Magnetic field effect on the benzophenone–sodium dodecyl sulphate system: influence of external additives

Ajay Misra, Rina Dutta, Debnarayan Nath, Subhasis Sinha, Mihir Chowdhury

Deparment of Physical Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

Abstract

Addition of small amphiphiles such as 1,4-dioxane is found to affect radical recombination and escape rates in micelles such as sodium dodecyl sulphate (SDS). This has been demonstrated with the hydrogen-abstracted product of triplet benzophenone as the probe molecule. This result has been interpreted on the basis of the ability of dioxane to form "mixed" micelles, which thereby affect the size, viscosity and reflectivity of the boundary of SDS. Studies in presence of magnetic fields up to 15 kG show that the magnetic field effect remains unaffected by the addition of dioxane. This has been explained as due to the combined effect of size, viscosity and reflectivity of the boundary of the micelle.

Keywords: Magnetic field effect; Geminate recombination; Micelle; Flash photolysis

1. Introduction

Micelles are favourite media for carrying out a variety of chemical reactions [1–3]. In particular, it has been found that micelles help to amplify the effect of a magnetic field on the process of recombination of radical pairs (RPs) [2–5]. The geminate recombination rate depends on both spatial evolution and spin evolution. An external magnetic field effect (MFE) is possible where two radicals, generated in a particular spin state at a certain distance, make a round-trip excursion to a distance where exchange interaction is small. An external magnetic field, or the internal magnetic field provided by magnetic nuclei, may affect the spin evolution process in between re-encounters and may thus influence the recombination rate. Micelles often increase the MFE on geminate recombination by confining the RPs and altering the round-trip diffusive excursion path of the two radicals [2–5].

The question of variation in the geminate recombination rate with micellar characteristics, such as size, viscosity and diffusibility across the boundary, is important and has been addressed by several workers [6–13]. Surfactants of different tail lengths and additives such as salts and alcohols were chosen to vary the micellar size, and geminate recombination rates were measured in the absence of a field. Depending on the nature of the RP and micellar parameters it is found that the geminate recombination rate may either decrease [8,9]

or increase [6,7] with increase in the size of the micelle. Corresponding rate measurements in the presence of a field are rather few [6b,10]. In these MFE studies it is found that the difference between the recombination probability at high fields and zero field is rather insensitive to the size of the micelle; the data of Tarasov et al. [6b] show that the field-induced change in recombination probability slightly increases on increasing the micellar size. The theory of MFE on RP recombination in micelles has been worked out by several groups assuming different models [6b,11,12]. All the calculations seem to point out that the relation between size and MFE is a function of the parameter; no simple generalization emerged from these models.

In this report we have addressed the same problem by adding certain small apolar aprotic molecules such as 1,4-dioxane to the micellar solutions. Recent small-angle neutron scattering (SANS) studies [14] show that such amphiphiles form mixed micelles of reduced size. We felt that it might be worth trying to see how the reduction in size (and viscosity) of the micelle affects rates and the MFE. Very recently we have investigated this problem with benzil as probe [15]. However, the multiplicity of the excited-state conformation of the labile molecule benzil created some problems in the analysis of the data. For example, analysis shows that the rate of escape from the micelle is dependent on the magnetic field, which is contrary to expectation. We have therefore chosen the well-studied, relatively more rigid molecule

benzophenone (BP) as probe in order to check the conclusions arrived at for benzil. We have found that the anomalous field dependence of the micellar escape rate observed in connection with benzil vanishes in the present case; other conclusions remain substantiated. Our results show that, while both exit and geminate recombination rates increased on addition of dioxane, the MFE remained rather insensitive.

