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Effect of variation of dielectric constant on the magnetic field modulation of exciplex luminescence

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Abstract. The effect of variation of dielectric constant on the relative magnetic field effect in singlet luminescence has been studied using a typical exciplex system at a saturating field. The study indicates strong specificity in the perturbation of the magnetic field effect by alcoholic solvents. In contrast to alcohols where relative singlet magnetic field effect is of the order of 2% only, the magnetic field effect in non-alcoholic medium reaches as high as 9%. Moreover, dielectric constant variation in alcohols yields curves which are distinctly different from those in non-alcoholic media. It turns out that this dependence of magnetic field effect on dielectric constant is similar in all non-alcoholic solvent mixtures. An analytical study based on Hong and Noolandi's solution of Smoluchowski equation has been made. Derived expressions can interpret experimental curves reasonably well.

Keywords. Radical pair reactions; magnetic field effect; exciplex luminescence; solvent effect of molecular interactions.

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1. Introduction

The phenomenon of magnetic effect on electron-spin-nonconserving chemical processes such as radical pair (RP) recombination has received considerable attention in recent years. The field has been competently reviewed by various workers (Atkins and Lambert 1975; Atkins 1976; Buchachenko 1976; Sagdeev *et al* 1977; Turro and Kraeutler 1980; Turro 1983; Gould *et al* 1984; Salikhov *et al* 1984; Basu *et al* 1988b; Steiner and Ulrich 1989). Exciplex luminescence in moderately polar solvent is one of the convenient ways to monitor the magnetic effect on the recombination of photo-generated radical ion pairs (RIP) (Petrov *et al* 1981) and two such magnetically sensitive exciplex systems have recently been studied by us (Nath and Chowdhury 1984a, b; Nath *et al* 1986, 1989; Basu *et al* 1987a, b, 1988a, b, 1989a, b). Following photo-excitation of one of the two partners of the exciplex, an electron is transferred from the donor to the acceptor to form solvent-separated radical ion pairs (SSIP) which then recombine to produce luminescent contact ion pair (CIP) or exciplex. A small fraction of the singlet-born RIPs, however, diffuses out to a domain where the exchange interaction between them is negligibly small and undergoes irreversible, hyperfine interaction (HFI)-induced intersystem crossing to the triplet state. A part of those still remaining in the singlet state after a diffusional excursion may recombine to form luminescent exciplex. A small magnetic field can lift the S-T degeneracy of the well-separated RIP to an extent greater than the widths of the levels and thus may cause a significant decrease in the rate of HFI-induced RIP intersystem crossing process. The suppression of the ISC process in the RIP by the small magnetic field, in turn, increases the singlet RIP recombination yield causing the exciplex luminescence to be magnetically sensitive. The diffusion provides the RIP the necessary time required for the comparatively slow spin-evolution process to occur and thus plays a major role in controlling the magnitude of the effect. For charged RIPs, the modification of the potential energy surface by electrostatic solvent interaction is large and this can cause an order of magnitude change in the diffusion rate. The purpose of this paper is to investigate the effect of dielectric constant (ε) variation on the magnetic effect of the pyrene-N,N-dimethylaniline (Py-DMA) system and explain the curves from a schematic theoretical model.

In order to find out whether any other specific property of the solvent, apart from ε, needs to be considered for cage effect of RIP, we have studied the magnetic effect in several iso-dielectric solvent mixtures. Our experiments show that the presence or absence of alcohols makes a significant difference. The ε variation in non-alcoholic media yields curves which are independent of the specific nature of the molecules comprising the solvent mixture, but this curve is distinctly different in the case of alcoholic media.

The analysis of the magnetic field effect requires an accurate knowledge of the HFI-induced spin motion, electrochemical potential induced spatial motion and the coupling between the two. A realistic formulation of the problem involves separate diffusion equation for singlet and triplet states, and a quantum mechanics based kinetic equation for singlet-triplet interconversion. Solutions for the coupled system of partial differential equations are not available, but can be computed. Freed and Pederson (1976) used the computational approach using finite difference algorithm for uncharged radicals. Schulten and Schulten (1977) and Werner *et al* (1977) have used the same approach for the ion pair case. Schulten and Epstein (1979) used a Monte Carlo path integral method. Mauzerall and Ballard (1982) used computed solutions with finite difference equations under more realistic conditions. In this paper we have attempted an analytical formulation of the magnetic effect on exciplex luminescence.

2. Experimental

An improved phase sensitive detection technique has been employed by us to study the magnetic field effect on exciplex luminescence and this has been described in detail in our previous works (Nath and Chowdhury 1984a, b). The lifetimes were measured with our correlated single-photon-counting set-up (Nath and Chowdhury 1984a; Nath *et al* 1986; Basu *et al* 1989a, b). Commercially available compounds of the highest quality were purified by zone refining (pyrene) and vacuum distillation (DMA). Trans-anethole (AN) and 9-cyanophenanthrene (CNP) were obtained from Aldrich (99% purity) and were used without further processing. Spectra-grade solvents methanol, 1-propanol, tetrahydrofuran (THF), dimethylformamide (DMF), acetone, ethylacetate, benzene, acetonitrile were used after distillation in inert atmosphere. The working samples were made with fixed acceptor and donor concentrations of $[\mathrm{Py}]:[\mathrm{DMA}] = 10^{-4}\,\mathrm{M}:6\times10^{-2}\,\mathrm{M}$ for Py-DMA exciplex system and $[\mathrm{CNP}]:[\mathrm{AN}] = 10^{-3}\,\mathrm{M}:8\times10^{-2}\,\mathrm{M}$ for CNP-AN exciplex system. All the samples were deoxygenated by either freeze-pump-thaw technique or by bubbling pure, dry nitrogen for 45 min and were used within one hour after preparation. Several checks were made during experiments for the possible degradation of the sample.

