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Combined kinetic and spectroscopic study of oxidation of azo dyes in surfactant solutions by hypochlorite

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Abstract

Combined kinetic, spectroscopic and thermodynamic investigations have been carried out to examine the influence of cationic, anionic and nonionic surfactants upon the oxidation of an azo dye, **II**, by hypochlorite. Oxidation rates were unaffected by the presence of anionic or nonionic surfactant (SDS or $C_{12}E_5$) either in micellar or submicellar regions: indicating the absence of any specific dye–surfactant interactions. On the other hand, specific interactions were observed with cationic surfactants, both in submicellar and micellar regions. Addition of CTAts to dye **II** produced a reduction in intensity of its UV–vis spectrum and caused oxidation rates to decrease. These are attributed to formation of a sparingly soluble 1:1 complex with the dye, via interactions with the sulfonate groups. Binding of DTAC to the dye in sub-micellar regions results in a slight enhancement in oxidation rates, which is attributed to break-up of small, soluble dye aggregates. In micellar regions, there was evidence that the dye becomes incorporated into the surface of micelles formed by both cationic surfactants, where they become inert to reaction with hypochlorite.

Keywords: Azo dyes; Hypochlorite; Cationic, amonic and nonionic surfactants; pK_A; UV spectroscopy; Kinetics

1. Introduction

Earlier investigations elucidated the mechanism of oxidation of azo dyes in alkaline solution by a range of oxidants, with particular emphasis upon the nature of the reactive species and the factors controlling oxidation [1–6]. This work is extended in this paper to include azo dye oxidation in the presence of cationic, anionic and nonionic surfactants in both submicellar and micellar concentration regions.

A number of recent studies have featured physico-chemical investigations of dye/surfactant interactions [7,8] and their oxidation by hydrogen peroxide or hypochlorite [9,10]. In particular, a potentiometric study was made [7] of the interactions of azo dyes containing a net negative charge (Orange II and Acid Red 88) with the cationic surfactants cetylpyridinium chloride (CPC) or dodecylpyridinium chloride (DPC) and with the anionic surfactant, sodium dodecyl sulfate (SDS). The technique utilised ion-selective electrodes to monitor surfactant monomer activities in submicellar regions to determine surfactant binding to the dyes.

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It was demonstrated that CPC quantitatively forms a 1:1 complex of low solubility with Orange II and that DPC binds much more weakly, possibly involving cooperative interaction between bound surfactant molecules. Overall, it was suggested that non-coulombic interactions make a sizeable contribution to the free energy of binding between cationic surfactants and the anionic dyes, a view generally accepted. On the other hand, no evidence was obtained for any interaction between SDS and Orange II in submicellar regions, presumably due to electrical repulsion.

Other investigations [8] have used UV–vis spectroscopy and focussed upon surfactant solutions above their critical micelle concentration; de-sulfonated Orange I was selected for examination as it exhibits an *azo-hydrazone* tautomeric equilibrium that is highly sensitive to changes in the immediate environment of the dye. Although the *hydrazone* form of Orange I dominates its UV–vis spectrum in water or in micellar solutions of anionic surfactant, the *azo* form is disproportionately displayed in micellar solutions of long chain nonionic surfactant ($C_{16}E_{20}$) — or in mixed anionic/nonionic micellar solutions. This suggests that Orange I becomes incorporated into the surface of nonionic-rich micelles.

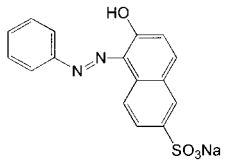
The oxidation of the azo dye, 1-(2-methylphenyl-azo)-2-hydroxy-3,6-naphthalene disulfonate by hypochlorite has been reported [9] in the presence of cationic, anionic and zwitterionic surfactants, namely dodecyl trimethylammonium bromide (DTAB) sodium dodecyl sulfate (SDS) and 2-(dodecyl-methylamino)-ethane-1-sulfate (SDAS). It was reported that spectral peaks due to the dye rapidly decreased in intensity upon addition of DTAB (or CTAB) and this, surprisingly, was interpreted in terms of immeasurably fast dye oxidation rates. It was also concluded that micelles did not influence observed rates. However, in our view, insufficient experimental detail was reported for firm conclusions to be drawn and certain key factors were not considered, in particular:

1. the authors recorded measurements at λ_{max} rather than the dye isosbestic point and did not report the pH at which experiments were recorded, nor how it was controlled,
2. the authors did not consider formation of large, sparingly soluble dye aggregates or precipitation by surfactants — which may equally be responsible for the rapid loss in intensity of the dye UV–vis spectrum, and
3. the influence of surfactants upon the dye pK_A was overlooked.

A further study examined the influence of three surfactant types upon the oxidation of the azo dye, Orange **II**, by hydrogen peroxide in alkaline media [10]. It was concluded that cetyl trimethyl-ammonium bromide (CTAB) enhanced the rate of oxidation but the effects were largely confined to surfactant concentrations below the critical micelle concentration (cmc) and the enhancements were considerably reduced above the cmc. Similar effects were reported with the anionic and non-ionic surfactants dodecyl benzene sulfonate (DBS) and polyethyleneglycol mono *p*-octylphenylether (PEOPE). Overall, effects were small in all cases and appeared to be close to the limits of experimental error. The influence of surfactants on the UV–vis spectra of Orange II were also recorded but no attempt was made to separate effects due to complexation, aggregation or precipitation, the influence upon the dye pK_A or the influence of solubilisation into micelles.

