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Photoinduced electron transfer between donors and acceptors on micelle surfaces

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Abstract

Fluorescence time-dependence and fluorescence yield data are used to examine photoinduced electron transfer between *N,N*-dimethylaniline and octadecylrhodamine B on the surfaces of dodecyltrimethylammonium bromide (DTAB) and Triton X-100 micelles. The data are analyzed with a detailed theory that includes diffusion of the chromophores over the micelle surface and models the reaction rate by a distance-dependent Marcus form. Good agreement between theory and experiment is obtained for reasonable choices of the transfer parameters for DTAB. However, for Triton X-100, there is reasonable agreement between theory and experiment only for values of the parameters that verge on unphysical. Possible explanations are discussed. © 1997 Elsevier Science B.V.

1. Introduction

In this Letter we present experimental results on forward electron transfer from *N,N*-dimethylaniline (DMA) to photoexcited octadecylrhodamine B (ODRB) on two aqueous micelles: dodecyltrimethylammonium bromide (DTAB) and Triton X-100. These chromophores are located preferentially on the micelle surfaces. The octadecyl tail of rhodamine B tethers it into the micelle, and previous studies of ODRB rotational relaxation place the chromophore selectively at the micelle surface [1,2]. NMR studies of *N,N*-dimethylaniline on cetyltrimethylammonium bromide show that the donor is localized at the micelle surface with a negligible fraction in the aqueous phase [3]. Additionally, the fluorescence spectra and reorientation time of DMA in DTAB and Triton X-100 are characteristic of an aqueous-like surrounding. This fact, combined with the NMR data and the low solubility of DMA in pure water, indi-

cates that the chromophore is dissolved near the micelle surface. (Somewhat deeper penetration into Triton X-100 may be possible due to the large size of the Triton X-100 head group, as discussed later.)

In a recent publication we discussed theoretically the role of diffusion in photoinduced intermolecular electron transfer on a micelle surface [4]. A detailed theoretical treatment was presented for forward electron transfer and geminate recombination between a photoexcited donor and *N* acceptors (or a photoexcited acceptor and *N* donors) on a micelle surface, without using approximations in the ensemble averaging techniques and with the diffusion of the chromophores over the micelle surface appropriately included. The theoretical results demonstrated how diffusion of the chromophores over the micelle surface significantly influences electron transfer dynamics. The significance of the theoretical treatment is that it permits the contributions to the electron transfer dynamics to be dissected and analyzed. Without a

rigorous statistical mechanical treatment of this sort, it is impossible to separate the role of diffusion and the effect of the DMA spatial distribution from that portion of the dynamics due directly to the distance-dependent rate coefficient.

The fluorescence upconversion and fluorescence yield data presented here for electron transfer between DMA and photoexcited ODRB on micelle surfaces are analyzed with the methods of reference [4], with particular emphasis placed on the role of diffusion. Although the data can be fit with static models, the resulting fits yield highly unreasonable values of the Marcus parameters. Inclusion of diffusion leads to good fits for reasonable values of the forward transfer parameters for the DTAB data. The Triton X-100 data, as discussed later, may not conform to the model of electron transfer presented here and in reference [4].

2. Theory

The model of the electron transfer system has been described in detail elsewhere [4,5]. Briefly, the donors and acceptors are taken to be curved disks on the surface of a spherical micelle of radius R . (See Fig. 1.) The micelle concentration is kept low, so that electron transfer from a donor on one micelle to an acceptor on another does not occur. Additionally,

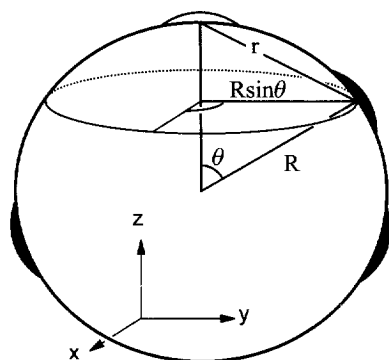


Fig. 1. Schematic illustrating the model system. The micelle is modeled as a sphere of radius R , with the chromophores assumed to be curved disks on the surface. The relevant electron transfer distance is taken to be r , the through-sphere (chord) distance. In the illustration, the unfilled disk denotes the ODRB (no more than one per micelle), while the filled disks are the DMA.

the ODRB concentration is extremely low so that there is at most one photoexcited acceptor per micelle; Förster excitation transfer does not occur. The mean number of DMA per micelle is denoted N . Diffusion over the surface of the micelle is characterized by a Fick diffusion constant, D , which is the sum of the donor (D_d) and acceptor (D_a) self diffusion coefficients: $D = D_d + D_a$ [6]. Photoexcitation of ODRB results in forward electron transfer from DMA to the excited acceptor.

