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Degradation of an Azo Dye by Sodium Hypochlorite in Aqueous Surfactant Solutions

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ABSTRACT

The degradation behaviour of sodium 1-(2-methylphenylazo)-2-hydroxy-3,6-naphthalenedisulphonate (o-TR) by sodium hypochlorite solution in the presence of three kinds of surfactants, viz. dodecytrimethylammonium bromide (DTAB), sodium dodecylsulphate (SDS), and sodium 2-(dodecylmethylamino)-ethane-1-sulphonate (SDAS) was investigated by means of visible absorption spectrum measurements. The degradation rate of o-TR was markedly dependent on the head groups of the surfactants. DTAB containing a quaternary ammonium head group significantly enhanced the degradation rate. SDS containing a sulphate head group enhanced the rate below the critical micelle concentration (CMC), whereas it did not change above CMC. SDAS containing a tertiary amino and suphonate group immediately degraded the dye existing outside of the micelle formed by SDAS, while the dye solubilized into the micelle remained without degradation. © 1998 Elsevier Science Ltd

Keywords: degradation, azo dye, surfactant, micelle, solubilization.

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INTRODUCTION

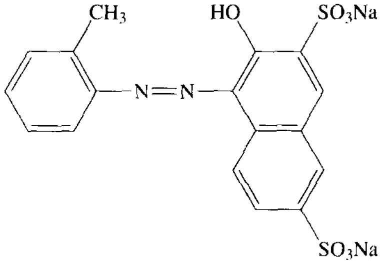
The degradation of water-soluble azo compounds by sodium hypochlorite was investigated in detail by Gregory and Stead [1], in which they determined the effect of pH on the reaction rate, the number of molecules of sodium hypochlorite involved in the decolorization reaction, and the nature of the decomposition fragments. Recently Kanazawa and Onami studied the degradation of Orange G and benzopurpurine and discussed the rate equation and kinetic values such as rate constants, activation energies and frequency factors [2]. Furthermore, the effects of surfactants [3] and water-soluble polymers [4] on the dye degradation were investigated, in which the mechanism of retardation and acceleration was argued.

In our previous paper [5], the effects of [3,3]- and [6,6]-ionene on the degradation of 1-(2-methylphenylazo)-2-hydroxy-3,6-naphthalene-disulphonate (*o*-TR) by sodium hypochlorite were studied. This study elucidated that the aggregation of the dye on the ionene chain depressed the degradation.

In the present study, the degradation of *o*-TR in the presence of dodecyltrimethylammonium bromide (DTAB), sodium dodecylsulphate (SDS), and sodium 2-(dodecymethylamino)ethane-1-sulphonate (SDAS) was investigated by means of visible absorption spectrum measurements. The effects of these surfactants on the rate constants and the activation energies are discussed.

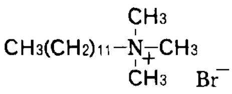
EXPERIMENTAL

The dye, 1-(2-methylphenylazo)-2-hydroxy-3,6-naphthalenedisulphonate (*o*-TR), was prepared as was described in the previous paper [5].



o–TR

Three kinds of surfactants, *viz.* dodecytrimethylammonium bromide (DTAB), sodium dodecylsulphate (SDS), and sodium 2-(dodecylmethylamino)ethane-1-sulphonate (SDAS) were used.

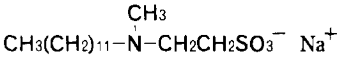


$$CH_3(CH_2)_{11}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3\ \ Br^-$$

DTAB

$CH_3(CH_2)_{11}-OSO_3^-\ Na^+$

SDS



$$CH_3(CH_2)_{11}-\overset{CH_3}{N}-CH_2CH_2SO_3^-\ \ Na^+$$

SDAS

DTAB and SDS were purchased from Tokyo Kasei Co. (Tokyo, Japan) and used without further purification. SDAS was prepared as follows [6].

