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# Interaction of methyl orange with cationic micelles and its effect on dye photochemistry

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**Abstract**

The interaction of the azo dye methyl orange with cationic and anionic surfactant micelles was studied by absorption and emission spectroscopy. The dye interacts strongly with the cationic micelles cetyltrimethylammonium chloride (CTAC) and cetyltrimethylammonium bromide (CTAB), but does not interact with the anionic micelle sodium dodecylsulphate (SDS). The association constants of the dye to CTAC and CTAB micelles are $5.6 \times 10^4$ and $5.9 \times 10^5$ respectively. The fluorescence quenching of pyrene by methyl orange in CTAC micellar solution occurs via non-radiative energy transfer. The variation of the relative fluorescence intensity agrees well with a model in which the dye is almost completely associated with the micellar phase. The photolysis of an aqueous solution of the dye in the presence of acetone gives rise to an irreversible photoreduction of the azo dye by the ketyl radical formed during photolysis. The presence of CTAB micelles reduces the photodecomposition rate of the dye. This effect is ascribed to the micellar cage effect which inhibits the second-order disproportionation reaction of the hydrazo compound formed.

*Keywords:* Methyl orange; Micelles; Photoreduction; Fluorescence quenching

## 1. Introduction

Azo dyes are a versatile class of coloured organic compounds which have been extensively used in the dyeing of synthetic fibres as well as in the formulation of many industrial pigments [1]. The investigation of the photophysical and photochemical properties of azo dyes is important for understanding their chemical photostability. It is well known that several azobenzene derivatives may undergo cis–trans photoisomerization, with partial fading of the colour in the visible region due to the formation of the cis isomer which usually absorbs strongly in the UV region [2,3]. In addition to cis–trans photoisomerization, several different reaction pathways of azo dyes can occur depending on the photolysis conditions [2,3]. For instance, when photolysis is performed in the presence of strong acids, azobenzene and other derivatives undergo photochemical cyclization by a disproportionation mechanism [2]. In aerated solutions, the presence of singlet oxygen can lead to photo-oxidative fading of the dye [4]. Photoreduction via hydrogen abstraction, which ultimately results in irreversible destruction of the azo bond, is also a well-known photoreaction for this class of compound [2,5].

Although these processes have been studied in homogeneous solution, interest in the photophysics and photochemistry of azo dyes in non-homogeneous solutions has appeared more recently [6–11]. The investigation of the photoisomerization and thermal isomerization processes of azobenzene derivatives in polymer matrices and liquid crystals is of current interest, in particular due to the use of these photoresponsive molecules as optical image storing devices [10,11]. Photocyclization in zeolite cavities and photoreduction in the presence of colloidal CdS have also been investigated [8,9]. Furthermore, a great deal of research has been devoted to the study of the interaction of azo dyes in micro-heterogeneous systems such as macromolecules in solution and cyclodextrins [12–16]. The characterization of the physical and chemical properties of azo dyes in the presence of these systems facilitates an understanding of their photochemistry.

In this paper, the interaction of the azo dye methyl orange with cationic micelles and its effect on the photochemical properties are presented. Steady state absorption and emission spectroscopy measurements are used to investigate the interaction of methyl orange with micelles. In the fluorescence emission measurements, the dye is used as a quencher of the singlet excited state of pyrene. Results are reported on the

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photoreduction of methyl orange in aqueous and micellar solution under different experimental conditions, such as in the presence of $O_2$ and acetone.

## 2. Experimental details

Methyl orange (Polyscience) was used as received. The surfactants sodium dodecylsulphate (SDS) (Merck) and cetyltrimethylammonium chloride and bromide (CTAC, CTAB) (Sigma and Aldrich) were recrystallized from acetone–ether (1 : 1) mixtures. Pyrene was recrystallized from benzene and kept in a desiccator. Milli-Q water was used to prepare all solutions. Acetone (Merck) was used as a triplet sensitizer of the azo dye for irradiated samples.

Working solutions were prepared by adding, via a microsyringe, the appropriate amounts of concentrated stock solutions of the dye in water and pyrene in methanol to the surfactant solutions, followed by sonication.

Absorption measurements were performed on a Hitachi U-2000 spectrophotometer. Fluorescence spectra were recorded on a Aminco-Bowman J8 spectrofluorometer. Fluorescence decays of pyrene were obtained by excitation at 330 nm using a nanosecond $H_2$ flash lamp (Edinburgh Instruments CD-900 single-photon-counting equipment). The decay profiles were analysed using standard deconvolution programs for exponential and biexponential decays. The photolysis experiments were carried out in a Rayonet photochemical mini-reactor (RMR-600) using a light source with a spectral energy distribution centred on 254 nm. When necessary, oxygen was removed from the samples by flowing $N_2$ prior to illumination.