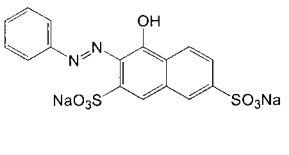
In this investigation, a more detailed and systematic investigation has been carried out of the influence of surfactants upon the oxidation of azo dyes. Particular attention has been paid to the influence of surfactants:

1. upon the dye pK_A — to examine whether rate enhancements arise from changes in dye speciation,
2. upon loss of the dye UV–vis spectral intensity due to formation of large, sparingly-soluble aggregates or formation of precipitates.
3. in promoting de-aggregation of small, soluble dye aggregates,
4. in changing UV–vis spectra due to forming complexes with the dye, and
5. above and below the cmc, particularly to examine whether localisation of reactants in micelles can enhance rates.



I

1-arylazo-2-naphthol-6-sulfonic acid (sodium salt)



II

2-arylazo-1-naphthol-3,6-disulfonic acid (sodium salt)

A special interest was to examine the observed rapid loss in dye absorbance [9] and in particular whether it arises from:

1. high observed rates due to increased concentrations of the reactive dye form — possibly as a result of formation of complexes between cationic surfactants and the reactive form of the dye, i.e. the common anion or phenolate form, or
2. the simple formation of complexes, followed by aggregation/precipitation.

All experiments, e.g. UV–vis spectra and oxidation rates, were determined over a wide pH range to explore key factors and to facilitate separation of the observed rate constant into absolute rate constants. Hypochlorite was investigated as oxidant since it behaves towards the dyes investigated like a typical peracid but is more reactive, i.e. oxidation is complete in comparatively short times, thus reducing the experimental errors that occur at longer times due to fluctuations in experimental conditions, e.g. pH control.

Two azo dyes were examined (**I**, **II**) which contain one and two sulfonate groups, respectively. These were selected to establish the stoichiometry for complexation with cationic surfactants and to probe the site of binding. Most of the work has been done with dye **II** as it has a structural motif that is representative of many commercial dyes and because the presence of two sulfonate groups reduces the likelihood of aggregation.[1]

Three surfactant types have been examined: the cationic surfactants cetyl trimethylammonium toluene sulfonate (CTAts, cmc = 0.92 mM) and dodecyl trimethyl ammonium chloride (DTAC, cmc = 16 mM) the anionic surfactant sodium dodecyl sulfate (SDS, cmc = 8 mM) and the nonionic surfactant, penta-ethyleneglycol mono *n*-dodecyl ether ($C_{12}E_5$, cmc = 0.065 mM). Toluene sulfonate (tosylate) or chloride counterions were chosen in preference to bromides to eliminate potential side reactions.

2. Experimental

2.1. Materials

CTAts (98%), DTAC (98%), SDS, (>99%) and $C_{12}E_5$ (>99%) were obtained from Sigma, Acros, BDH and Chesham Chemicals, respectively, all in the UK. Sodium hypochlorite solution (5% active chlorine) was obtained from Acros and dyes **I** and **II** (each 71% pure isomer, with the remainder NaCl and H_2O) were synthesised in-house as described previously [4]. EDTA (diaminoethane tetraacetic acid, disodium salt, >98%) was sourced from Sigma-Aldrich, again in the UK.

2.2. Determination of dye pK_A by UV–vis spectroscopy

The pH dependence of the absorption spectra in dilute dye solutions (up to 0.1 μM) was used to determine dye pK_As at 25°C. The method utilises the principle that where isosbestic points[2] are present, the spectra of the undissociated dye (HD) and the dissociated dye (D^-) are additive. Thus, one may write for the absorbance (A) at a given pH and wavelength:

$$A = \left(x_{(HD)}.A_{o(HD)}\right) + \left(x_{(D-)}.A_{o(D-)}\right) \quad (1)$$

where $x_{(HD)}$ and $x_{(D-)}$ are the mole fractions of HD and D^-, respectively, and $A_{o(HD)}$ and $A_{o(D-)}$ are the absorbance values of the pure forms HD and D^- measured at extreme values of pH, usually ~pH 4 and ~pH 13. With only two species present $x_{(D-)} = 1 - x_{(HD)}$ which, when substituted into

[1] Although the Beer–Lambert Law holds for these dyes, it does, not necessarily rule out a limited degree of aggregation. For example, related dyes form small, soluble aggregates, like dimers [11], over the concentration range of interest.

[2] Isosbestic points arise where dye spectra at differing pH values intersect at one or more characteristic wavelengths.

Eq. (1) and rearranged, gives:

$$x_{(HD)} = \left(A - A_{o(HD)}\right)/\left(A_{o(HD)} - A_{o(D-)}\right) \qquad (2)$$

The fractions $x_{(HD)}$ and $x_{(D-)}$ were calculated according to Eq. (2) at a given wavelength (λ_{max} of HD) and plotted versus pH. The pK_A value was determined graphically at the point where $x_{(HD)}$ and $x_{(D-)}$ were equal to 0.5, since pK_A is defined as the pH at which half the molecules are dissociated. A collection of UV–vis spectra exhibiting an isosbestic point due to ionisation of dye as the pH is increased is illustrated in Fig. 1.

Measurements were carried out in a double-walled glass water jacket, thermostatted with a digital reading circulator. A small overhead stirrer was used to achieve homogeneity. The pH was controlled by a VIT90 titration system in conjunction with a ABU93 autoburette and pH electrodes PHG201 and REF401, all by Radiometer. The dye solution was circulated with a peristaltic pump via silicone rubber tubing through a quartz flow cell (path length 10 mm) mounted in a double-beam Perkin-Elmer Lambda 14 spectrophotometer. The flow was maintained at such a rate that no significant temperature losses occurred between the reaction vessel and the flow cell. Solutions were prepared using water that was double-distilled from demineralised water using a Fisons 'Fi-Streem' 4BD Still.

