Magnetic Field Effects on Exciplex Luminescence in Water−Tetrahydrofuran and Water−Dioxane Mixtures[†]

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Magnetic-field-modulated exciplex luminescence in different solvent media has been studied to verify the solvent microheterogeneity effect. In particular, mixtures of a low-polarity component, such as dioxane and tetrahydrofuran, and a highly polar component, such as water, have been used as media where the microheterogeneity has been further modulated by addition of salt and variation of temperature. The results are analysed in light of several proposed models for the solvent effect on MFE's, but no model is found to be completely satisfactory. It has been suggested that multiple intermediate states, instead of a single intermediate state, are formed during the electron-transfer process.

1. Introduction

Exciplex luminescence in semipolar neat solvents and polar−nonpolar mixed solvents has been found to increase in intensity on application of a small magnetic field.[1] This observation has been explained as follows. In solvents of medium polarity, an electron jumps from the donor to the photoexcited acceptor (or from the photoexcited donor to the acceptor), forming a solvent-shared radical ion pair (SSRIP).[2] If the precursor {A*,D} or {A,D*} is in a singlet spin state, which is normally the case, the SSRIP, born from it, is also in a spin-correlated singlet state. When the coupling between the spins of the two radicals of the SSRIP is small, singlet-to-triplet evolution, assisted by hyperfine interaction which compensates for electron spin change by nuclear spin change, could occur.[3,4] In medium dielectric constant environment, this singlet-to-triplet evolution competes with the singlet-state radical recombination and subsequent luminescence process.[4] If an external field, large enough to cause the Zeeman splitting to exceed the hyperfine width, is applied, it blocks the two channels of $S \rightarrow T_{\pm 1}$ spin evolution and thus considerably decreases the $S \rightarrow T$ evolution rate.[3,4] This results in increased singlet radical pair recombination and, hence, increased exciplex luminescence intensity.

Nath and Chowdhury found that for various neat and mixed aprotic solvents, the magnetic field effect (MFE), as measured by $\Delta\phi/\phi$, where ϕ is the total luminescence yield and $\Delta\phi$ the increase in luminescence yield on application of a saturating magnetic field, reaches a maximum near a solvent dielectric constant of 16.[5] According to these authors, the magnetic-field-induced increase in luminescence depends on the complex interplay between spatial and spin evolution within the SSRIP.[6] If the dielectric constant of the medium is too low, the luminescent contact ion pair (CIP) is formed directly by electron transfer from the donor to the excited acceptor, and the CIP/SSRIP has to climb a steep potential energy surface to reach a distance large enough for the exchange coupling between the pair of radicals to be nearly zero. On the other hand, a medium of large dielectric constant is suitable for the dissociation of the SSRIP but not for their recombination after a diffusional excursion during which the correlated spin evolution into the triplet state occurs. The solvent of intermediate dielectric constant is suitable for the SSRIP to reach a distance where hyperfine-induced singlet-to-triplet transformation can easily take place, but the recombination probablity is also not too low. Thus, the magnetic-field-modulated emission of the exciplex, formed from the SSRIP, shows a maximum at an intermediate solvent dielectric constant.

Petrov et al. invoked the idea of preferential solvation in a polar−nonpolar binary solvent mixture and introduced the concept of microheterogeneity in such solvents.[7,8] By approximate calculation, they were able to explain why the $\Delta\phi/\phi_{\max}$ vs ϵ curve shows a maximum near $\epsilon = 15$.[7a] They also found out a correlation between $\Delta\phi/\phi$ and a difference between the solubility parameters of the solvent components of the binary solvent mixtures.[8] The dynamics of preferential solvation has also recently been investigated.[7b]

Recently, Werner and Staerk studied the relative magnetic-field-modulated exciplex luminescence $\Delta\phi/\phi$ of polymethylene-linked pyrene−DMA systems.[9] They found that these systems also show the maximum of $\Delta\phi/\phi$ at the same intermediate dielectric constant as that for the unlinked system. They pointed out that the chain lengths of the polymethylene-linked pyrene−DMA systems are several times smaller than the Onsager radius, and hence, these are not expected, by the two previously stated diffusion based models, to show a decrease in $\Delta\phi/\phi$ in polar solvents. Werner and Staerk observed a correlation between $\Delta\phi/\phi$ and the lifetime of the exciplex, $\Delta\phi/\phi$ increasing with increasing lifetime in polar solvents. They ascribed the low value of $\Delta\phi/\phi$ in nonpolar solvents to direct formation of the CIP instead of indirect formation from SSRIP. In polar solvents, they suggested that a SSRIP is formed first, and the lifetime of the SSRIP is governed by the back-electron-transfer (BET) rate of the SSRIP. Assuming a rapid equilibrium between the CIP and SSRIP, they argued that since a long-lived SSRIP spends more time in the region suitable for hyperfine-induced spin evolution, it should show higher MFE's. They related the MFE of the linked system with the lifetime and the lifetime with $\Delta G(\epsilon)$ variation of the BET process in the "Marcus inverted region".

It is obvious that the above three proposed models are speculative and need to be checked against additional experimental data. In particular, we thought that in the background of Petrov et al.'s idea of microheterogeneity, it might be interesting to choose water as one component of the polar−nonpolar solvent mixture. Water is an important component

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of most biological substances, and hence, a better understanding of biological MFE's may arise from emission studies in a water-containing medium. It has been reported that MFE on exciplex luminescence can be increased substantially by choosing DMSO−benzene solvent mixtures.[9] The microheterogeneity is expected to increase in mixtures of a nonpolar solvent with water, and hence, our expectation was that it should increase the MFE still further. Only a few nonpolar solvents are, however, miscible with water in all proportions so as to allow us to vary the dielectric constant significantly. Here we report our experiments with some exciplex systems in THF−water and dioxane−water solvent mixtures. Water is normally treated as an undesirable component in MFE studies of exciplex luminescence, and all solvent mixtures are usually thoroughly dried before MFE studies. We, however, observed considerable MFE's in water−THF mixtures. Water-containing solvent mixtures permitted us to study the effect of salt on the MFE's, which was not possible in other organic solvent mixtures. We have critically examined our results in light of the three proposed models but found none of them to be completely satisfactory. The necessity of a new approach has been pointed out.