## 3. Results and discussion

### 3.1. Interaction of methyl orange with surfactants investigated by absorption and emission spectroscopy

Pronounced changes in the UV–visible spectra of the dye are observed in dilute aqueous solutions of methyl orange on addition of the cationic surfactants CTAB and CTAC. Fig. 1 shows the spectral shift of the absorption maximum of a methyl orange dye solution on addition of CTAC, and Fig. 2 presents the change in absorbance at 428 nm at different dye to cationic surfactant ratios.

At low surfactant concentration (below the critical micelle concentration, cmc), the observed changes can be ascribed to the formation of dye–surfactant ion pairs and large aggregates containing the dye in a dimeric or higher aggregation state [17]. Close to the cmc, the spectral maximum of the dye shifts towards that observed

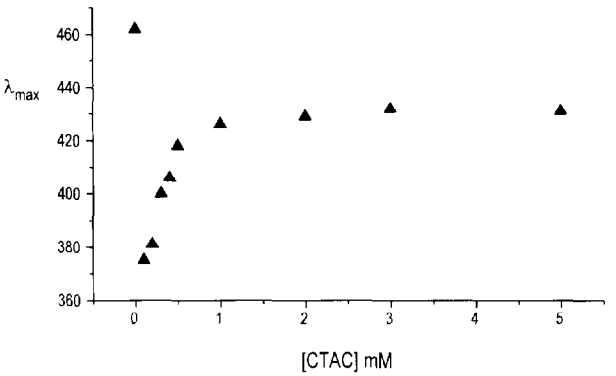



Fig. 1. Spectral shift of the absorption maximum of a methyl orange dye solution as a function of CTAC concentration.

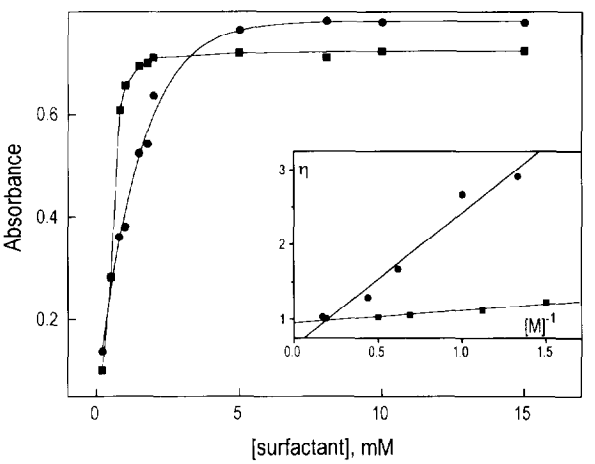



Fig. 2. Change in the absorbance of methyl orange at 428 nm in aqueous solution ($3\times10^{-5}$ M) as a function of surfactant concentration: •, CTAC; ■, CTAB. Inset: data treatment according to Eq. (7).

in pure water due to the nucleation of surfactant molecules onto the premicellar aggregates with the formation of normal micelles. In this process, the dye is redistributed over the micelles formed. The spectral changes observed are typical of general dye behaviour in the presence of surfactants of opposite charge [17–21].

No spectral changes are observed on addition of the anionic surfactant SDS. In aqueous solution at neutral pH, methyl orange is an anionic species. Thus the electrostatic repulsion between surfactant and dye does not allow for the formation of ion pairs, and the propagation to premicellar aggregates.

The dye redistribution process over the micelles formed may be represented approximately by the following equilibrium

$$A + M = M' \quad (1)$$

where A is the surfactant–dye premicellar aggregate, M is a normal micelle which nucleates onto the aggregate and M′ is the resulting micelle containing all the surfactant and dye molecules. At equilibrium

$$K_a = \frac{[M']}{[A][M]} \quad (2)$$

where $K_a$ is defined as the association constant of the dye to the micellar pseudophase.