Sodium 2-(methylamino)ethane-1-sulphonate (65% in water, 37.5 g, 0.15 mol) and 25.1 g (0.1 mol) of dodecyl bromide were allowed to react in refluxing ethanol for 60 h in the presence of 37.5 g of $NaCO_3$. The alkylation product which crystallized upon cooling was repeatedly recrystallized from ethanol and dried at 393 K *in vacuo*. The purity of SDAS thus obtained was confirmed by elemental analysis (Calculated for $C_{15}H_{32}NO_3SNa$: C, 54.68; H, 9.79; N, 4.25%. Found: C, 54.25; H, 9.90; N, 4.24 %).

The degradation rate was determined by monitoring the change of absorption with time using a cell unit (Shimadzu UV-240 spectrometer) shown in Fig. 1 after 0.5 ml of sodium hypochlorite solution containing 7×10^{-3} mol dm^{-3} of Cl^+ was added to 3 ml of the aqueous dye/surfactant solution. The visible absorption spectra of the aqueous dye solutions with a constant concentration (8.44×10^{-5} mol dm^{-3}) in the presence of various concentrations of SDAS were measured at 300 K using a Shimadzu UV-240 spectrometer.

RESULTS AND DISCUSSION

The addition of DTAB significantly enhanced the degradation rate of *o*-TR, so that the change of absorbance with time could not be monitored. Such enhancement was also observed for the addition of hexacetyltrimethyl-

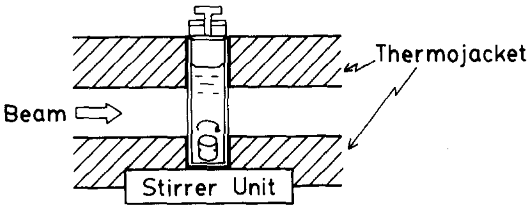


Fig. 1. Cell unit in the visible absorption spectrometer.

ammonium bromide [3]. Furthermore, the fast degradation reaction was found in the presence of ionenes [5]. These results might indicate that the ammonium groups contained in the above additives play an important role in the enhancement of the dye degradation.

The degradation curves of *o*-TR in the presence of SDS (Fig. 2). were depicted by monitoring the spectral change with time, where the dye concentration at each time was calculated using the extinction coefficients measured at 498 nm in aqueous SDS solutions of various concentrations. Although the condition of the dye in the solution changes with dye degradation, it is assumed that the ε values do not vary during the measurement. Figure 2 indicates that the degradation curves thus determined were dependent upon the SDS concentration, [SDS].

The degradation rate constants, k_1, were estimated from the relationship as follows. On the basis of the degradation mechanism proposed by Gregory and Stead [1], $k >_1$ is expressed by eqn (1):

$$-\frac{\mathrm{d[Dye]}}{\mathrm{d}t} = k_1 \cdot [\mathrm{Cl}^+] \cdot [\mathrm{Dye}] \tag{1}$$

where [Dye] and $[\mathrm{Cl}^+]$ are the concentrations of dye and chloronium ion respectively. Since Cl^+ is present in excess, eqn (2) can be derived from eqn (1):

$$\ln\,[\mathrm{Dye}] = -k_1' \cdot t + \ln\,[\mathrm{Dye}]_0 \tag{2}$$

where $[\mathrm{Dye}]_0$ is the initial dye concentration and $k_1' = k_1[\mathrm{Cl}^+]$. As shown in Fig. 3, the plots of ln [Dye] against time gave good linearity and the pseudo first-order rate constants, k_1', were determined from the gradient of the plots. The $[\mathrm{Dye}]_0$ values estimated from the intercept of the plots were 7.0–7.8$\times10^{-5}$ mol dm^{-3}, which are consistent with the actual initial dye concentration, 7.23$\times10^{-5}$ mol dm^{-3} calculated by considering the addition of aqueous sodium hypochlorite solution (0.5 ml) to the aqueous dye solution (3 ml, 8.44$\times10^{-5}$ mol dm^{-3}). This confirms the validity of ε used for the calculation of dye concentrations.