2. Experimental Section

Compounds. Anthracene, 9-cyanophenanthrene, and anethole were supplied by Aldrich Chemical Co. and used as supplied. Pyrene was supplied by Aldrich and used after purification by column chromatography using silica gel as the static medium and cyclohexane as the mobile phase. *N*,*N*-Dimethylaniline (DMA) was supplied by BDH and used after vacuum distillation. All salts of analytical grade were supplied by Loba Chemicals and used as supplied.

Solvents. All solvents of spectroscopy grade or HPLC grade were supplied by SD Chemical and used as supplied, except tetrahydrofuran, which was used after distillation. Purity of a solvent was checked before use by measuring the background fluorescence. Triple distilled water was used for all experiments.

Spectra. Absorption spectra were determined on a JASCO UV/vis spectrometer, Model 7850. Steady-state emission and excitation spectra were recorded on a Perkin-Elmer fluorescence spectrometer, MPF-44B. All samples were degassed by purging with nitrogen gas for 30 min. The temperature was controlled within 5−60 °C by a Neslab thermostat using water as the heat carrier.

Fluorescence Decays. Fluorescence decays were determined by the time-correlated single-photon-counting (TCSPC) technique. The apparatus has been described elsewhere.[10] Fluorescence decay curves were analyzed by the deconvolution technique using a global analysis program of PTI.

Magnetic Field Effect. To find out the magnetic field effect on exciplex luminescence, a phase-sensitive detection system has been employed, the details of which have been discussed elsewhere.[11] The experiment has been done within a magnetic field range of 0−250 G. Between 5 and 50 °C, the temperature was controlled by a Neslab thermostat using water as the heat carrier.

Transient Absorption Spectra. Transient absorption spectra of the pyrene−DMA system were measured by the laser flash photolysis technique. The details of our laser flash photolysis apparatus are given elsewhere.[12] The third harmonic output of Nd-YAG (355 nm) with a 5-ns pulse width was used to pump the sample and 200-W Xe pulse to monitor the transient species. An IP28 photomultiplier with a detection time constant of around 15 nm was employed to detect the light transmitted through the sample. The transient absorption spectra were recorded by a digital oscilloscope (TDS-350).

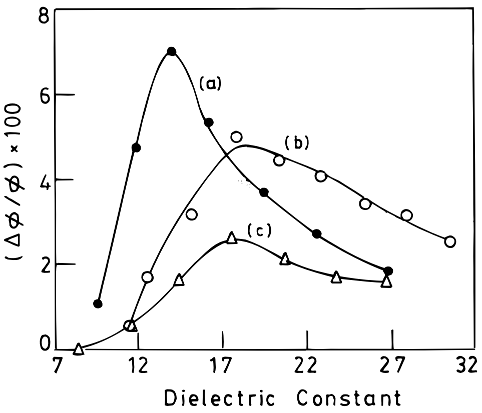


Figure 1. Variation of the ratio of the magnetic-field-induced change in the exciplex luminescence intensity to the exciplex luminescence intensity in the absence of the magnetic field, $\Delta\phi/\phi$, of the pyrene−DMA system with medium dielectric constant: (a) THF/water, (b) THF/methanol, and (c) dioxane/water at 520 nm. The compositions of solvent the mixtures corresponding to the maximum of the $\Delta\phi/\phi$ vs ϵ curves are 10% of water by volume in the THE/water mixture, 40% of methanol in the THF/methanol mixture, and 20% of water in the dioxane/water mixture.

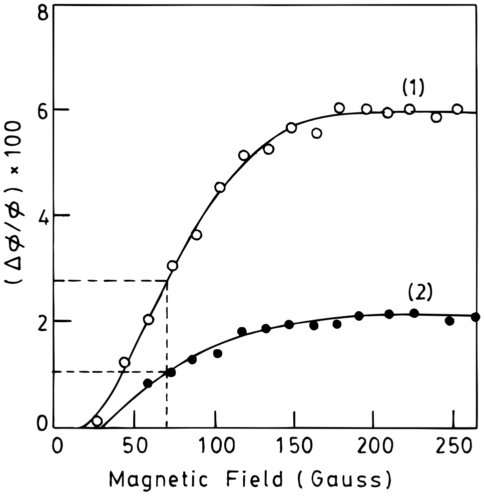


Figure 2. Dependence of $\Delta\phi/\phi$ on the magnetic field strength for the pyrene−DMA system in (1) THF/water and (2) dioxane/water at 520 nm.

3. Results

3.1. Solvent Effect on the MFE's. The effects of the dielectric constant on the relative magnetic-field-induced change in the exciplex luminescence ($\Delta\phi/\phi$) of the pyrene−DMA system in some new binary solvent mixtures (THF/water, dioxane/water and THF/methanol) are shown in Figure 1. For all solvent mixtures, the $\Delta\phi/\phi$ vs ϵ curve passes through a maximum. There is a small variation in ϵ_{max} (i.e., the dielectric constant corresponding to the maximum in the $\Delta\phi/\phi$ vs ϵ curve) from one solvent mixture to another. In THF/water and THF/acetone, the maximum appeared at an ϵ value of around 15 and in THF/methanol and dioxane/water around $\epsilon = 17$. In all mixtures, there occurs very little MFE below $\epsilon = 10$. The curve is asymmetrical around ϵ_{max}, the rising part at low ϵ being much steeper than the descending part at higher ϵ.

The variations of $\Delta\phi/\phi$ in THF/water and dioxane/water with the magnetic field strength, *B*, are shown in Figure 2 for the pyrene−DMA system. The nature of the curves in both solvent mixtures are almost the same. From the figure, it is found that the $B_{1/2}$ values (i.e., the strength of the magnetic field at which $\Delta\phi/\phi$ becomes half of $\Delta\phi/\phi_{max}$) in both solvents are almost

TABLE 1: Variation of $\Delta\phi/\phi_{max}$ of Different Exciplexes in Different Binary Solvent Mixtures

		$\Delta\phi/\phi_{max} \times 100$		
solv mix[a]	η_{av}, cP	Pyrene–DMA	anth–DMA	cyanoanth–anethole
B/D	1.01	10.9	7.7	3.8
T/Dm	0.79	8.3	7.8	3.7
T/Ac	0.42	8.1	7.2	3.6
B/Ac	0.42	7.8	6.9	2.6
T/W	0.55	7.2	4.5	2.5
Cy/Ac	0.46	5.3	4.2	1.3
D/W	1.11	2.6	0.4	0.0

[a] B/Dm, benzene/DMSO; T/Dm THF/DMSO; T/Ac THF/acetone; B/Ac, benzene/acetone; T/W, THF/water; Cy/Ac, cyclohexane/acetone; D/W, dioxane/water.