2. Experimental details

The details of our flash-photolysis apparatus have already been published elsewhere [16]. For high field studies, we have employed a pulsed home-built electromagnet, where the pulsed current is provided by discharge of capacitors through an air-core coil (Kapitza's technique). A schematic diagram of the circuitry is shown in Fig. 1. The pulsed duration is about 7.8 ms. An Xe lamp is triggered about 1.8 ms after the trigger of the capacitor discharge unit (i.e. at the commencement of the plateau region of the magnetic field profile). The laser is triggered after a delay of about 200 μs (i.e. at the flat portion of the lamp profile) and the transient absorption followed by an oscilloscope. We have ensured that the magnetic field remained constant during the transient decay measurement (10–100 μs). The pulsed current was measured and the
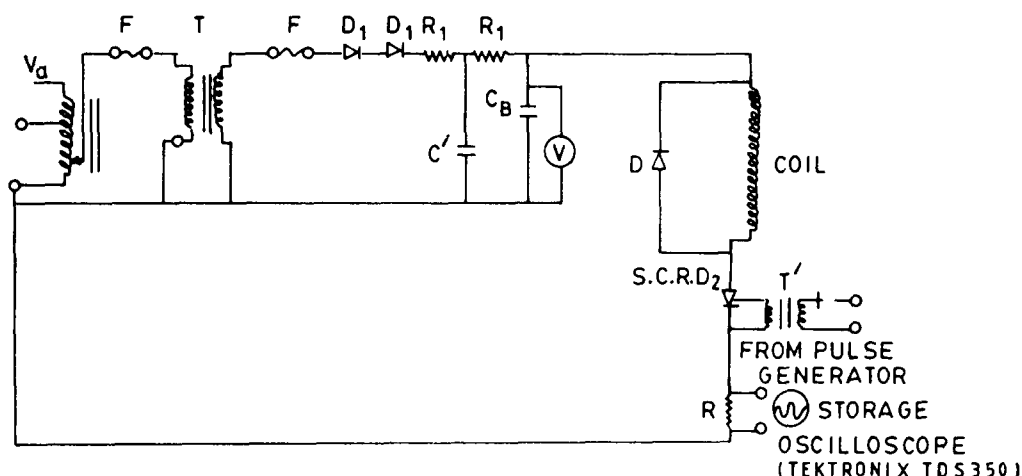
V   AUTO TRANSFORMER (VARIAC)
F   FAST BLOWN FUSE (0.5 Amp)
T   STEP-UP TRANSFORMER (1:10)
D_1 RECTIFIER DIODE (BY 127)
D   FAST RECTIFIER DIODE (DSA216A)
D_2, 1600 PIV 100A (STEADY) TYPE
S.C.R.
T' PULSE TRANSFORMER (1:1)
C_B MAIN CAPACITOR BANK 300 μF/1100 V
L   100 μH INDUCTOR
V   VOLTMETER
R   0.01 Ω NON INDUCTIVE STANDARD RESISTANCE
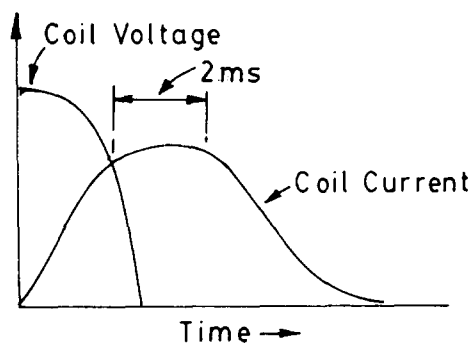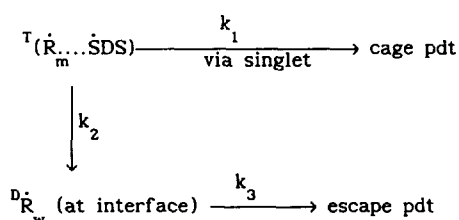C' 100 μF/(1200 V)
R_1 1 KΩ/20 W

Fig. 1. A schematic circuit diagram of our pulsed magnetic field set-up.

field was calibrated using a Hall probe. The output signal was fed to a digital oscilloscope (TDS 350). Subsequent signal processing was done by a standard IBM PC-AT computer.

BP (Merck) was purified by recrystallization from alcohol (Uvasol, Merck). Sodium dodecyl sulphate (SDS) from Koch-Light was used as supplied. Triply distilled deionized water was used for preparation of solutions. The concentrations of BP and SDS were 5×10^{-4} M and 0.2 M respectively throughout the experiments. Spectroscopic grade 1,4-dioxane (from Merck) was used without further purification. The solutions were degassed by repeated freeze–pump–thaw cycles and then transferred to the microcell (specially prepared for pulsed magnetic field studies) under a nitrogen atmosphere.

3. Results and discussion

The triplet–triplet absorption spectra of BP and its H-abstracted product (BPH') in SDS medium have been reported earlier [17]. ^{3}BPH' absorbs strongly in the 330–550 nm region. We have analysed the decay curves by the following kinetic scheme:

$$^T(\dot{R}_m....\dot{S}DS) \xrightarrow[\text{via singlet}]{k_1} \text{cage pdt}$$

$$\Big\downarrow k_2$$

$$^D\dot{R}_w \text{ (at interface)} \xrightarrow{k_3} \text{escape pdt}$$

where $\dot{R}_m$ stands for the benzophenone ketyl radical in micellar core, and $\dot{R}_w$ for the escaped radical at the interface.

