Dyes and Pigments, Vol. 33, No. 2, pp. 97–105, 1997
Copyright © 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
PII: S0143-7208(96)00040-X 0143-7208/97 $17.00+0.00

ELSEVIER

Deaggregation of Benzimidazolone Azo Dyes

Jerzy Szadowski & Zbigniew Niewiadomski

Institute of Dyes, Technical University of Łódź, 90-924, Łódź, Poland

(Received 21 February 1996; accepted 23 April 1996)

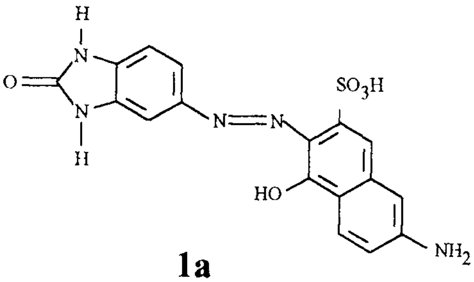
ABSTRACT

The influence of temperature on the aggregation and deaggregation of monoazo dyes containing imidazolone residues has been examined under conditions similar to those in a conventional dye bath. It was found that only certain dyes could be deaggregated. An explanation is given to relate the effect of aggregation on the affinity of some imidazolone dyes to cellulose fibres. © 1997 Elsevier Science Ltd. All rights reserved

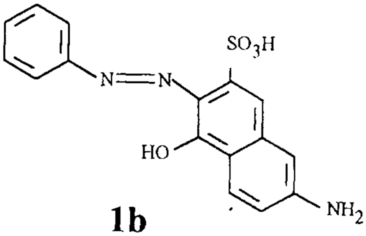
INTRODUCTION

In previous studies on direct dyes containing imidazolone residues,[1–3] it was found that in most cases these dyes show an increased affinity to cellulose fibres in comparison with dyes containing no imidazolone residues. However, the effect of the imidazolone residue on the dye affinity to cellulose is variable and depends on the location of the imidazolone residue in the dye molecule; in some cases the presence of the imidazolone residue brings about no increase in affinity.[4] In the light of these findings, the previously reported concept[1–3] on the formation of a monoazo imide dye dimer appears to be an insufficient explanation of the increased affinity of some dyes and the lack of affinity in other dyes of apparently similar structure. It is now proposed that imidazolone dye molecules with various structures form aggregates with different stabilities, this resulting in their different behaviour in the dyebath.

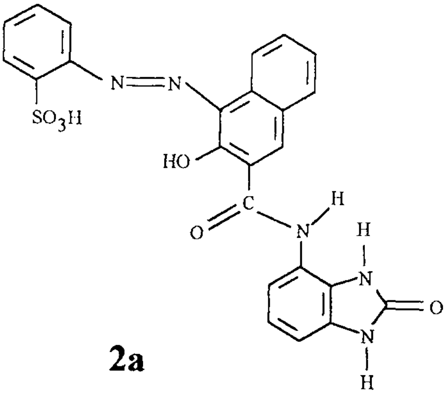
In order to evaluate this hypothesis it was therefore attempted to show to what extent the dyes are aggregated under conditions similar to those during dyeing. Four pairs of simple imidazolone dyes **1–4a** and their analogues containing no imidazolone groups **1–4b** were examined.