TABLE 2: Variation of Lifetime, Fluorescence Intensity, and Percentage Magnetic-Field-Modulated Luminescence of Pyrene–DMA Exciplex with Average Viscosity and a Characteristic Parameter, $V_{mp}(\delta_p - \delta_n)^2$, of Several Binary Solvent Mixtures at the Isodielectric Constant ($\epsilon \approx 15$), except for Dioxane/Water ($\epsilon \approx 17$)

solvent[a]	η_{av} cP[b]	$V_{mp}(\delta_p - \delta_n)^2$,[c] cal mol^{-1}	τ_{ex},[d] ns	ϕ at 510 nm[e]	$\Delta\phi/\phi_{max}$, %
B/Dm	1.01	559	13.7	17	10.9
T/Ac	0.42	47	24.5	47	8.1
B/Ac	0.42	36		63	7.8
T/W	0.55	3680	14.9	29	7.5
E/Dm	0.92	345	21.8	66	7.4
E/Ac	0.48	1	10.9	18	7.3
cy/Ac	0.46	214		63	5.3
C/Ac	0.41	27	22.1	43	3.9
C/Dm	0.90	520	20.1	44	2.6
D/W	1.11	3232	22.3	28	2.6

[a] B, benzene; Cy, cyclohexane; T, tetrahydrofuran (THF); Dm, dimethyl sulfoxide (DMSO); C, chloroform; E, ethylene dichloride; D, dioxane; Ac, acetone; W, water. [b] η_{av}, average viscosity of binary solvent mixture. [c] V_{mp}, molar volume of polar component. [d] τ_{ex}, exciplex lifetime. [e] Arbitrary units.

equal, around 70 G. This value may be compared with 70 ± 2 G obtained for nonprotic solvent mixtures at the same concentration.[13]

The variation of $\Delta\phi/\phi_{max}$ for different exciplexes (pyrene–DMA, anthracene–DMA, and 9-cyanophenanthrene–anethole) in several binary solvent mixtures are given in Table 1. Here, all solvent mixtures are nearly isodielectric. It is found that the magnitude of $\Delta\phi/\phi_{max}$ varies considerably from one solvent mixture to another for all exciplexes, and these variations are very similar for all exciplexes. The average viscosities of these solvent mixtures have been calculated by the mixing rule assuming no interaction between components. The same table shows that there is hardly any correlation between $\Delta\phi/\phi_{max}$ and the average bulk viscosity.

$\Delta\phi/\phi_{max}$, ϕ (relative), and the decay time (τ) of the pyrene–DMA exciplex have been measured and are given in Table 2. The quantity $V_{mp}(\delta_p - \delta_n)^2$, which has been found to be of significance by Petrov et al., has also been calculated for our binary solvent mixtures, where V_{mp} is the molar volume of the polar component and δ_p and δ_n represent the solubility parameters of the polar and nonpolar solvent components, respectively. Figure 3 shows the variation of $\Delta\phi/\phi_{max}$ against $V_{mp}(\delta_p - \delta_n)^2$. There is hardly any correlation between the two for this enlarged group of solvent mixtures. Nor could we find any correlation between $\Delta\phi/\phi_{max}$ and the lifetime of the exciplex for the set considered by us. $\Delta\phi/\phi_{max}$ has also been studied in the ternary solvent mixture benzene/DMSO/acetone, the last one being in small proportion. The idea is that acetone, which is soluble in both DMSO and benzene, should reduce the number of microscopically heterogeneous clusters that are supposed to exist in the benzene/DMSO mixture. However, no appreciable variation in $\Delta\phi/\phi_{max}$ could be found.

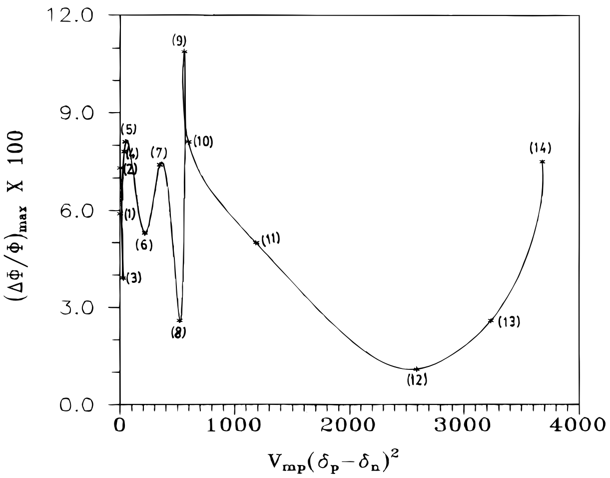


Figure 3. Variation of $\Delta\phi/\phi$ with the solvent parameter, $V_{mp}(\delta_p - \delta_N)^2$, in several binary solvent mixtures at around $\epsilon = 15$: (1) acetone (pure), (2) ethylenedichloride/acetone, (3) chloroform/acetone, (4) benzene/acetone, (5) THF/acetone, (6) cyclohexane/acetone, (7) ethylenedichloride/DMSO, (8) chloroform/DMSO, (9) benzene/DMSO, (10) THF/DMSO, (11) THF/methanol, (12) butanol/water, (13) dioxane/water, and (14) THF/water.

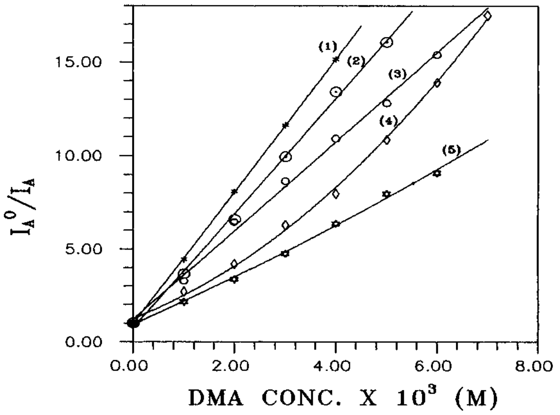


Figure 4. Variation of the pyrene fluorescence intensity ratio (I_A^0/I_A) with DMA concentration in (1) THF/acetone, (2) benzene/ acetone, (3) cyclohexane/acetone, (4) benzene/DMSO, and (5) dioxane/water.

