

A WATER-SOLUBLE BENZOPHENONE IN REVERSE MICELLES: KINETICS AND SPECTROSCOPY

DANIEL-JOSEPH LOUGNOT[†] and J. C. SCALANO

Department of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6 (Canada)

(Received September 22, 1983; in revised form November 1, 1983)

Summary

A water-soluble benzophenone, 4-sulphomethylbenzophenone (SMBP), was studied in reverse micelles of Aerosol OT and in the parent microemulsions obtained on cyclohexanol addition. The rate constants corresponding to the interaction of SMBP with the different components of the microemulsion were measured and compared with the available data in pure water and direct micelles. The situation where a monomer is incorporated in the microheterogeneous assembly is also considered. An important reduction in the efficiency of the interaction taking place between the carbonyl triplet and the monomer is observed in this system which could therefore prove of particular interest in photopolymerization experiments.

1. Introduction

The photochemistry of both large and small molecules solubilized in microheterogeneous media has been the subject of intensive work during recent years [1 - 8]. Very large changes in reaction rates have been observed in many instances and are generally accounted for by two specific properties of micellar assemblies.

(i) The micelle solubilizes one of the two reactants in any zone of the micellar volume, thereby introducing a heterogeneity in the local concentrations of the reactants and hence changing the reaction rate; the case where the two reactants are soluble in the micelle corresponds to the same approach with, as a consequence, the reaction rates increasing drastically [9, 10].

(ii) The micelle-bulk solvent interface can be the site of unusual reactions owing to unique properties which result either from the existence of an

[†]Permanent address: Laboratoire de Photochimie Générale, Ecole Nationale Supérieure de Chimie, Equipe de Recherche associée au CNRS 386, 68093 Mulhouse Cédex, France.

intense electric field or from the very pronounced discontinuity in several physical properties of the "solvent" in this region [11].

For carbonyl compounds dissolved in direct micelles (oil in water), many specific topics have received particular attention: photoreduction [12], Norrish type I and II reactions [8, 13], spectral properties [14], dynamics of entry and exit processes [15], photodimerization [16] and photoinitiation of polymerization [17].

However, detailed quantitative studies of reverse micellar assemblies are rather scarce. These micelles have polar cores, which may accommodate rather large amounts of water, and a hydrophobic bulk phase. Although these systems are not as common as "direct" micelles, they are used very extensively in the industrial world. Moreover, as a result of the segregation effect introduced between the bulk organic phase and the polar core, reverse micelles are able to protect enzymes against denaturation; hence they are of interest in biology and photobiology [18].

Finally, a point which seems to be worth thinking about is the photopolymerization of acrylic monomers in the presence of a carbonylic initiator. It is now well recognized that the process which essentially limits the quantum yield of photoinitiation is the quenching of the excited triplet state of the carbonyl compound by the olefin. This process is obviously detrimental to the overall quantum yield since it consumes most of the potentially active excited states. Thus, segregation of the different species in the different phases of micellar assemblies could be an attractive idea to prevent the initiator and the monomer from coming into close contact during the first moments of the triplet lifetime and thereby to prevent quenching from becoming the dominant triplet decay path. This assumption has been proved to be valid for direct micelles with a water-soluble initiator and methyl methacrylate (MMA) [19]. However, the difficulty in finding a water-soluble carbonyl compound which is highly insoluble in the micelle makes it difficult to rationalize the mechanism of the sequence of reactions that finally lead to the polymer.

In the present paper information is provided on the location, the lifetime, the quenching rates and the transient spectra of a water-soluble benzophenone solubilized in reverse micelles of Aerosol OT (AOT). The purpose of this study is to collect the data and the mechanistic evidence which are essential to the understanding of any photopolymerization in reverse micelles.

2. Experimental details

Benzophenone (Janssen Chimica) was recrystallized twice from ethanol-water mixtures. Cyclohexanol and *n*-decane (Janssen Chimica) were used as received. Pure di-(2-ethylhexyl) sodium sulphosuccinate was supplied commercially as AOT by the American Cyanamid Company and was used without further purification. MMA (Janssen Chimica) was washed with 0.2

M sodium hydroxide, washed twice with water, then dried over anhydrous magnesium sulphate and finally distilled under a reduced pressure.

The water-soluble benzophenone, the sodium salt of 4-sulphomethylbenzophenone (SMBP), was synthesized and purified according to the procedure recently described by Green and coworkers [20]. The crude product was washed with ether and then recrystallized twice from slightly alkaline ethanol. After the product had been dried, elemental analysis gave the following results: 56.30% C; 3.76% H; 10.7% S. $C_{14}H_{11}NaO_4S$ requires 56.37% C, 3.72% H and 10.75% S.