Full details of the theory are given in reference [4], and we briefly state the key result for the forward transfer. The ensemble-averaged probability of finding ODRB excited as a function of time, $\langle P_{\text{ex}}(t) \rangle_N$, is:

$$\langle P_{\text{ex}}(t) \rangle_N = \left[\int_{\theta} S_{\text{ex}}(t|\theta) \frac{\sin \theta}{2} d\theta \right]^N, \quad (1)$$

where $S_{\text{ex}}(t|\theta)$ satisfies the differential equation with associated initial and boundary conditions:

$$\begin{aligned} \frac{\partial}{\partial t} S_{\text{ex}}(t|\theta) &= D \nabla_{\theta}^2 S_{\text{ex}}(t|\theta) - k_f(\theta) S_{\text{ex}}(t|\theta), \\ S_{\text{ex}}(0|\theta) &= 1, \\ 2\pi R^2 \sin \theta_c D \frac{\partial}{\partial \theta} S_{\text{ex}}(t|\theta) \Big|_{\theta=\theta_c} &= 0. \end{aligned} \quad (2)$$

$S_{\text{ex}}(t|\theta)$ is the survival probability for a donor with a single acceptor located initially at θ . The diffusion operator is defined:

$$D \nabla_{\theta}^2 = \frac{D}{R^2 \sin \theta} \frac{\partial}{\partial \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \right], \quad (3)$$

where R is the micelle radius. θ_c is the donor-acceptor contact distance in radians. The forward transfer rate constant is given by a standard Marcus-type expression:

$$\begin{aligned} k_f(\theta) &= \frac{2\pi}{\hbar} J^2 \exp[-2R\beta(\sin(\theta/2) - \sin(\theta_c/2))] \\ &\times \frac{1}{\sqrt{4\pi\lambda(\theta)k_B T}} \exp\left[\frac{-(\Delta G_f + \lambda(\theta))^2}{4\lambda(\theta)k_B T} \right], \end{aligned} \quad (4a)$$

where

$$\lambda(\theta) = \frac{e^2}{2} \left(\frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right) \left(\frac{1}{r_d} + \frac{1}{r_a} - \frac{1}{R \sin(\theta/2)} \right). \quad (4b)$$

Here, ϵ_{op} and ϵ_s are the high frequency and static dielectric constants, respectively. r_d and r_a are the half-arc length of the donor and acceptor, respectively, and ΔG_f is the free energy change due to the forward transfer. e , h and k_B are the fundamental charge, Planck's and Boltzmann's constants. The Marcus J and β parameters characterize the magnitude and distance-dependence of the transfer rate, respectively. For the purposes of this letter we have chosen to use the form of the reorganization energy derived by Marcus for charges in a three-dimensional dielectrically-isotropic environment. A more detailed treatment of the reorganization energy for micelles requires the solution of the Poisson equation for the micelle geometry or the Poisson–Boltzmann equation if counterions are included. This is a relatively complex numerical problem that will be addressed in a subsequent publication. The implications of using Eq. (4b) will be discussed in more detail in Section 4.

We note that Eq. (1) gives $\langle P_{\text{ex}}(t) \rangle_N$ for 1 ODRB and N DMA per micelle surface. (Micelles without any ODRB will not contribute to the experimentally observed signal.) In an experiment, the number of DMA per micelle is assumed to follow a Poissonian distribution about the mean N . Thus, the actual experimental observable is:

$$\langle P_{\text{ex}}(t) \rangle = e^{-t/\tau} \sum_{n=0}^{\infty} \frac{e^{-N} N^n}{n!} \langle P_{\text{ex}}(t) \rangle_n. \quad (5)$$

In Eq. (5) the term $e^{-t/\tau}$ has been included to account for the ODRB fluorescence decay. τ is the excited state lifetime in the absence of electron transfer. Since this pathway is independent of the transfer event, it can be included as a multiplicative factor.