3. Results

Figure 1 shows the dependence of relative magnetic effect $\Delta\phi/\phi$ (ϕ = exciplex luminescence, $\Delta\phi$ = enhancement in presence of a saturating magnetic field of 240 G) on the ε for Py-DMA system when ε has been varied using various compositions of the following non-alcoholic solvent pairs: THF and DMF, ethylacetate and DMF, ethylacetate and acetonitrile, THF and acetonitrile, THF and acetone, acetone and DMF etc; and mixtures of methanol and *n*-propanol for alcoholic environment. Figure 2 shows the same for the total luminescence ϕ in a typical non-alcoholic environment (THF-DMF mixtures) and in mixtures of methanol and *n*-propanol. When ε has been varied using mixtures of different alcohols the data closely correspond to those reported by Petrov *et al* (1981) for alcoholic solvents. While ϕ decreases monotonically with increase in ε, $\Delta\phi/\phi$ shows a maxima at an intermediate dielectric constant ($\varepsilon = 29$). The $\Delta\phi/\phi$ versus ε plots for non-alcoholic solutions, however, differ markedly from the plot in alcoholic solution. The salient features of the curves are: (a) The $\Delta\phi/\phi$ versus ε curve in non-alcohols shows a rapid increase after the onset at $\varepsilon = 9$, followed by a slow decrease with increase in ε. In alcohols $\Delta\phi/\phi$ shows a gradual increase, followed by a decrease with increase in ε. (b) The peak position of $\Delta\phi/\phi$ versus ε curve *does not depend on the nature of the non-alcoholic solvent chosen or the exciplex system*; this stays within the limit $15 < \varepsilon < 20$ for different choice of components. Similarly, the basic nature of the ϕ versus ε curve remains the same for

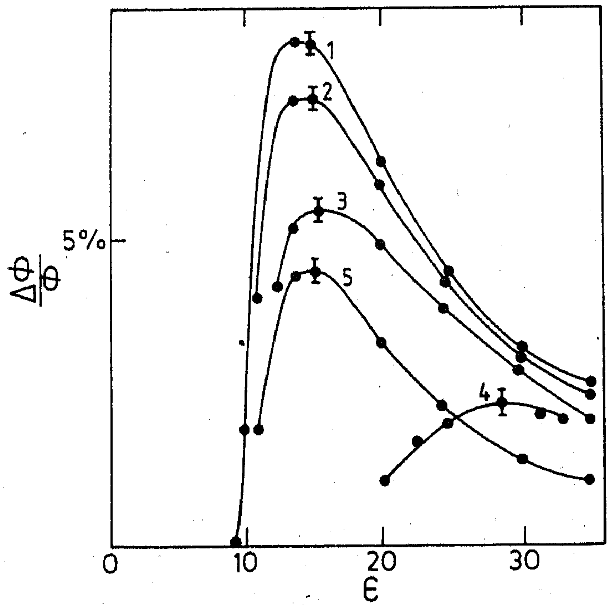

Figure 1. Change in $\Delta\phi/\phi$ with ε. Curves 1 to 4 stand for Py-DMA exciplex in THF/DMF, ethylacetate/DMF, ethylacetate/acetonitrile and 1-propanol/methanol mixed solvents respectively. Curve 5 stands for CNP-AN system in THF/DMF. The relative errors in the data-points are shown by vertical bars.

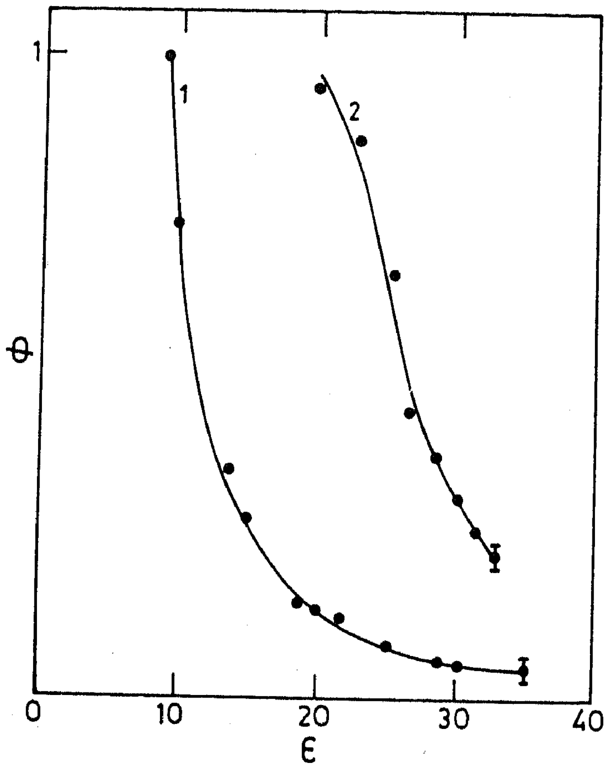

Figure 2. Change in ϕ with variation in ε for Py-DMA system in THF/DMF (curve 1) and in 1-propanol/methanol (curve 2). The scale of ϕ has been adjusted so that for THF/DMF $\phi = 1$ at $\varepsilon = 9$.

non-alcoholic solvent mixtures. But the $\Delta\phi/\phi$ versus ε curve in alcohol does not display any system-independent characteristic. While the peak for Py-DMA system occurs at $\varepsilon = 29$, that for the CNP-AN system shifts to $\varepsilon > 40$ (Basu *et al* 1987b; Nath *et al* 1989). (c) In alcohols the $\Delta\phi/\phi$ value is much less than that in non-alcohols. (d) In isodielectric situation the total luminescence (ϕ) and life-time (τ) of the exciplex is larger in alcohol. Our experiment shows, when $\varepsilon = 28{\cdot}5$, the lifetime of the exciplex is 17 ns in alcohol, while this drops to 4 ns in THF/DMF mixture. However, for both alcohols and non-alcohols, as ε is increased τ decreases while the lifetime for pyrene decay remains the same ($\simeq$ 3 ns) over the range of observation of magnetic field effect.

