Effects of Preferential Solvation Revealed by Time-Resolved Magnetic Field Effects

Van Thi Bich Pham, Hao Minh Hoang, Günter Grampp, and Daniel R. Kattnig

Institute of Physical and Theoretical Chemistry, Graz University of Technology, Stremayrgasse 9/1, A-8010 Graz, Austria
Ho Chi Minh City University of Technology and Education, Vo Van Ngan 01, Linh Chieu Ward, Thu Duc District, Ho Chi Minh City, Vietnam
Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, U.K.

ABSTRACT: External magnetic fields can impact recombination yields of photoinduced electron transfer reactions by affecting the spin dynamics in transient, spin-correlated radical pair intermediates. For exciplex-forming donor–acceptor systems, this magnetic field effect (MFE) can be investigated sensitively by studying the delayed recombination fluorescence. Here, we investigate the effect of preferential solvation in microheterogeneous solvent mixtures on the radical pair dynamics of the system 9,10-dimethylanthracene (fluorophore)/N,N-dimethylaniline (quencher) by means of time-resolved magnetic field effect (TR-MFE) measurements, wherein the exciplex emission is recorded in the absence and the presence of an external magnetic field using time-correlated single photon counting (TCSPC). In microheterogeneous environments, the MFE of the exciplex emission occurs on a faster time scale than in iso-dielectric homogeneous solvents. In addition, the local polarity reported by the exciplex is enhanced compared to homogeneous solvent mixtures of the same macroscopic permittivity. Detailed analyses of the TR-MFE reveal that the quenching reaction directly yielding the radical ion pair is favored in microheterogeneous environments. This is in stark contrast to homogeneous media, for which the MFE predominantly involves direct formation of the exciplex, its subsequent dissociation to the magneto-sensitive radical pair, and re-encounters. These observations provide evidence for polar microdomains and enhanced caging, which are shown to have a significant impact on the reaction dynamics in microheterogeneous binary solvents.

I. INTRODUCTION
Solvent polarity strongly affects the mechanism of photoinduced electron transfer (ET) reactions. In polar solvents, the process usually involves complete ET from the electron donor to the acceptor, thereby forming spin-correlated radical ion pairs (RIPs). In nonpolar solvents, the formation of excited-state charge transfer complexes, so-called exciplexes, is often observed. Expectedly, in moderately polar solvents, both quenching reactions may contribute simultaneously and radical ions can result from direct ET as well as dissociation of the exciplex.1–8 Due to similar spectral footprints of ion pairs and exciplexes, it is generally difficult to elaborate which channel dominates.9–12 The magnetic field effect (MFE) on the exciplex emission provides a versatile tool for the study of this intricate dynamics. The approach has been applied to homogeneous solvents as well as under conditions of preferential solvation, which often occur in binary solvent mixtures of solvents of vastly different polarity.13–18 The term “preferential solvation” subsumes nonspecific and specific interactions of solutes with specific components of binary solvent mixtures. It often induces microheterogeneity in the solvent, which is characterized by the spatially nonuniform distribution of the solvent components in the vicinity of polar or ionic solutes. These microclusters of polar solvent molecules have a pronounced effect on the mutual diffusion and reactivity of radical ion pairs and, thus, the MFEs they elicit. So far, microheterogeneous solvation has only been studied by steady-state MFE measurements.16,19,20 This severely limits the insights in the radical pair dynamics in these systems, because only time-resolved MFE measurements allow one to discriminate the initial reaction products.1,2

The MFE relevant to this study results from the radical pair mechanism. In short, the overall singlet and triplet states of the radical pair are coherently interconverted by the hyperfine interactions (HFIs) of the magnetic nuclei of the radicals.21–25 An external magnetic field will remove the degeneracy of the three electronic triplet sublevels (T0 and T±) of the spin-correlated pair (in the absence of significant exchange or electron–electron dipolar coupling). When the energy separation between these states exceeds the size of the mixing interactions, T± cannot mix with the singlet state S. In this way, the external magnetic field reduces the probability of