Light and small-angle X-ray scattering studies of Triton X-100 indicate that the micelle is almost monodispersed [7,8]. For DTAB, a spherical micelle with a fairly small cmc value, the size distribution should also be quite narrow [9]. In the event of

polydispersity, a final integral should be performed over the micelle size distribution.

3. Experimental procedures

ODRB was obtained from Molecular Probes and used as received, while DMA was of the highest commercial grade available from Aldrich. DTAB and Triton X-100 were from Aldrich. All experimental samples were prepared in deionized water for micelle concentrations, $[M]$, slightly above the cmc ($[M] = 206 \mu\text{M}$ for both micelles). The ODRB concentration was a factor of 10 less, while DMA concentrations ranged from 0–15 mM, corresponding to up to a 6% fractional occupancy of the micelle surface. (For these low fractional occupancies, DMA–DMA excluded volume may be safely neglected [5].)

ΔG_f was obtained from the Rehm–Weller equation [10], using redox potentials for rhodamine B and DMA measured by cyclic voltammetry (CV) in acetonitrile. Fluorescence spectra of DMA in DTAB and Triton X-100 indicate that the local dielectric constant lies somewhere between that of acetonitrile ($\epsilon_s = 37$) and water ($\epsilon_s = 78$). Since DMA has low solubility in pure water and since the free energy difference is expected to be similar in highly polar solvents [11], the CV experiments were performed in acetonitrile. The difference between the oxidation potential of DMA and the reduction potential of rhodamine B was 1.6 eV. Fits to the electron transfer data using the methods of section II were found to be relatively insensitive to variations in ϵ_s within the range of 37–78.

Fluorescence upconversion experiments were performed using dual dye lasers pumped by a frequency-doubled mode-locked and Q -switched Nd:YLF laser. Photoexcitation was performed at 568 nm, on the red-edge of the ODRB absorption spectrum. The upconverting beam was provided by a second dye laser tuned to 850 nm. The time-resolved fluorescence was detected by a dry-ice cooled PMT connected to a gated integrator. The overall instrument response was 45 ps. The time dependence was obtained using a delay line to scan the arrival time of the excitation pulse at the sample relative to the fixed time of the upconversion pulse.

The fluorescence yield measurements were performed with the same experimental system, except using a red-sensitive PMT. The relative fluorescence-yield, Φ , is a time-independent measurement of the ratio of the total fluorescence for a sample containing no DMA to that of sample with identical ODRB concentration, but containing DMA.

$$\Phi = \frac{\tau}{\int_0^{\infty} \langle P_{\text{ex}}(t) \rangle dt} \quad (6)$$

The yield data provides an independent verification of fits to the upconversion data, since only fits with the correct short-time decay (within the instrument response) will also give agreement with the yield data.

4. Results and discussion

Fig. 2 shows fluorescence upconversion and fluorescence yield data for ODRB and four DMA concentrations on DTAB. The theoretical fits to the data were generated using Eq. (5). Application of the theory requires values for the Marcus parameters J and β along with a reasonable estimate of the diffusion constant for lateral diffusion over a micelle surface. Additionally, the solvent reorganization energy, λ , must be known or calculated. For the purposes of this Letter, we have chosen to use Eq. (4b), even though it was derived for an isotropic dielectric continuum. In a future publication, we present experimental evidence that the reorganization energy changes with micelle size for a homologous series of micelles. The distance dependence of the reorganization energy contributes to the overall distance dependence of electron transfer. However, the major contributor to the distance dependence is the electronic interaction. We suspect that the use of Eq. (4b) will only introduce a relatively small error in the results and will not change the conclusions regarding the influence of diffusion on electron transfer on micelle surfaces. This will be tested in detail subsequently [12]. The additional parameters needed in Eqs. (1)–(5) have been measured or calculated. Once J , β and D are specified, Eq. (5) can be used to predict the time decays of all four concentrations, and Eq. (6) should give the experimental yield values. Without any information about J , β or D , all three could