4. Discussion

4.1 *Description of the proposed model*

The potential energy diagrams of the various uncharged ground and excited states and charged RIP states are shown schematically in figure 3. At large inter-radical distances ($r > 6A^0$) the potential energy of the singlet RIP (solid curve) is represented by Coulombic interaction. At smaller r, however, the simple Coulombic energy diagram is modulated by the presence of an activation barrier (E_a, E_a') which arises due to the specific interaction of the solvent molecules with the radicals. This barrier originates from the work done in the reorientation of the solvent molecules in the process of SSIP$\rightleftharpoons$CIP interconversion.

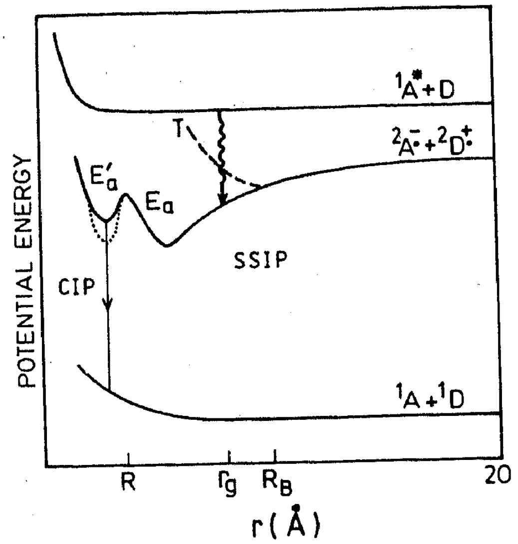

Figure 3. Schematic representation of the dependence of energy levels of the ($^2Py^{\bar{\cdot}} + {}^2DMA^{\dot{+}}$). RIP system on the inter-radical distance (r) in a moderately polar solvent. The dashed curve represents the triplet state of the RIP and the dotted curve represents the possible CIP stabilisation in the case of alcoholic solvents to account for the anomalous effect in alcohols (see text and figure 10).

The energy of the RIP state depends on the orientation of polar solvent molecules surrounding it. The orientation of solvent molecules is fluctuating and for some specific orientations the RIP energy may degenerate with the initial $^1A^* + D$ state making the radiationless transition facile. We consider a simple model where direct transition to the RIP state is assumed to take place only at r_g where r_g is greater than the reaction distance R. The idea of long-range electron transfer is in conformity with Staerk *et al* (1985) and Petrov *et al* (1981) conclusion. Lastly, we have assumed a minimum inter-radical distance R_B, characterized by $\omega_{\mathrm{HFI}} = V_{\mathrm{ST}}(R_B)$, below which spin-evolution cannot occur. To have observable magnetic effect it is essential for the RIP to undergo diffusional excursion in the domain $r > R_B$.

Extensive work has been reported on the theory of diffusion controlled reactions, the classical Smoluchowski equation being the starting point of all such pursuits (Mauzerall 1980; Calef and Deutch 1983; Newton and Sutin 1984; Hynes 1985). Most of the theoretical developments, however, pertain to neutral species. The diffusion process of oppositely charged RIP in their mutual potential field (F) according to Smoluchowski equation is given by

$$\frac{d\rho}{dt} = \nabla\left\{D\left(\nabla\rho + \frac{\rho}{kT}\nabla F\right)\right\}, \tag{1}$$

where ρ is the probability per unit volume for finding two radicals at a relative distance r at a time t; D is the mutual diffusivity of two radicals, k, the Boltzman constant, T, the absolute temperature, F, the potential over the surface governing the radical motion. The following boundary conditions are pertinent to the problem at hand:

at $t = 0$; $\rho \rightarrow \frac{\delta(r - r_g)}{4\pi r_g^2}$

i.e. RIPs are generated at a distance $r_g > R$;

$$\text{at } r \to \infty, \quad \rho \to 0; \tag{2}$$

$$\text{at } r \to R \text{ (reaction radius); } D\left(\frac{\delta\rho}{\delta r} + \frac{\rho}{kT}\frac{\delta F}{\delta r}\right) \to h\rho. \text{ (diffusive flux).}$$