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intersystem crossing in the radical pair and, thus, alters the relative concentrations of singlet and triplet reaction products (see Scheme 1a). The hyperfine-induced spin mixing between S and \( T_0 \) and \( T_\pm \) using magnetic-field interactions depends exponentially on the distance between the radical ions, this implies that only dilute radicals can undergo \( S/T \)-conversion. Eventually, the singlet RIP lifetime of the RIP increases due to a smaller depth of the dielectric traps. This is a consequence of the RIPs evading swift recombination by their diffusive escape from the trap. Accordingly, the extrapolated \( B_{1/2} \) values in the limit of zero donor concentration, \( B_{1/2}(0) \), are larger than expected for long-lived RPs but decrease with increasing macroscopic dielectric constant, in contrast to what is seen in homogeneous solvents. Nath and co-workers have recently suggested that two populations of exciplexes exist for the pyrene/N,N-dimethylaniline donor–acceptor system in comparably polar THF/DMF and benzene/acetanilide solvent mixtures. The authors argue that the effect is attributed to (incomplete) relaxation of the solvent shell surrounding the contact ion pair.

The aforementioned steady-state approaches usually do not take the exciplex kinetics into account. The mechanism of fluorescence quenching by electron transfer is, however, ambiguous; i.e., the initial quenching products are a RIP via distant ET (pathway 2B of Scheme 1b) or the exciplex (pathway 2A). Several studies have illustrated the use of time-resolved MFEs of the exciplex to identify the initial quenching products in homogeneous solvents and solvent mixtures. In this work, we describe the solvent polarity dependence of the time-resolved MFE in homogeneous and micro-heterogeneous binary solvent mixtures as measured by time-correlated single photon counting (TCSPC). The well-studied donor–acceptor system N,N-dimethylaniline (quencher)/9,10-dimethylanthracene (fluorophore) serves as a magnetosensitive probe (see Scheme 1c). Our study gives detailed insights into the peculiar RP dynamics in microheterogeneous solvents. Throughout this work, we use the terms “preferential solvation” and “microheterogeneous medium” interchangeably, although, strictly speaking, the former refers to specific and nonspecific solute–solvent interactions, while the latter signifies the nonuniform solvent structure, which the former induce. In the present context, this semantic distinction is immaterial.

**II. EXPERIMENTAL SECTION**

**Sample and Solvent Preparation.** 9,10-Dimethylanthracene (DMAn, Aldrich 99%) was used as received. N,N-Dimethylaniline (DMA, Aldrich 99.5%) was distilled under reduced pressure and subsequently handled under an argon atmosphere. The concentration of the fluorophore was constant at 1.5 \( \times 10^{-5} \) M, while that of the quencher was 0.06 M. Solutions were prepared in septa-sealed fused silica cuvettes. All solutions were purged with solvent-saturated nitrogen gas for 15 min to remove dissolved oxygen before adding the quencher through the septum using Hamilton syringes. A series of solvent mixtures of propyl acetate (PA, Aldrich 99.5%) and butyronitrile (BN, Fluka 99%), dimethyl sulfoxide (DMSO, Aldrich 99.9%), and dimethylaniline (DMA, Aldrich 99.5%) with widely varying dielectric constants, \( \varepsilon \), were prepared. The dielectric constants of these mixtures are given by eq 1 and eq 2 for the PA/BN and TO/DMSO systems, respectively (at 295 K):  \[
\varepsilon = w_{PA}\varepsilon_{PA} + (1 - w_{PA})\varepsilon_{BN} \tag{1}
\]
\[ \varepsilon_s = 62.5 \exp \left[ \frac{1-x_{\text{DMSO}}}{0.78} \right] - 15.6 \]  

Here, \( w_{PA} \) is the mass fraction of PA and \( x_{\text{DMSO}} \) is the mole fraction of DMSO. The homogeneous mixtures of PA/BN allow systematic variation of the solvent dielectric constants within a range of 6–24.7 (at 295 K) while keeping the viscosity (\( \eta \)) and the refractive index (\( n \)) almost constant. The Peker factor, \( \gamma = (1/\varepsilon_\infty - 1/\varepsilon_s) \approx (1/n^2 - 1/\varepsilon_s) \), which governs the outer-sphere electron transfer reorganization energy, increases only moderately with increasing permittivity. For the microheterogeneous mixtures of TO/DMSO, the solvent dielectric constant was varied from 4.3 to 15.5. The viscosity and the bulk Peker factor \( \gamma \) of TO/DMSO mixtures slightly increase with increasing DMSO concentration. We are not aware of a microheterogeneous solvent mixture for which this could be avoided.