The quenching of pyrene fluorescence with DMA has been investigated in various isodielectric binary solvent mixtures, and the corresponding Stern–Volmer plots are shown in Figure 4. All the curves are linear except that in benzene/DMSO. In different isoviscous media, the quenching rate constant is a measure of the quenching radius in the solvent.[14] For two sets of isoviscous solvents (also isodielectric), one dioxane/water and benzene/DMSO and the other cyclohexane/acetone, benzene/acetone, and THF/acetone, the quenching constants are in the following order: dioxane/water < benzene/DMSO and cyclohexane/acetone < benzene/acetone < THF/acetone. From Table 2, it is found that the magnitude of $\Delta\phi/\phi_{max}$ also varies in the same order in these mixed solvents. This table also shows that the relative exciplex fluorescence yields in the same set of solvents are in reverse order.

3.2. Temperature Effect on ϕ and $\Delta\phi/\phi$. The temperature dependence of ϕ for the pyrene–DMA system in various binary solvent mixtures has been studied within the temperature range of 283–323 K. Figure 5 shows how the logarithm of the ratio of exciplex emission peak intensity to pyrene emission peak intensity, $\ln(I_E/I_A)$, varies with the inverse of temperature. The

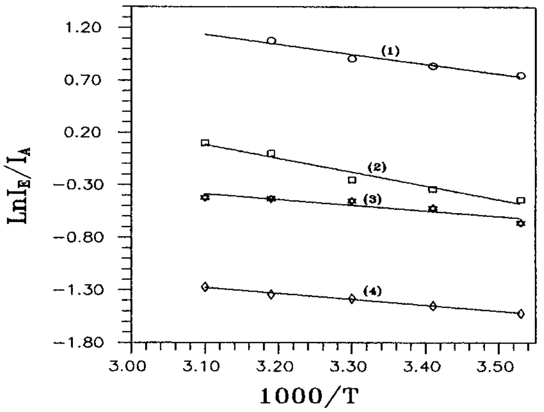


Figure 5. Influence of temperature on the ratio of the exciplex emission intensity to that of its locally excited state (I_E/I_A) of the pyrene−DMA system in (1) cyclohexane/acetone, (2) THF/water, (3) dioxane/water, and (4) benzene/DMSO.

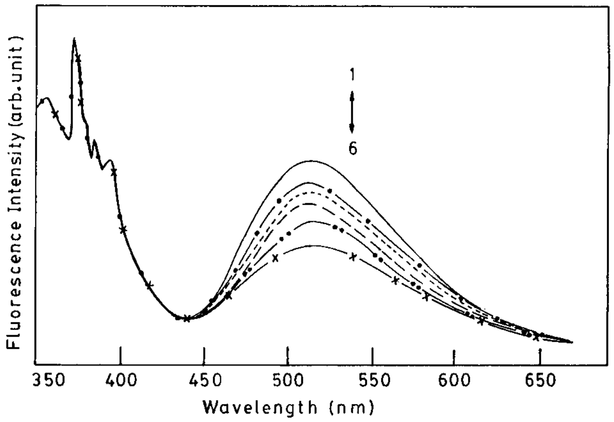


Figure 6. Effect of salts on the exciplex emission intensity of the pyrene−DMA system in THF/water: (1) Na_2SO_4, (2) NaF, (3) without salt, (4) NaCl, (5) NaBr, and (6) $LiClO_4$ (the concentration of all salts is 9.6×10^{-3} N).

slopes of the curves measure the effective exciplex formation activation energies.[15] From the slopes, the activation energies are found to be 5 kJ mol^{-1} in benzene/DMSO, 5 kJ mol^{-1} in dioxane/water, 7.5 kJ mol^{-1} in cyclohexane/acetone, and 11 kJ mol^{-1} in THF/water. Note that all the activation energies are less than 0.13 eV (≈12.5 kJ mol^{-1}), a figure reported for polymethylene-linked pyrene−DMA systems.[16]

The effect of temperature variation on $\Delta\phi/\phi_{max}$ of the pyrene−DMA system has been measured in different binary solvent mixtures. There is no significant change of $\Delta\phi/\phi_{max}$ with temperature.

3.3. Salt Effects on ϕ and $\Delta\phi/\phi$. The effects of salt on exciplex fluorescence, ϕ, of the pyrene−DMA system in THF/water have been studied at a salt concentration of around 9.6 × 10^{-3} N. The corresponding fluorescence spectra for a few salts are given in Figure 6. There is negligible change in the pyrene emission intensity on addition of different kinds of salts. The exciplex intensity, on the other hand, depends on the specific nature of the added salts. The exciplex intensity increases on addition of NaF, Na_2SO_4, $MgSO_4$, or Na_2S whereas the same decreases on addition of $LiClO_4$, NaBr, or NaCl. The quenching capacities of the exciplex emissions are in the following order: $LiClO_4$ > NaBr > NaCl. The effect of salts on the pyrene emission in the absence of DMA has also been found, and there is no apparent change in the pyrene emission in the absence of DMA on addition of these salts, except perhaps NaBr, where a slight decrease occurs. It seems that the change in exciplex luminescence intensity is not due to any interaction between excited pyrene and salts. The effects of salts on $\Delta\phi/\phi_{max}$ for the pyrene−DMA system are shown in Table 3. There is no change on $\Delta\phi/\phi_{max}$ with addition of NaF, Na_2S, Na_2SO_4, and $MgSO_4$, but NaCl, NaBr, and $LiClO_4$ quench the magnitude of the MFE's; that is, $\Delta\phi/\phi_{max}$ decreases with salt concentration. The MFE quenching ability of these salts follows the same order as that for exciplex emission quenching, i.e, $LiClO_4$ > NaBr > NaCl.

