

## BROMIDE ION QUENCHING OF MICELLIZED HYDROCARBON FLUORESCENCE: A SEARCH FOR EFFECTS OF EMITTER LIFETIME ON THE QUENCHING BEHAVIOUR

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### Summary

A study is made of the quenching by bromide ions of the fluorescence of the aromatic hydrocarbons anthracene, azulene, naphthalene, ovalene, perylene and triphenylene solubilized in the cationic micelle cetyltrimethylammonium bromide. Quenching is observed with all the hydrocarbons except perylene, indicating that the fluorescence lifetime has little effect on the quenching behaviour. The fact that quenching is observed even with the short-lived azulene  $S_2$  fluorescence rules out a quenching mechanism involving diffusion of aromatic hydrocarbon from the centre of the micelle to the micellar surface. The behaviour can, however, be explained on the basis of a channel model in which the aromatic hydrocarbon distorts the micellar structure to produce a water-filled channel down which quencher ions can penetrate. Stern-Volmer plots for the quenching are non-linear, partly due to the fact that the concentration of bromide ion in the Stern layer is not directly proportional to the total bromide concentration. In addition, it is suggested that contributions to the quenching from aromatic hydrocarbon in both micellar and aqueous phases are important.

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### 1. Introduction

Recently, considerable interest has been shown in the luminescence of aromatic hydrocarbons in aqueous micelles [1] and in the quenching of such luminescences by suitable ions or molecules [2 - 7]. For quenching by ions of the fluorescences of hydrocarbons solubilized in charged micelles, it is observed that quencher ions of opposite charge to the micelle are more ef-

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fective than ions of the same charge, reflecting the importance of ions in the micellar electrical double layer in the quenching process [2, 4]. The ionic quenching rate has been found to increase with the total quencher concentration in a non-linear fashion, and this has been interpreted in terms of a multiple-equilibrium model for the equilibration of the quencher ion between the solution and the electrical double layer [7]. Two models have been presented for the quenching process. Graetzel and Thomas [4] have suggested that, for quenching to occur, the excited aromatic hydrocarbon has to diffuse from its equilibrium position within the micelle to a quencher ion situated at the micelle-water interface. This model has subsequently been criticized by Rodgers and da Silva [6], largely on the basis that the diffusion process is too slow to account for quenching in such cases as iodide ion quenching of the pyrene singlet state in cetyltrimethylammonium bromide (CTAB) micelles [6]. In this case the fluorescence lifetime can be reduced to 13 ns, whereas calculations using the model given in ref. 4 gave a lower limit of 90 ns for the lifetime of pyrene quenched in the micelle by a diffusion-controlled process. Rodgers and da Silva [6] have proposed an alternative model in which the solubilized hydrocarbon perturbs the micellar structure; a water-filled channel is introduced and the lipid-water interface in this channel may lie close to the hydrocarbon. Quenching then occurs via diffusion of the quencher ion into this channel. Spectral studies on pyrene solubilized in various micelles [8, 9] strongly suggest that water penetrates close to the site of solubilization of the aromatic molecule.

Both of these models were introduced originally to attempt to explain quantitatively the quenching of the excited singlet state of pyrene, a molecule which has a particularly long fluorescence lifetime. Our objectives were to study the quenching of the fluorescence of solubilized hydrocarbons which have a wide range of singlet-state lifetimes, so that any effects that the lifetime may have on the quenching kinetics could be identified. We chose quenching by bromide ions of hydrocarbons solubilized in CTAB micelles, and used the technique of steady state luminescence quenching because this affords great sensitivity in studying small variations in lifetimes for short-lived fluorescences. It has previously been observed that steady state quenching and lifetime studies give comparable results in quenching studies of the CTAB system [7].

## 2. Experimental

The aromatic hydrocarbons, potassium bromide, sodium fluoride and CTAB were either of scintillation grade or of the most pure commercially available grade. They were used without further purification. Triply distilled water was used for the preparation of all solutions.

To avoid problems associated with changes in the micellar structure with changing ion concentration [10], the CTAB concentration was kept at  $2 \times 10^{-3}$  mol dm<sup>-3</sup> which is just above the critical micelle concentration.

Whilst there may be slight changes in micellar size with varying ionic concentration under these conditions, there are no electrolyte-induced phase changes in the aggregate, in contrast with the behaviour at high surfactant concentrations [5].