While the second boundary condition is obvious, the first and the third conditions need a few comments: (a) Evidence for electron transfer at a distance greater than molecular contact distance R, as implied in the first boundary condition of (2), has been provided by various workers (Carapellucci and Mauzerall 1975; Brugger *et al* 1981; Borsenberger *et al* 1978; Crawford *et al* 1981; Boxer *et al* 1983). Evidence for electron tunnelling in molecular system has been discussed by Brockelhurst (1973), Miller (1975), Libby (1977), Chance and Devault (1979) and Devault (1980). In our system, the quenching constant of pyrene fluorescence yields a r_g of $8A^0$ (Weller 1967).
(b) The third boundary condition of (2) contains an adjustable parameter h defined by

$$h = \kappa U_0/4 \tag{3}$$

where U_0 is an effective velocity of crossing the potential barrier at the reaction radius and κ is a transmission coefficient. In our system κ is governed ultimately by the interconversion rates CIP$\rightleftharpoons$SSIP. The condition $h = \infty$ means a perfectly absorbing sink, as assumed commonly, while $h = 0$ corresponds to non-reaction. If some of the CIPs formed from SSIP dissociate back, instead of irreversibly and radiatively coming down to the ground state, h will be finite.
(c) It is to be noted that in practice, fixing a value for R depends on our knowledge of F. In all our analysis we have considered F to be represented by a pure Coulombic potential and thus the minimum R one can choose in a working theoretical model is the SSIP minima, below which the Coulombic model fails. If, however, we assume that the activation barrier induced perturbation is negligible and the Coulombic law extends all the way up to CIP minima then R can be conceptually taken as the CIP minima. In such a case the disappearance of RP through transitions to the ground state will be irreversible, and h will be given by the sum of radiative and non-radiative decay rates of the CIP or exciplex. The point we would like to emphasize that the interpretation of h will depend on the choice of R in the model.

Onsager (1934, 1938) was the first to modify the Smoluchowski equation to describe Brownian motion of ions under the influence of an external field and their own Coulomb attraction. Debye (1942) generalized Smoluchowski's result for steady-state reaction rate to include the effect of potential interaction. The stationary solutions of modified Smoluchowski equation for ion pair in presence of scavenger and/or electric field have been obtained in elegant ways by Monchik (1956), Berlin *et al* (1980), Sano and Baird (1982), Sano (1983), Tachiya (1978, 1979), Raaen and Hemmer (1982), Naqui *et al* (1979), Waldenstrom *et al* (1981). Non-stationary solutions describing time-evolution of the neutralization process have been obtained mostly by numerical techniques (Fries and Patey 1984; Rzad and Bakale 1973; Ludwig 1969; Abell and Mozumder 1972; Abell *et al* 1972; Hummel and Infelta 1974) and such a numerical approach has been attempted by Schulten and Schulten (1977) and Schulten and Epstain (1979) to discuss magnetic effect in geminate recombinations of RIPs. Approximate analytical methods for the time-dependent equation have been suggested by Montroll (1946), Mozumder (1968, 1974). Belloni *et al* (1977), Deutch (1972) and

Berlin (1976). *Exact analytical solution for Coulomb field* has been obtained and applied by Hong and Noolandi (1978a, b, c) and Sano and Tachiya (1979).

The exact analytical solution is given in terms of the Laplace transform variable S. The long-time behaviour can be described by simple expressions and is particularly easy to handle. In the long time limit (for $Dt \gg r_g^2, r_c^2$), the evolution of the reactivity $R(t)$ and the survival probability $\Omega(t)$ are given by Hong and Noolandi (1978a, b, c) as

$$R(t) = \frac{r_c}{(4\pi D t^3)^{1/2}} \frac{U(r_g)}{[U(\infty)]^2}, \tag{4}$$

$$\Omega(t) = \frac{U(r_g)}{U(\infty)} \left[1 + \frac{r_c}{U(\infty)(\pi D t)^{1/2}} \right] \tag{5}$$

where the Onsager radius $r_c = e^2/\varepsilon kT = \dfrac{547\cdot2}{\varepsilon} A^0$ at room temperature, (6)

and

$$U(r) = \exp(r_c/r) + [(Dr_c/hR^2) - 1] \exp(r_c/R). \tag{7}$$

The yield of free ions is simply the survival probability at infinite time and is given by

$$Y = \frac{U(r_g)}{U(\infty)}. \tag{8}$$

In the present case of exciplex fluorescence from CIP, the total exciplex fluorescence yield (ϕ) is given by

$$\phi = 1 - Y = 1 - \frac{U(r_g)}{U(\infty)} \tag{9}$$

assuming negligible role of other modes of decay of RIP.

As mentioned before, the diffusion process and the spin rephasing dynamics are decoupled in our model. For calculating ϕ, we limit ourselves to the Smoluchowski equation with complete neglect of the spin hamiltonian while, to calculate the enhancement in magnetic field ($\Delta\phi$), we attribute a phenomenological leakage to its expressions. However, such an assumption is justified because ϕ is substantially higher than $\Delta\phi$. Thus, we treat the intersystem crossing phenomenologically as a leakage to the triplet surface (linear with time) represented by (figure 4)

$$\begin{aligned} \rho_T &= At \quad \text{for } t < 10\,\text{ns} \\ \rho_T &= A_{sat} \quad \text{for } t \geqslant 10\,\text{ns}, \end{aligned} \tag{10}$$

where A is the HFI induced ISC rate in absence of magnetic field. The simple expression (10) is assumed on the basis of the theoretical computation of Werner *et al* (1977) for the Py-DMA system. Actually, however, ρ_T will deviate from (10) at small times, but the computed curve, as reproduced in figure 4 shows that the deviations from (10) are too small to change the conclusions arrived at finally. The time t at which the saturation occurs is assumed to be independent of the magnetic field; a justification for this has been provided in our earlier paper (Basu *et al* 1989a, b). We further assume that the S-T degeneracy extends up to the reaction radius i.e. $R_B = R$.