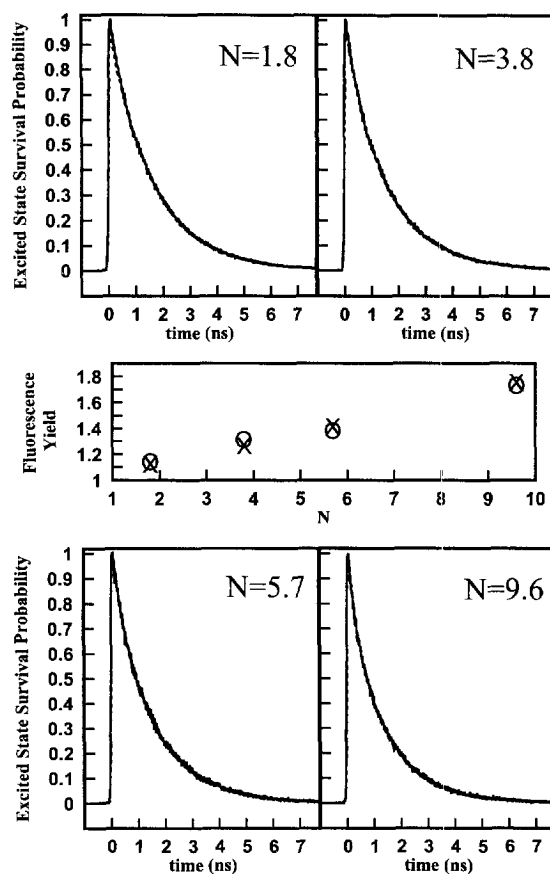


Fig. 2. Fluorescence upconversion data (solid lines) and theoretical fits using Eq. (5) (dashed lines) for ODRB and four concentrations of DMA ($N=1.8, 3.8, 5.7$ and 9.6 DMA per micelle) on DTAB. The center panel shows fluorescence yield data (circles) and the fits (crosses) from Eq. (6). The DTAB radius was taken to be 16.7 \AA [33], and the ODRB and DMA radii were 4.45 and 3.05 \AA , respectively. (Estimates of molecular radii of DMA and the ODRB head group were obtained from molecular modeling and from crystallographic data on similar compounds.) The theoretical fits shown are for parameters: $J = 48 \text{ cm}^{-1}$, $\beta = 1.0 \text{ \AA}^{-1}$, $D = 5.4 \text{ \AA}^2/\text{ns}$, $\tau = 1.76 \text{ ns}^{-1}$, $\epsilon_{\text{op}} = 1.77$ and $\epsilon_s = 78$. The calculated yield numbers are within the error bars on the data.

be used as adjustable parameters. With three adjustable parameters, it is possible to generate fits to the DTAB data with the same quality as those shown in Fig. 2; however, the fits are not unique. In fact, though, it is not necessary to treat the data with three adjustable parameters. Many detailed studies of electron transfer in proteins, glasses and liquids have been performed in the last several decades [13–17], and very general agreement now exists that the

Marcus β parameter should have a value close to 1.0. Furthermore, there have been numerous attempts to measure lateral diffusion constants over micelle surfaces. These are difficult numbers to obtain because of the indirect nature of the experimental probes [18]. Nonetheless, a wide variety of experiments, including ^{13}C NMR, fluorescence depolarization, and microviscosity measurements, have generally yielded values for lateral diffusion constants on micelle surfaces in the range of 2–15 $\text{\AA}^2/\text{ns}$ [19–22]. In generating the fits shown in Fig. 2, we chose to fix β at 1.0 \AA^{-1} . Both J and D were treated as adjustable parameters. Under these conditions, a unique fit to the DTAB upconversion and yield data is obtained. Fig. 2 shows the fit for $J = 48 \text{ cm}^{-1}$ and $D = 5.4 \text{ \AA}^2/\text{ns}$, obtained from a χ^2 minimization algorithm [23]. For any set of inputs to the calculation (e.g. the micelle dielectric constant or the donor and acceptor sizes), there is a fairly steep, global minimum to the χ^2 value.

The error bars on J and D , then, are primarily determined by the accuracy of certain key physical quantities. One source of uncertainty is the micelle dielectric constant, which we conservatively estimate to be somewhere between 37 and 78. Also, the donor–acceptor contact distance (7.5 \AA) could also be in error by 5, or possibly even 10%. From adjusting these inputs within their error bars and fitting J and D , we place J in the range of $50 \pm 20 \text{ cm}^{-1}$ and D from $5 \pm 1 \text{ \AA}^2/\text{ns}$. Additional error is introduced by using the form of the reorganization energy appropriate for a homogeneous medium. We will be addressing this issue in more detail in a future publication [12,24]. The form of the reorganization energy may change the values of J reported here. The important result is that we are able to get very good agreement between data and theory for a complex system and that information about the transfer rate can be extracted from data on a diffusing system with a complex geometry.