In a typical pK_A determination 200 ml dye solution, containing 20 μM EDTA was adjusted to pH 3 with addition of a small volume of 10% sulfuric acid. The spectrum was recorded at 25°C once the temperature and pH had stabilised. The pH was raised in increments using small volumes of 0.2 M NaOH dosed using the autoburette. Spectra were thus obtained until the pH was so high that no further changes were observed. At elevated pH (>11) it was necessary to switch to manual addition of a more concentrated NaOH solution (10% w/v) to avoid diluting the dye solution, and above pH 12.5 solid NaOH pellets were added.

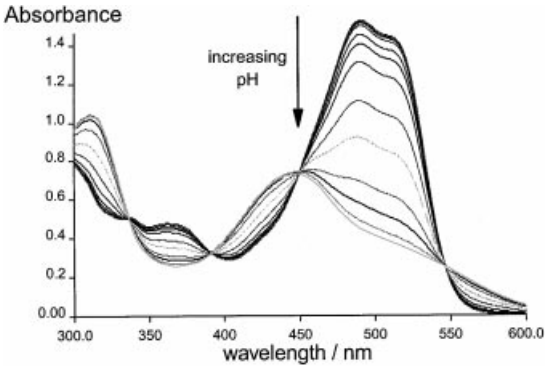


Fig. 1. UV–vis spectra of 50 μM dye **II** as a function of pH at 25°C. pH values range from 4 to 13.

2.3. Kinetic measurements

Oxidations of dye with NaOCl were carried out using the same experimental set up at 25°C in the presence of an 8-fold excess of hypochlorite, producing a pseudo first-order reaction with respect to [dye]. All experiments were carried out at low ionic strengths to minimise dye aggregation. Accordingly, the pH was maintained by the automatic addition of 0.2 M $NaOH_{(aq)}$ from a pH stat rather than with buffer solutions. The λ_{max} or, preferably, an isosbestic point was monitored (the absorbance at the isosbestic point is pH independent) depending on which was the more convenient.

In a typical reaction 200 ml of dye solution containing 20 μM EDTA was circulated for at least a minute to warm up the cell and tubing and to allow stabilisation of pH and temperature. At some pre-determined time, an aliquot of NaOCl solution, pre-adjusted to the reaction pH, was added such that [NaOCl] was 200 μM. The hypochlorite stock was titrated against standardised sodium thiosulfate and was diluted such that <1 ml in 200 ml would give the required concentration, again to avoid needless dilution of the dye solution. The absorbance was monitored at 3 s intervals for a period of 10–20 min.

The rate law for dye oxidation has been elucidated earlier [1,2]

$$\begin{aligned} -\mathrm{d[D]}/\mathrm{d}t &= k_2(\mathrm{obs})[\mathrm{HOC1}]_T.[\mathrm{D}]_T \\ &= k_2[\mathrm{HOC1}].[\mathrm{D}^-] \end{aligned} \qquad (3)$$

k_2(obs) is calculated from the time dependence of the absorbance [1,2]

$$k_2(\text{obs}) = \mathrm{d}(\ln A)/\mathrm{d}t/[\mathrm{HOCl}]_T \quad (4)$$

Absorbance is directly proportional to the dye concentration, so the rate of change in absorbance is equal to the rate of change of [dye]. The observed rate k_2(obs) (units M^{-1} s^{-1}) is found to pass through a maximum with pH and, using the hypochlorite and the dye pK_A values to calculate speciation, the rate constant k_2 is obtained from the best theoretical fit to the experimental results. The rate of hypochlorite bleaching of 25 μM dye **II** in the absence of surfactant was 9.7×10^3 M^{-1} s^{-1} (± 50%) using the determined pK_A value of 11.3. The error margin is large since the rate is very sensitive to the value of pK_A used in the calculations, because the concentrations of the reacting species are so low.

3. Results and discussion

3.1. Interactions with cationic surfactants

3.1.1. Precipitation of dyes *I* and *II* with CTAts

Upon addition of CTAts to dyes **I** and **II**, the UV–vis absorption spectrum rapidly reduces in intensity — even in the absence of an oxidant — and there is visible evidence for precipitate formation (Figs. 2–4). Evidently, a key factor in reducing the intensity of the UV–vis absorption spectrum is not oxidation of the dye, but complexation and ultimate precipitation with CTAts and the effect is observed at all pH values. The decrease in spectral intensity of the UV–vis spectrum for dye **I** (50 μM) at low pH is depicted in Fig. 2.

The influence of CTAts on the absorbance at λ_{max} (482 nm) of 50 μM dye **I** at pH 5–6 (where the dye is primarily in the hydrazone tautomeric form) is illustrated in Fig. 3.

This shows that there is a linear decrease in absorbance with increasing [CTAts]/[dye] up to a 1:1 ratio, where there is a 60% loss in intensity. As the dye is predominantly in the hydrazone tautomeric form, this suggests electrostatic interactions with the sulfonate group play a key role.

A similar plot is depicted in Fig. 4 for dye **II**, which contains two sulfonate groups, but in this case the total intensity loss is less (20%). Fig. 4 shows that the absorbance at λ_{max} (492 nm) of the hydrazone form of dye **II** (50 μM) at pH 5–6 linearly decreases with increasing [CTAts]/[dye] up to a 2:1 ratio. Evidently, complexes form with CTAts

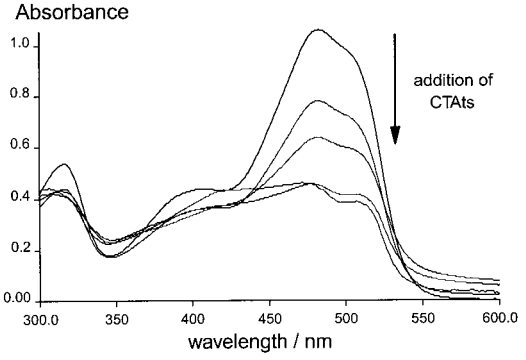


Fig. 2. UV–vis spectra of 50 μM dye **I** as a function of added CTAts at pH ~5 and 25°C.