At a high surfactant concentration, the dye will be completely loaded in the micellar pseudophase. In this saturation limit, the absorbance at a given wavelength is

$$A_m^{\infty} = \epsilon_m^{\lambda}[C_t]L \quad (3)$$

where $\epsilon_m^{\lambda}$ is the molar absorptivity coefficient of the dye in the micellar phase, $[C_t]$ is the analytical dye concentration and $L$ is the optical path length. The absorbance at the lowest surfactant concentration is related to the dye which forms premicellar aggregates, and may be represented approximately by

$$A_a = \epsilon_a^{\lambda}[C_t]L \quad (4)$$

where $\epsilon_a^{\lambda}$ is the molar absorptivity coefficient of the premicellar aggregates. At any intermediate surfactant concentration, the absorbance will be given by

$$A = \epsilon_m^{\lambda}[M']L + \epsilon_a^{\lambda}[A]L \quad (5)$$

Using the conservation relation

$$[A] + [M'] = [C_t] \quad (6)$$

together with Eqs. (2)–(5), the following expression can be derived

$$\eta = \frac{A_m^{\infty} - A_a}{A - A_a} = 1 + (K_a[M])^{-1} \quad (7)$$

The association constant $K_a$ is determined from a plot of $\eta$ against $[M]^{-1}$. The micelle concentration [M] formed on addition of surfactant may be calculated by dividing the surfactant concentration increment by the aggregation number of the micelles close to the cmc. In the present treatment, we have assumed that the aggregation numbers of CTAC and CTAB are 80 and 90 respectively. The inset in Fig. 2 shows a plot according to Eq. (7). The values obtained for the association constant of methyl orange with CTAC and CTAB micelles were $5.6\times10^4$ and $5.9\times10^5$ respectively. These values are within the range observed for the association of various kinds of dyes to micelles and polyelectrolytes [21,22].

The time-resolved profile of the quenching of pyrene by methyl orange in CTAC micelles is shown in Fig. 3. It is composed of a fast decay due to intramicellar quenching in the subset of micelles containing one excited pyrene and at least one dye molecule, and a slow decay related to the fraction of micelles which are free of dye but contain pyrene. The inverse of the fast decay time is about $4\times10^8$ $s^{-1}$. This value is much higher than that predicted for an intramicellar diffusion-controlled quenching process in CTAC spherical micelles [23], so that this fast decay component should be related to quenching via non-radiative energy transfer [24]. An increase in the micellar concentration leads to a dilution of the dye and pyrene micellar occupancy, thereby reducing the contribution of the short decay component which is ascribed to intramicellar quenching by an energy transfer process. Under these experimental conditions, the fluorescence intensity observed in continuous excitation experiments will be determined mainly by the fraction of micelles containing the fluorophore but free of quencher molecules. If we assume that the dye molecules are distributed over the micelles according to a Poisson distribution law, the relative fluorescence intensity in this limit is reduced to the Perrin limit [25]

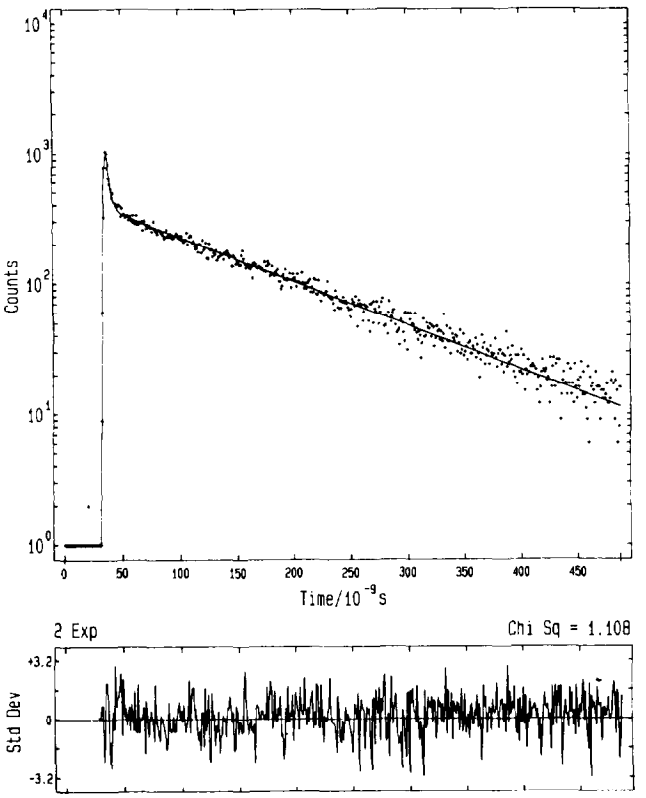



Fig. 3. Fluorescence quenching of pyrene ($1.5\times10^{-5}$ M) by methyl orange ($10^{-4}$ M) in CTAC solution ($6.0\times10^{-3}$ M). Biexponential fitting resulted in decay times of 2.52 and 128 ns.