The rate law governing the decay of $\dot{R}_m$ is

$$-\frac{d[\dot{R}_m]}{dt} = (k_1 + k_2)[\dot{R}_m] \tag{1}$$

and that for the production of $\dot{R}_w$ is

$$\frac{d[\dot{R}_w]}{dt} = k_2[\dot{R}_m] - k_3[\dot{R}_w] \tag{2}$$

The total radical yield $Y(t)$ at any time (t) is given by

$$Y(t) = [\dot{R}_m](t) + [\dot{R}_w](t) \tag{3}$$

From (1)–(3), we get

$$Y(t) = [\dot{R}_m](0)\Big(\exp[-(k_1+k_2)t]$$

$$+ \frac{k_2 \exp[-(k_1+k_2)t]}{k_3-(k_1+k_2)} + \frac{k_2 \exp(-k_3 t)}{(k_1+k_2)-k_3}\Big) \tag{4}$$

where $[\dot{R}_m](0)$ is the concentration of BP ketyl radical at $t = 0$. Experimentally one obtains the total radical yield Y, for both $\dot{R}_m$ and $\dot{R}_w$ have the same spectrum and hence cannot be distinguished. We have calculated k_1, k_2 and k_3 from the

$Y(t)$ curve. The effect of field and dioxane is discussed in terms of the changes in the values of the three constants.

3.1. Effect of the magnetic field on the benzophenone-sodium dodecyl sulphate system

Fig. 2 shows the agreement of our model (Eq. (4)) with the experimentally obtained decay curves. The geminate recombination rate of the BPH' and SDS' radical within the micelle is represented by k_1 and is a complex function of interdependent spin and spatial motion. The spin evolution rate of ^{3}BPH' → ^{1}BPH' is the major factor determining k_1, i.e. the decrease in k_1. This dependence of k_1 is shown in Fig. 3.
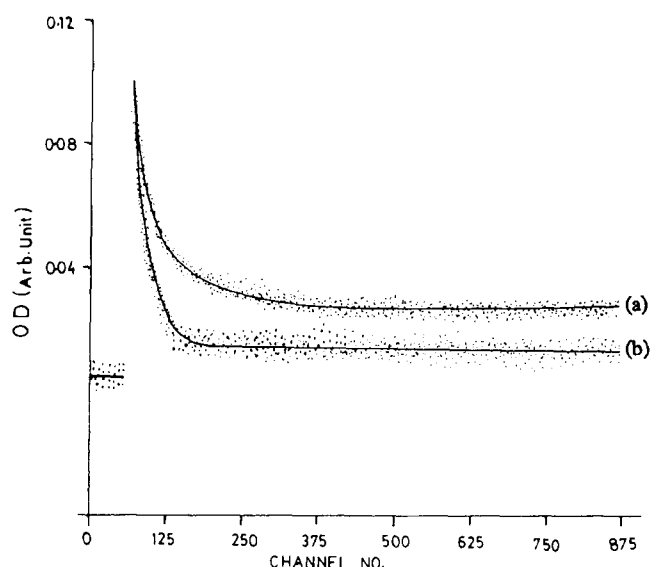
Fig. 2. Agreement of Eq. (4) ((a) line) with the experimentally obtained decay (OD) curve (b) of a BP:SDS RP (at 525 nm) at 0 kG (curve a) and 14 kG (curve b) magnetic field.
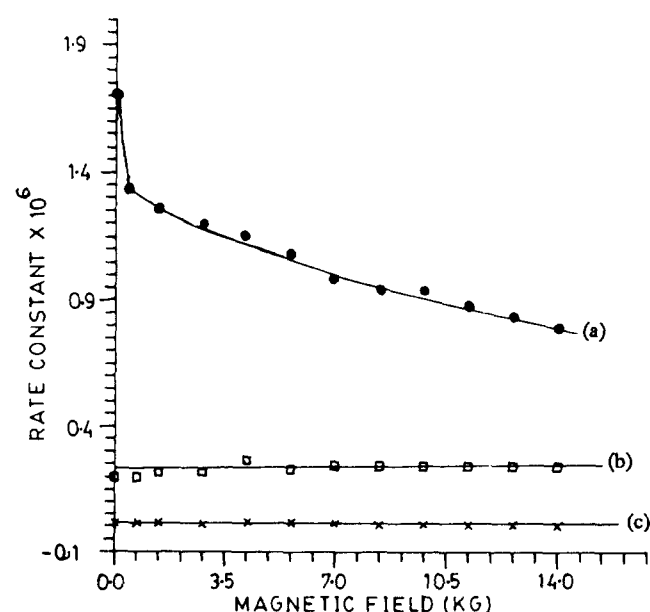
Fig. 3. Plots of k_1 (curve a), k_2 (curve b) and k_3 (curve c) (of a BP:SDS RP at 525 nm) vs. magnetic field in aqueous SDS solution.

