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Relationship between Aggregation and Degradation of an Azo Dye in Aqueous 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 ionenes was investigated by means of visible absorption spectrum measurements. The degradation rate of* o*-TR markedly changed with the ionene concentration. The visible absorption spectra of the aqueous dye solutions in the presence of the ionenes were measured to clarify the situation of* o*-TR in the ionene solutions. It was found that dye* o*-TR aggregated in a solution with a certain ionene concentration, this concentration being consistent with the concentration at which the degradation rate became the slowest. It is therefore concluded that the degradation rate of the dye aggregate is significantly slower than that of the dye monomer.*

1 INTRODUCTION

In flower colour variations the stacking of dyes plays an important role. Hoshino *et al.* investigated the self-association of anthocyanins, which develop flower colour, by means of circular dichroism and nuclear magnetic resonance measurements.[1–3] Whilst the aggregation behaviour of synthetic dyes has been a subject of much interest, the effects of dye stacking on the degradation rate of dyes have rarely been investigated.

The degradation of water-soluble azo compounds by dilute sodium hypochlorite solution has been studied by Gregory and Stead,[4] who suggested that electronic, steric and possibly other effects influence the reaction rate. On the basis of their study we have investigated the effects of functional groups on the rate of degradation by sodium hypochlorite

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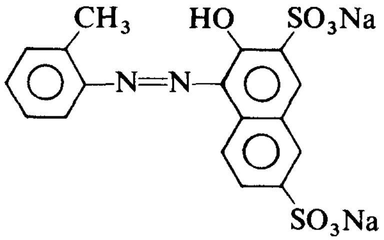


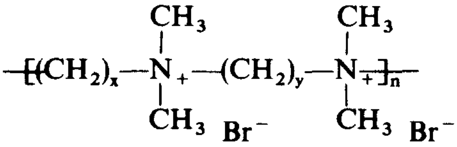
o-TR

solution[5] of azo dyes derived from the use of the sodium salt of R acid (sodium 2-naphthol-3,6-disulphonate) as coupling component. Dyes containing a methyl group showed a simpler degradation mechanism, in which the degradation rate was proportional to the dye and chloronium ion concentration. Furthermore, the degradation rate changed with the orientation of the methyl group, the dye containing a methyl group in the phenyl ring at an ortho position to the azo linkage showing the slowest degradation. Since it is relatively easier to measure the slower degradation, sodium 1-(2-methylphenylazo)-2-hydroxy-3,6-naphthalenedisulphonate (*o*-TR) was used in this present study, which is concerned with the aggregation behaviour of *o*-TR on [3,3]- and [6,6]-ionene chains by means of visible absorption measurements. On the basis of these results the effects of the aggregation on the degradation rate of *o*-TR by sodium hypochlorite solution are discussed.

2 EXPERIMENTAL

The dye, *o*-TR, was prepared by coupling diazotized 2-methylaniline with sodium 2-naphthol-3,6-disulphonate in alkaline conditions. After repeated salting-out with NaCl and reprecipitating the aqueous solution with acetone, the dye purity was confirmed by elemental analysis. [3,3]- and [6,6]-ionene were synthesized from the corresponding *N*,*N*,*N*′,*N*′-tetramethyldiaminoalkane and dibromoalkane.

The visible absorption spectra of the aqueous dye solutions with a constant concentration ($8{\cdot}44 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$) in the presence of various concentrations of the ionenes were measured at 300 K using a Shimadzu UV-240 spectrometer. The degradation rate was determined by monitoring



$$-\!\!\left[(CH_2)_x-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3\ Br^-}{N^+}}-(CH_2)_y-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3\ Br^-}{N^+}}\right]_n\!\!-$$

$x = 3$, $y = 3$: [3,3]-ionene; $x = 6$, $y = 6$: [6,6]-ionene the change of absorption with time 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/polymer solution.