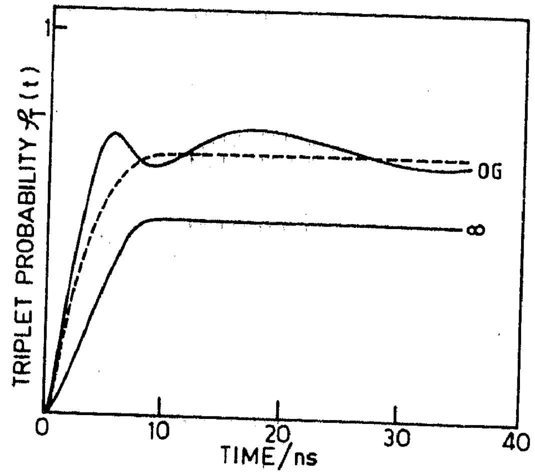

Figure 4. Time-evolution of the hyperfine interaction induced triplet probability $\rho_T(t)$ for the ($^2Py^- + {}^2DMA^+$). RIP system in absence (0 G) and in presence of saturating magnetic field (∞ G) as calculated by Werner *et al* (1977). The linearly approximated time-evolution curve is shown as the dashed line.

Assuming that an exciplex can be formed from a singlet RIP only, the rate of exciplex formation in absence of external magnetic field is given by

$$\chi(t, B=0) = (1 - At)R(t). \tag{11}$$

In the presence of a saturating magnetic field $S \to T_{\pm 1}$ channels are blocked and ISC rate reduces to $A/3$; the exciplex formation rate is thus given by

$$\chi(t, B=B_S) = \{1 - (A/3)t\} R(t). \tag{12}$$

So the time-dependent magnetic field induced enhancement is given by

$$\Delta\chi(t) = (2/3) AtR(t). \tag{13}$$

Equations (11) to (13) hold for $t < t'$; $t' \simeq 10\,\text{ns}$. For $t > t'$,

$$\Delta\chi(t) = (2/3) A_{sat} R(t). \tag{14}$$

Thus, the total magnetic field induced enhancement is given by

$$\Delta\phi = \frac{2}{3}\frac{Ar_c}{(4\pi D)^{1/2}}\frac{U(r_g)}{[U(\infty)]^2}\left[\int_0^{t'} t^{-1/2}\,dt + \int_{t'}^{\infty} (A_{sat}/A)t^{-3/2}\,dt\right]. \tag{15}$$

The integrals within the third bracket are finite and there is no need of truncation as required in many approaches. Convergence could also have been ensured by introducing a finite lifetime of the RIP state due to the effect of the scavengers or non-radiative processes. It may be noted that after a long time the recombination is a homogeneous process with hardly any magnetic effect. Thus we get

$$\Delta\phi = \tfrac{2}{3} AB \frac{r_c}{(4\pi D)^{1/2}} \frac{U(r_g)}{[U(\infty)]^2} \tag{16}$$

where B stands for the integrals within the bracket. From (9) the total luminescence yield (ϕ) is given by

$$\phi = \frac{1 - \exp(r_c/r_g)}{1 + (\bar{\alpha} r_c/R^2 - 1)\exp(-r_c/R)} \tag{17}$$

where

$$\bar{\alpha} = (D/h) \times 10^8 = 10^9/\mathrm{h} \tag{18}$$

for $D = 10^{-5}\,\mathrm{cm}^2/\mathrm{s}$; R, r_g and r_c are in A^0 unit and h is given in cm/s. From (17), (16) and (9) we obtain

$$\frac{\Delta\phi}{\phi} = \frac{2}{3}\frac{AB}{(4\pi D)^{1/2}}\frac{r_c(1-\phi)}{1-\exp(-r_c/r_g)} \tag{19}$$

$$= \tfrac{2}{3} \times \text{constant} \times \frac{r_c}{1-\exp(-r_c/r_g)} \times \left[\frac{(\bar{\alpha} r_c/R^2 - 1)\exp(-r_c/R) + \exp(-r_c/r_g)}{1 + (\bar{\alpha} r_c/R^2 - 1)\exp(-r_c/R)}\right]. \tag{20}$$

[The factor A is effectively constant for a particular donor-acceptor system; the form of the time integral B used in (15) also renders it independent of solvent composition. For the sake of simplicity, we also neglect any effect of variation in D through the factor $1/(4\pi D)^{1/2}$, because in different solvent mixtures the order of D remains the same; effect of its variation is further reduced by the square-root dependence. That is why the second term in the right-hand-side of (20) is taken as a constant.]

The variation of ϕ and $\Delta\phi/\phi$ with ε can be studied with various fitting values for R, r_g and $\bar{\alpha}$. In the case of $\Delta\phi/\phi$, we consider the variation of the bracketted term (20) only.

4.2 *Computed curves and its comparison with experiment*

4.2.1 *Theoretical fit of the experimental ϕ versus ε curves*: In trying to achieve an empirical fit, we have kept in mind the restriction $r_g > R$ of our model. The effect of variation of r_g, R and $\bar{\alpha}$, one at a time, on ϕ versus ε curve is shown in figure 5. Generally ϕ remains unity up to a threshold value of ε, after which it drops to a saturation value. As r_g increases, the threshold shifts towards lower value. The slope of the curve is insensitive to variation of r_g, particularly at large R and $\bar{\alpha}$. In comparison to r_g-variation, R-variation is more pronounced. As R increases, the slope is slightly affected, but the threshold ε rapidly decreases. On the other hand, the variation of $\bar{\alpha}$ affects the slope of the curve and not so much the threshold ε.