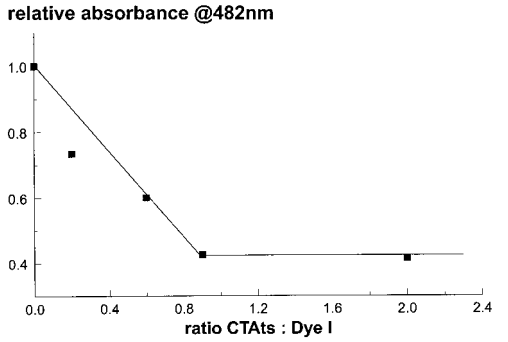


Fig. 3. Influence of CTAts on relative absorbance at λ_{max} of 50 μM dye **I** at pH ~5 and 25°C.

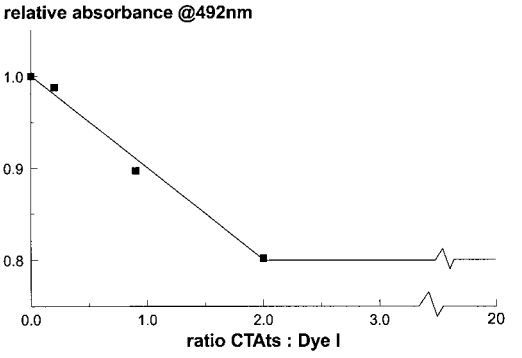


Fig. 4. Influence of CTAts on relative absorbance at λ_{max} of 50 μM dye **II** at pH ~5 and 25°C.

and dyes **I** and **II** with stoichiometry of 1:1 and 2:1, respectively. This reinforces the view that complexation between cationic surfactant and dye occurs with the negatively charged sulfonate groups, leading to ultimate precipitation.

Furthermore, as solution complexation alone is unlikely to lead to effects of the magnitude observed, the main source of intensity loss can be attributed to precipitation. The loss in intensity for dye **I** is higher than for dye **II** for two reasons:

1. dye **II** is more soluble than dye **I**, due to the presence of the extra sulfonate group, and
2. the free energy for surfactant binding to sulfonate groups is expected to be of similar magnitude in both cases.

There was no evidence of any precipitation or intensity loss when CTAts was replaced with the shorter chain cationic surfactant, DTAC, which has a lower free energy of surfactant binding [7]. However, there was spectroscopic evidence for formation of complexes in solution and this will be discussed later.

3.1.2. Influence of CTAts on kinetics of dye oxidation

A typical plot of k_2(obs) versus solution pH is illustrated in Fig. 5, which, in accordance with Eq. (3), exhibits a maximum at ~pH 9.2, which is halfway between the pK_A values of the oxidant and dye.

In general, the rate profiles measured using 25 μM dye **II** are more accurate than those for 50 μM dye **II** as the isosbestic points were better defined in the presence of CTAts, due to less aggregation/precipitation (see below). The maximum value of k_2(obs) (at pH 9.2) is plotted for 50 μM dye **II** as a function of [CTAts] in Fig. 6.

Clearly, observed rate constants decrease upon addition of CTAts, reaching a minimum at [CTAts] of 0.2–0.5 mM ([CTAts]:[D] = 4:1–10:1), then gradually increasing as the cmc is reached and exceeded.

Superimposed on Fig. 6 is a corresponding plot of the absolute rate constant k_2 determined using the dye pK_A obtained from the theoretical fit to measured rates (Table 1). This follows the same trend as k_2(obs) since there are no observed changes in pK_A values.

Whilst formation of insoluble complexes, sparingly-soluble dye aggregates or precipitation can result in a reduction in the intensity of the dye UV–vis spectrum, formation of soluble complexes can only do so if their extinction coefficients are substantially less than those of the original dye. On the other hand, the reduction in observed rates can only explained by the equilibrium formation of soluble complexes/aggregates if these complexes are less kinetically active. Consistent with this view, UV–vis spectra became much better resolved due to complexation (see below).

Although specific complexation could conceivably occur between cationic surfactant, CTA^+, and the dye common anion (D^-) (see Appendix A), there was no evidence for a reduction in pK_A of the residual solution spectrum either in micellar or

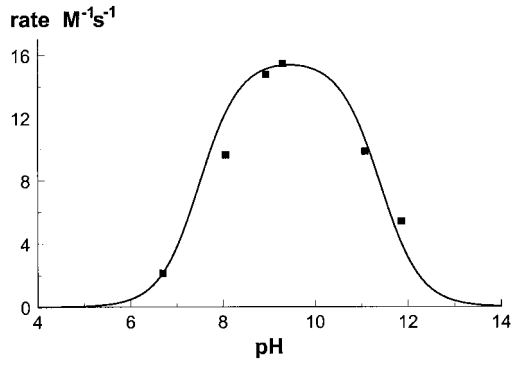


Fig. 5. Effect of pH on k_2(obs) for the oxidation of 25 μM dye **II** with sodium hypochlorite at 25°C.