$$\frac{I_o}{I} \approx \exp[\bar{n}] \quad (8)$$

where $\bar{n}$ is the average number of quencher molecules per micelle. In the present case, the dye has a high affinity for the micellar phase of CTAC as demonstrated previously. In such a situation, $\bar{n}$ can be calculated from

$$\bar{n} = \frac{[dye]}{[M]} = N_{agg}\frac{[dye]}{([Surf] - cmc)} \quad (9)$$

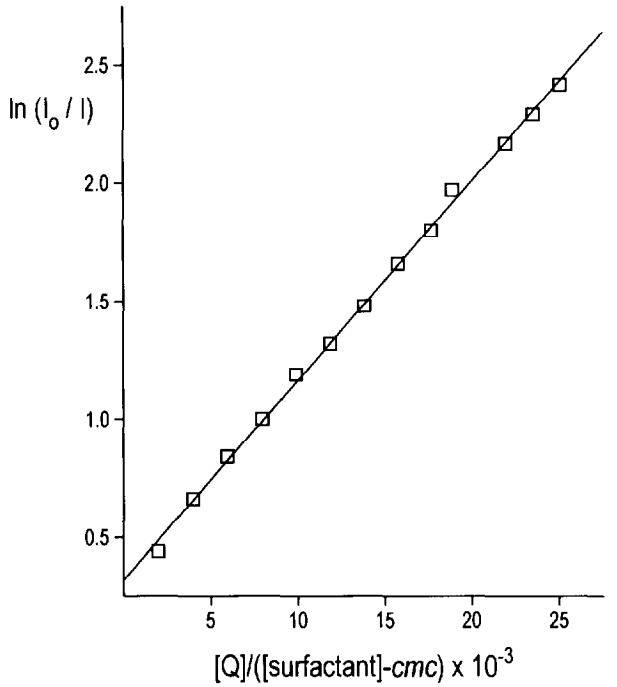



Fig. 4. Relative fluorescence intensity of pyrene ($1.5\times10^{-5}$ M) in CTAC solution ($3.0\times10^{-3}$ M) as a function of the ratio of the dye to micellized surfactant. The line shows the linear fitting according to Eq. (8).

where [dye], [Surf], cmc and $N_{agg}$ are the analytical concentration of the dye and surfactant, the critical micelle concentration and the aggregation number of CTAC micelles respectively. It follows that a logarithmic plot of the relative fluorescence intensity vs. [dye]/([Surf]−cmc) should be linear with a slope equal to $N_{agg}$. Fig. 4 shows this plot, and a value of $N_{agg}=84\pm2$ is obtained. This value agrees well with previously reported values of the aggregation number of CTAC micelles in this surfactant concentration range [26].

### 3.2. Photolysis experiments

When dilute aqueous solutions of methyl orange containing acetone are irradiated with UV light, fading of the dye is observed. After irradiation, samples stored at 40 °C in the dark recover less than 2% of their initial absorbance. This indicates that the changes observed cannot be ascribed to the isomerization of the dye. In experiments in which oxygen is removed from the dye solution, faster fading of the dye is observed. On the other hand, the photodecomposition rate of the dye is reduced by about 40% in experiments in which CTAB micelles are present. Fig. 5 shows plots of the absorbance at 462 nm as a function of time in these experiments. It should be noted that, in both water and CTAB air-equilibrated solutions, the initial rates follow zero-order kinetics with respect to the dye concentration, while in the absence of oxygen, a first-order process is observed. Changes in the concentration of acetone (0.5, 1, 2, 3 and 5 vol.%) do not alter appreciably the zero-order rate constant for the photodecomposition of methyl orange in aqueous solution. However, in the absence of acetone fading of the dye does not occur. Fig. 6 shows a plot of the spectral changes in the visible region observed during irradiation of the dye in water in the presence of 2 vol.% of acetone. The photodecomposition rate constants determined for the different experimental conditions are summarized in Table 1. An interesting point is that the rate constant in aqueous CTAC solution is 30%–40% lower than that observed in the absence of surfactant.