Figure 6 shows the best theoretical fit for ϕ versus ε curve in THF/DMF mixed solvents with parameter values $R = 6A^0$, $r_g = 8A^0$, $\bar{\alpha} = 1000$. The fit is more-or-less unique with respect to the values of R and $\bar{\alpha}$, but it is not sensitive to r_g for assumed R and $\bar{\alpha}$. From (18) the estimated value of the boundary parameter h is 1 cm/s.

Figure 7 shows the theoretical fit for ϕ versus ε in alcoholic solvents with a set of parameters ($r_g = 4A^0$, $R = 2{\cdot}5A^0$, $\bar{\alpha} = 900$). A characteristic feature in this case is that unlike non-alcohols, the fit is not unique with respect to the value of $\bar{\alpha}$. For example, almost equivalent fit can also be obtained with the following sets of parameters

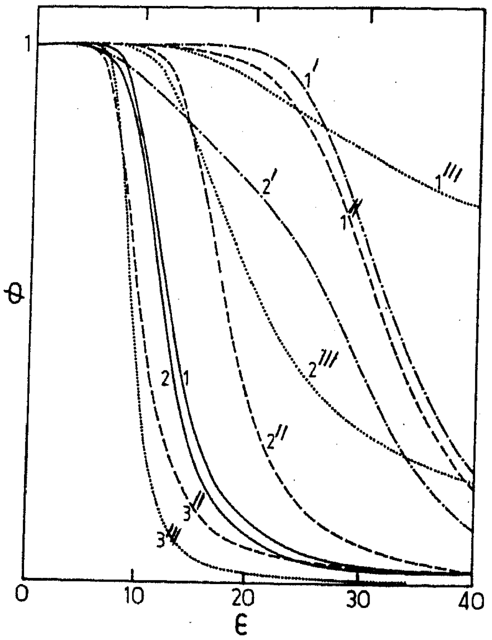

Figure 5. Theoretical ϕ versus ε curve for Py-DMA system. Curves with (———) represent $r_g=4A^0$ (1) and $20A^0$ (2) with $R=6A^0$, $\bar{\alpha}=1000$; (—·—·—) curves for $r_g=4A^0$ (1′) and $20A^0$ (2′) with $R=2A^0$, $\bar{\alpha}=1000$; (— — —) curves represent variation of R for $2A^0$ (1″), $4A^0$ (2″) and $8A^0$ (3″) with $r_g=8A^0$ and $\bar{\alpha}=1000$; (····) curves are for $\bar{\alpha}=10$ (1‴), 100 (2‴) and 10000 (3‴) keeping $r_g=8A^0$ and $R=6A^0$.

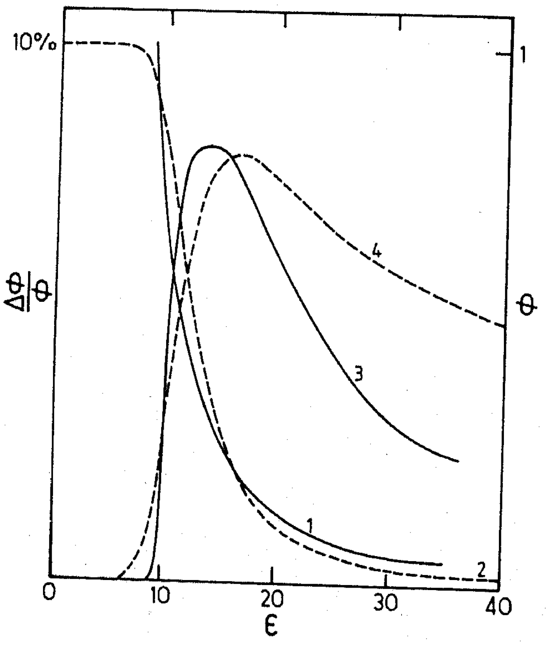

Figure 6. Comparison of the theoretical $\Delta\phi/\phi$ versus ε (plot 4) and ϕ versus ε (plot 2) curves (dotted lines) for Py-DMA exciplex with the best curves (plots 3 and 1) drawn through experimental points (solid lines) in THF/DMF. Parameter values for the theoretical curves are $R=6A^0$, $r_g=8A^0$, $\bar{\alpha}=1000$.

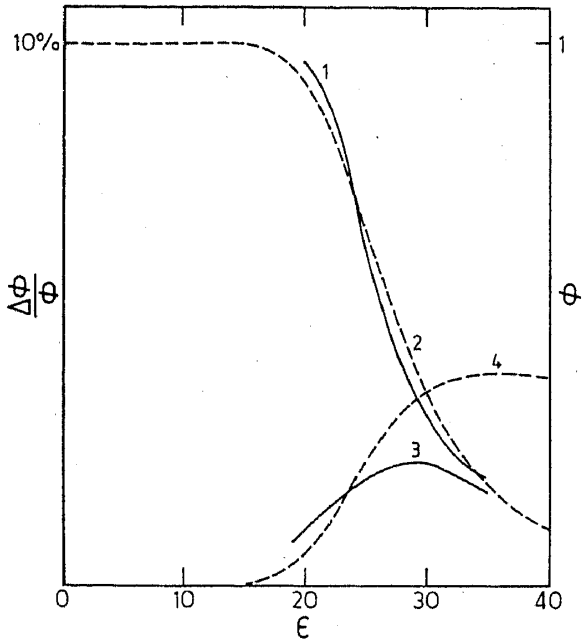

Figure 7. Comparison of the theoretical $\Delta\phi/\phi$ versus ε (plot 4) and ϕ versus ε (plot 2) curves (dotted lines) for Py-DMA exciplex with the best curves (plots 3 and 1) drawn through experimental points (solid lines) in 1-propanol/methanol. Parameter values for the theoretical curves are $R = 2{\cdot}5A^0$, $r_g = 4A^0$, $\bar{\alpha} = 1000$.