**Steady-State MFE Measurements.** Using the experimental setup described in ref. 32, the exciplex emission was recorded at 550 nm under continuous excitation of the sample at 374 nm. For each sample, the fluorescence intensities were acquired three times under conditions of zero and saturating magnetic field excitation for 60 s each. Field-on and field-off measurements were recorded in an alternating fashion. The excitation slit width was 2 nm, the emission slit width 6 nm, and the spectrometer time constant 1 s. Measurements were conducted at 295 K. The three repetitions were analyzed independently, and the experimental errors were obtained according to the method described in ref. 32. The absolute MFE, \( \chi_{\text{SS}} \), was evaluated from

\[ \chi_{\text{SS}} = \frac{T(\lambda_{\text{em}}, B_{\text{sat}}) - T(\lambda_{\text{em}}, B_0)}{T(\lambda_{\text{em}}, B_0)} - \frac{\Delta \chi_{\text{TR}}(\lambda_{\text{em}}, B_0)}{I/I_0} \]  

Here, \( T(\lambda_{\text{em}}, B_{\text{sat}}) \) and \( T(\lambda_{\text{em}}, B_0 = 0) \) are the mean intensities at \( \lambda_{\text{em}} \) in a saturated magnetic field (\( B_{\text{sat}} = 62 \text{ mT} \)) and in the absence of an additional magnetic field, respectively. \( I/I_0 \) is the residual emission of the locally excited fluorophore at \( \lambda_{\text{em}} \) in the absence of quencher. \( I \) and \( I_0 \) are the intensities of prompt emission of the fluorophore in the presence and absence of the quencher, respectively, which have been obtained from the decomposition of the fluorescence spectra. \( \Delta \chi_{\text{TR}}(\lambda_{\text{em}}, B_0) \) is the mean background intensity.

**Time-Resolved MFE Measurements and Modeling.** Time-resolved data of the MFEs on the exciplex were obtained by the TCSPC technique. In order to investigate the effect of an external magnetic field on the exciplex emission (Figure 1), a saturating magnetic field (\( B_0 = 62 \text{ mT} \)) was applied. The fluorophore is excited at 374 nm by a laser diode (Picoquant, LDH-P-C-405), and a 550 nm long-pass filter in front of the detector ensured that only the exciplex luminescence was detected. A detailed description of the experimental setup is given in refs 1 and 2.

The raw data of a typical time-resolved MFE measurement are shown in Figure 1. The time traces rise with a time constant of approximately 2 ns, almost independent of the magnetic field intensity. The decay kinetics of the exciplex emission includes the dissociation into free ions and recombination giving rise to delayed exciplex emission. The time-resolved MFE (TR-MFE) is given as the difference in the exciplex emission intensity, \( \Delta I(t) \), in the absence and presence of the external, biasing magnetic field:

\[ \Delta I(t) = I(t, B_0) - I(t, B_0 = 0) \]  

In order to determine the MFE, the amplitudes within the first nanosecond after the excitation pulse were matched. We integrated the time traces so obtained to determine the steady-state MFE of the exciplex, \( \chi_{\text{TR}} \), from the time-resolved MFE measurements:

\[ \chi_{\text{TR}} = \frac{\int_0^\infty \Delta I(t) \, dt}{\int_0^\infty I(t, B_0 = 0) \, dt} \]  