As expected, k_1 decreases with increasing magnetic field. On going from zero field to 600 G, there is a sharp drop in k_1. This is obviously a consequence of the hyperfine mechanism of ISC, where a transition from all three degenerate triplet sublevels to a singlet is possible. An externally applied magnetic field causes Zeeman splitting of the triplet levels and consequently lifts their degeneracy. This stops the $S \leftrightarrow T_+$ and $S \leftrightarrow T_-$ transition, thus leading to an overall decrease in ISC rate. This range has been studied with greater field resolution by Fujiwara et al. [4,18]. In the case of the process dominated by the hyperfine interaction (HFI), the MFE usually saturates out at fields much less than kG. Although the rapid drop (Fig. 3) between 0 and 700 G may be attributed to this HFI mechanism, the expected complete saturation at around 600 G does not occur. The slow approach to saturation is, however, consistent with the relaxation mechanism [19]. In the relatively high field region (1–15 kG), although the Zeeman splitting has separated the triplet levels beyond their hyperfine width, there is still leakage from the $T_\pm \leftrightarrow T_0$ sublevel, which is then followed by the $T_0 \leftrightarrow S$ ISC process. This residual leakage needs a larger field for it to saturate.

Fig. 2 also shows the variation in k_2 with magnetic field. k_2 remains constant with magnetic field, as it should. This is in contrast with what we observed for the benzil–SDS radical pair system [15]. We ascribe this difference to the rigidity of the S_1 conformation of BP in contrast with the lability of benzil in the S_1 state. No such correction is, however, needed for the present case. It may be pointed out that the k_2 obtained in the present case is very close to the k_2 observed for benzil.

k_3 corresponds to the usual decay process of the escape radicals. As expected, this is independent of magnetic field (Fig. 3). Its value of 0.01×10^6 s^{-1} is comparable with that of benzil ($k_3 = 0.015 \times 10^6$ s^{-1}). However, because of its pseudo-first-order nature, its value might depend on the light intensity and micellar concentration.

3.2. Effect of addition of dioxane

3.2.1. In the absence of a magnetic field

The intercepts of curves a, b and c on the ordinate of Fig. 4 show the effect of 1,4-dioxane (10% v/v) on the BP–SDS system in the absence of a field. Both k_1 and k_2 are found to increase, but the effect on k_2 is more prominent. k_1^D/k_1^0 and k_2^D/k_2^0 (the superscripts D and 0 corresponding to the presence and the absence respectively of dioxane) were found to be 1.2 and 2 respectively. Dioxane also increases the yield of escape radicals by about 100%. k_3, however, remains unchanged, as expected.

This increase in k_2 can be explained in a straightforward way in terms of the reduction in micellar size, viscosity and reflectivity of the micellar boundary on addition of dioxane. Dioxane is a molecule soluble in both water and micellar core and, as such, may be expected to increase the permeability of the micelle and hence of k_2. The reduction in the size of the micelle on addition of dioxane increases the surface-to-volume ratio and as such increases the exit rate. Our measure-
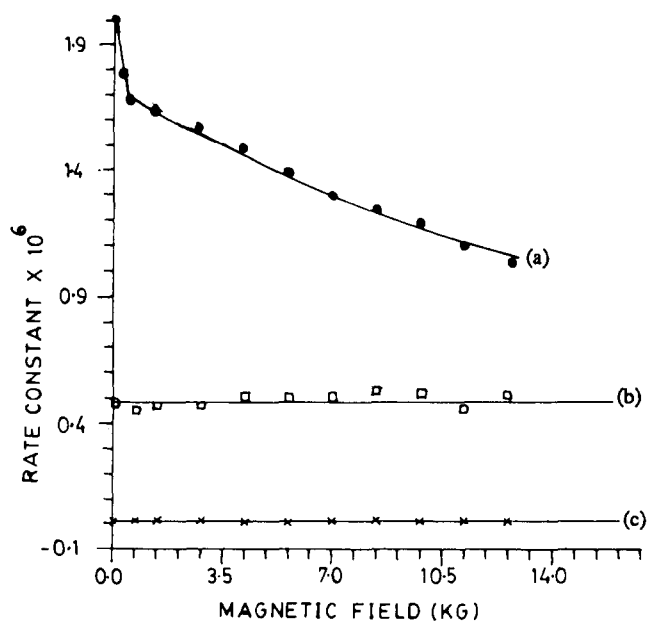

