COMMENTS

Comment on the "Magnetic Field Effects on Exciplex Luminescence in Water−Tetrahydrofuran and Water−Dioxane Mixtures"

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Cage recombination of radical ion pairs (RIP) produced during the course of photoinduced electron transfer in polar solutions of exciplex systems can be affected by a weak external magnetic field $B \sim 100$ G (for review see ref 1). Because of the law of spin conservation, the multiplicity of the product formed by geminate recombination is the same as that of its radical-ion precursor. The RIP, which is created, say, as a pure singlet state, undergoes spin evolution during its lifetime (∼10 ns) to form a triplet state via hyperfine interaction (HFI) of its unpaired electrons. Applied magnetic fields affect the spin mixing, removing the degeneracy of the triplet sublevels of RIP, T_0, and $T_{\pm1}$. When the energy separation between them exceeds the size of HFI, only T_0 can mix with the RIP singlet state S. Thus, external magnetic fields diminish the probability of intersystem crossing and, therefore, change the concentration of both the singlet and triplet states of the RIP. Magnetic fields affect the spin evolution of the geminate RIP rather than that of pairs generated via random bulk recombination. A convenient method for detecting the magnetic field effect (MFE) on cage recombination of RIP is based on detecting exciplex fluorescence; the transition from the singlet state of RIP to exciplex is possible even in moderately polar solvents.

Studying the MFE on exciplex fluorescence of pyrene/*N*,*N*-dimethylaniline solution in binary solvents, components of which were considerably different in terms of dielectric permittivity, we have found[2] that values of a relative enhancement of exciplex fluorescence caused by magnetic fields may be as large as 18% at $B = 300$ G in a benzene/dimethyl sulfoxide (DMSO) liquid mixture when the volume fraction of the polar component is ca. 0.26. This value of the MFE is considerably larger than those obtained in intermolecular exciplexes in neat solvents (typically 3−6%) and is the same order of magnitude as the MFE detected by Staerk et al.[3] in polar solutions of polymethylene-linked pyrene/*N*,*N*-dimethylaniline systems. A characteristic features of these intramolecular systems is that dissociation of RIP is completely eliminated. Therefore, the bulk (homogeneous) recombination of free radical ions, which also results in exciplex fluorescence but unaffected by magnetic fields, is actually absent. This provides favorable conditions for detecting large values of the MFE (up to 47% depending on the length of polymethylene chain[3]). By analogy with intramolecular exciplex systems, we have assumed that in the binary liquid solvents, owing to preferential solvation, microdomains of polar-component molecules are created around radical ion pairs, keeping radical ions within the cage.[2]

The physical meaning of such a cage effect enhancement is as follows. When ions have the separated solvation shells (see Figure 1), this interaction is determined by ϵ_m. If the solvation shells of partner ions intersect each others (Figure 1a), Coulombic forces are strongly diminished by a factor of ca. ϵ_l/ϵ_m. Here ϵ_l is the dielectric constant of the polar component (ca. 50 for DMSO) and ϵ_m is that of the mixture. (For a benzene/DMSO (25 vol %) mixture, ϵ_m is ca. 11 as measured by the capacity method.) So that the common solvation shell plays the role of a trap that increases the yield of cage recombination of radical ion pairs.

Fluctuations of the polar component concentration is supposed to be a physically meaningful source of producing relatively large polar clusters. It is worth noting that concentration fluctuations in nonideal binary mixtures can considerably exceed a stochastic level, and the concept of microheterogeneous structure of binary mixtures has been involved in explaining experimental results on light scattering in binary mixtures.[4]

Recently, Chowdhury et al.[5] have questioned the maximum value of MFE we had found earlier for the benzene/DMSO mixture. (These authors have reported ca. 11% as a greatest possible value; the lifetime of exciplex fluorescence corresponding to this MFE is 13.7 ns [ref 5, Table 2].) On the other hand, the above concept of microheterogeneity is actually based on the main experimental fact that in the binary mixture there exists a value of MFE significantly larger than that in neat solvents. Therefore, we have reproduced our old results,[2] repeating it under different experimental conditions in the MFE laboratory of the Max-Plank Institute of Biophysical Chemistry (Goettingen, FRG).