TABLE 3: Effect of Salt on $\Delta\phi/\phi_{max}$ at Different Salt Concentrations

NaF	10^3conc, N	0.0	2.4	4.8	7.2	9.6	12.0
	$\Delta\phi/\phi_{max}$, %	7.5	7.4	7.5	7.3	7.2	7.3
NaCl	10^3conc, N	0.0	2.4	4.8	7.2	9.6	12.0
	$\Delta\phi/\phi_{max}$, %	7.4	5.4	4.7	4.1	4.0	4.0
NaBr	10^3conc, N	0.0	2.4	4.8	7.2	9.6	12.0
	$\Delta\phi/\phi_{max}$, %	7.5	5.7	4.4	3.8	3.7	3.3
Na_2SO_4	10^3conc, N	0.0	2.4	4.8	7.2	9.6	12.0
	$\Delta\phi/\phi_{max}$, %	7.6	7.5	7.7	7.4	7.5	7.7
Na_2S	10^3conc, N	0.0	2.4	4.8	7.2	9.6	12.0
	$\Delta\phi/\phi_{max}$, %	7.3	7.1	7.2	6.9	7.1	7.1
$LiClO_4$	10^3conc, N	0.0	2.4	4.8	7.2	9.6	12.0
	$\Delta\phi/\phi_{max}$, %	7.3	6.1	4.7	3.7	3.5	3.3

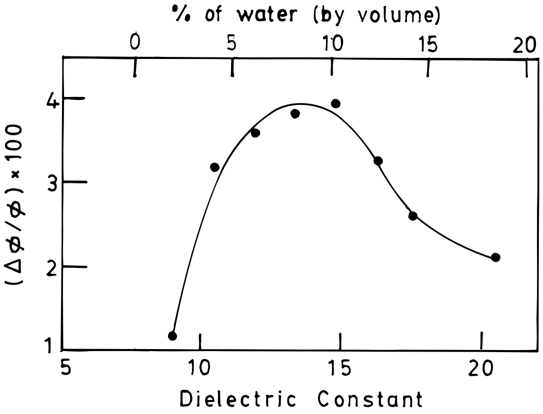


Figure 7. Variation of $\Delta\phi/\phi$ of the pyrene−DMA system with medium dielectric constant in THF/water in the presence of NaCl at concentration of 7.2 × 10^{-3} mol dm^{-3}.

The variation of $\Delta\phi/\phi$ with dielectric constant, in the presence of NaCl of concentration 7.2 × 10^{-3} N, is shown in Figure 7. The $\Delta\phi/\phi$ vs ϵ curve passes through a maximum, and the maximum appears at around $\epsilon = 15$. The maximum, however, is broadened in comparison to that in the absence of salt. In the presence of NaCl, the lifetime of the pyrene−DMA system in THF/water at $\epsilon = 15$ has been measured, and there is no significant change in the lifetime on the addition of salt.

The effects of the magnetic field strength, B, on $\Delta\phi/\phi$ in the presence of salt have been studied and are shown in Figure 8. The nature of the curves is similar to that found in a pure binary solvent mixture. The $B_{1/2}$ values in the presence of all kinds of salt are nearly the same, around 70 G.

The transient absorbance behavior of the pyrene−DMA system in THF/water in the absence and in the presence of salt has been investigated by a flash photolytic technique, and a few of them are presented in Figure 9. The relative absorbances (in arbitrary units) at 420 and 490 nm in the presence and absence of salt are given in Table 4. The absorbance at 420 and 490 nm are due to pyrene triplet (^{3}Py)[17] and pyrene anion radical (^{2}Py$^-$),[18] respectively. It is found that on addition of salt, there is no change in the triplet yield, but the pyrene radical ion yield increases 1.5−2 times. Figure 9 also shows that the decay rates of pyrene triplet with and without addition of salts are almost the same; however, for pyrene radical anion, a small decrease in the decay rate is observed in microsecond time scale on addition of salt.

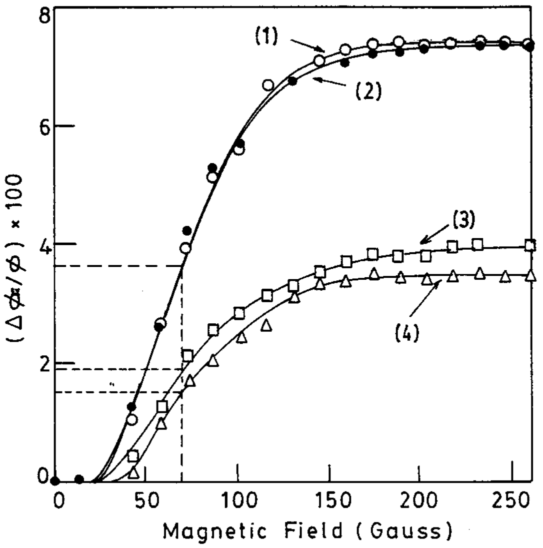


Figure 8. Dependence of $\Delta\phi/\phi$ on the magnetic field strength for the pyrene−DMA system in THF/water in the presence of (1) NaF, (2) Na_2SO_4, (3) NaCl, and (4) NaBr (the concentration of all salts is 9.6×10^{-3} N).

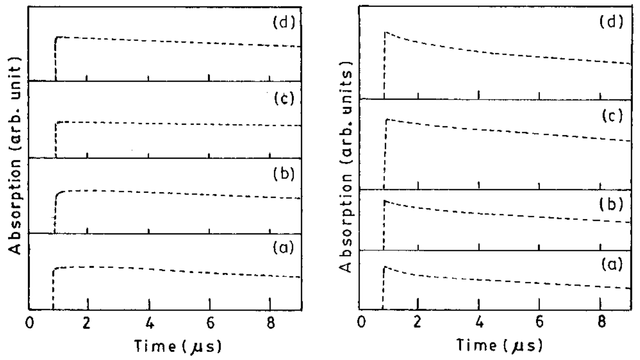


Figure 9. Transient absorption of the pyrene−DMA system at (a, left) 420 and (b, right) 490 nm in THF/water in absence and presence of salt: (a) without salt, (b) Na_2SO_4, (c) $LiClO_4$, and (d) NaF (the concentration of all salts are 9.6×10^{-3} N).

4. Discussion

Our experimental results show that the variations in magnetic-field-induced exciplex luminescence for different exciplexes in different binary solvent mixtures are very similar. This indicates that for a particular exciplex, the variation in the magnitude of $\Delta\phi/\phi_{max}$ in different solvents is due to solvent characteristics rather than that of the exciplex system. For a given exciplex, the magnitude of $\Delta\phi/\phi$ shows the maximum value at an intermediate dielectric constant (ϵ_{max}) which varies between 14 and 18. However, there is a large variation in the magnitude of $\Delta\phi/\phi_{max}$ from one solvent mixture to another; e.g., for pyrene−DMA, it varies from 2.5% to 11%, for anthracene−DMA 0.4% to 8%, and for 9-cyanophenanthrene−anethole 0% to 4.5%. In what follows, we discuss possible models which might be put forward as an explanation of this variation of MFE's.