Our laser photolysis uses the pulses from a Molelectron UV-24 nitrogen laser for excitation (337 nm; about 8 ns and up to 10 mJ). Further details have been given previously [21]. The absorption measurements were made on a Varian spectrophotometer (model Cary 219).

Diverse micellar solutions were prepared by dissolving appropriate amounts of AOT in decane (typically 60 g l^{-1}), then adding a precise volume of an aqueous solution of SMBP to the required concentration (unless otherwise specified the final concentration of benzophenone was $1.6 \times 10^{-2} \text{ M}$) and sonicating the mixture overnight at room temperature. The reverse microemulsions, *i.e.* AOT-water-cyclohexanol-decane-benzophenone, were prepared by incorporating a suitable amount of cyclohexanol in the corresponding micellar solutions and sonicating the mixture to obtain "macroscopically homogeneous" solutions.

All the samples were degassed by means of nitrogen bubbling in vessels designed for this purpose (with a large spout so that they were not overwhelmed by foam).

3. Results and discussion

3.1. The location of 4-sulphomethylbenzophenone in reverse micelles

As a result of the strong interaction of the carbonyl group with the solvents, the solvatochromic shifts of the $n \rightarrow \pi^*$ transition can be used as a probe to investigate the location of the compound in the micellar assembly. Fendler *et al.* [22] have found evidence of a good correlation between ν_{\max} of the $n \rightarrow \pi^*$ transition and the $E_T(30)$ value for benzophenone. Taking advantage of this correlation, they propose to use the ν_{\max} measured in a particular micellar solution as the function and to deduce the corresponding value of the variable, *i.e.* the $E_T(30)$ value for that particular "solvent". By entering this value on the E_T scale, a local equivalent polarity can be assigned to the solvent, which denotes a more or less deep site of solubilization in the micelle. However, the greatest care must be taken in interpreting these results since the equivalent local polarity determined in this way corresponds to a statistical analysis which cannot account for the possible partition of the probe between several sites with similar polarities. With this approach we have determined ν_{\max} for the $n \rightarrow \pi^*$ transition for SMBP in various solvents (Figs. 1 and 2).

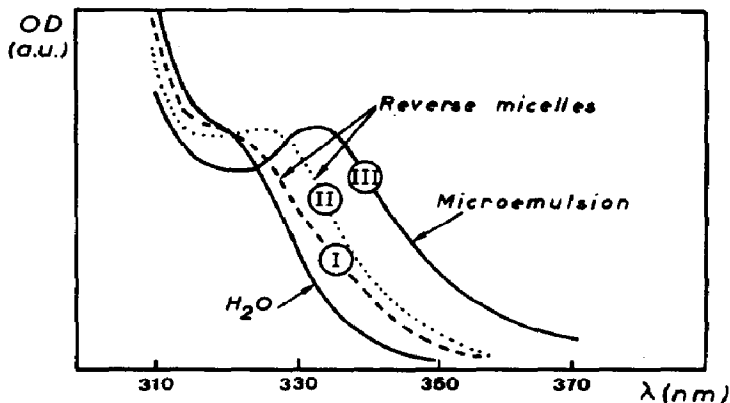


Fig. 1. UV spectra of SMBP in water, in reverse micelles (with two or three SMBP molecules per micelle (curve I) and with 25 - 30 SMBP molecules per micelle (curve II) and in a microemulsion (with $[H_2O]/[AOT] \approx 7$ (curve III)).

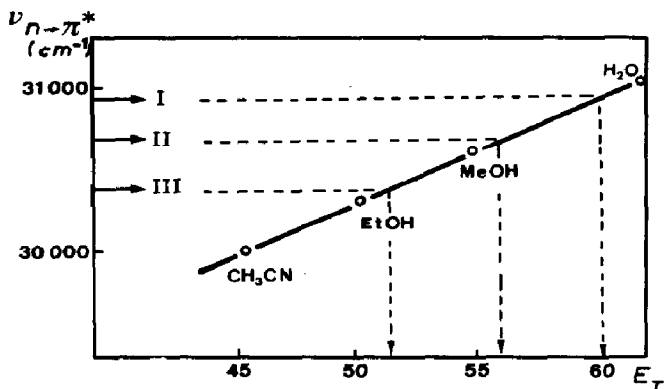


Fig. 2. $\nu_n \rightarrow \pi^*$ as a function of E_T for SMBP (MeOH \equiv methanol, EtOH \equiv ethanol).

On examination of Fig. 2, it can be unambiguously concluded that SMBP lies inside the highly polar droplet. However, small changes are observed when the micelle is swollen with water or when the aggregates form a reverse microemulsion on addition of cyclohexanol or when the occupancy is increased.