Scheme 1b shows the pertinent reaction pathways for fluorescence quenching by electron transfer. The abcissa can be expressed as the projection of a two-dimensional reaction coordinate comprising the distance between the fluorophore and the quencher and the outer-sphere electron transfer reaction coordinate. The ordinate corresponds to the free energy. An increase in the intensity of the exciplex emission (6) is due to the enhancement of the population of the singlet RIP, which can reform the exciplex via (4). The singlet RIP can be indirectly generated via exciplex dissociation (3), e.g., following a quenching reaction yielding the exciplex (2A), or directly, via a remote electron transfer reaction (2B). Note that the ET reactions preserve the overall spin of the reactant pair; i.e., both the exciplex and the RIP are formed as singlet entities. The external magnetic field gives rise to an increase in the singlet RIP probability and hence the exciplex via pathway 4. As a consequence of the exciplex dissociation here being a slow process, the MFEs generated by the direct ET route (2B) will be observed on a faster time scale than those formed by the exciplex route (2A). In this way, time-resolved MFEs of the exciplex emission can distinguish the reaction channels populating the magneto-sensitive RP state (2B versus 2A).

To simulate the experimental data, we used the model introduced in ref 2. In this model, both initial quenching...
products (exciplex or RIP) are possible. The probability that the radical pair system exists as an exciplex, \( \rho_E(t, B_0) \), is given by

\[
\rho_E(t, B_0) = \phi_E + \phi_i R(t, B_0) E \tau
\]

\[
+ k_d \int_0^\tau \rho_E(\tau) R(t - \tau, B_0) d\tau \nonumber
\]

\[
- (k_d + \tau^{-1}_E) \int_0^\tau \rho_E(\tau) d\tau
\]

(6)

where \( \phi_i \) is the probability that the RIP is initially generated (pathway 2B in Scheme 1b), \( k_d \) denotes the rate constant of exciplex dissociation, \( r_1 \) is the distance of RIP formation via distant ET, and \( R(t, B_0)E \tau \) is the probability that a RIP formed at distance \( r_1 \) at \( t = 0 \) has recombined by time \( t \). \( \tau_E \) refers to the contact distance of the fluorophore and quencher, at which the transition of the RIP to the exciplex (or contact ion pair) occurs. \( \phi_E = 1 - \phi_i \) is the initial exciplex probability (pathway 2A in Scheme 1b), and \( \tau^{-1}_E \) is the intrinsic exciplex lifetime (without dissociation). The contributions to the exciplex probability in eq 6 can be described as follows: The first term is the probability that the exciplex is formed initially, while the second term accounts for the probability that the initially generated RIP reforms an exciplex at \( t \). The third term describes the probability that the exciplex dissociated at time \( \tau \) is reformed at \( t \), and the last term models the depopulation of the exciplex by dissociation \( (k_d) \) and radiative/nonradiative decay with the rate constant \( \tau^{-1}_E \). \( R(t, B_0)E \tau \) is field dependent and has been calculated in the low-viscosity limit as described in detail in refs 1 and 2. The radical pair was assumed to diffuse in a potential of mean force approximately accounting for the microheterogeneous environment. This potential was calculated following an approach based on the \( D-E_0 \) theorem as outlined in refs 18 and 20. Note that more elaborate schemes of treating the diffusion-influenced reversible exciplex kinetics have been derived on the basis of the integral encounter theory. \( \phi_i \) While also comprehensively applicable to highly viscous mixtures, this approach is difficult to employ for radical pairs with a multitude of magnetic nuclei (as is the case here) and beyond the scope of the current presentation. Figure 2 illustrates the microheterogeneous medium structure to clarify typical length scales and the extent of the local enrichment of the polar component as predicted on the basis of the continuum model from ref 20.