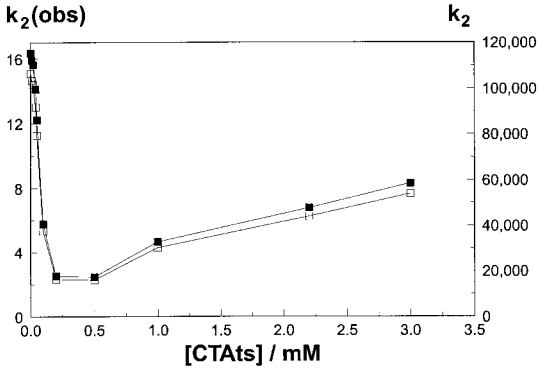


Fig. 6. Effect of [CTAts] on k_2(obs) ■ and k_2 □ for the oxidation of 50 μM dye **II** with sodium hypochlorite at 25°C and pH 9.2.

Table 1
Measured and derived dye pK_As and spectral peaks at visible wavelengths for dye **II** as a function of [DTAC]

[Dye] (μM)	[CTAts] (mM) (dye:CTAts)	pK_A (from spectra)	pK_A (from rate vs pH plot)[a]	A of HD[b]	HD peak resolved?[c]	HD, D peaks (nm)
50	9	11.1	11.1	1.51	No	(492, 510 sh) 448
50	0.01 (5:1)	11.17	–	1.50	No	(491, 511 sh) 449
50	0.045 (1:0.9)	11.03	–	1.36	No	(490, 511 sh) 448
50	0.050 (1:1)	–	11.5		—	—
50	0.100 (1:2)			1.22	Yes	(488, 515) 415
25	0	11.3	11.3	0.74	Slight	(496, 516 sh) 448
25	0.025 (1:1)	–	11.4		—	—
25	0.075 (1:3)	11.20	–	0.57	Yes	(492, 520) 498
25	0.10 (1:4)	12.8	–	0.56	Yes	(492, 520) 464
25	0.25 (1:10)	> 13	11.3	0.56	Yes	(492, 519) 471
25	1.0 (1:40)	> 13		0.58	Yes	(493, 519) 480

[a] pK_A that gave the closest fit between the experimental results and theoretical rate profile.
[b] Absorbance of the most intense peak (~490 nm) when all of the dye is in the HD form.
[c] The peak of the HD form has two peaks, the less intense peak being a shoulder on the main peak without CTAts present. The shoulder can resolve into a peak in the presence of CTAts, as the peak widths decrease.

sub-micellar concentration ranges, indicating it can be ruled out. Consequently, it is considered that solution complexes or aggregates are formed that solely involve electrostatic interactions between the sulfonate groups and cationic surfactant (see Appendix B).

For both dyes, it was found that as the CTAts: dye ratio increased there was evidence of loss of the isosbestic points and increasing dye aggregation, leading to an increase in the baseline up to 0.07 A at 600–700 nm (Fig. 2), indicating aggregates large enough to scatter light (> 600 nm in diameter). The aggregation also increased with increasing pH. Loss of isosbestic points due to pH-dependent precipitation/aggregation and an increase in the baseline at 600–700 nm are clearly evident in comparing Figs. 7a–c as the [CTAts]/[dye] ratio increases.

3.1.3. Formation of solution complexes with CTAts

To provide more insight into complexation of dye **II** by CTAts, further examination was carried out by UV–vis spectroscopy and pK_A values were determined at various [CTAts]/[D] ratios. First of all, it was noticed that the pK_A determined for 25 μM dye **II** was 11.3 as opposed to 11.1 at the higher concentration and the spectrum was slightly sharper, indicating that soluble aggregates are present at 50 μM dye. The results are given in Table 1. Secondly, as pH-dependent aggregation makes it difficult to get accurate rate vs pH profiles, the dye concentration was lowered to 25 μM to see if the aggregation decreased. The UV–vis spectra became sharper and better resolved at [CTAts]/[D] of > 2:1. (This was especially evident at the lower dye concentration where there is less precipitation.) The isosbestic point (455 nm) shifts to higher wavelength (Fig. 8a).

This indicates that complexation results in a sharpening and shifting of the observed spectrum and this may reflect restriction of the vibrational modes of the molecule upon complexation. Clearly, the UV–vis spectrum represents a superposition of uncomplexed and complexed species, which have similar extinction coefficients. Although the reduction in intensity is influenced by both precipitation and complexation in solution in the case of CTAts, later we shall see that complexation with DTAC causes only a small reduction in extinction coefficient.

In the presence of 75 μM CTAts the resolution was increased and the base increased to 0.12 A above pH 10, indicating aggregation. With 100