At low occupancies (two or three SMBP molecules per micelle) the UV spectrum is very similar to that observed in pure water (Fig. 1, spectrum I): the environment of SMBP is highly polar and most of these two or three molecules of SMBP must be considered to be dissolved in a homogeneous droplet of water. When the occupancy is increased to 25 - 30 (Fig. 1, spectrum II), SMBP behaves as if it were cramped for room in the droplet; a statistically less polar environment corresponding to a lower E_T is an indication of "jaunts" beyond the polar heads of the surfactant.

On addition of water the micelles are known to be swollen and also to associate to form larger aggregates [23]. These changes seem to have no

appreciable effect on the location of SMBP, the UV spectrum of which denotes an unmodified highly polar environment.

The addition of cyclohexanol, which is known to induce a progressive change in the structure and in the size of the aggregate, in concentrations of up to 1.3 mol l^{-1} results in the formation of a reverse microemulsion comprising colloidal aggregates with much larger radii (about 100 \AA). In this environment SMBP is located in a region of intermediate polarity, which is expected to be close to the surface region (Fig. 1, spectrum III).

It is also important to note that the addition of MMA does not affect the UV spectrum of SMBP and as a consequence its location in any of the situations described above. This observation clearly excludes any interaction between the monomer and the surface of the micelle. It should be noted that all these ideas strictly apply to the ground state, but in the absence of large polarity changes they probably also apply to the triplet state.

3.2. 4-sulphomethylbenzophenone solubilized in the system Aerosol OT-decane-water

The only characteristic feature which is worth mentioning for the AOT-decane-water system is the strong interaction of SMBP triplet with the so-called "surface" of the micelle. In fact, the lifetime of the triplet is determined by the strong interaction with the alkyl chain of either the surfactant or the decane molecules. This interaction, which induces the generation of a radical pair through hydrogen abstraction from the alkyl chain, was first recognized for direct micelles of either anionic or cationic surfactants and seems to behave analogously for reverse micelles [24]. Figure 3 shows the transient absorption signals recorded at 620 nm , a region where only the triplet absorbs light. The triplet lifetime is measured to be 630 ns . It is important to note that the progressive change in the absorption recorded in small time windows as the decay progresses is very similar to that observed in pure water at neutral pH ($\lambda_{\text{max}} = 530 \text{ nm}$ for the triplet and $\lambda_{\text{max}} = 555 \text{ nm}$ for the ketyl radical) [25].

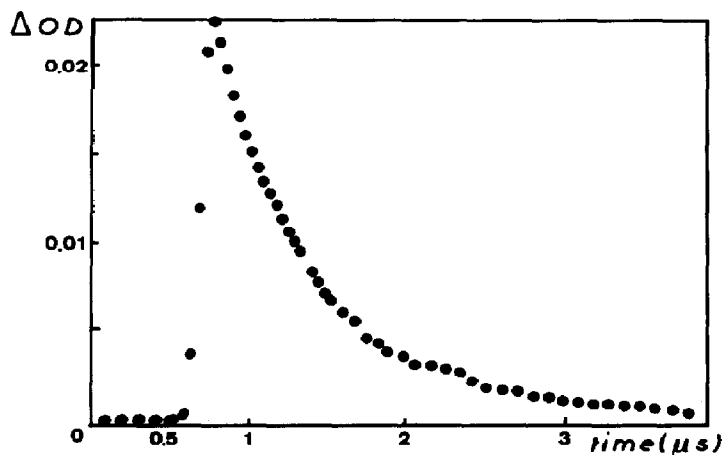


Fig. 3. Time evolution of the transient absorption observed at 620 nm ($\tau_T \approx 630 \text{ ns}$).

Moreover, the triplet lifetime seems to be independent of the amount of water solubilized by the aggregate with $[AOT] = 0.13 \text{ M}$ when the molar ratio $[H_2O]/[AOT]$ is changed from 5 to 75.

3.3. 4-sulphomethylbenzophenone in the system Aerosol OT–decane–water–cyclohexanol

This study has been confined to the region of the diagram where only colloidal aggregates are present. According to the recognized terminology and under this condition, the four-component mixture AOT–decane–water–cyclohexanol is a microemulsion, which implies a progressive increase in the particle size as increasing amounts of alcohol are incorporated. Specific effects could reasonably be expected to take place in those microheterogeneous solutions where the reagents are, on the one hand, segregated between the interior and the exterior of the droplets and, on the other hand, stratified into the swollen aggregate.

However, the AOT–decane–water–cyclohexanol system does not seem to be the site of any specific or intricate phenomenon. Figure 4 illustrates the quenching of the triplet state of SMBP by cyclohexanol; the rate constant derived from Stern–Volmer treatment ($k_H = 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) compares fairly well with the value we obtained in pure water ($k_{\text{water}} = 1.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$). In this system, the maxima of the spectra corresponding to the transient species have been measured to be 535 nm for the triplet and 555 nm for the ketyl radical respectively.