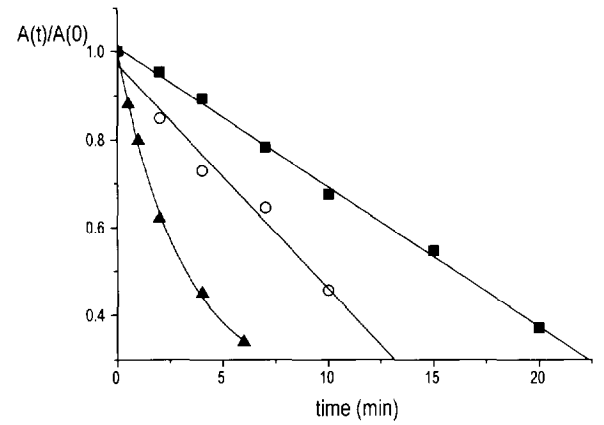



Fig. 5. Relative absorbance of methyl orange ($[C_1]=4\times10^{-5}$ M) vs. irradiation time in different photolysis conditions: ○, air-equilibrated aqueous solution; ▲, degassed aqueous solution; ■, $2\times10^{-2}$ M CTAB. All solutions contain 3 vol.% of acetone. $\lambda_{max}$ in water is 462 nm; $\lambda_{max}$ in CTAB solution is 428 nm.

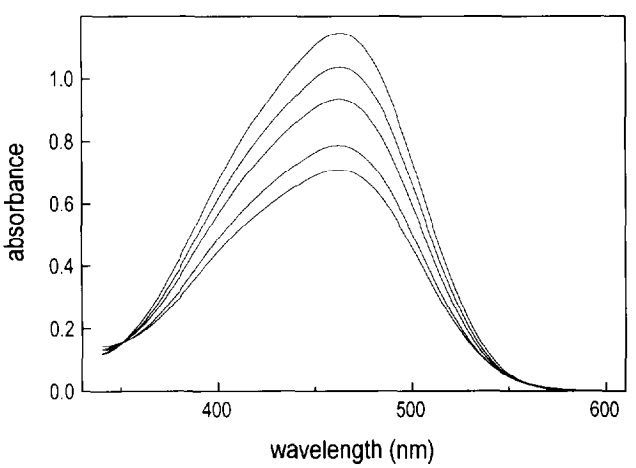



Fig. 6. Methyl orange spectra after different irradiation times.

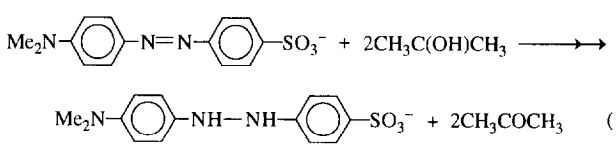
Recently, Peral and Mills [9] have observed that the photoreduction of methyl orange in the presence of CdS is faster in the absence of $O_2$. The initial rate of reduction is zero order with respect to the dye concentration.

Since oxygen is an effective quencher of the triplet state of many compounds due to its very low triplet

Table 1
Zero- and first-order rate constants for the photodecomposition of methyl orange in different experimental conditions

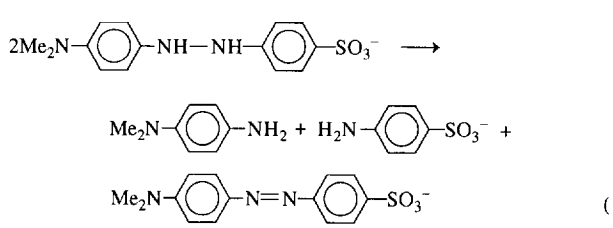
| Conditions | $k^0/C_t$ ($s^{-1}$) | $k^1$ ($s^{-1}$) |
|---|---|---|
| Water + 3% acetone, air-equilibrated | 0.051 | |
| Water + 3% acetone, degassed | | 0.327 |
| CTAC (20 mM) + 3% acetone | 0.037 | |
| CTAB (20 mM) + 3% acetone | 0.032 | |
| Water + 2% acetone + KBr (5 mM) | | 0.313 |
| Water + 2% acetone + KBr (10 mM) | | 0.265 |
| Water + 2% acetone + KBr (40 mM) | | 0.232 |
| Water + 2% acetone + $NaNO_3$ (10 mM) | 0.0558 | |
| Water + 2% acetone + $NaNO_3$ (20 mM) | 0.0513 | |
| Water + 2% acetone + $NaNO_3$ (30 mM) | 0.0505 | |
| Water + 2% acetone + $NaNO_3$ (40 mM) | 0.0482 | |

energy, it may be assumed that the triplet states of the dye and acetone are important precursor species in the photoreaction. In the previous section, it has been demonstrated that methyl orange interacts strongly with cationic micelles, and is almost completely associated with the micellar phase. The acetone triplet has a lifetime of about 4200 ns in pure water. However, this lifetime is reduced to 1700 and 1240 ns in 0.01 and 0.05 M CTAC solutions respectively [27]. The quenching process involves the photoreduction of the acetone triplet by the surfactant giving rise to a ketyl radical. Most of the triplets are generated in the aqueous pseudophase, and are extremely mobile species in micellar solution, with exit and entry rate constants above $10^8\ s^{-1}$ and $10^{10}\ M^{-1}\ s^{-1}$ respectively [27]. Ketyl radicals can also be formed by hydrogen abstraction from the ground state. It is well known that ketyl radicals are efficient hydrogen donors and can reduce azobenzene dyes [2]. In the present case, this reaction would be