($r_g = 8A^0$, $R = 2A^0$, $\bar{\alpha} = 3000$); ($r_g = 8A^0$, $R = 2{\cdot}8A^0$, $\bar{\alpha} = 500$). However, all the fits demand R to be less than $3A^0$. A value of r_g less than $8A^0$ gives a slightly better fit. A study of figures 6 and 7 leads to the conclusion that parameter R carries the information for the behavioral difference between alcohols and non-alcohols (see later).

4.2.2 *Theoretical fit of the experimental* $\Delta\phi/\phi$ *versus* ε *curves*: Figures 6 and 7 also contain the theoretical $\Delta\phi/\phi$ versus ε curves corresponding to the set of parameters which fit ϕ versus ε curves nicely. The initial rising part of the curve matches well with the experimental curve for both alcohols and non-alcohols. The general features of the variation (e.g. maxima etc.) are also reproduced. However, in the theoretical curve $\Delta\phi/\phi$ drops more slowly with increase in ε (for $\varepsilon > 15$ in non-alcohols and $\varepsilon > 30$ in alcohols) in comparison to the experiment. One of the possible causes of the anomaly might be our assumption that the spin-evolution rate is independent of r_g once r_g is greater than R. In reality, however, this may not hold, specially for a low value of R; ISC is probably operative only for $r > R_B$. If that be the case, $\Delta\phi$ is contributed to only by those RIPs which are in the diffusion domain $r > R_B$ (figure 3) whereas ϕ receives contribution from the entire diffusion domain. The increase in outward diffusion process with increase in ε, which reduces the recombination, will then affect $\Delta\phi$ *more* in comparison to ϕ causing $\Delta\phi/\phi$ to decrease faster than the theoretical curve.

4.2.3 *Estimate of the order of A*: Let us calculate from (19) AB for THF/DMF mixed solvent corresponding to $\varepsilon = 15$. We have

$$\Delta\phi/\phi = 0{\cdot}081 \text{ (experimental data)}$$

$$\phi = 0{\cdot}26 \text{ (experimental data)}$$

$$D = 3 \times 10^{-5}\,\text{cm}^2/\text{s}$$

$$r_g = 8A^0 \text{ (assumed value)}$$

and

$$r_c = 36{\cdot}48A^0.$$

Expression (19) yields

$$AB = 8{\cdot}63 \times 10^3\,\text{s}^{-1/2}.$$

Considering (15) and the linear approximation (figure 4)

$$A_{sat} = At,$$

we get

$$B = [2t^{1/2}]_0^{t'} + t'[-2t^{1/2}]_{t'}^{\infty}$$

$$= 4t'^{1/2}$$

$$= 4 \times 10^{-4}\,\text{s}^{1/2}$$

Thus

$$A = 0{\cdot}2 \times 10^8\,\text{s}^{-1}.$$

The order matches nicely with the HF-induced ISC rate in Py-DMA system.

4.2.4 *Non-typical behaviour of alcoholic solvents*: The alcohols can influence magnetic field effect either by altering the static potential energy surface of the RIP, particularly at small inter-radical distances, or by reduction of effective HFI through dynamic involvement (Nath *et al* 1989). Here, we will only discuss the significance of the parameters in relation to the static potential energy surface. The first point we would like to make is that the difference in $\Delta\phi/\phi$ versus ε curve between alcoholic an non-alcoholic solvents is arising through the solvent effect on ϕ itself. Since the parameter $\bar{\alpha}$ may vary with ε, a better alternative is to use the experimental ϕ in the expression of $\Delta\phi/\phi$ (19). The $\Delta\phi/\phi$ versus ε curves so obtained for non-alcohols and alcohols are shown in figure 8 ($r_g = 8A^0$) and figure 9 ($r_g = 4A^0$) respectively. The ϕ versus ε curve for alcoholic solvent differs drastically from that for non-alcoholic solvent; hence, $\Delta\phi/\phi$ versus ε curve also shows non-typical features. The difference of $\Delta\phi/\phi$ at isodielectric solvent mixtures arises mainly due to the factor $(1-\phi)$.

The essential difference between non-alcohols and alcohols, with respect to the parameter values for a good fit, is that for non-alcohols the required R is $6A^0$ whereas alcohols demand distinctly lower values of R i.e. $R < 3A^0$. As the whole analysis is based on a purely Coulombic potential, the fit with $R \simeq 2{\cdot}8A^0$ for alcohols may be interpreted as that the Coulombic potential is valid up to an inter-radical distance of $\simeq 3A^0$ which nearly corresponds to the CIP minima. The boundary parameter h in such a situation should be interpreted as an irreversible radiative and non-radiative decay rate of the exciplex. The experimental observation that the life time τ also