The hydrocarbons were dissolved in micellar systems by stirring warm solutions (approximately 60 °C) of the micelles in the presence of a few crystals of hydrocarbon for about 20 h and then filtering off undissolved hydrocarbon. The hydrocarbon concentrations were determined from electronic absorption spectra. Because of potential problems from aging of the micelles and from slow equilibration of the micellar systems on dilution [11], solutions were prepared by adding microlitre quantities of concentrated quencher solution directly to known volumes of freshly prepared micellized hydrocarbon solutions in the fluorescence cells. The quenching data were corrected for the slight volume change this process introduced. The solutions were degassed by bubbling with nitrogen.

Fluorescence spectra were recorded in 1 cm cells on a Perkin-Elmer MPF-3 spectrofluorimeter. The sample cell was thermostatted at  $30 \pm 0.5$  °C in all cases, except for the variable temperature studies on anthracene.

### 3. Results and discussion

The fluorescence spectra of anthracene, azulene, naphthalene, ovalene, perylene and triphenylene solubilized in  $2 \times 10^{-3}$  mol dm<sup>-3</sup> CTAB solutions were recorded. The emission spectra in all cases were similar to those recorded for monomer fluorescence in homogeneous solution. Relevant details of concentrations, literature fluorescence lifetimes, and excitation and emission wavelengths used in the quenching studies are given in Table 1.

TABLE 1

Aromatic hydrocarbon concentrations, excitation and emission wavelengths used in fluorescence quenching studies in  $2 \times 10^{-3}$  mol dm<sup>-3</sup> CTAB, and fluorescence lifetimes in solution

Hydrocarbon	Concentration (mol dm <sup>-3</sup> )	$\lambda_{\text{excit}}$ (nm)	$\lambda_{\text{emiss}}$ (nm)	$\tau$ (ns) <sup>a</sup>
Anthracene	$1 \times 10^{-5}$	360	390	4.9
Azulene	$1 \times 10^{-4}$	336	370	1.4 <sup>b</sup>
Naphthalene	$3 \times 10^{-4}$	356	410	53
Ovalene	$1 \times 10^{-6}$	360	430	360 <sup>c</sup>
Perylene	$6 \times 10^{-5}$	413	430	6.4
Triphenylene	$4 \times 10^{-5}$	338	360	36.6

<sup>a</sup> Values in degassed cyclohexane solution taken from ref. 12 unless otherwise stated.

<sup>b</sup> For S<sub>2</sub> fluorescence.

<sup>c</sup> Value obtained for ovalene in an epoxy resin at room temperature by the extrapolation of Fig. 4 in ref. 13.