The k_1' values thus determined were plotted as a function of SDS concentration (Fig. 4). At all temperatures, k_1' had a maximum value around the critical micelle concentration (CMC) of SDS (8.1$\times10^{-3}$ mol dm^{-3} at 298 K) [7]. The k_1' values above CMC were equal to or smaller than those in the absence of SDS. For further evaluations, activation energies, E_a for the degradation were calculated from the temperature dependence of k_1' using eqn (3):

$$\ln k_1' = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln A \tag{3}$$

where R is the gas constant, T the absolute temperature, and A the pre-exponential factor. The dependence of the activation energies, E_a, on SDS

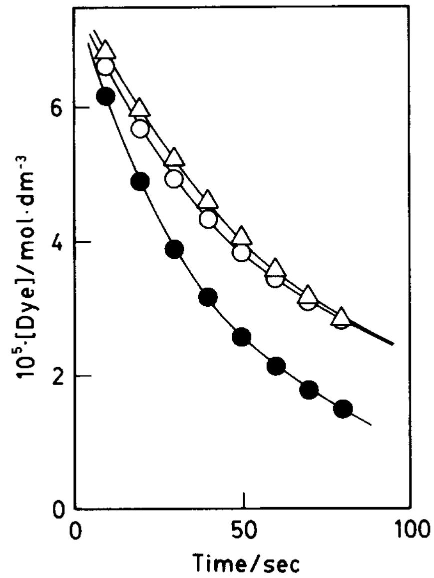


Fig. 2. Degradation curves ([Dye] vs time) in the presence of SDS at 300 K. ○, [SDS] = 0 mol dm^{-3}; ●, [SDS] = 3.43×10^{-3} mol dm^{-3}; △ [SDS] = 2.06×10^{-2} mol dm^{-3}.

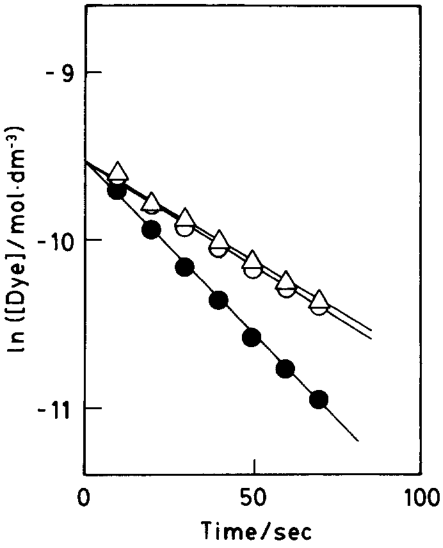


Fig. 3. Plots of ln [Dye] against time in the presence of SDS at 300 K. ○, [SDS] = 0 mol dm^{-3}; ●, [SDS] = 3.43×10^{-3} mol dm^{-3}; △ [SDS] = 2.06×10^{-2} mol dm^{-3}.

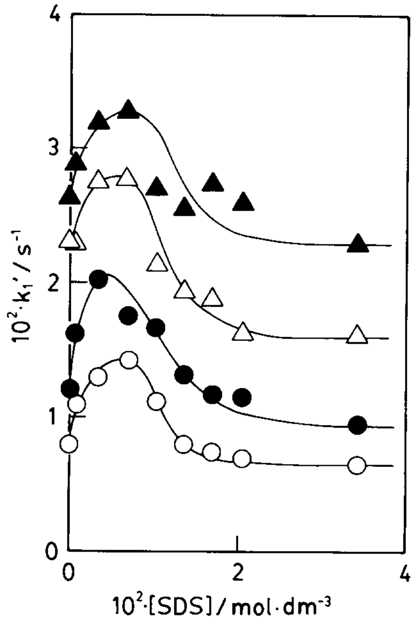


Fig. 4. Dependence of k_1' on the SDS concentration. ○, 292 K; ●, 300 K; △, 310 K; ▲, 319 K.

concentration is shown in Fig. 5. The minimum value of E_a was also found around CMC and the E_a values above CMC were consistent with that in the absence of SDS. The above results demonstrate that SDS micelles do not influence the dye degradation, but that SDS monomers or premicelles do.