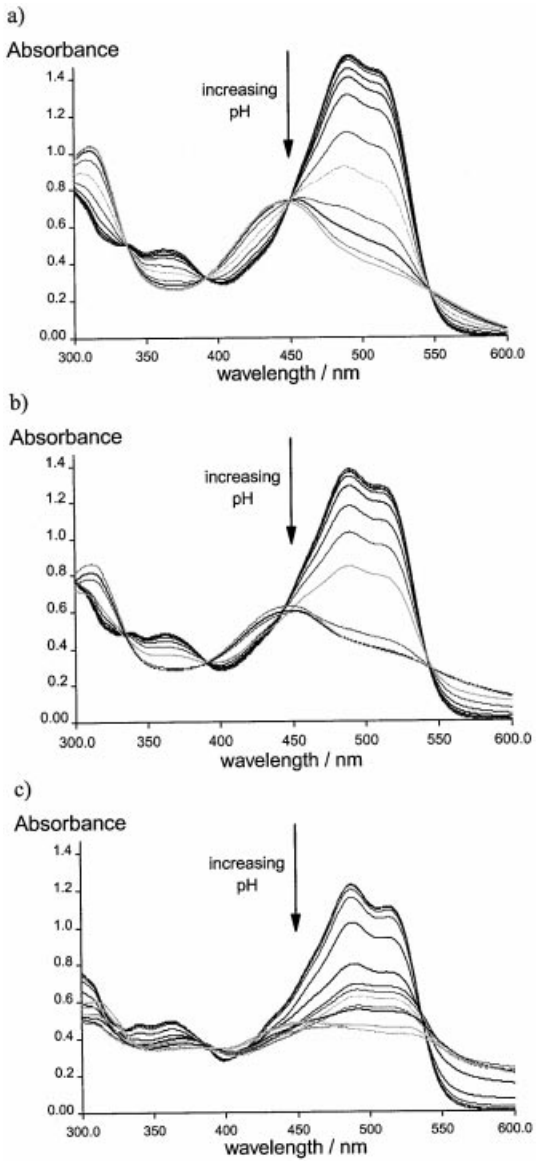


Fig. 7. UV–vis spectra of dye **II** in the presence of CTAts at 25°C as a function of pH: (a) 50 μM dye **II**, no CTAts, (b) 50 μM dye **II**, 50 μM CTAts (1:1), (c) 50 μM dye **II**, 100 μM CTAts (1:2).

μM CTAts, aggregation appears to decrease, isosbestic points are better defined and the baseline only rises to 0.03 A. With 250 μM there is only a slight baseline increase above pH 12 and the same is true with 1000 μM indicating aggregation is lessened using a lower dye concentration (Fig. 8a).

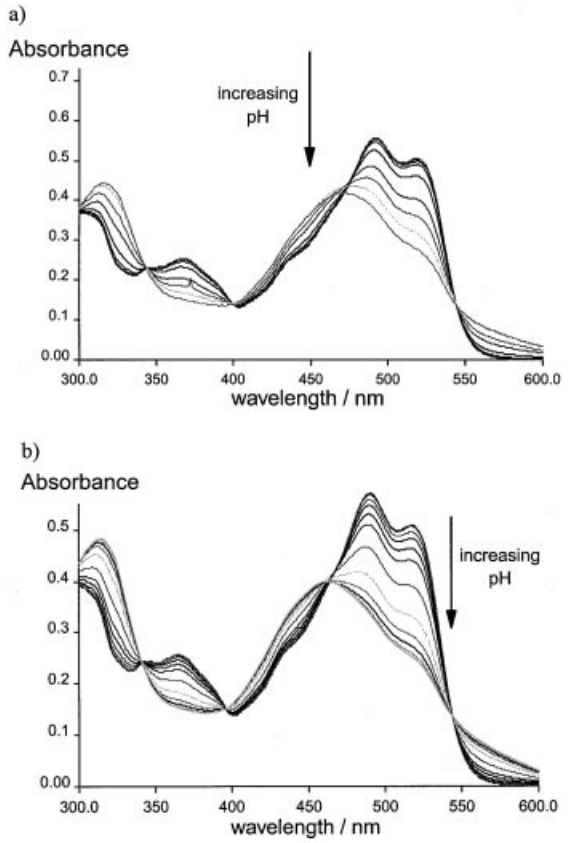


Fig. 8. UV–vis spectra of 25 μM dye **II** in the presence of CTAts or DTAC as a function of pH at 25°C: (a) 25 μM dye **II**, 1 mM CTAts (ratio 1:40); (b) 25 μM dye **II**, 5.25 mM DTAC (ratio 1:200).

Furthermore, extremely high pK_A values (~13) were obtained at [CTAts]/[D] ratios higher than 4 ([CTAts] > 0.1 mM), and all spectra are similar (Fig. 8a). However, the observed rate constant profile with pH can be fitted only by assuming the pK_A of the uncomplexed dye and not of complexed dye (Table 1). This indicates that the dye experiences two environments and suggests that it may be acting as a nucleating site for micelle formation, with micelle-bound dye not contributing to overall rates.

A typical plot is illustrated in Fig. 9 for DTAC and dye **II** (see below).

3.1.4. Summary for CTAts

Overall, it is concluded that loss in intensity of the UV–vis absorption spectra results from the

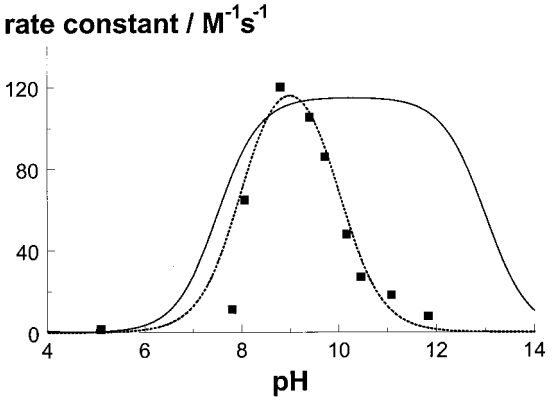


Fig. 9. Plot of observed second-order rate constants for the oxidation of 25 μM dye **II** with 0.2 mM NaOCl in the presence of 14 mM DTAC at 25°C. ■ = experimental data, the broken line is the theoretical fit for a dye pK_A of 11.6, the solid line is for a pK_A of 13.0.

formation of insoluble complexes, due to strong interactions of CTAts with sulfonates on the dye. The reduction in observed rates of oxidation arises initially from formation of complexes in solution — which may be aggregated to varying degrees — and subsequently from micelle formation in which dye acts as a template. Complexation results in an increase in spectral resolution and an increase in measured pK_A values to 13 above 0.1 mM CTAts. However, the pK_A determined from the rate vs pH profile appears to be fairly independent of [CTAts] indicating that there are two dye environments; the pK_A measured from the UV–vis spectra being an average of the two pK_As. The two environments are free dye in solution and immobilised dye: either aggregated or bound to micelle. Aggregated dye would be unable to react with the bleach, which would account for the rate decrease. The aggregates must be small (<400 nm diameter), as there is no shift in the baseline, and have a very similar UV–vis spectra to the free dye.