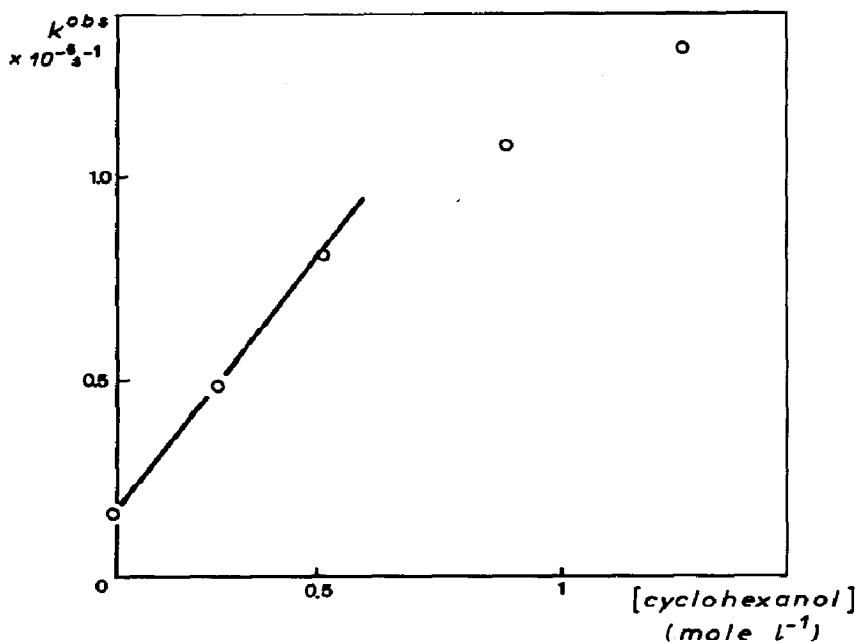


Fig. 4. The observed decay rate constant k^{obs} vs. the cyclohexanol concentration in the quenching of SMBP triplet by cyclohexanol ($[H_2O]/[AOT] \approx 25$; $k_Q \approx 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).

In fact, SMBP seems to behave as if it were dissolved in homogeneous droplets of water with increasing concentrations of cyclohexanol; the presence of an important electric field around the reaction site has no significant influence on the reaction mechanism.

3.4. 4-sulphomethylbenzophenone in the system Aerosol OT-decane-water-methyl methacrylate

As part of the examination of all the possible interactions taking place in a polymerizable mixture (containing an initiator, a hydrogen donor and a monomer in a micellar solution), it is critical to understand the four-component system AOT-decane-water-MMA. As mentioned before, the physical quenching of the excited triplet state by the olefin is often the process that limits the ability of a monomer to be photopolymerized in the presence of a benzophenone derivative as the initiator. In homogeneous solutions the quenching constants may exceed $10^9 \text{ M}^{-1} \text{ s}^{-1}$ for styrene derivatives and in direct micelles this process remains a problem, the negative effects of which are heightened by confinement of the monomer and of the initiator in the same microphase. In sodium dodecylsulphate micelles the triplets of benzophenone derivatives are quenched by MMA with apparent rate constants exceeding $10^9 \text{ M}^{-1} \text{ s}^{-1}$, an order of magnitude faster than in homogeneous solution ($6.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in benzene) [19]. It is important to note that such a "homogeneous-like" treatment is only made possible by the absence of any static component in the quenching process [26] (Fig. 5). Moreover, the "bimolecular-like" constants are used only to compare macroscopically the efficiency of the quenching reactions occurring in photopolymerizable mixtures.

The results obtained in reverse micelles where the monomer and the initiator are dissolved (the monomer in the oil phase and the initiator somewhere in the water droplet) seem to be rather encouraging. The rate constant corresponding to the quenching of SMBP by MMA is $2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 5). Since this process involves the crossing of a reactant through the surface of the micelle, we have measured its rate constant as a function of the amount of water swelling the micellar assembly. Owing to the small amounts of water added, $12 \leq [\text{H}_2\text{O}]/[\text{AOT}] \leq 32$, the aggregation number does not change significantly [23] and the surface area S of the aggregate can be considered to be proportional to the volume V of water incorporated ($dS/dV = 2/R$ where R is approximately constant). As can be seen from Fig. 6, the rate constant is roughly proportional to the amount of water incorporated, *i.e.* to the total area of the interface between the two phases. This observation can be regarded as circumstantial evidence for the existence of a limiting step in the course of the quenching process; the limiting step could correspond to the crossing of the interface, a process which occurs with increasing probability as the area of the interface increases. This limiting step could also be the equilibrium between MMA in the bulk organic phase and water.