(A) Can these large variations of $\Delta\phi/\phi_{max}$ be due to hopping of electrons between donor radical cation and neutral donor molecule? It is known that electron hopping increases $B_{1/2}$ depending on the exchange rate.[19] But in our case, there is no apparent change in $B_{1/2}$ in different solvent mixtures or on addition of salts. We, therefore, did not further consider this approach.

(B) The observed effects of NaCl, NaBr, and $LiClO_4$ on $\Delta\phi/\phi_{max}$ suggest that the variation of $\Delta\phi/\phi_{max}$ could be due to external spin−orbit coupling.[20] However, the results of the flash photolytic experiments show that there is no significant change in the triplet yield in the presence of these salts. Moreover, though a S atom and a Cl atom occupy adjacent positions in the periodic table, S compounds (Na_2S and Na_2SO_4) do not quench $\Delta\phi/\phi_{max}$ in THF/water medium at the same salt concentration as that of NaCl. On the basis of spin−orbit coupling interaction, it is difficult to explain why ClO_4^- quenches both ϕ and $\Delta\phi$ more than Cl^-; for in ClO_4^-, the heavier Cl atom is rather insulated by a tetrahedron of four lighter oxygen atoms. The $\Delta\phi/\phi_{max}$ values of pyrene−DMA in different solvents are given in Table 2. There is no direct correlation between the chlorine content of the binary solvent mixture and $\Delta\phi/\phi_{max}$. So we conclude that the external spin−orbit coupling is not a major factor in the variation of the $\Delta\phi/\phi_{max}$ from one binary solvent mixture to another.

TABLE 4: Transient Absorption of Pyrene and Pyrene−DMA Systems in THF/Water in the Presence and Absence of Salt

compd	wave length, nm	transient absorption, %					
		w/o salt	NaF	NaCl	NaBr	$LiClO_4$	Na_2SO_4
pyrene	420	1.5		1.6	1.8	1.7	
	490	0.6		0.0	0.5	0.8	
pyrene−	420	2.9	3.5	3.0	2.8	2.9	3.4
DMA	490	5.5	8.8	7.8	8.6	9.5	6.7

[a] Salt concentration: 9.6×10^{-3} N.

(C) Petrov et al. suggested that there is microheterogeneity in binary solvent mixtures due to the difference in solubility parameters of its components, the SSRIP being preferentially solvated by the polar component, which leads to the formation of a microdomain.[7] The concept of preferential solvation was supported by picosecond dynamical studies,[7b] and the MFE was correlated with the microheterogeneity.[7a,8] The excess stabilization energy of the radical ion pair, i.e., the excess energy (E_b) required to diffuse out a radical pair from a polar domain to bulk, was approximately given by the following expression:

$$E_b \approx e^2(1/\epsilon_m - 1/\epsilon)(1/r_i - 1/r_b) \tag{1}$$

where e is the electronic charge of each radical, ϵ_m and ϵ are the dielectric constants of the bulk and polar domain, respectively, and r_i and r_b the inter-radical distance within the SSRIP and the radius of the polar domain, respectively. Assuming that the geminate recombination of the SSRIP to the CIP, but not the homogeneous recombination, is affected by the magnetic field, these authors estimated that the relative CIP formation (via geminate recombination) would be maximum when $k_a/k_b = {}^1/_2$, where k_a is the formation rate constant of the CIP and k_b the dissociation rate constant of the SSRIP. Assuming a constant CIP formation activation energy equal to 0.13 eV and the same preexponential factor for recombination and dissociation, they estimated that $\Delta\phi/\phi$ would be maximum when the average dielectric constant of the binary solvent mixture was about 15. Depending on the size and stability of the polar microdomains, the magnitude of $\Delta\phi/\phi$ varies from one solvent mixture to another. According to a later paper[8] of these authors, the polar microdomains are formed due to fluctuation of the chemical potential (μ_p) of the polar component, which was given by the following expression:

$$(\Delta x_p)^2 = RT/(\partial\mu_p/\partial x_p)_{V,T} \approx x_p/[1 - 2V_{mp}(\delta_p - \delta_n)^2 X_p/RT] \tag{2}$$

where x_p and V_{mp} are the mole fraction and molar volume of the polar component, respectively, and δ_p and δ_n are the solubility parameters of the polar and nonpolar components, respectively. The above expression shows that the fluctuation would be maximum for $x_p \le 1/2$, when $V_{mp}(\delta_p - \delta_n)^2/RT \le 1$. Experimentally, they also showed that there is a correlation between $\Delta\phi/\phi_{max}$ and the solvent parameter $V_{mp}(\delta_p - \delta_n)^2$. $\Delta\phi/\phi$ passes through a maximum with $V_{mp}(\delta_p - \delta_n)^2$ when the latter is about 500 cal mol^{-1}.