Fig. 4. Plots of k_1 (curve a), k_2 (curve b) and k_3 (curve c) (of a BP:SDS RP at 525 nm) vs. magnetic field in the presence of a 10:1 (v/v) water: dioxane mixture.

ment of the viscosity of the micelle by the polarization technique [20] with diphenylhexatriene (DPH) as probe shows that the viscosity of SDS micelles is lowered from 80 to 10 cP by the addition of 10% dioxane [15]. This decrease in viscosity is expected to increase the mobility of radicals, and hence the escape rate k_2. The increase in the free radical yield Y_0 is a direct consequence of the increase in k_2. However, the observed increase in k_2 due to addition of dioxane is less than that of benzil reported earlier [15], as summarized in Table 1. The reason for this probe dependence of the influence of dioxane is not immediately obvious. It seems to be related to the difference in the locations of the two probes in the micelle. In the excited state, benzil is known to be trans-planar [21] where the dipole moment should be zero. Thus the benzil triplet is likely to be in the core region while the BP triplet with a larger dipole moment should prefer the peripheral region. It is quite possible that dioxane, which is also a molecule of nearly zero dipole moment, affects the core (size or viscosity) more than the peripheral region. In fact, the viscosity measured by DPH polarization pertains to the core and indicates that the core viscosity is affected considerably on addition of dioxane. The larger effect of dioxane on the core than the peripheral region of micelles brings about a relatively larger change in k_2 for benzil compared with that of BP.

The explanation of the increase in k_1 is less obvious. The predictions of different theoretical models are not clear cut [6,9a,11,12]. The value of k_1 depends jointly on the frequency of re-encounters and the extent of spin conversion between two encounters. The frequency of re-encounters may be expected to increase with increase in the reflection coefficient [11] of the boundary (which in some sense is equivalent to an increase in the depth of the potential well in the

Table 1
Rate constants $k(0)$ at zero magnetic field and $k(H)$ at 14 kG magnetic field

	$k_1(0)$ $(\times 10^6 \text{ s}^{-1})$	$k_1(H)$ $(\times 10^6 \text{ s}^{-1})$	$k_2(0)$ $(\times 10^6 \text{ s}^{-1})$	$k_2(H)$ $(\times 10^6 \text{ s}^{-1})$	$k_3(0)$ $(\times 10^6 \text{ s}^{-1})$	$k_3(H)$ $(\times 10^6 \text{ s}^{-1})$
(1) BP in SDS micellar solution	1.70	0.80	0.25	0.25	0.01	0.01
(2) BP in SDS (10:1 v/v water:dioxane) micelle	2.00	1.00	0.5	0.52	0.01	0.01
(3) Benzil in SDS micelle	0.70	0.08	0.27	0.11	0.01	0.01
(4) Benzil in SDS (10:1 v/v water:dioxane) micelle	1.86	0.20	1.07	0.70	0.02	0.01

micelle [12]), decrease in the viscosity and decrease in the size of the supercage micelle. The extent of triplet to singlet spin evolution is sensitive to the above-mentioned micellar parameters only if the T ↔ S conversion time is of the same order as the round-trip excursion time, which in turn depends on viscosity and size of micelle. A reduction in size decreases the time interval between two successive encounters and increases the exchange interaction; thus it tends to diminish the extent of spin evolution [6b]. The effect of paramagnetic relaxation, on the other hand, is most pronounced in large micelles [6b]. Whether the overall rate of geminate recombination will increase or decrease on reduction in the micellar size, viscosity and reflectivity of the boundary depends delicately on the sum total of opposite effects [6,9a,11,12]. Experimentally, a reduction in micellar size has been found to increase [8,9] as well as to decrease k_1 [6,7]. Our observation of an increase in k_1 is in agreement with the results obtained by previous workers. This only means that the increase in number of encounters due to decrease in micellar size (and viscosity) more than compensates for the decrease in encounters due to decrease in reflectivity of the boundary and decrease in spin evolution due to increase in spin exchange [6]. The normal micellar size is 50–100 Å, which after 40% reduction on addition of dioxane becomes 30–60 Å. The inter-radical distance is still quite large and the distance-dependent exchange interaction possibly plays a minor role in the present case.