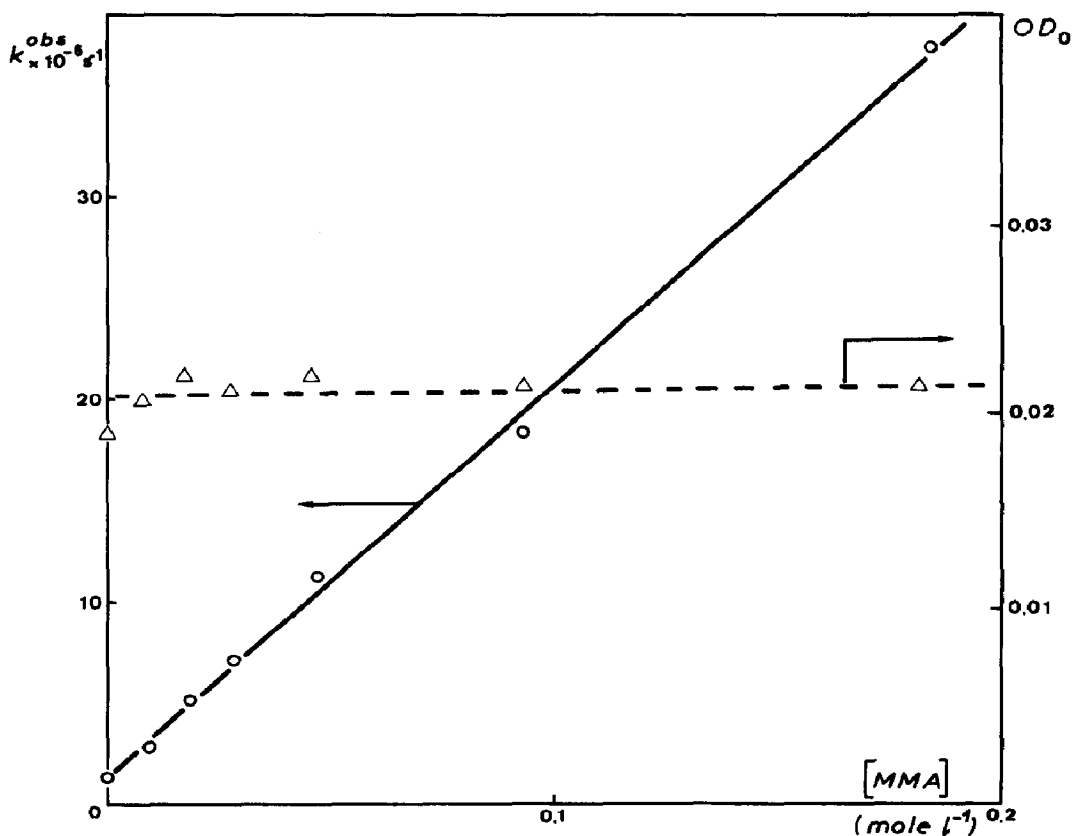


Fig. 5. The observed decay rate constant k^{obs} (—, ○) and the initial transient optical density OD_0 (---, △) vs. the MMA concentration in the quenching of SMBP triplet by MMA ($[H_2O]/[AOT] \approx 12.5$; $k_Q^{\text{MMA}} \approx 2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$).

It should be noted that the final experimental datum point on the curve of Fig. 6 ($125 \mu\text{l ml}^{-1}$) is not an indication of saturation in this correlation; as a matter of fact, with water concentrations greater than $110 \mu\text{l ml}^{-1}$, the micellar solution becomes turbid and forms an emulsion. Finally, with regard to the interaction between SMBP and MMA, another observation is worth mentioning: on addition of very large amounts of MMA, the quenching process seems to saturate progressively. Thus, a 1 M solution of MMA leads to a triplet lifetime of the order of 12 ns instead of 5 ns if the quenching process were linear up to such a concentration and, with $[MMA] > 1 \text{ M}$, the triplet lifetime remains almost unaffected. Although this observation is not quantitative it could have decisive consequences for photopolymerizations in reverse micelles.

3.5. 4-sulphomethylbenzophenone in the system Aerosol OT–decane–methyl methacrylate–cyclohexanol

The four-component mixture AOT–decane–MMA–cyclohexanol corresponds to a reverse microemulsion containing all the reactants to be involved in a photopolymerizable formulation.