If the microheterogeneous structure is responsible for the amplification of the MFE, we can expect that the variation of $\Delta\phi/\phi_{max}$ in different types of exciplexes should be the same from one solvent mixture to another. From Table 1, we indeed find that for three exciplexes, $\Delta\phi/\phi_{max}$ varies almost in a similar way from one solvent mixture to another. However, the following observations are not consistent with the concept of a microheterogeneity−MFE correlation. (1) The crucial observation on which the model is based is higher MFE's in the benzene−DMSO mixture compared to neat solvents such as acetone.[7] The difference in polarity between the two components is still higher for the dioxane−water mixture compared to the benzene−DMSO mixture, but we find that the MFE in the former solvent mixture is about 3 times less than the latter. (2) The THF−water mixture, where the polarity difference is less than the dioxane−water mixture, shows a much higher MFE!! Preferential solvation in the polar solvent sheath does not explain how the nonpolar component could have such a large effect. (3) Petrov et al.[8] reported a correlation between $\Delta\phi/\phi_{max}$ and $V_{mp}(\delta_p - \delta_n)^2$ where δ_p and δ_n are the Hildebrand solubility parameters for the polar and nonpolar components, respectively, and V_{mp} is the molar volume of the polar component. When we tried the same correlation (Figure 3) with a larger set of data, we could hardly find any correlation. (4) According to the model, the MFE is related to the fluctuation of the chemical potential of the polar component. We have modified this fluctuation of the chemical potential of the polar component in the binary solvent mixture by changing the temperature and/or adding salts. The temperature should change the distribution of the size of the microdomains and their dissolution times. However, we have not noted any significant change in the MFE over the temperature range studied by us. (5) We have tried to influence the miscibility of the two components by adding salts. The salt that is known to increase the miscibility is $LiClO_4$, and those which decrease the miscibility are NaCl, NaBr, Na_2S, Na_2SO_4, and $MgSO_4$. However, here the observed change in the MFE does not depend on the "salting in" and "salting out" character of the salt.[21] Although flash kinetic experiments indicate that all salts increase the radical ion yield as expected, most salts, univalent or bivalent, are without any effect on the MFE. A few, such as NaCl, NaBr, and $LiClO_4$, quench both ϕ and $\Delta\phi/\phi_{max}$. Why do a few salts quench both ϕ and $\Delta\phi/\phi_{max}$ while others increase ϕ and have no effect on $\Delta\phi/\phi_{max}$—this specificity is not understandable in terms of the microdomain model. (6) We have also tried to increase the miscibility of the two solvents by adding a third component which dissolved in both; however, the MFE was not affected by the addition of acetone in the benzene/DMSO mixture. (7) From Figure 3, it is found that there are some binary solvent mixtures in which the pyrene−DMA exciplex shows lower magnitude of $\Delta\phi/\phi_{max}$ than in acetone (where it is around 6%). It has also been found by Basu and Aich that for some exciplex systems, the MFE is greater for neat solvents than polar−nonpolar mixed solvents.[22] Pertov et al.'s model cannot explain such behavior of the MFE in mixed solvent. (8) Petrov et al. assumed the exciplex formation activation energy to be almost constant at (≈12.5 kJ mol^{-1}), but from the temperature variation of the exciplex luminescence intensity, it is found that the activation energy does indeed vary from solvent to solvent (section 3.2). We therefore conclude that the microheterogeneity does not play an important role as envisaged by Petrov et al., at least not in the dioxane−water or THF−water solvents studied by us.

(D) With a simple mathematical formulation, Nath and Chowdhury showed analytically that the exciplex luminescence and the relative magnetic-field-modulated exciplex luminescence $\Delta\phi/\phi$ are approximately related with the solvent parameters by the following expression:[6a]

$$\phi = \frac{1 - \exp(r_c/r_g)}{1 + (\alpha r_c/R^2 - 1)\exp(-r_c/r_g)} \qquad (3)$$

$$\frac{\Delta\phi}{\phi} = \frac{2}{3}\frac{AB}{(4\pi D)^{1/2}}\frac{r_c(1-\phi)}{1 - \exp(-r_c/r_g)} \qquad (4)$$

$$\alpha = \frac{4D}{\chi U_0}10^8 \qquad (5)$$

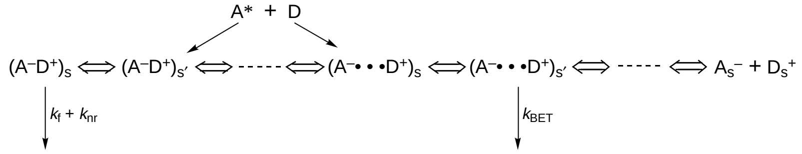
where D is the diffusion coefficient of the ion, R the SSRIP-to-CIP conversion radius, r_g the SSRIP-generating radius from donor and excited acceptor, and r_c the Onsager radius ($=e^2/\epsilon kT$). U_0 and χ are the effective barrier crossing velocity and transmission coefficient from the SSRIP to the CIP, respectively, at reaction radius R, and A is the HFI-induced ISC rate in the absence of magnetic field. B is a constant which depends on time; however, after 10 ns, its variation with time is negligible. Equation 5 indicates α is the measure of the SSRIP dissociation to CIP formation ratio. For the pyrene−DMA exciplex, Nath and Chowdhury showed that the expressions approximately fitted the experimental $\Delta\phi/\phi$ vs ϵ curves if the fitting parameters (R, r_g, and α) are varied from solvent mixture to solvent mixture.

Equations 3 and 4 show that ϕ and $\Delta\phi/\phi_{max}$ are dependent on a number of parameters. If we confine ourselves to a set of nearly isodielectric, isoviscous solvent mixtures, the number of variable parameters may be decreased. If we assume that r_c, R, D, and α are more or less constant for a set of isodielectric and isoviscous solvent mixtures, r_g might be expected to correlate with ϕ and $\Delta\phi/\phi_{max.}$ A good measure of r_g is the quenching radius, which can be determined from the plot of $I_A{}^0/I_A$ vs donor concentration. Our data (Figure 4 and Table 2) indeed show a correlation between ϕ (or $\Delta\phi/\phi_{max}$) and r_g (section 3.1).

Our observation of the increase of the Py^- yield on salt addition, irrespective of the nature of the salt, indicates that the dissociation rate of the SSRIP increases, which in turn indicates an increase in the value of α and/or r_g and/or r_c. A change in r_c is unlikely, for ϵ_{max}, the dielectric constant at which$\Delta\phi/\phi$ peaks, remains unchanged on addition of salt (Figure 7). Let us explore the consequence of a change of α on ϕ and $\Delta\phi/\phi_{max}$. Equations 3 and 4 predict that an increase of α on salt addition should decrease ϕ and increase $\Delta\phi/\phi_{max}$. We, however, find that the effect of salt on ϕ and $\Delta\phi/\phi_{max}$ is highly specific. For example, the magnitude of $\Delta\phi/\phi_{max}$ hardly changes on addition of NaF, Na_2SO_4, Na_2S, and $MgSO_4$ but is affected by NaCl, NaBr, and $LiClO_4$. It is this specificity of the effect which is difficult to understand from the model. In this model, the CIP, triplet state (responsible for $\Delta\phi$), and radical anion are assumed to be formed from the same intermediate state, the SSRIP. A single SSRIP model does not explain why $\Delta\phi/\phi_{max}$ remains unchanged on addition of salts such as NaF, Na_2S, Na_2SO_4, and $MgSO_4$, although ϕ and Py^- yield are increased.