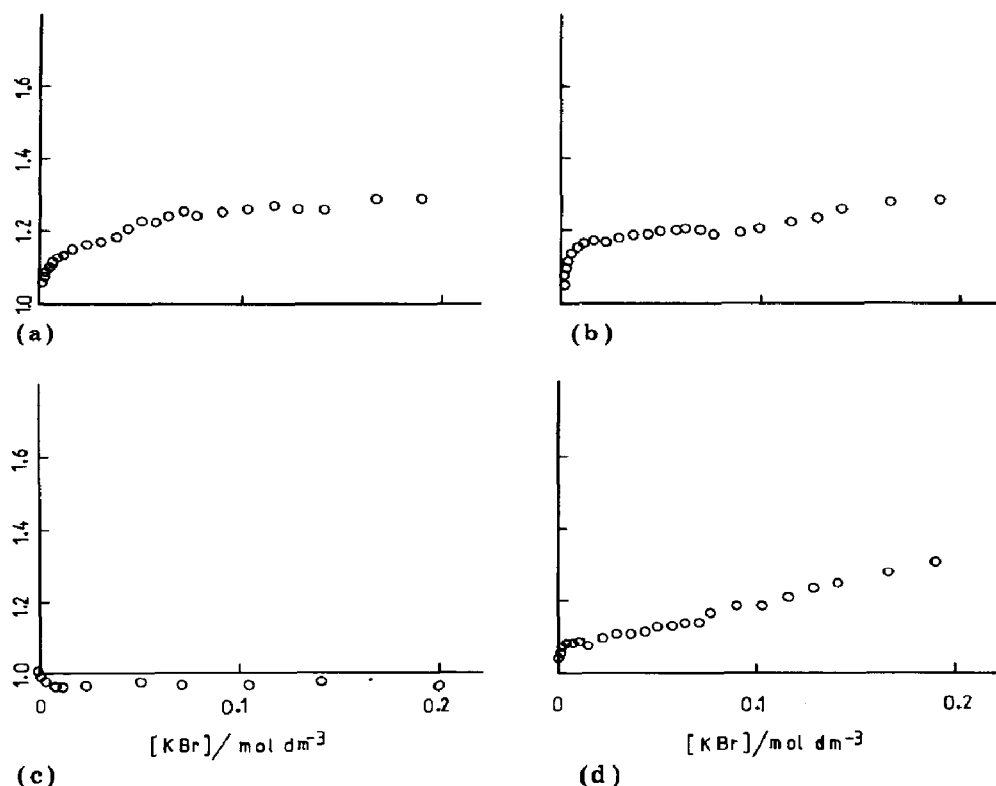


Fig. 1. Stern-Volmer plots for the quenching of the fluorescence of aromatic hydrocarbons in degassed  $2 \times 10^{-3}$  mol dm $^{-3}$  CTAB micelles by KBr at 30 °C: (a) naphthalene; (b) ovalene; (c) perylene; (d) triphenylene.

The fluorescences of these solutions were studied in the presence of potassium bromide of concentration varying between approximately  $10^{-3}$  mol dm $^{-3}$  and 0.2 mol dm $^{-3}$ . In spite of the wide range of fluorescence lifetimes, quite strong quenching was observed in all cases except for perylene. To obtain further information on the kinetic dependence of the quenching, the data were analysed in the form of Stern-Volmer plots (Figs. 1 - 3). As in the case of fluoranthene [7], the plots were non-linear. This has been interpreted using a multiple-equilibrium model in terms of the non-linear relationship between the concentration of effective quencher ions in the Stern layer and the total bromide ion concentration [7].

An alternative explanation for the non-linear behaviour is that changing the ionic strength alters the micellar size [14], and that the fluorescences of the hydrocarbons solubilized in the micelles of different sizes are quenched with different efficiencies. However, studies of fluorescence quenching by halide ions of micellized hydrocarbons at constant ionic strength have revealed similar non-linear behaviour [7], supporting the idea that, at this surfactant concentration, the main origin of the non-linearity is the relationship between the quencher ion and the total ion concentration.

As temperature is observed to alter the micellar size [14], the quenching of anthracene was studied at 30, 40 and 50 °C (Fig. 3). Although the

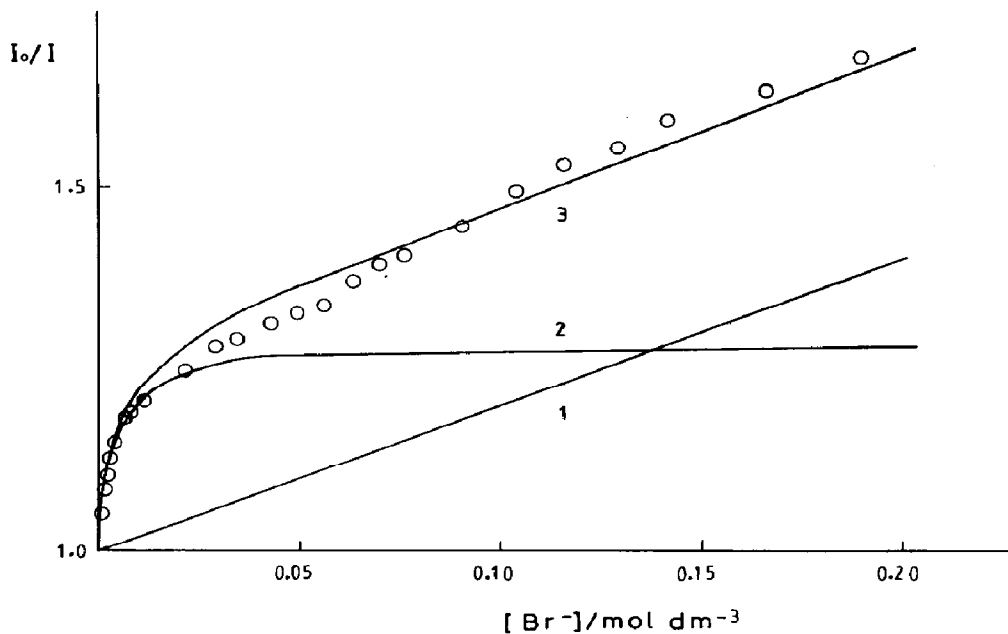


Fig. 2.  $\circ$ : Experimental data for the quenching by bromide ion of the fluorescence of azulene in degassed  $2 \times 10^{-3}$  mol  $dm^{-3}$  CTAB at 30 °C. Simulation of azulene quenching behaviour: curve 1, the contribution to the quenching by azulene molecules in the aqueous phase; curve 2, the contribution to the quenching by azulene molecules in the micelle; curve 3, simulated quenching of azulene in both phases using eqn. (4).