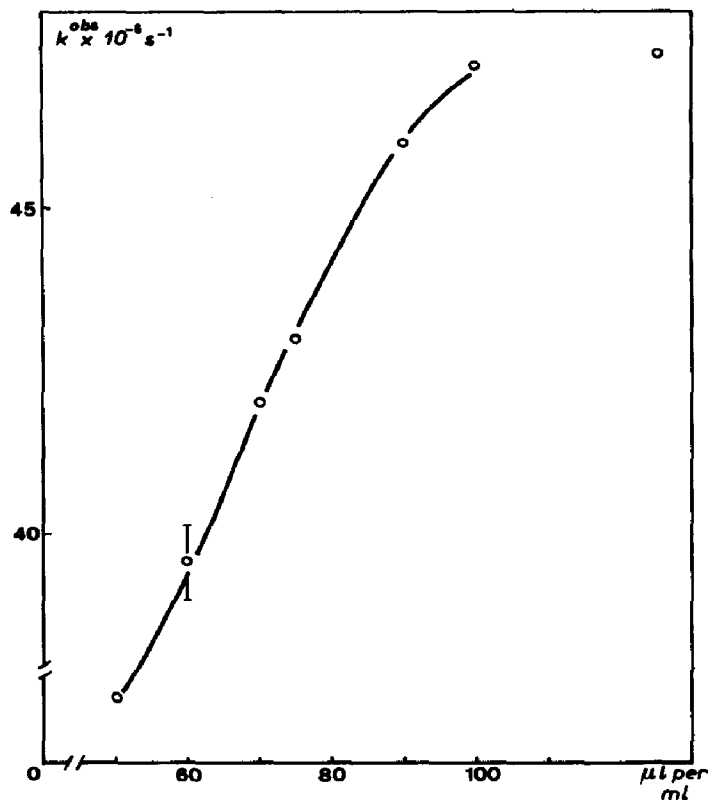
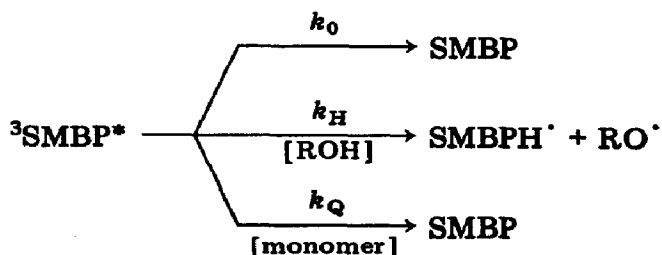


Fig. 6. Observed rate constants for the triplet decay of SMBP in the presence of MMA as a function of the volume of water added ($12 < [\text{H}_2\text{O}]/[\text{AOT}] < 32$; $[\text{MMA}] = 0.18 \text{ M}$).

In the absence of MMA a transient signal which results from overlap of the triplet and ketyl absorptions is observed. Owing to their very different lifetimes, it is interesting to record the transient signal in a wavelength range where these two absorptions are present. In fact, the Stern-Volmer treatment of the observed rate constant for the triplet decay as the concentration of MMA is increased provides an estimate of the rate constant for the concurrent quenching by this monomer. Moreover, by correlating the amount of ketyl radical present at the end of the decay of the triplet state with the concentration of the monomer, this estimate can be corroborated and it can be confirmed that the system under investigation is only a system involving two concurrent quenching processes:



where k_0 is the pseudo-first-order rate constant including spontaneous decay and quenching by the surfactant and/or the oil, k_H ($= 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) is the rate constant for quenching by cyclohexanol and k_Q is the rate constant for quenching by the monomer.

$$OD_{\infty} = OD_0 \frac{\epsilon_K}{\epsilon_T} \frac{k_H[\text{ROH}]}{k^{\text{obs}}}$$

and

$$\frac{OD_0}{OD_{\infty}} = A + B[\text{MMA}]$$

with

$$A = \frac{\epsilon_T}{\epsilon_K} \left(1 + \frac{k_0}{k_H[\text{ROH}]} \right)$$