Evidently, UV–vis spectra are sensitive to (a) precipitation of dye: producing a reduction in intensity, and (b) to complexation in solution. These changes accompany changes in dye pK_A values and changes in spectral resolution. The analysis presented here indicates that observations made previously [9,10] can be interpreted accordingly.

3.1.5. Influence of DTAC on kinetics of dye oxidation

Unlike CTAts, DTAC does not induce precipitation of dye **II** at any concentration or pH. The UV/vis spectra show no baseline shift, or loss of isosbestic points at any of the DTAC concentrations measured. However, it does form soluble complexes, which influence the dye pK_A and UV–vis spectral resolution. (Table 2).

Inspection of Table 2 indicates that addition of DTAC causes an increase in the dye pK_A from 11.3–11.6 over the range 25–500 μM and there is a small detectable increase in spectral resolution. When the concentration of DTAC reaches 5mM, the measured pK_A sharply increases to >12.6, an observation common to CTAts just below its cmc. Similarly, at these concentrations, the UV–vis spectra become sharper and better resolved (though this happens at much lower concentrations with CTAts) and complexation produces a shift in the isosbestic point that represents the equilibrium with the common anion (Fig. 8b).

DTAC differs from CTAts not only in that it exhibits no loss in dye UV–vis spectral intensity but in measured dye oxidation rates, i.e. k_2(obs) actually increases in sub-micellar regions (Table 2).

Data in Table 2 also indicate that rate enhancements in the region 25–500 μM DTAC (dye:DTAC ratios from 1:1 to 1:20) reach a maximum at ~14 mM but diminish above the cmc. The enhancement in rates coincides with the increase in the dye pK_A from 11.3 to 11.6 (Table 2).

Although the Beer–Lambert Law holds good for dyes **I** and **II** over the concentration range of interest, we have earlier seen that initial dye solutions do, nonetheless, contain some degree of aggregation as do many similar dyes [11]. However, as there is no significant intensity loss, they are likely to be small, water-soluble aggregates. Thus the initial increase in observed rate constant up to 500 mM, the concomitant small increase in pK_A and the slight sharpening of spectral peaks are all indicative of de-aggregation of the dye due to formation of weak complexes between DTAC and dye **II**.

Interestingly, the increase in the pK_A would normally be expected to give rise to a rate decrease. This observation suggests that similar

Table 2
Measured and derived dye pK_As and spectral peaks at visible wavelengths for dye **II** as a function of [DTAC]

[Dye] (μM)	[DTAC] (mM) (dye:DTAC)	pK_A from spectra	pK_A from rate vs pH plot[a]	Abs of HD[b]	HD peak resolved?[c]	HD, D peaks (nm)	k_2(obs) (M^{-1} s^{-1})
25	0	11.3	11.3	0.74	Slight	(496, 516 sh) 448	15.8
25	0.025 (1:1)	11.6	11.6	0.75	Slight	(493, 512 sh) 451	18.9
25	0.050 (1:2)	11.55	11.55	0.75	Slight	(492, 511 sh) 449	16.2
25	0.500 (1:20)	11.65	11.6	0.72	Improving	(492, 512 sh) 451	59.0
25	5.25 (1:210)	> 12.6	10.4	0.57	Yes	(490, 518) 464	69.7
25	10 (1:400)	> 13.1	–	0.58	Yes	(490, 517) 466	86.0
25	14 (1:560)	–	11.1	–	–	–	124
25	17.5 (1:700)	> 12.6	–	0.59	Yes	(491, 517) 464	14.8
25	21 (1:840)	> 12.6	11.1	0.60	Yes	(491, 516) 469	6.4

[a] pK_A that gave the closest fit between the experimental results and theoretical rate profile.
[b] Absorbance of the most intense peak (~490 nm) when all of the dye is in the HD form.
[c] The peak of the HD form has two peaks, less intense peak being a shoulder on the main peak without DTAC present. The shoulder can resolve into a peak in the presence of DTAC as the peak widths decrease

rate enhancements observed elsewhere in sub-micellar regions [10] may have similar origin.

Around the cmc, the profile for k_2(obs) with pH can only be fitted assuming a pK_A of 11.6, even though measured pK_A values are ~13. A typical rate vs pH plot is given in Fig. 9. This observation parallels that with CTAts and evidently suggest that the dye experiences two environments above 5 mM (Table 2) and that the new environment does not contribute significantly to dye oxidation.

This suggests that the environment is micelle-like and the dye either becomes unreactive — possibly due to the higher pK_A — or because it is either inaccessible to HOCl, or that HOCl has insignificant concentrations at the micelle surface. The magnitude of the observed rate constant indicates that the dye bound to the micelles can be regarded as an entirely separate phase, i.e. any equilibrium between dye in these two phases is slowly established. The increased spectral resolution in the UV–vis spectrum is consistent with this view as the vibrational modes of the molecule will be restricted in a micelle-like environment. Thus it is suggested that the dye acts as a site for promoting micellisation and that this also explains the shift in pK_A. For example, complexation with the sulfonates may reduce their electron-withdrawing power and provide increased steric hindrance, two factors that are known to influence pK_A values [4]. Above the cmc, the micelle-like arrangement may be re-organised somewhat but it seems likely that the dye is located within the surface of the micelle.