Experimental Results and Discussion

The relative change in the exciplex fluorescence caused by external magnetic fields, the magnetic field effect (MFE), was detected under steady-state conditions through an OG515 Schott filter during the course of excitation of pyrene by a xenon arc lamp (BG18+UG11 Schott filters). Magnetic field applied to a sample cell were produced by a Bruker electromagnet and measured with a Hall probe. All experiments were carried out at room temperature. Nitrogen was bubbled through the solutions before measurements for ca. 20 min in order to remove oxygen. A typical concentration of zone purified pyrene was ca. 10^{-5} mol/L and that of *N*,*N*-dimethylaniline (distilled under reduced pressure), 3×10^{-2} mol/L. Toluene and DMSO (Merk, Uvasol) of spectroscopic grade were used as solvents. Fluorescence lifetimes were determined with a single-photon-counting fluorometer (Edinburgh Instruments).

We have repeated the measurements of the saturation value of the MFE at $B = 600$ G on exciplex fluorescence in pyrene solution with excess of *N*,*N*-dimethylaniline in toluene/DMSO binary solvent mixtures as a function of the volume fraction of DMSO (see Figure 2). In spite of using compounds and solvents of a different grade as compared with that we used earlier and a different type of experimental setup, we have obtained the results that are in a good agreement with our previous ones. At 25 vol % of DMSO we have observed a 20% (!) enhancement

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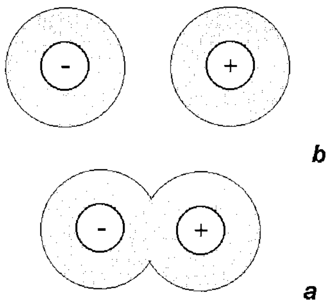

Figure 1. A schematical sketch of radical ion pair solvation: (a) overlapping of the polar solvation sheath (shadowed area) of partner ions; (b) each radical ion has its own solvation sheaths.

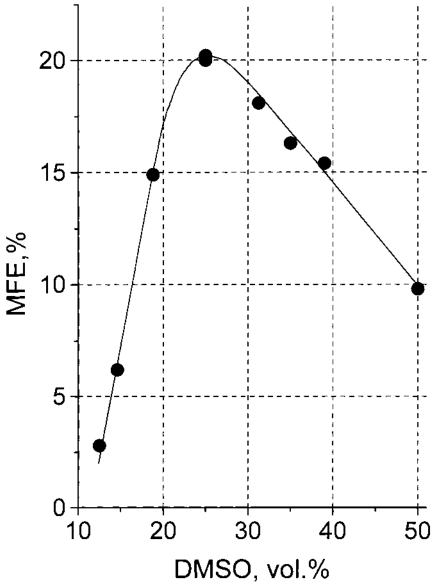

Figure 2. Magnetic field effect on exciplex fluorescence at $B = 600$ G as function of the DMSO volume fraction.

of exciplex fluorescence (18% at 26 vol % of DMSO have been reported in ref 2). The important point is that we have reproduced the MFE maximum value that is significantly higher than that measured in neat solvents.

Lifetimes of exciplex fluorescence were also measured. These are 58.2 ns at 15 vol % of DMSO, 21.4 ns at 25 vol %, and 9.1 ns at 40 vol %. The more polar the medium is, the shorter the exciplex lifetime; it is a well-known trend in such systems.[6] Although it is difficult to explain an actual reason for the discrepancy with results obtained by Chowdhury et al.[5] (it is out of the scope of this comment indeed), the lifetime data indicate that these authors might have worked with a more polar composition of solvent mixture rather than with one that corresponds to a 25 vol % of DMSO, when the MFE is at its maximum.

In conclusion, it is worthwhile to mention an interesting but crucial feature of the paper by Chowdhury et al:[5] the use of aqueous mixtures in order to check the microheterogeneous model against additional experimental data. This is what these authors allege in the introduction of their article; but from the above it is clear (see Figure 1) that an aqueous mixture is hardly suitable to study this case. Pyrene is a strongly hydrophobic compound while our model assumes that both acceptor and donor should be soluble in a polar component of the mixtures used in order to be effectively kept in the dielectric trap.

Conclusion

A relative enhancement of exciplex fluorescence caused by an external magnetic field in binary mixtures can be significantly larger than that observed in neat solvents. The verification of this fact more than once makes it a reliable basis for developing the adequate theoretical model. A forthcoming publication is addressing a partial aspect, the transient dynamics of solvatochromic shift of exciplex fluorescence in binary solvent mixtures.[7]

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References and Notes

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