The quality of fits shown in Fig. 2 is quite good. The theory misses the lowest concentration somewhat at early times but yields essentially perfect agreement for the higher three concentrations. The simultaneous fit to the yield data is also very good. The theoretical treatment, using J and D as adjustable parameters, leads to a diffusion constant $D = D_d + D_a$ in the expected range. Furthermore, if

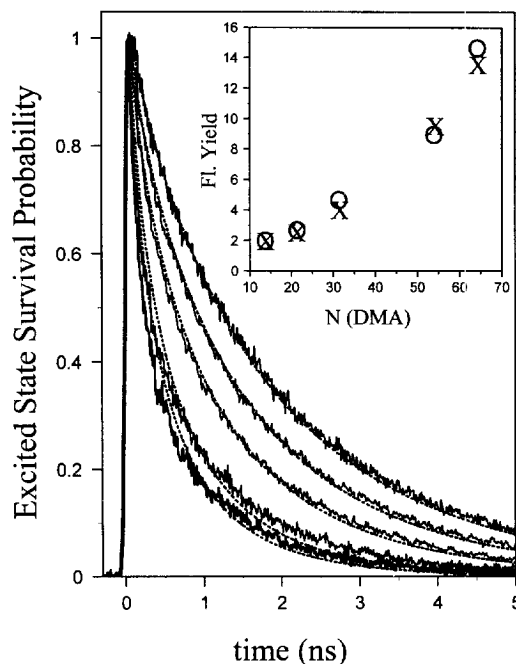


Fig. 3. Fluorescence upconversion data (solid lines) and theoretical fits using Eq. (5) (dashed lines) for ODRB and five concentrations of DMA ($N = 13.6, 20.9, 31.1, 53.9$ and 64.1) on Triton X-100. (Decays get faster as DMA concentration increases.) The inset shows fluorescence yield data (circles) and the fits (crosses) from Eq. (6). The fits are for a micelle radius of 42 \AA [26,34] and $J = 1768 \text{ cm}^{-1}$, $\beta = 1.0 \text{ \AA}^{-1}$, $D = 30.0 \text{ \AA}^2/\text{ns}$, $\tau = 2.85 \text{ ns}^{-1}$, $\epsilon_{\text{op}} = 1.77$ and $\epsilon_s = 37$. Agreement between theory and experiment is not good for the highest two concentrations.

instead of fixing β at 1.0 \AA^{-1} , β is fixed at values in the range 0.8–1.2 \AA^{-1} , unique fits are obtained for each β value, with J and D within the error bars reported above. Thus, in addition to describing electron transfer on micelle surfaces, a measure of the lateral diffusion constant is obtained.

In reference [4], we showed by theory and Monte Carlo simulation that inclusion of diffusion in the electron transfer problem is important. The DTAB data shown in Fig. 2 can be fit with $D = 0$, but only if a value $\beta < 0.3 \text{ \AA}^{-1}$ is assumed. Such a low β value is highly unphysical.

Fig. 3 shows fluorescence upconversion and yield data for ODRB and five concentrations of DMA on Triton X-100 micelles. If β is fixed at 1.0 \AA^{-1} , agreement between theory and experiment can only be obtained for $J > 1765 \text{ cm}^{-1}$ and $D > 30 \text{ \AA}^2/\text{ns}$. Although it is conceivable that a small molecule like

DMA might have a lateral diffusion constant higher than $30 \text{ \AA}^2/\text{ns}$, the large values of J are extreme. $J = 1765 \text{ cm}^{-1}$ corresponds to a transfer rate at contact of 76000 ns^{-1} , or a transfer time of 13 fs. This is more than 1000 times faster than for the same donor and acceptor on DTAB micelles. Additionally, these parameters give poor agreement with the short to medium time behavior of the two highest concentrations. Somewhat better fits can be obtained if β is allowed to take on values $< 0.5 \text{ \AA}^{-1}$, but such long-range, through-solvent electron transfer seems unphysical.