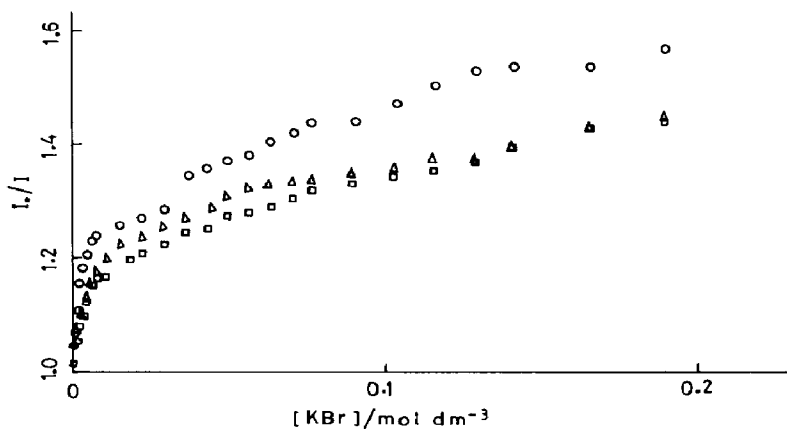


Fig. 3. Stern-Volmer plots for the quenching of the fluorescence of anthracene in degassed CTAB micelles by KBr at various temperatures:  $\circ$ , 30 °C;  $\square$ , 40 °C;  $\triangle$ , 50 °C.

slope at high bromide concentrations appears to be slightly steeper at 30 °C, the overall form of the graphs at the three temperatures seems to be quite similar.

Since quenching has been suggested to occur only via ions in the Stern layer, it may be anticipated that, if a non-quenching ion such as fluoride is added instead of bromide ion to the micellar system, fluoride will replace

bromide in the Stern layer and lead to an increase of the fluorescence intensity\*. The fluorescence spectra were recorded of a solution of anthracene in  $2 \times 10^{-3}$  mol dm<sup>-3</sup> CTAB and of the same solution in the presence of 0.17 mol dm<sup>-3</sup> sodium fluoride. In agreement with predictions, whilst the shapes of the spectra were the same in both cases, in the presence of F<sup>-</sup> ion the emission intensity increased by a factor of two because of replacement of Br<sup>-</sup> by F<sup>-</sup> in the Stern layer. This parallels the increases in fluorescence lifetime of micellized fluoranthene [7] and anthracene [3] observed upon addition of chloride ions to the CTAB solutions.

In both models which have been presented to explain the quenching by ions of the fluorescence of aromatic hydrocarbons solubilized in charged micelles it is suggested that quenching occurs via ions in the Stern layer. However, in one model [4] it is suggested that quenching occurs by diffusion of excited hydrocarbon from its equilibrium position in the micelle to the micellar surface, whilst in the other [6] it is suggested that inclusion of the solute in the micelle distorts the structure and creates water-filled channels down which quencher ions can penetrate. In cyclohexane solution the hydrocarbons studied have fluorescence lifetimes varying between 1.4 and 360 ns. However, in all cases except perylene, bromide ion is observed to quench the fluorescence of the solubilized hydrocarbon. The fact that quenching is observed even in the case of the short-lived azulene singlet state suggests quite strongly that the model for quenching involving diffusion of excited aromatic solute [4] cannot be used in these systems, since the calculated minimum diffusion time (90 ns) is considerably longer than the fluorescence lifetime of many of the hydrocarbons studied in this work. In contrast, with the channel model [6] the root mean square displacement of a Br<sup>-</sup> ion in water is given by

$$(\overline{x^2})^{1/2} = (2Dt)^{1/2} \quad (1)$$

Using a diffusion coefficient  $D$  of  $2 \times 10^{-9}$  m<sup>2</sup> s<sup>-1</sup>, this means that during the lifetime of excited azulene (the fluorescer with the shortest lifetime studied in this work) the bromide ion could be up to 2.4 nm from the fluorescer and still give quenching<sup>†</sup>. This distance can be compared with the micellar radius of about 2 nm, indicating that the model can satisfactorily explain the observed behaviour by considering that the ions in the Stern layer are responsible for the quenching.