The degradation curves of *o*-TR in the presence of SDAS are shown in Fig. 6. The addition of SDAS resulted in degradation curves which were linear plots parallel to the abscissa, suggesting that part of the dye is degraded immediately after the addition of aqueous sodium hypochlorite solution, whereas the remaining part exists in the solution without degradation. Considering that the higher concentration of SDAS enlarges the remaining part, it is believed to be solubilized into micelles formed by SDAS.

Assuming that one dye is solubilized into one micelle, the following equilibrium eqn (4) exists in the dye/SDAS system:

$$D + M \rightleftarrows D \cdot M \qquad (4)$$

where **D**, **M**, and **D·M** expresses the dye, the SDAS micelle, and the dye/micelle complex, respectively. When the concentrations of the total SDAS, the bound dye (the complex), and the free dye are [SDAS], C_b, and C_f

respectively, the binding constant of the dye with the micelle, $K_{\mathrm{bind}}{}^{\mathrm{M}}$, is represented by eqn (5):

$$K_{\mathrm{bind}}{}^{\mathrm{M}} = \frac{C_b}{C_f \cdot ([\mathrm{SDAS}]/n - C_b)} \qquad (5)$$

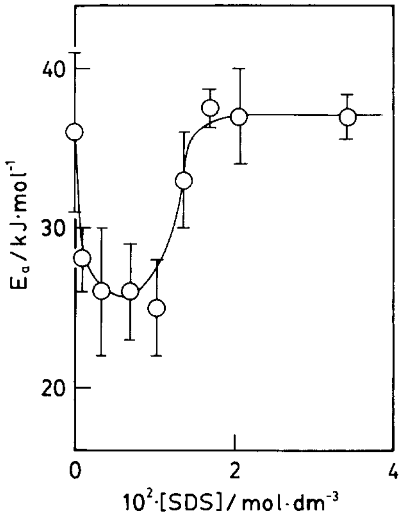


Fig. 5. Dependence of E_a on the SDS concentration.

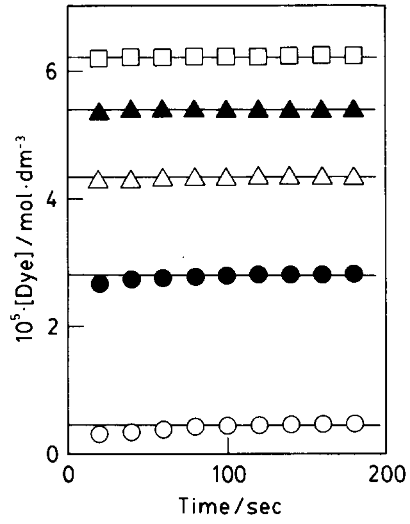


Fig. 6. Degradation curves ([Dye] vs time) in the presence of SDAS at 300 K. ○, [SDAS] = 1.81×10^{-3} mol dm^{-3}; ● [SDAS] = 3.62×10^{-3} mol dm^{-3}; △, [SDAS] = 7.23×10^{-3} mol dm^{-3}; ▲, [SDAS] = 1.09×10^{-2} mol dm^{-3}; □, [SDAS] = 3.62×10^{-2} mol dm^{-3}.