and

$$B = \frac{\epsilon_T}{\epsilon_K} \frac{k_Q}{k_H[\text{ROH}]}$$

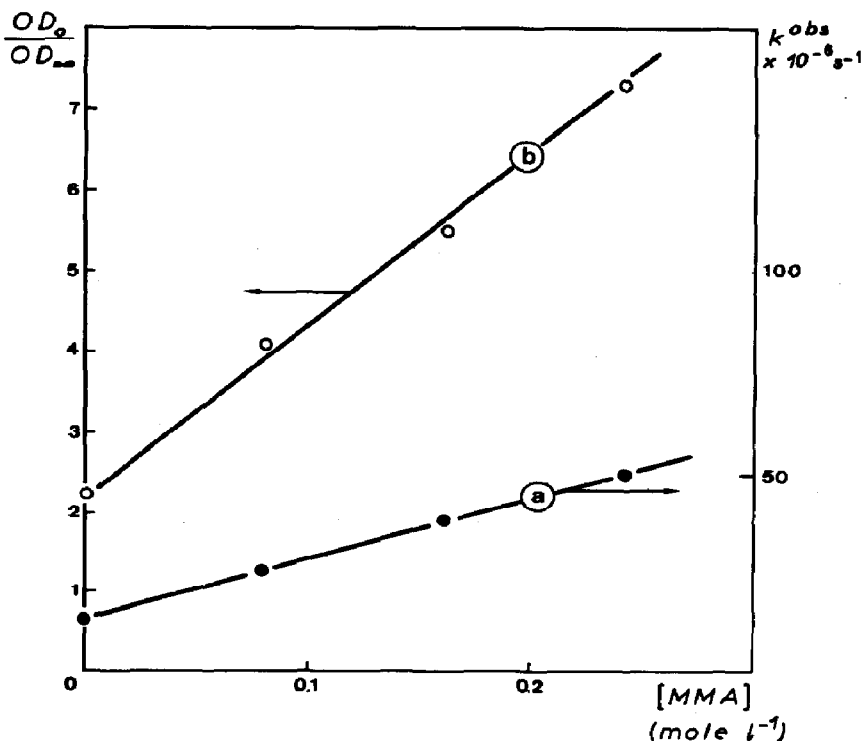


Fig. 7. Stern-Volmer treatment of the quenching of triplet SMBP by MMA in a micro-emulsion (line a) and the evolution of the ratio OD_0/OD_{∞} as a function of $[\text{MMA}]$ (line b) ($[\text{H}_2\text{O}]/[\text{AOT}] = 25$; $[\text{cyclohexanol}]/[\text{AOT}] = 7$).

where $k^{\text{obs}} \equiv \Sigma k = k_0 + k_H[\text{ROH}] + k_Q[\text{MMA}]$, OD_0 and OD_∞ are the optical densities at zero time and after complete decay of the triplet and ϵ_T and ϵ_K are the extinction coefficients of the triplet and ketyl species at the wavelength considered (540 nm).

The experimental data are processed according to the above procedures and the results derived are as follows.

(i) From the Stern-Volmer treatment of the triplet lifetime the rate constant k_Q for quenching by MMA is estimated to be $1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, a value significantly less than that obtained for reverse micelles of AOT-decane-MMA (Fig. 7, line a).

(ii) The quenching constant k_Q derived from the concurrent quenching treatment is equal to $1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 7, line b).

(iii) The ratio ϵ_T/ϵ_K is estimated to be 2.4.

The good agreement between the values of k_Q obtained from the two different probes in the system and the reasonable estimation of ϵ_T/ϵ_K provide proof of self-consistency.

4. Conclusion

As seen from this paper, several interactions must be taken into account to describe this system as satisfactorily as possible. Most of the interactions are present in homogeneous solutions and also in direct micelles. However, the relative importances of the interactions are significantly affected by going to reverse microheterogeneous assemblies. In particular, the rate of the quenching process taking place between an acrylic monomer (MMA) and a water-soluble carbonyl compound (SMBP) is slowed down to such an extent that photoinitiation of photopolymerization of this monomer in reverse micelles should not be disturbed by this type of interaction. In effect, although the system MMA-SMBP does photopolymerize in reverse micelles, much more work is still needed to optimize the photopolymerization. Studies are now in progress with this objective, the results of which will be reported in a forthcoming paper.

Acknowledgments

One of us (D.J.L.) thanks the National Research Council of Canada (NRCC) for support received as a guest worker in the Department of Chemistry of NRCC in Ottawa. We are grateful to Mr. S. E. Sugamori for his technical assistance and to Dr. P. N. Green for the gift of a pure sample of SMBP.

References

- 1 D. G. Whitten, *Angew. Chem., Int. Edn. Engl.*, **18** (1979) 440.
- 2 J. K. Thomas, F. Grieser and M. Wong, *Ber. Bunsenges. Phys. Chem.*, **82** (1978) 937.
- 3 N. J. Turro, M. Graetzel and A. Braun, *Angew. Chem., Int. Edn. Engl.*, **19** (1980) 675.