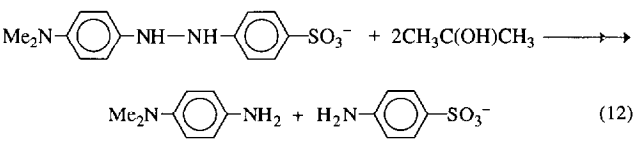
(10)

The reaction product is an unstable hydrazo compound which may be converted into one molecule of the original azo dye and two molecules of amino compounds by a disproportionation reaction



(11)

or be reduced by ketyl radicals



(12)

The observed decrease in the rate constants in the presence of added salt ($NaNO_3$ and KBr up to 40 mM) can be traced to the competition between reactions (11) and (12). The disproportionation of the charged hydrazo compounds should increase at higher ionic strength. Nevertheless, this reaction will re-form one molecule of the original dye, whereas the reduction reaction with ketyl radicals will decompose all of it. Thus an increase in the former reaction will result in a decrease in the overall decomposition rate of the dye.

On the other hand, the hydrazo compound can revert to the azo dye by oxidation in air-saturated solution. This fact, and also the observation of the highest stationary acetone triplet concentration in $O_2$-free solution, would explain why, in degassed solution, the photodecomposition rate is larger than in air-equilibrated solution. The less effective photodecomposition rate in the presence of cationic CTAB micelles could be ascribed to the intrinsic property of the micellar solutions. It is well known that micelles provide a molecular cage which allows compartmentalization of reactants. The surfactant solution containing acetone, on irradiation at 254 nm, will generate acetone triplet mostly in the aqueous pseudophase. As these are extremely mobile species, they will enter into the micelles and be quenched by the surfactant molecules or by the dye which is almost exclusively solubilized in the micellar pseudophase.

Since hydrogen abstraction by the triplet state of the azo dye has a low quantum yield, the most probable reaction pathway will involve the reduction of the dye by ketyl radicals, as shown in Eq. (10).

The decrease in the rate of the irreversible photodecomposition of the dye in micellar solution could be explained if the disproportionation reaction is partially inhibited by the micellar cage effect. At a low dye to micelle concentration ratio, micelles will be mostly free of dye or contain a single dye molecule. In this situation, no more than one molecule of hydrazo compound will be formed on a given micelle. The disproportionation reaction will only occur when two molecules of hydrazo compound are in the same micelle, and this condition is a function of the dye occupancy, the intermicellar migration rate of the hydrazo compound and the oxidation rate. The difference between the rate constants in CTAC and CTAB may be a result of the highest degree of micellar association, and hence less effective intermicellar migration of the hydrazo compound, in CTAB solution than in CTAC solution. However, the small difference between the fading rate in aqueous

and micellar solution may be ascribed to opposing factors operating in the micellar phase. On the one hand, the cage effect inhibits the disproportionation reaction. However, once two molecules of hydrazo compound are present in the same micelle, their intrinsic disproportionation rate constant may be higher than in the aqueous phase due to the electrostatic shielding of the anionic hydrazo compound provided by the ionic micellar surface.

## 4. Conclusions

In this investigation of the photochemistry of the azo dye methyl orange, it has been demonstrated that the dye interacts strongly with the cationic micelles CTAC and CTAB with estimated association constants of about $5.6\times10^4$ and $5.9\times10^5$ respectively. The high affinity of the dye for cationic micelles is confirmed by fluorescence quenching experiments employing pyrene as the probe and the dye as the quencher. The photolysis of aqueous solutions of the dye in the presence of acetone gives rise to irreversible photoreduction of the azo dye by the ketyl radical formed during photolysis. Experiments in the presence of CTAB micelles result in lower photodecomposition rates of the dye than in the absence of added surfactant. The less effective fading rate in micellar CTAB solution is explained by the micellar cage effect which reduces the second-order disproportionation reaction of the hydrazo compound formed.

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