As has been noted previously [3], no significant quenching by Br<sup>-</sup> was found for the micellized perylene singlet state. The Stern-Volmer constant

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\*It should be noted that the fluorescence lifetime of triphenylene solubilized in  $5 \times 10^{-3}$  mol dm<sup>-3</sup> CTAB ( $\tau = 9.6$  ns [15]) is considerably shorter than that in cyclohexane ( $\tau = 36.6$  ns [12]), demonstrating that Br<sup>-</sup> counter-ions from CTAB are efficient quenchers even in the absence of any added bromide ions.

<sup>†</sup>It is assumed that quenching is diffusion controlled in this case. Whilst we have been unable to obtain any information on the quenching of <sup>1</sup>azulene\* by bromide, the quenching of the azulene fluorescence by a wide range of other quenchers has been found to be diffusion controlled [16].

for the quenching of the perylene fluorescence by bromide ions in 10% ethanol-water is approximately  $1 \text{ dm}^3 \text{ mol}^{-1}$  [17] from which, using the fluorescence lifetime in water [3], a quenching rate in this solvent of about  $2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  can be estimated. This is close to the rates of bromide ion quenching of the fluorescence of many of the other hydrocarbons in this study [18]. Perylene has a relatively short lifetime and, as suggested by Patterson and Vieil [3], the hydrocarbon is probably solubilized at a site far from the micelle-water interface -- in terms of the channel model it may be imagined that distortion of the micellar structure for perylene does not give any significant water-filled channel, but occurs instead via rearrangement of the hydrocarbon chains of the micelle around the perylene. It should be noted that the perylene lifetime in CTAB [3] is similar to that in hydrocarbon solvents [12].

In earlier studies on the quenching of the fluoranthene fluorescence by bromide ions in CTAB micelles [7], the Stern-Volmer plots were observed to plateau at high bromide concentrations. Such simple behaviour was not, however, observed in this work. The studies of Hautala *et al.* [2] on quenching of the naphthalene singlet state in ionic micelles provide considerable insight into what could be happening. They found two fluorescence decays, one corresponding to naphthalene inside the micelle and one corresponding to naphthalene in aqueous solution [2]. Different quenching characteristics are observed in the two phases. In aqueous solution simple bimolecular quenching occurs, whilst in the micelle the quenching may be expected to show similar behaviour to fluoranthene [7]. The forms of the Stern-Volmer plots in the present study can be clearly understood if it is assumed that there is a similar partitioning of the hydrocarbon between the aqueous phase and the micellar phase; then these are composite plots for quenching in the two phases. We have attempted to analyse this theoretically for the case of azulene. In aqueous solution the quenching is expected to follow normal Stern-Volmer behaviour:

$$(I_0/I)_{\text{aq}} = 1 + K_{\text{sv}}[\text{Br}^-] \quad (2)$$

The equation has to be modified for micellized azulene, because only bromide ions in the Stern layer are effective in quenching. The bromide ion concentration in the Stern layer can be related to the total ion concentration using a multiple-equilibrium model [7], from which a modified Stern-Volmer equation can be obtained for the quenching of micellized azulene:

$$(I_0/I)_{\text{mi}} = 1 + \frac{K'_{\text{sv}}nK[\text{Br}^-]}{1 + K[\text{Br}^-]} \quad (3)$$

where  $K'_{\text{sv}}$  is the Stern-Volmer constant for quenching in the micelle,  $n$  is the number of active sites per micelle and  $K$  is an association constant. Combining eqns. (2) and (3) and allowing for the partitioning of azulene between the two phases, an expression for the quenching in both phases as a function of the ion concentration can be obtained:

$$(I_0/I)_{\text{total}} = 1 + A[\text{Br}^-] + \frac{B[\text{Br}^-]}{1 + K[\text{Br}^-]} \quad (4)$$

$A$  and  $B$  are the products of the Stern–Volmer terms in eqns. (2) and (3) and the fraction of azulene molecules in the aqueous phase and the micellar phase respectively. A reasonable fit with the experimental data was obtained with  $A = 2.00 \text{ dm}^3 \text{ mol}^{-1}$ ,  $B = 80 \text{ dm}^3 \text{ mol}^{-1}$  and  $K = 220 \text{ dm}^3 \text{ mol}^{-1}$  (Fig. 2). Theoretical plots for the quenching in each of the two phases are also included in this figure.

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