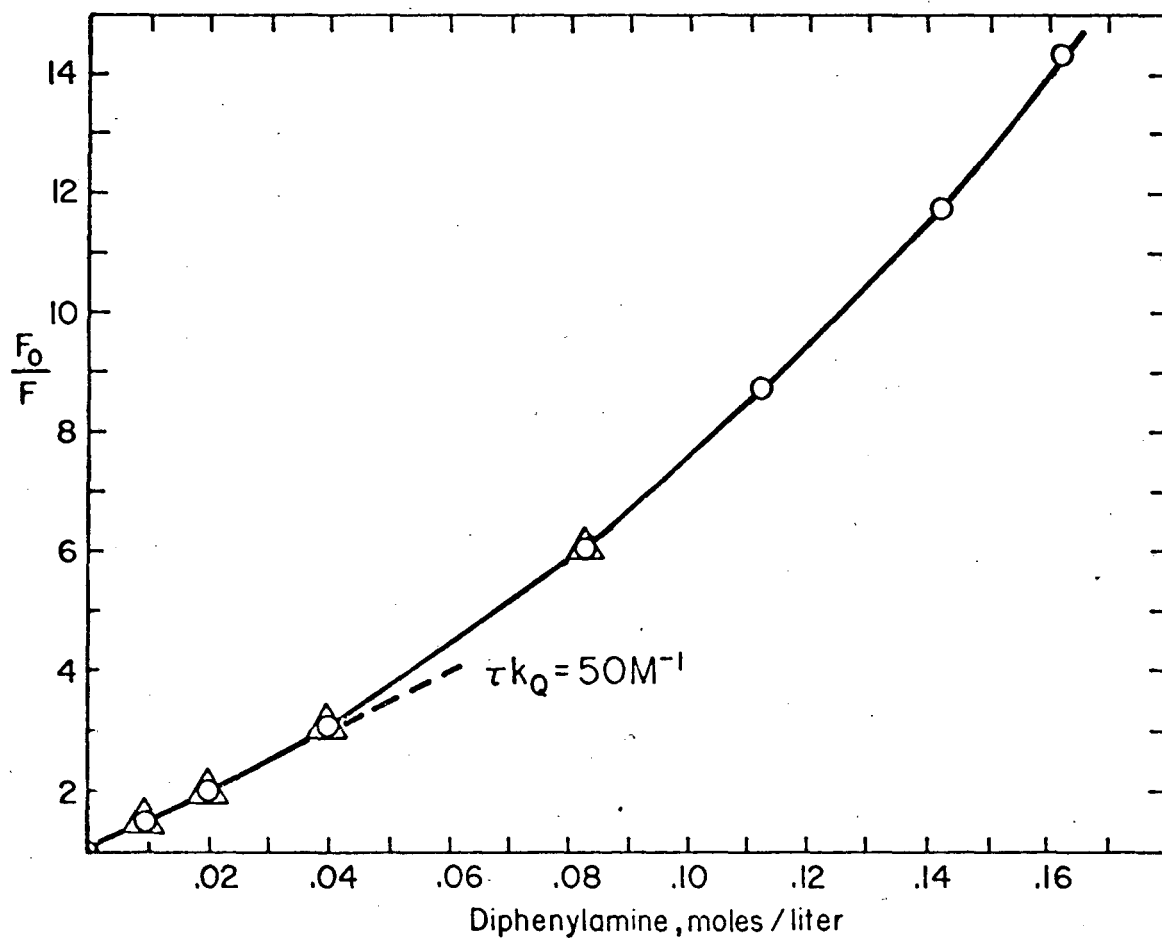
- Figure 1. Rhodamine 101 in methanol (—) absorption spectrum (E, Molar decadic coefficient); (---) quantum spectrum of fluorescence (arbitrary units).
- Figure 2. Fluorescence quenching of rhodamine 101 by N,N-dimethylaniline (DMA, -□-) N-methyldiphenylamine (MDPA, -o-), triethylamine (TEA -○-) in methanol.
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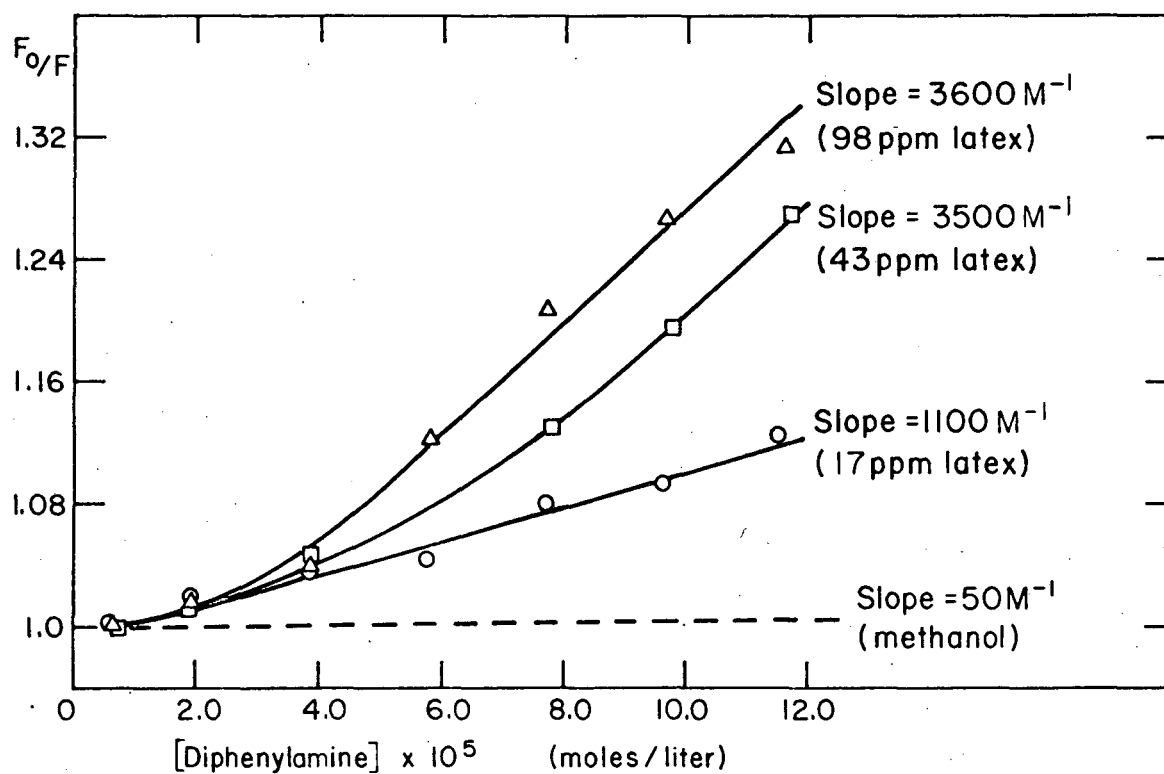


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Quenching of Rhodamine 101 by Diphenylamine
as a Function of Latex Concentration



XBL 787-4081

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