3.1.6. Summary for DTAC

Overall, it is concluded that DTAC weakly interacts with sulfonates on the dye, resulting in some de-aggregation, leading to enhanced rates of dye oxidation and increasing dye pK_A values. DTAC interacts weakly, evidenced by a comparatively small increase in spectral resolution until a ratio of 20:1 [DTAC]/[dye] is reached. Above 5.25 mM DTAC the measured pK_A and the pK_A of the reacting species is different: the dye appears to be in two different environments, and the pK_A measured is an average of the two. This means that the UV–vis spectrum is a combination of the spectrum of the dye in the two environments, but the spectra are of a similar shape, with the complexed species having a slightly lower extinction coefficient than the dye in solution (Table 2). The dye's new environment is either an aggregate or in the top layer of a spherical micelle formed by the DTAC, with the sulfonates interacting with the ammonium ions in the head group and the rest of the dye molecule in the micelle. The sharpening and shifting of the UV–vis spectrum is evidence for this as the vibrational modes of the molecule will be restricted in the micelle and aggregates. The reduction in rate constant above the CMC of DTAC — returning close to the rate for pure dye —

Table 3
Increase in rate, $k_2(\text{obs})_{max}$ for oxidation of 25 μM dye **II** at pH ~9.1 and 25°C as a function of [SDS]

Rate, k_2(obs) (M^{-1} s^{-1})	17.2	17.3	19.7	22.4	26.5	25.3	26.7	30.0
[SDS] (mM)	0.0	16.0	32.0	62.5	100	125	160	204

suggests that (a) uncomplexed dye is present in the aqueous phase, (b) that oxidation occurs exclusively in the aqueous phase, and (c) that dye incorporated in micelles can be treated as a separate phase from that in solution.

3.2. Interactions with anionic and nonionic surfactants

Unlike cationic surfactants, no changes were observed in the dye pK_A, in the dye spectral resolution or in observed rate constants at all pHs in the sub-micellar regions of SDS or even at concentrations just in excess of the cmc. The results are consistent with earlier reports that SDS does not exhibit any interactions with dyes at submicellar [7] or micellar [8] regions, due to unfavourable electrostatic repulsion. However, inspection of Table 3 indicates that $k_2(\text{obs})_{max}$ for dye **II** does increase at higher SDS concentrations. This can be explained by the corresponding decrease in the dye pK_A (Table 4) since calculated absolute rate constant remains constant. This increase in $k_2(\text{obs})_{max}$ is explained by the increase in ionic strength of the solution at high SDS concentrations.

Table 4
Increase in effective pK_A of dye **II** as a function of [SDS]

[SDS] (mM)	pK_A determined experimentally	pK_A required for k_2(obs) to remain constant
0	11.3	—
100	10.9	11.08
200	11.1	11.03

No corresponding increase is evident in solutions of nonionic surfactant $C_{12}E_5$ and dye **II** (25 μM) at pH 9.3 and 25°C where the ionic strength remains low (Table 5). Indeed, there is little evidence at all for interactions between $C_{12}E_5$ and dye **II**, either in micellar or sub-micellar solutions (Table 5). This suggests that, unlike Orange I [8], it either does not become incorporated into the surface of nonionic micelles or that localisation into micelles does not hinder its reactivity towards HOCl. If the former, the presence of two sulfonate groups may confer higher solubility in the aqueous medium; if the latter, both reactants must be just as freely accessible in the micelle as in aqueous media.

4. Conclusions

A detailed analysis has been given of the factors influencing (i) UV–vis spectra of dyes, (ii) dye pK_A values, and (iii) the rates of oxidation by hypochlorite upon addition of surfactants. These are illustrated by reference to dye **II** in the presence of anionic, nonionic and cationic surfactants.

Overall, UV–vis spectra are sensitive to precipitation of dye — reducing in intensity — and to complexation in solution, producing improvements in spectral resolution. Complexation is also manifested in reduction in oxidation rates and by changes in dye pK_A values. The measured pK_A

Table 5
Effect on [$C_{12}E_5$] on $k_2(\text{obs})_{max}$ for oxidation of 25 μM dye **II** at pH ~9.3 and 25°C

[$C_{12}E_5$] (mM)	0.00	0.025	0.250	0.500	1.00
$k_2(\text{obs})_{max}$	19.7	19.6	19.9	18.2	19.1
Rate constant, k_2 ($HOCl/D^-$)	128 000	127 500	130 000	118 000	124 000

value in micellar solutions of cationic surfactant differs from that estimated from oxidation rate profiles with pH. This indicates that the dye experiences two environments: one where it is 'free' in aqueous solution and the other where it is incorporated into micelles, where it becomes inert to reaction with hypochlorite.

Appendix A. Complexation between cationic surfactant and dye common ion

$$DH \rightleftharpoons D^- + H^+ \tag{5}$$

$$CTA^+ + D^- \rightleftharpoons CTAD \tag{6}$$

$$\text{effective } pK_A = [H^+]([D^-] + [CTAD])/[DH] \tag{7}$$

Appendix B. Complexation between cationic surfactants and dye sulfonate groups

The appropriate rate law can be derived from Eqs. (3) and (6):

$$-d[D]/dt = k_2^u[HOC1][D^-] + k_2^c[HOC1][CTAD] \tag{8}$$

where superscripts u and c refer to uncomplexed and complexed dye, respectively.

Thus:

$$k_2\text{obs} = k_2^u[D^-]/[D^-]_T + k_2^c[CTAD]/[D^-]_T \tag{9}$$

where $[D^-]_T$ is the total dye concentration:

$$[D^-]_T = [D^-] + [CTAD] \tag{10}$$

If it is assumed that k_2^c is negligible, i.e. complexed dye is inactive, then it follows that the sevenfold reduction in rate means that a maximum of 14% of the dye remaining in solution is uncomplexed.

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