III. RESULTS AND DISCUSSION

Figure 3 illustrates the dependence of the MFE of the DMAnt/DMA system on the solvent dielectric constant, \( \epsilon_s \), of the microheterogeneous TO/DMSO mixture as determined from steady-state (blue filled triangles) and time-resolved MFE (red filled stars with barely visible error bars reflecting the statistical error of the registration process) measurements in solvent mixtures of TO/DMSO (upper panel). The lower panel compares the MFE in the homogeneous and microheterogeneous solvent mixtures.

radical pair. The onset of the MFE is found at \( \epsilon_s = 6 \) (with \( \chi = 0.1 \% \)) and \( \epsilon_s = 4.3 \) (with \( \chi = 1.6 \% \)) in the PA/BN and TO/DMSO mixture, respectively. In the homogeneous PA/BN mixtures, the MFE is small for \( \epsilon_s < 10 \) but rises sharply for \( \epsilon_s \sim 13 \) to attain its maximum value around \( \epsilon_s \sim 18 \) (11%). For larger solvent polarities, it decreases slightly as a larger population of the radical pairs dissociates indefinitely without reencountering (within the coherence time of the radical pair). In the microheterogeneous TO/DMSO mixtures, the onset of the MFE occurs at a lower bulk permittivity and the maximal value (14.5%) is already observed at \( \epsilon_s = 8.3 \). In essence, the MFE appears to report a more polar environment than would be expected on the basis of the bulk permittivity. These peculiarities in the MFEs can be explained on the basis of a...
dielectric enrichment of the polar component (DMSO) in the vicinity of the magneto-sensitive RIP. As a consequence, the effective dielectric constant, $\varepsilon_{\text{eff}}$, of the enriched solvation shell is increased over the bulk dielectric constant, $\varepsilon_s$. This specific solvation increases the reencounter probability of the geminate RP without impeding the spin-conversion by too tight binding, which in homogeneous solvents of low polarity is seen to hamper the MFE by confining the radical pairs to configurations with large exchange coupling. As a consequence, larger MFEs are possible in the microheterogeneous environments as compared to homogeneous solutions.

For various dielectric constants, the time-resolved MFEs are shown in Figure 4 together with least-squares fits applying the model given by eq 6. The maximum of the TR-MFEs occurs in the range from 10 to 75 ns after photoexcitation, with larger values occurring at lower dielectric constants. For all samples, the MFEs reached the noise level of the experiment within 400 ns after excitation.

The exciplex lifetime, $\tau_E$, is one of the central parameters characterizing the time evolution of the MFE. We have determined $\tau_E$ from the initial decay of the TCSPC traces of the exciplex, for which the RP recombination is negligible. Figure 5 shows that the apparent exciplex lifetime decreases with increasing bulk dielectric constant, $\varepsilon_s$, in both binary solvent mixtures. Furthermore, as expected in view of the above discussion, the exciplex lifetimes are considerably smaller in the TO/DMSO mixtures as compared to the iso-bulk dielectric PA/BN mixtures. Note also that the exciplex is an excited charge-transfer complex with correspondingly large dipole moment. As a consequence, its formation is expected to enhance the diffusive enrichment of polar solvent molecules in its surrounding. In this way, the exciplex can act as a catalyst to its own dissociation (pathway 3 in Scheme 1b). As the exciplex lifetime is considerably larger than the characteristic time of solvation, these dynamic aspects can however not be resolved here.

The exciplex kinetics are also characterized by the association constant $K_a = k_a/k_d$ (top panel in Figure 6) and the exciplex dissociation quantum yield $\phi_d$ (middle panel in Figure 6). $\phi_d$ was estimated from the dependence of $\tau_E$ on dielectric constants assuming that the intrinsic, radiative and nonradiative decay rates are independent of solvent composition. $K_a$ has a strong effect on the shape, i.e., the temporal evolution, of the time-resolved MFEs and can thus be extracted from the experimental data by modeling the TR-MFE. The solid lines have been added to guide the eye.
function of \( \varepsilon_r \). In general, \( \phi_f \) increases with \( \varepsilon_r \), likely because polar environments reduce the exciplex stabilization free energy by increasing the reorganization energy.\(^{3,32}\) This effect is indeed found and much more pronounced in the microheterogeneous environment as compared to the homogeneous one. For TO/DMSO, the exciplex dissociation quantum yield approaches \( \phi_d = 1 \) for a bulk dielectric constant as low as \( \varepsilon_r = 8 \), while for PA/BN mixtures this is only the case at \( \varepsilon_r \approx 22 \).