- 4 K. Kalyanasundaram, *Chem. Soc. Rev.*, 7 (1980) 453.
- 5 S. S. Atik, M. Nam and L. A. Singer, *Chem. Phys. Lett.*, 67 (1979) 75.
- 6 N. J. Turro and A. Yekta, *J. Am. Chem. Soc.*, 100 (1978) 5951.
- 7 P. P. Infelta, *Chem. Phys. Lett.*, 61 (1979) 88.
- 8 D.-J. Lougnot, P. Jacques and J. P. Fouassier, *J. Photochem.*, 19 (1982) 59.
- 9 D. Hindmann and J. Jacobus, *Tetrahedron Lett.*, 17 (1974) 1619.
P. A. Brugger and M. Graetzel, *J. Am. Chem. Soc.*, 102 (1980) 2461.
D. G. Whitten, D. W. Eaker, B. E. Horsey, R. H. Schmehl and P. R. Worsham, *Ber. Bunsenges. Phys. Chem.*, 82 (1978) 858.
- 10 K. Mandal and J. N. Demas, *Chem. Phys. Lett.*, 84 (1981) 410.
M. P. Pileni, *Chem. Phys. Lett.*, 81 (1981) 603.
- 11 J. K. Thomas, *Acc. Chem. Res.*, 10 (1977) 133.
- 12 R. Breslow, S. Kitabatake and J. Rothbard, *J. Am. Chem. Soc.*, 100 (1978) 8156.
J. C. Scaiano and E. B. Abuin, *Chem. Phys. Lett.*, 81 (1981) 209.
- 13 B. Krautler and N. J. Turro, *Chem. Phys. Lett.*, 70 (1980) 270.
N. J. Turro, D. R. Anderson and B. Krautler, *Tetrahedron Lett.*, 21 (1980) 3.
H. Hayashi, Y. Sakaguchi and S. Nagakura, *Chem. Phys. Lett.*, 72 (1980) 1149.
N. J. Turro, K.-C. Liu and M. F. Chow, *Photochem. Photobiol.*, 26 (1977) 413.
P. R. Worsham, D. W. Eaker and D. G. Whitten, *J. Am. Chem. Soc.*, 100 (1978) 7091.
J. C. Scaiano and J. C. Selwyn, *Photochem. Photobiol.*, 34 (1981) 29.
- 14 P. de Mayo, J. Miranda and J. B. Sothers, *Tetrahedron Lett.*, 22 (1981) 509.
F. M. Menger, J. M. Jerkunica and J. C. Johnston, *J. Am. Chem. Soc.*, 100 (1978) 4676.
- 15 J. C. Scaiano and J. C. Selwyn, *Can. J. Chem.*, 59 (1981) 2368.
- 16 K. H. Lee and P. de Mayo, *Photochem. Photobiol.*, 31 (1980) 311.
D. Avenir, L. J. Johnston, P. de Mayo and S. K. Wong, *J. Chem. Soc., Chem. Commun.*, (1981) 958.
- 17 D.-J. Lougnot, A. Merlin, P. Jacques and J. P. Fouassier, *Makromol. Chem., Rapid Commun.*, 1 (1980) 687.
A. Merlin and J. P. Fouassier, *Polymer*, 21 (1980) 1363.
C. E. Larabee, Jr., and E. D. Sprague, *J. Polym. Sci., Polym. Lett. Edn.*, 17 (1979) 749.
- 18 P. J. Curtis, *Biochim. Biophys. Acta*, 255 (1972) 833.
K. Martinek, A. V. Levaskov, N. L. Kluachko and I. V. Berezin, *Dokl. Akad. Nauk S.S.S.R.*, (1978) 236.
P. P. Luisi, F. J. Bonnier, A. Pellegrini, P. Wiget and R. Wolf, *Helv. Chim. Acta*, 62 (1979) 740.
- 19 J. P. Fouassier and D.-J. Lougnot, *Polym. Photochem.*, 3 (1983) 79.
R. A. Caldwell, *J. Phys. Chem.*, 92 (1969) 1439.
G. Amirzadeh, R. Kuhlmann and W. Schnabel, *J. Photochem.*, 10 (1979) 133.
I. E. Kochevar and P. J. Wagner, *J. Am. Chem. Soc.*, 94 (1972) 3859.
- 20 P. Barker, R. A. Bottom, J. T. Guthrie, A. A. Godfrey, P. N. Green and J. R. A. Young, *Res. Discl.*, 93 (1981), no. 20221.
- 21 J. C. Scaiano, *J. Am. Chem. Soc.*, 102 (1980) 7747.
- 22 J. H. Fendler, E. J. Fendler, G. A. Infante, P. Sushih and L. K. Patterson, *J. Am. Chem. Soc.*, 97 (1975) 89.
- 23 S. G. Frank and G. Zografis, *J. Colloid Interface Sci.*, 29 (1969) 27.
M. Zurlauf and H.-F. Eicke, *J. Phys. Chem.*, 83 (1979) 480.
T. Assih, F. Larché and P. Delord, *J. Colloid Interface Sci.*, 89 (1982) 35.
- 24 J. C. Scaiano, E. B. Abuin and L. C. Stewart, *J. Am. Chem. Soc.*, 104 (1982) 5673.
- 25 D.-J. Lougnot, P. Jacques, J. P. Fouassier and J. C. Scaiano, submitted to *J. Phys. Chem.*
- 26 A. J. Frank, M. Graetzel and J. J. Kozak, *J. Am. Chem. Soc.*, 98 (1976) 3317.
P. P. Infelta, M. Graetzel and J. K. Thomas, *J. Phys. Chem.*, 78 (1974) 190.