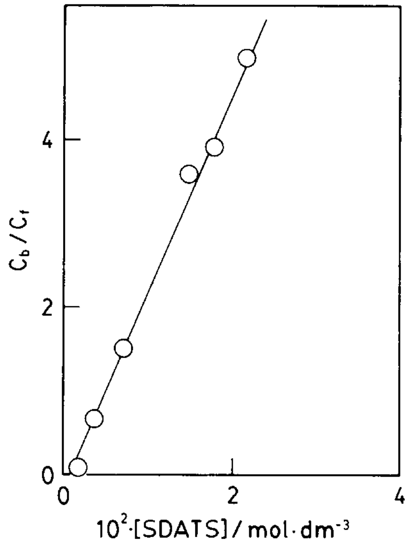


Fig. 7. Plot of C_b/C_f against [SDAS] at 300 K.

where n is the aggregation number of the SDAS micelle. The assumption of [SDAS] $>>C_b$ leads to eqn (6):

$$K_{bind}{}^{M} = \frac{C_b}{C_f \cdot [SDAS]/n} \tag{6}$$

Equation (6) can be rewritten as follows:

$$\frac{C_b}{C_f} = \frac{K_{bind}{}^{M}}{n} \cdot [SDAS] \tag{7}$$

C_b/C_f was estimated from Fig. 6 and plotted as a function of [SDAS] (Fig. 7). The plot shows good linearity and passes through the origin closely, indicating that eqn (7) is valid for the dye/SDAS system. $K_{bind}{}^{M}/n$ was determined as 238 dm^3 mol^{-1} from the slope of the plot. On the other hand, the binding constant, $K_{bind}{}^{M}$ can be also estimated by means of visible absorption spectrum measurement. The $K_{bind}{}^{M}$ value for the dye/SDAS system was calculated using eqn (8), which was derived in a similar manner to the deviation for the dye/poly(vinylpyrrolidone) systems reported in a previous paper [8].

$$\varepsilon = \frac{\varepsilon_f - \varepsilon}{[SDAS]} \cdot \frac{1}{K_{bind}{}^{M}/n} + \varepsilon_b \tag{8}$$

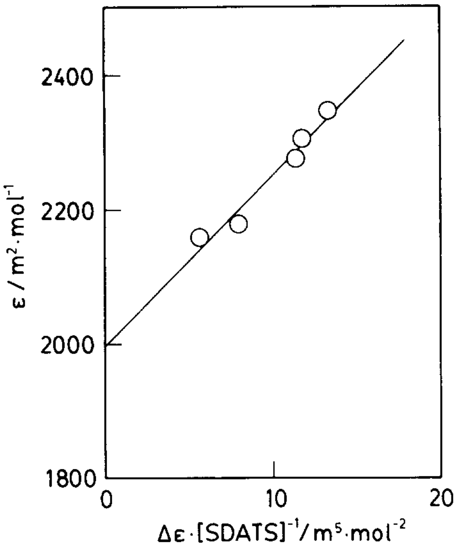


Fig. 8. Plot of ε against $\Delta\ \varepsilon$/[SDAS] at 498 nm and 300 K.

where ε_b and ε_f are the extinction coefficients of the bound and free dye, respectively, and ε is the observed extinction coefficient at 498 nm. The plot of ε against $\Delta\varepsilon$/[SDAS]($\Delta\varepsilon = \varepsilon_f - \varepsilon$) (Fig. 8) became linear and $K_{\mathrm{bind}}{}^{\mathrm{M}}$ was estimated as 39 dm^3 mol^{-1}. The distinction between the $K_{\mathrm{bind}}{}^{\mathrm{M}}$ values determined from the degradation curves and visible absorption spectrum measurement is due to the existence of sodium hypochlorite in the solutions used for the measurements of the dye degradation: sodium hypochlorite affects the binding process of the dye with the SDAS micelle.

From the above results, it is concluded that the effects of surfactants on the dye degradation significantly depend on the kind of their head groups. Particularly, the behaviour of SDAS is very interesting, which makes it possible to degrade the desired amounts of dyes by controlling SDAS concentrations in the dye solutions.

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