It may be argued that the specific effect may be built into the model if we propose that salts have some effect on one of

SCHEME 1



the two constants, *A* or *B*, appearing in eq 4. *B* is dependent on the lifetime of the exciplex. We, however, find no significant effect of salt on the exciplex lifetime (which we suppose to be the same as the lifetime of the SSRIP because of rapid equilibrium[9] between the two), which could be correlated with the specificity of the salt effect. Had the salts affected the ISC rate *A*, there would have been changes in $B_{1/2}$ on salt addition, but experimentally, this has not been observed. Besides, there should have been a correlation with the SO coupling parameter of the heavy atom of the salts. It is, however, possible that salt affects ϕ and $\Delta\phi/\phi_{\max}$ through its influence on r_g. We could not find any correlation with the ionization potential or the redox potential of the anions of the salts.

(E) Werner and Staerk have recently highlighted the importance of back electron transfer (BET) in determining the magnitude of the MFE on the RIP recombination process in different solvent mixtures, particularly for polymethylene-linked donor−acceptor systems, where they found a correlation between the exciplex lifetime and the MFE.[9] It is pertinent to find out whether the same is true for our unlinked systems. The correlation between $\Delta\phi/\phi_{\max}$ and lifetime was sought earlier by us.[23] Our present data are summarized in Table 2 and show that there is hardly any correlation between the exciplex lifetime and the MFE in different solvents. The BET process should be affected by the ionic strength of the solution. Our water-containing solvent mixtures indeed permit us to test this point, as is known that salt can affect the back-electron-transfer rate.[24] Our flash photolysis experiment shows that on addition of salt the Py^- yield increases, indicating that the BET rate decreases. On the other hand, $\Delta\phi/\phi_{\max}$ depends on the nature of the salt. The contrasting behavior of certain salts (compare the effects of NaCl, NaBr, and $LiClO_4$ with those of NaF, Na_2S, $NaSO_4$, and $MgSO_4$) is rather intriguing.

In the THF /water solvent mixture, the $\Delta\phi/\phi_{\max}$ of pyrene−DMA decreases with addition of NaCl, but there is no corresponding change in the lifetime; this is contrary to Werner and Staerk's expectation. Werner and Staerk's proposed model is also unable to explain satisfactorily the salt effect on triplet yield for our unlinked system.

(F) Mataga's multiple state model is as follows. The basic assumption in the above three models is that free ions, exciplexes, and triplets are all formed from the same intermediate state, namely, thermalized SSRIP. However, exciplex fluorescence intensity, Py^- yield, $\Delta\phi/\phi_{\max}$, and exciplex lifetime indicate that there is hardly any direct correlation between these. The above assumption, therefore, may not be quite correct. The results from all salt effect on ϕ, $\Delta\phi/\phi$, and free ion yield seem to indicate the existence of several intermediate states instead of a single intermediate SSRIP formed after electron transfer from donor to acceptor. From simultaneous measurement of transient ion current and fluorescence, Mataga et al. proposed the multiple state model, which assumes the existence of various kinds of exciplexes and geminate ion pairs (SSRIP) which undergo partial interconversion between each other as expressed in Scheme 1,[25] where s and s′ are possible different solvent configurations around all exciplex and SSRIP. Similarly, there are different configurations of exciplexes and geminate ion pairs depending on the orientation of donor and acceptor with respect to each other. Each of the intermediate states may undergo a back-electron-transfer process with a distance-dependent energy gap law.[26c,d] This multistate model needs to be invoked for explaning our rather complicated experimental results.

It seems that processes such as fluorescent CIP formation, back electron transfer leading to the ground state, HFI-induced S−T conversion, etc., are dependent on the nature of the RIP, the distance and the orientation between partners of the RIP, and the nature of solvent.[26c,d] Mataga et al. have shown that in both charge separation (CS) and charge recombination (CR) processes, the distance distribution is important; for example, the energy gap law for the CR process is different for loose RIPs and compact RIPs. One can therefore reasonably expect ϕ, $\Delta\phi/\phi_{\max}$, and Py^- yield to depend on the nature of the salt, which can modify all initial and relaxed distributions by influencing the medium-dependent rates of formation and decay of conformers. The rates of interconversion between conformers and relaxation of the distance distribution can very well depend on the specific nature of the salt. The nonspecific increase in Py^- yield on addition of any kind of salt may simply be due to stabilization of long-lived loose RIPs by an ionic atmosphere of salts, which shifts the distribution in favor of loose RIPs compared to compact RIPs.[26c] The less electronic coupling interaction between the partner radical ions within loose RIP favor free ion formation compared to back electron transfer. On the other hand, the negligible effect of ionic atmosphere on the exciplex emission process or the S−T conversion process is most probably due to the short lifetimes of those conformers in which these processes predominantly occur. The time taken by the ionic atmosphere to form in an organic solvent[27] may indeed considerably exceed the time taken for the formation of the exciplex and the ISC process in some relatively short-lived conformers.[28] Thus, the specific interaction between the salt and the conformer, rather than the nonspecific ionic strength effect, might dominate the ISC, the exciplex formation, and the geminate recombination processes.

On the basis of the multiple-ET-state model, the effect of the dielectric constant of the medium on $\Delta\phi/\phi_{\max}$ could be interpreted as follows. The relative stabilities of the conformers may vary with ϵ. At low ϵ, fluorescing CIP, at high ϵ, ion-forming SSRIP, and at intermediate ϵ, a triplet-forming ETstate may dominate. That will explain why the $\Delta\phi/\phi_{\max}$ vs ϵ curve shows a maximum.

5. Conclusion

Different exciplex models have been examined in light of our experimental results on magnetic-field-modulated luminescence. None of the models are completely satisfactory. The multiple-state model of Mataga et al. might have an advantage over others; however, it considerably increases the conceptual and mathematical complexity and therefore is not amenable to prediction of the MFE. An impediment to the understanding of environmental effects on MFE's is our lack of knowledge of the D−A distance distribution as a function of solvent polarity and the ΔG^* (the free energy of activation for the back-electron-transfer reaction) of the radical ion pair system. The time-dependent distribution of several conformers (e.g., CIP, compact RIP, and loose RIP) will affect considerably the back-electron-transfer rates and the MFE. Prediction has to wait until it can be treated quantitatively.

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