Likewise, the association constant \( K_a \) is expected to decrease with polarity, as is clearly evidenced in Figure 6 for the homogeneous PA/BN solutions. While \( K_a \) in general also decreases with increasing polarity for TO/DMSO, it is nearly constant in the range from \( \varepsilon_r = 8 \) to 12. This surprising behavior suggests that \( k_a \) increases in this region in parallel to \( k_d \) such that \( K_a \) is approximately constant. This can likely be attributed to an increased association rate brought about by the microheterogeneous solvation impeding the separation of the radical ions with respect to the homogeneous environment.

Just as \( K_a \) the probability of the initial RIP formation, \( \phi_0 \) governs the time evolution of MFEs of the exciplex and was extracted from the experimental data by least-squares fitting.\(^1,2\) The extracted \( \phi_0 \) values are also shown in Figure 6 as a function of the dielectric constant. The data reveal that, for the DMAnt/DMA system with moderate free energy of charge separation \( \Delta G_{se} = -0.28 \) eV,\(^{33,34}\) the direct exciplex formation (pathway 2A in Scheme 1b) contributes at all dielectric constants in homogeneous and microheterogeneous environments. Furthermore, the probability of distant ET quenching increases with increasing solvent polarity. Note that the requirement to detect the exciplex luminescence limits the accessible \( \varepsilon_r \) range to the indicated range; beyond the respective limits, the exciplex emission is insufficient for the accurate determination of \( \Delta I \). In both solvent mixtures, \( \phi_1 \) levels off at \( \phi_1 = 0.55 \). For TO/DMSO, this is the case for \( \varepsilon_r \geq 9 \), and for PA/BN, for \( \varepsilon_r \geq 20 \), in agreement with the general bearing. Distant electron transfer quenching is more favored in polar solutions, where it leads to a better solvation of the reaction products (RIPs). This holds true despite a minor increase in the reorganization energy resulting from the increasing polarity. In the low-viscous solutions studied here, the diffusive approach of the reactants is fast enough compared to the intrinsic electron transfer rate to always form a contact complex (exciplex) at the contact distance. As a consequence, \( \phi_1 \) is smaller than unity, even for the most polar and hardly emissive solutions.

IV. CONCLUSIONS

In this work, we have employed time-resolved MFE measurements to study the exciplex and RIP dynamics of the DMAnt/DMA system in homogeneous and microheterogeneous solvent mixtures of various bulk permittivities. We use a model accounting for the reversible exciplex dissociation to identify the peculiarities resulting from microheterogeneous solvent environments in solvent mixtures of TO and DMSO. The exciplex dynamics and the initial quenching products depend strongly on the solvent properties. In microheterogeneous solvents, specific solvation of the exciplex and RIP gives rise to an environment that is significantly more polar than that observed in homogeneous solvents of comparable bulk permittivity. For low permittivities, this brings about a larger dissociation quantum yield of the exciplex, a lower exciplex lifetime, and a larger probability that the system undergoes distant electron transfer quenching. Specific solvation furthermore impedes the radical separation such that, in the permittivity region from 7 to 15, the association constant decays only slowly with the solvent polarity in the TO/DMSO mixtures. In both environments, the probability of the initial formation of RIPs is always less than unity; i.e., the exciplex formation contributes at all \( \varepsilon_r \). In microheterogeneous solution, the local concentration of DMSO in the solvation shell around the exciplexes and RIPs plays an important role in the exciplex kinetics and the fluorescence quenching mechanism. Together with earlier works, this study demonstrates that time-resolved MFE studies have the potential to provide detailed insights into the reaction dynamics of RIPs and exciplexes. Since the reaction dynamics of the geminate radical pair are very sensitive to small changes in the local dielectric environment, the technique is here recognized as a versatile tool in revealing and characterizing the phenomenon of specific solvation in solvent mixtures.

AUTHOR INFORMATION

Corresponding Author
E-mail: daniel.kattnig@chem.ox.ac.uk.

ORCID
Daniel R. Kattnig: 0000-0003-4236-2627

Notes
The authors declare no competing financial interest.

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