3 RESULTS AND DISCUSSION

The absorption spectra of dye *o*-TR in the presence of [3,3]- and [6,6]-ionene are shown in Fig. 1. The absorption spectra changed greatly with the

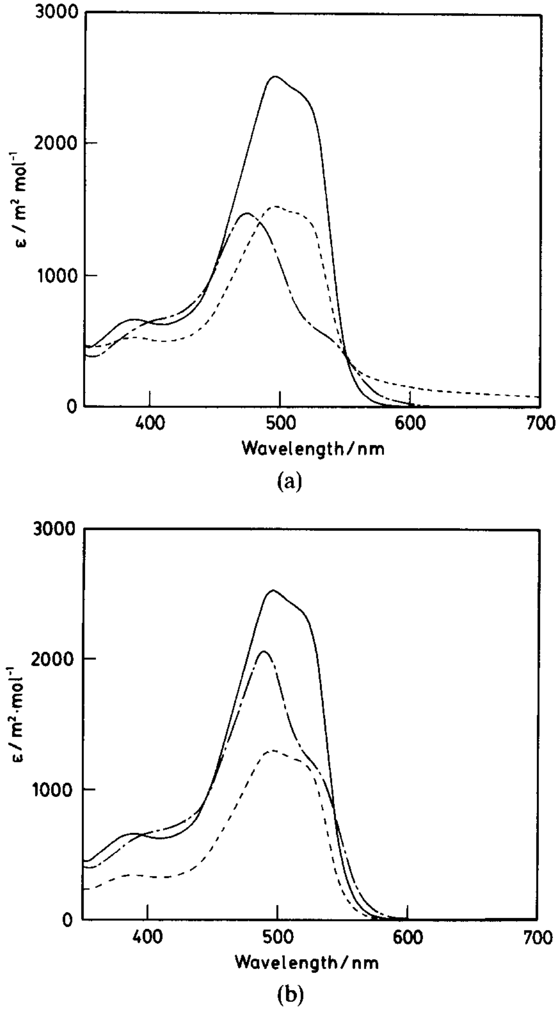


Fig. 1. Visible absorption spectra of *o*-TR aqueous solutions ($8{\cdot}44 \times 10^{-5}$ mol dm^{-3}) in the presence of (a) [3,3]-ionene and (b) [6,6]-ionene at 300 K. ——, $P/D = 0$; – – –, $P/D = 0{\cdot}5$; –·–·–, $P/D = 10$.

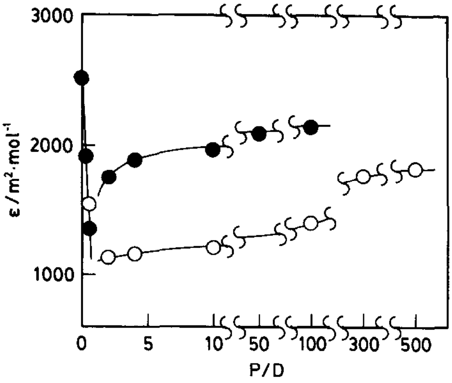


Fig. 2. Plots of the extinction coefficients, ε, against P/D at 498 nm. ○, [3,3]-ionene; ●, [6,6]-ionene.

polymer and dye concentration ratio, P/D, where the polymer concentration is expressed in monomer units: the intensity of the spectra decreased without change in shape until $P/D = 1$, after which it increased, also showing a different wavelength of maximum absorption. Figure 2 shows the change of the extinction coefficient at 498 nm with variation in P/D. The results are similar to those of aqueous Acridine Orange solutions in the presence of poly(styrenesulphonic acid),[6] suggesting that a dye monomer/aggregate equilibrium exists. From this it is concluded that the dye forms an aggregate at small P/D, and the extent of the aggregate decreases with increasing P/D. Furthermore, the difference in the recovery of ε between [3,3]- and [6,6]-ionene indicates that the dye aggregates more easily on [3,3]- than [6,6]-ionene chains.

The degradation curves of *o*-TR in the presence of the ionenes (Fig. 3) 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 the polymers with 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, because of the very short measuring time and the small change of ε in the region of $P/D > 1$ (Fig. 2). The degradation curves thus determined were dependent upon the ionene concentration.

To elucidate this dependence the degradation rate constants, k_1, were estimated. On the basis of the degradation mechanism proposed by Gregory and Stead,[4] k_1 is expressed by eqn (1):

$$-\frac{d[\mathrm{Dye}]}{dt} = k_1 . [\mathrm{Cl}^+] \cdot [\mathrm{Dye}] \qquad (1)$$

where [Dye] and $[\mathrm{Cl}^+]$ are the concentrations of dye and chloronium ion,