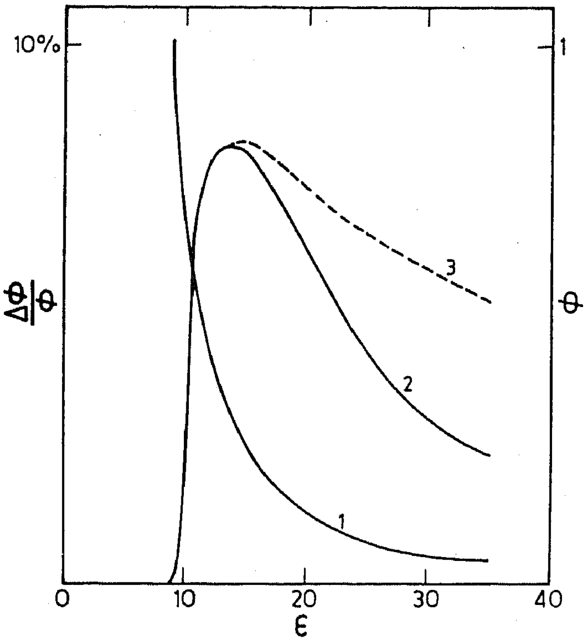

Figure 8. Theoretical $\Delta\phi/\phi$ versus ε curve (dotted curve 3) for Py-DMA exciplex in THF/DMF evaluated with experimental ϕ values (curve 1) following (19). Curve 2 represents $\Delta\phi/\phi$ versus ε curve drawn through experimental points.

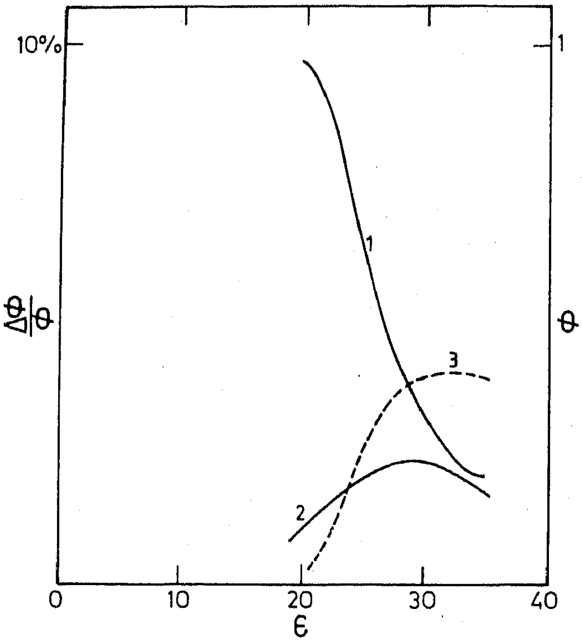

Figure 9. Theoretical $\Delta\phi/\phi$ versus ε curve (dotted curve 3) for Py-DMA exciplex in 1-propanol/methanol evaluated with the experimental ϕ values (curve 1) in (19). Curve 2 represents $\Delta\phi/\phi$ versus ε curve drawn through experimental points.

increases in alcohol agrees with the assumption that energetically the CIP is lower than the SSIP in this medium. Figure 10 gives a qualitative presentation of the schematic potential energy diagram of the RIP in alcohols on the basis of the above argument.

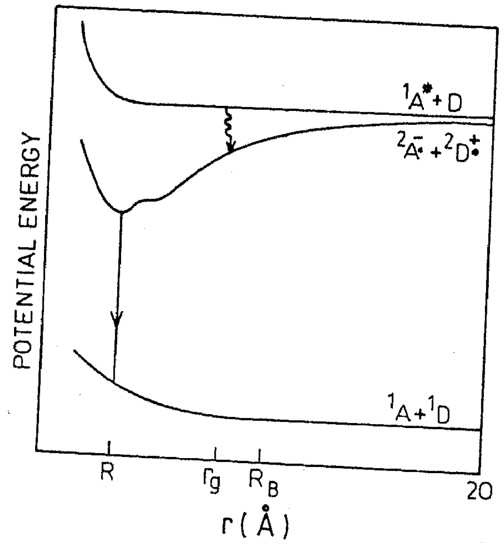

Figure 10. Schematic representation of the dependence of the singlet-state potential energy of the ($^2Py^{\bar{\cdot}}$ + $^2DMA^{\dot{+}}$). RIP system on the inter-radical distance (r) in a moderately polar alcoholic solvent.

4.2.5 *A few additional comments on further improvement of the crude theory may be pertinent:* (1) In the experiment D decreases with increase in ε for THF/DMF mixed solvents whereas for alcohols it increases. The inclusion of its variation in the factor $1/(4\pi D)^{1/2}$ improves the fit in the case of alcohols but the reverse happens for THF/DMF mixed solvents. (2) The parameter r_g may also vary with ε. At low values of ε the charge transfer distance may reduce slightly. The inclusion of this variation in (19), through the factor $r_c/(1 - \exp(r_c/r_g))$, will further reduce the slope of the $\Delta\phi/\phi$ versus ε curve. However, this effect is quite negligible. (3) It is to be noted that our starting eq. (4) is valid only for $t > r_c^2/D$ (Basu *et al* 1989a, b). In practice, for THF/DMF mixture at $\varepsilon = 9$, this reduces to $t > 12$ ns. Thus, at the lower limit of ε the starting equation is only valid at a time domain where ISC has attained saturation. This introduces an error in our theoretical $\Delta\phi/\phi$. A more complicated expression, such as the exact one derived by Hong and Noolandi (1978a, b, c) through Laplace transformation or the approximate one derived by Mozumder (1974) on the basis of prescribed diffusion, is needed for treating short times analytically. However, the simplicity of the present analytical treatment will then be lost.

5. Conclusion

We have tried to develop an analytical working model for ε-variation of magnetic effect. Considering the simplicity of the model and lack of our knowledge of parameters, the success achieved is satisfying. However, a more solid conclusion requires more substantial effort. A rigorous analysis where the spin dynamics and the diffusion dynamics are coupled will certainly give a better picture of the phenomenon. However, such an analysis will be vastly more complicated where a numerical approach needs to be followed.

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