3.2.2. In the presence of a magnetic field

If the magnetic field is increased from zero, k_1 decreases. As expected, k_2 (Fig. 4(b)) and k_3 (Fig. 4(c)) remain independent of magnetic field. A comparison of Fig. 3 and Fig. 4 shows that the shape of k_1 vs. H curve remains unaltered; this suggests that the mechanism of spin evolution of the system is same in water as in the water–dioxane mixture. The escape radical yield also shows a dependence on magnetic field (Fig. 5). The MFE on the yield (defined as $[(Y_H - Y_0)/Y_0] \times 100$, where Y is the radical concentration at a long time (14 μs) and $H = H_{sat} = 15$ kG), turns out to be 64% for the water–SDS medium as against 53% for the benzil in water–SDS medium.

The observed constancy of MFE with respect to the dioxane addition, despite large changes in the geminate recombination and micellar exit rates, is rather surprising. A number of factors are simultaneously operative and need to be considered. First, the viscosity is reduced on the addition of
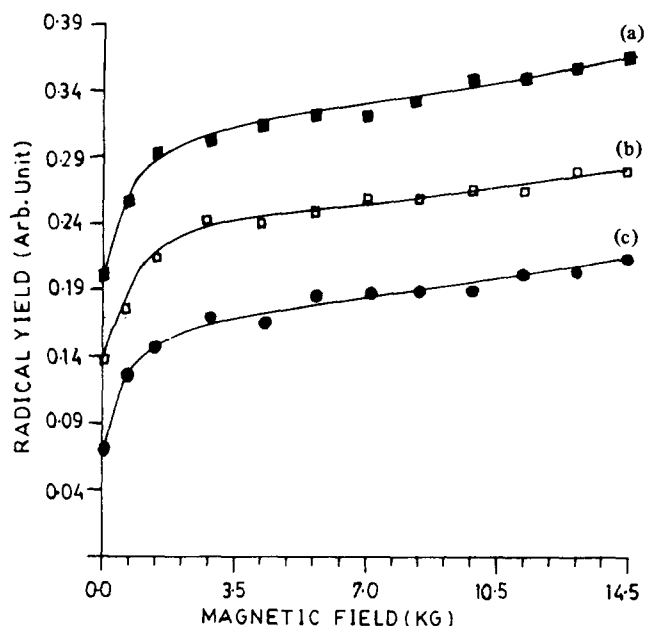

Fig. 5. Plot of radical yield vs. magnetic field (the yield has been calculated from the ratio of counts at $t = 14$ μs to the counts at $t = 0$): curve a, without dioxane; curve b, 10:1 dioxane; curve c, 10:2 dioxane.

dioxane. The theoretical models do not make clear-cut predictions as regards viscosity effect; however, calculations with reasonable parameters do not indicate any large dependence of MFE on viscosity [11,12]. Empirically it has been observed that in case of a homogeneous medium the MFE often increases marginally on increase in the viscosity [22]. It is therefore possible that in the present case the reduction of viscosity reduces the MFE to a small extent.

Secondly, dioxane, which is soluble in both water and the non-polar medium, is expected to increase the permeability of the micelle boundary. This means that the reflection coefficient [11] of the boundary will decrease on addition of dioxane. In other words, the potential which confines the RPs within the micelle [12] will also decrease. The calculations of Luders and Salikhov [11] and of Shusin et al. [12] seem to indicate that this should cause a decrease in MFE.