There are several possible explanations for the reduced quality of the agreement between theory and experiment for the Triton X-100 system. First, recent small angle neutron scattering results indicate that Triton X-100 may be an oblate ellipsoid [25]. For a large micelle like Triton X-100, it seems unlikely that curvature errors would substantially affect the short-range electron transfer process. Calculations where the curvature of the spherical micelle is adjusted to match the curvature of regions of the ellipsoid (while maintaining a constant DMA packing fraction) show almost no difference in the predicted $\langle P_{\text{ex}}(t) \rangle$ decays. Additionally, even if the mean number of DMA per micelle is held constant, but the micelle radius is decreased by 15%, extreme parameters are still required to fit the data. This result indicates that including polydispersity in the theory would not lead to more reasonable parameters.

In order to consider whether the use of Eq. (4b) for the reorganization energy could account for the poor fits to the Triton X-100 data, the data were fit using a purely exponential form of the rate constant: $k_f(\theta) = J^2 \exp[-2R\beta(\sin(\theta/2) - \sin(\theta_c/2))]$. Using this form of $k_f(\theta)$, reasonable agreement between theory and experiment is obtained only for the lowest three concentrations using $D = 25 \text{ \AA}^2/\text{ns}$; the fits to the two highest DMA concentrations are inferior. A value of $25 \text{ \AA}^2/\text{ns}$ for the diffusion coefficient is also significantly higher than is expected. Thus, although it is possible that an inaccurate form of the solvent reorganization energy accounts for the poor agreement between theory and experiment for Triton X-100, we believe that this is unlikely in view of another, possibly more significant factor.

The treatment of intermolecular electron transfer in diffusing systems where there are multiple donors or acceptors available for transfer is extremely sensitive to the spatial distribution of the chromophores. The functional form of the data on Triton X-100 is not well-described by diffusion on a two dimensional surface. However, good fits to the data can be obtained for reasonable Marcus parameters provided that the motion of DMA on Triton X-100 is considered to be three dimensional. To understand this, we note that for DTAB, a spherical micelle with small head groups, the DMA can be realistically considered to be on the surface of a sphere. However, the polyoxyethylene head group of Triton X-100 is approximately 17 \AA in length [26], so that the DMA (and perhaps the ODRB) may penetrate a substantial way into the micelle. Since 17 \AA is substantial on the distance scale of the electron transfer, the Triton X-100 problem may more realistically involve diffusion and electron transfer from within a thick spherical shell. Developing theory for this complicated geometry is difficult and has not been done to date. This problem is approximately one of electron transfer in a bounded three dimensional space. If we calculate a crude "three dimensional" concentration by dividing the mean number of DMA by the volume of the spherical shell and then calculate the electron transfer $\langle P_{\text{ex}}(t) \rangle$ observable as for a liquid, good fits to the data are obtained for reasonable J , β and D parameters. Thus, when reaction in a spherical shell is improperly modeled as reaction on a spherical surface, unreasonably large and long-range parameters may result in order to compensate for the reduced dimensionality.

5. Conclusions

We have presented experimental data on photoinduced electron transfer between chromophores localized on micelle surfaces. There has been considerable interest in micelle-bound electron transfer systems [27–29,19,30–32], since control over geometry may be useful in promoting long-term ion survival. We have analyzed the data with a detailed theory of electron transfer that utilizes no approximations in the ensemble average over particle positions, includes diffusion of the chromophores over the mi-

celle surface, and uses a distance-dependent Marcus-type of transfer rate. We have observed good agreement between theory and experiment for DTAB micelles. Further, we have demonstrated the ability of the theory to distinguish between contributions due to diffusion and those due to the distance-dependent transfer rate, $k_f(\theta)$, by using a detailed statistical mechanical theory. This theory is applied here for the first time to experimental data on micelle surfaces. For DTAB micelles, which are expected to be well-modeled by chromophores on a spherical surface, the results are consistent with theory and give a reasonable estimate for the lateral diffusion coefficient. For Triton X-100, extension of the theory to thick spherical shells may be necessary.

We are currently at work studying electron transfer between ODRB and DMA on other micelle surfaces as well as in bulk liquids. We are also investigating the role of the reorganization energy, which may make a significant contribution to understanding electron transfer dynamics in micelle systems.

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