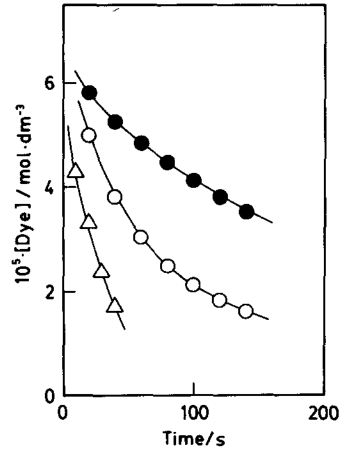


Fig. 3. Degradation curves ([Dye] *versus* time) in the presence of [3,3]-ionene at 300 K. ○, $P/D=0$; ●, $P/D=2$; △, $P/D=10$.

respectively. Since Cl^+ is present in excess, eqn (2) can be derived from eqn (1):

$$\ln[\text{Dye}] = -k_1'.t + \ln[\text{Dye}]_0 \qquad (2)$$

where $[\text{Dye}]_0$ is the initial dye concentration and $k_1' = k_1.[Cl^+]$. Plots of ln [Dye] against time gave good linearity, as shown in Fig. 4, and the pseudo first-order rate constants, k_1', were determined from the gradient of the plots. It is worthwhile to note that the $[\text{Dye}]_0$ values estimated from the intercept were $5{\cdot}9$–$6{\cdot}4 \times 10^{-5}$ mol dm^{-3}, which are different from the actual initial dye concentration, $7{\cdot}23 \times 10^{-5}$ mol dm^{-3} calculated by considering the addition of aqueous sodium hypochlorite solution (0·5 ml) to the aqueous dye solution (3 ml, $8{\cdot}44 \times 10^{-5}$ mol dm^{-3}). This is mainly due to the deviation of the start time in the measurements. For example, deviation of 10 s results in a change

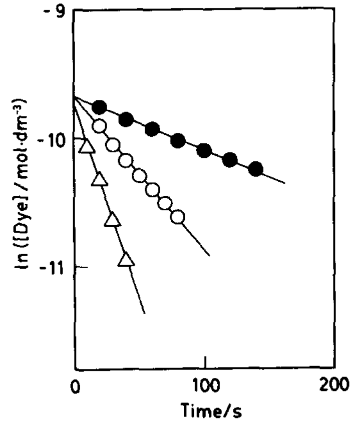


Fig. 4. Plots of ln [Dye] against time in the presence of [3,3]-ionene. ○, $P/D=0$; ●, $P/D=2$; △, $P/D=10$.

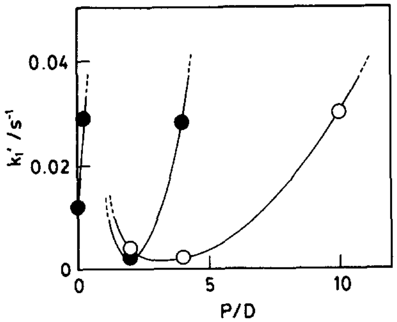


Fig. 5. Plots of the pseudo first-order rate constants, k_1', against P/D. ○, [3,3]-ionene; ●, [6,6]-ionene.

from $7 \cdot 2 \times 10^{-5}$ to $6 \cdot 4 \times 10^{-5}$ mol dm^{-3} of the initial dye concentration in the case of $k_1' = 0 \cdot 012$ s^{-1}. Thus the deviation of the start time affects $[\text{Dye}]_0$ values in such a rapid reaction.

The k_1' values determined at various P/D are shown in Fig. 5. For both [3,3]- and [6,6]-ionene the degradation rates at $0 \cdot 25 < P/D < 1$ and $P/D > 10$ were so fast that the k_1' values could not be estimated in this region. This might be due to the catalytic action of the ionenes. At $P/D = 2$–4, however, the k_1 values were much smaller than in the absence of the ionenes. Considering the aggregation behaviour of *o*-TR, the above results suggest that the dye aggregate degrades more slowly than the dye monomer. It is thus concluded that the dye stacking markedly depresses the degradation.

It is of interest to discuss whether the aggregated dyes without the ionenes behave similarly to those with them. Since it is concluded that the reason why dye stacking depresses the degradation is that chloronium ions are not easily accessible to the azo linkage because of the neighbouring dye molecules being present in the aggregate, the aggregated dyes without the ionenes presumably behave in a similar manner to those with them. However, the formation of the aggregated dyes without the ionenes requires high dye concentration. It is difficult to monitor the degradation of dyes in such high concentration, even if the aggregation depresses the degradation rate, because the degradation rate is proportional to dye concentration. Therefore it is impossible to compare the degradation of the aggregated dyes with and without the ionenes from an experimental point of view. The ionenes, however, do play an important role in the formation of the aggregate in the low dye concentration region.

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