Thirdly, the size of the micelle is shown to decrease 40% on addition of dioxane by a SANS study [14]. The data calculated by Luders and Salikhov [11] and Shusin et al. [12] with reasonable parameters seem to indicate an increase in MFE with reduction in micellar size. Empirically it has been found that in a linked system the MFE increases with increasing chain length for small links but decreases with

increasing chain length for large links [23,24]. For micelles possibly the latter situation is appropriate. We therefore believe that the observed constancy of MFE on addition of dioxane is due to the opposite influences of size and reflectivity of the boundary (i.e. potential depth) of micelle. The calculations of Tarasov et al. [6b] indicate that the variation in the geminate recombination rate and the MFE on micellar size delicately depends upon several factors: frequency of forced encounters, distance-dependent electron spin exchange and paramagnetic relaxation. Our knowledge of these factors at the present juncture is not detailed enough to make a clear prediction in a particular case so that it could be compared with experimental result. Further experiments with different kinds of additives might clarify the situation.

Acknowledgement

References

[1] K. Kalyansundar, *Photochemistry in Microheterogeneous Systems*, Academic Press, New York, 1987.

[2] I.R. Gould, N.J. Turro and M.B. Zimmt, *Adv. Phys. Org. Chem., 20* (1984) 1.

[3] M. Tachiya, *Kinetics of Nonhomogeneous Processes*, Wiley, New York, 1987.

[4] U.E. Steiner and T. Ulrich, *Chem. Rev., 89* (1989) 51.

[5] K. Bhattacharya and M. Chowdhury, *Chem. Rev., 93* (1993) 507.

[6] (a) V.F. Tarasov, N.D. Ghatlia, A.L. Buchachenko and N.J. Turro, *J. Am. Chem. Soc., 114* (1992) 9517.
(b) V.F. Tarasov, N.D. Ghatlia, N.I. Avdievich, I.A. Shkrob, A.L. Buchachenko and N.J. Turro, *J. Am. Chem. Soc., 116* (1994) 2281.

[7] N.J. Turro, M.B. Zimmt, X.G. Lei, I.R. Gould, K.S. Nitsche and Y. Cha, *J. Phys. Chem., 91* (1987) 4544.

[8] C.H. Evans, J.C. Scaiano and K.U. Ingold, *J. Am. Chem. Soc., 114* (1992) 140 and other references [16–20,24] cited therein.

[9] (a) H. Hayashi, *Bull. Chem. Soc. Jpn., 57* (1984) 1753.
(b) T. Ulrich and U.E. Steiner, *Chem. Phys. Lett., 112* (1984) 365.

[10] Y. Tanimoto, C. Jinda, Y. Fujiwara, M. Itoh, K. Hirai, H. Tomioka, R. Nakagaki and S. Nagakkura, *J. Photochem. Photobiol. A; Chem. 47* (1989) 269.

[11] K. Luders and K.M. Salikhov, *Chem. Phys., 98* (1985) 259.

[12] A.I. Shusin, J.B. Pedersen and L.I. Lolle, *Chem. Phys., 188* (1994) 1.

[13] N.J. Turro, A.L. Buchachenko and V.F. Tarasov, *Acc. Chem. Res., 28* (1995) 69.

[14] P. Thiyagrajan and D.M. Tiede, *J. Phys. Chem., 98* (1994) 10 343.

[15] A. Misra, R. Dutta and M. Chowdhury, *Chem. Phys. Lett., 243* (1995) 308.

[16] R. Dutta and M. Chowdhury, *J. Photochem. Photobiol. A: Chem., 55* (1990) 197.

[17] A.V. Buettner and J. Dedinas, *J. Phys. Chem., 75* (1971) 187.

[18] Y. Fujiwara, M. Mukai, T. Tamura, Y. Tanimoto and M. Okazaki, *Chem. Phys. Lett., 213* (1993) 89.

[19] U.E. Steiner and H.F. Wolff, in J.F. Rabek (ed.), *Photochemistry and Photophysics*, Vol. IV, CRC Press: Boca Raton, FL, 1991, Chapter 1.

[20] M. Shinitzky and Y. barenholz, *Biochem. Biophys. Acta, 515* (1978) 369.

[21] K. Bhattacharya, D.S. Roy and M. Chowdhury, *J. Lumin., 22* (1980) 95.

[22] L.A. Margulis, I.V. Khudyakov and V.A. Kuzmin, *Chem. Phys. Lett., 119* (1985) 244.

[23] H.G. Busmann, H. Staerk and A. Weller, *J. Chem. Phys., 91* (1989) 4098.

[24] S. Basu, D.N. Nath, M. Chowdhury and M.A. Winnik, *Chem. Phys., 162* (1992) 145.