H
N
O
N
H
N=N
SO$_3$H
HO
NH$_2$

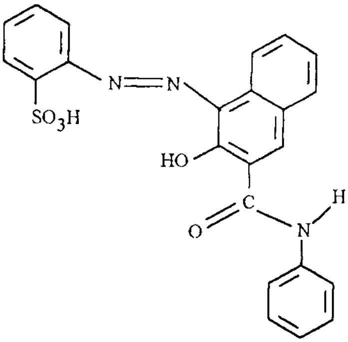
1a


N=N
SO$_3$H
HO
NH$_2$

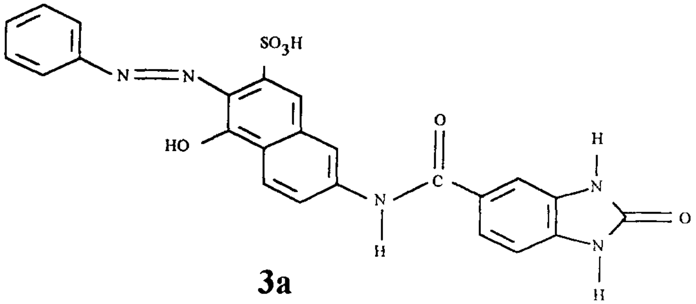
1b


N=N
SO$_3$H
HO
C
O
N
H
H
N
O
N
H

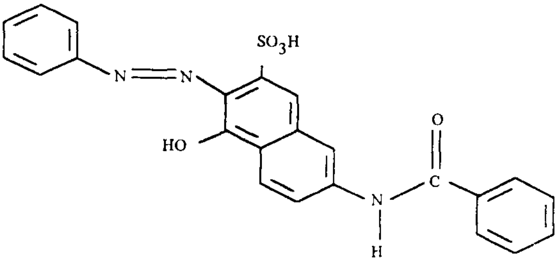
2a


N=N
SO$_3$H
HO
C
O
N
H

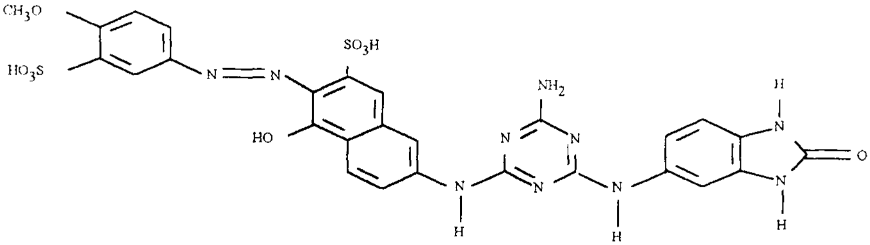
2b


SO$_3$H
HO
N
N
O
C
N
H
H
N
O
N
H

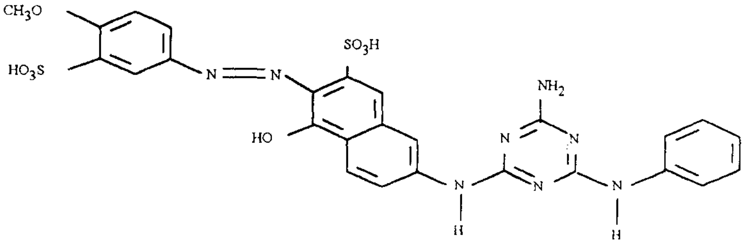
3a


SO$_3$H
HO
N
N
O
C
N
H

3b


CH$_3$O
HO$_3$S
SO$_3$H
HO
N
N
NH$_2$
N
N
N
N
H
N
H
H
N
O
N
H

4a


CH$_3$O
HO$_3$S
SO$_3$H
HO
N
N
NH$_2$
N
N
N
N
H
N
H

4b

EXPERIMENTAL

The synthesis of the dyes has been described in previous papers.[1–4] The homogeneity of the dyes was determined chromatographically (Whatman paper 1, eluent–DMF:MeOH:H_2O = 3:1:1).[5] The content of NaCl in the dye samples was determined potentiometrically.[6] The content of pure dye in samples was confirmed by the determination of sulphonic groups by titration with Hyamine solution.[7]

Exhaustion degree

The degree of dye exhaustion by cellulose fibres was determined by dyeing bleached and mercerized cotton fabric (150 g/m^2) samples in a Roaches-Rotec dyeing apparatus, using 1% omf of dye and 0.5% of Na_2SO_4 at a liquor ratio of 1:30. The dyebath was heated for 2 h up to 95°C and dyeing was continued at this temperature for 1 h. The bath was then cooled to 60°C for 1 h and the dyed samples were thoroughly rinsed and dried. The degree of dye exhaustion from the bath E was determined colorometrically, measuring the dye concentrations before (c_1) and after dyeing (c_2): using Equation (1)

$$E = \frac{c_1 - c_2}{c_1} 100\%. \tag{1}$$

The measurements were made at λ_{max} of the dye, at 20°C.

Spectrophotometric measurements

Standard solutions were prepared by dissolving 0.025 g dye samples in 100 ml of water with 0.04 g of Na_2SO_4. The dye deaggregation was examined using dye solutions prepared by diluting 5 ml of a standard solution to a volume of 100 ml. Ethanol solutions were prepared by diluting 5 ml of a standard solution with 96% ethanol to a volume of 100 ml. All samples were stored in the dark for 24 h prior to measurement. Measurements were then carried out using a Specord M-40 spectrophotometer C.Zeiss, Jena, using a thermostatted glass cell 10 mm in thickness. Once the required temperature was reached, the measurement of absorbance was repeated every few minutes until two equal results were obtained. The results of the measurements are shown in the form of plots of absorbance A versus temperature t (Figs 1–4). The temperature constant of deaggregation (K_d) was calculated for the linear segments of the aggregation curves using Equation (2):

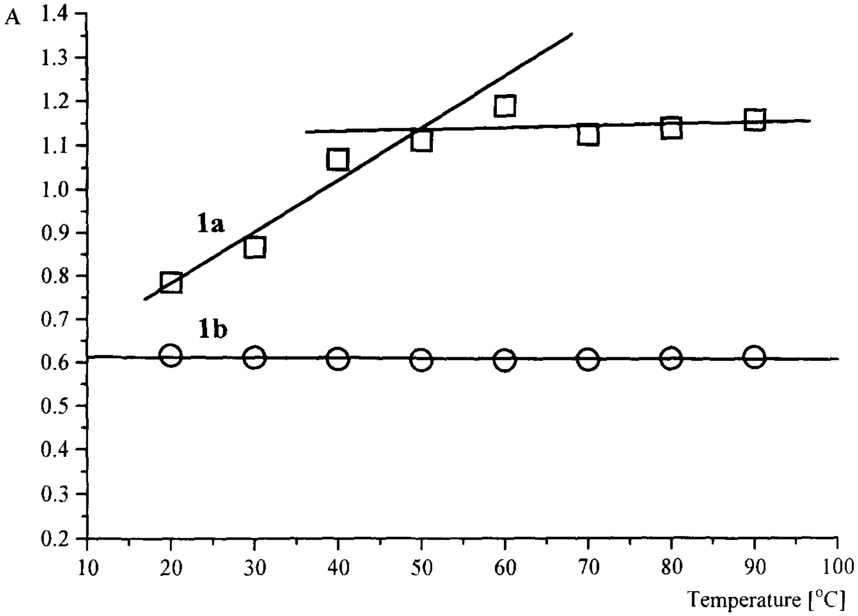


Fig. 1. Relationship between absorbance *A* of dye **1a** and **1b** and temperature *t*.

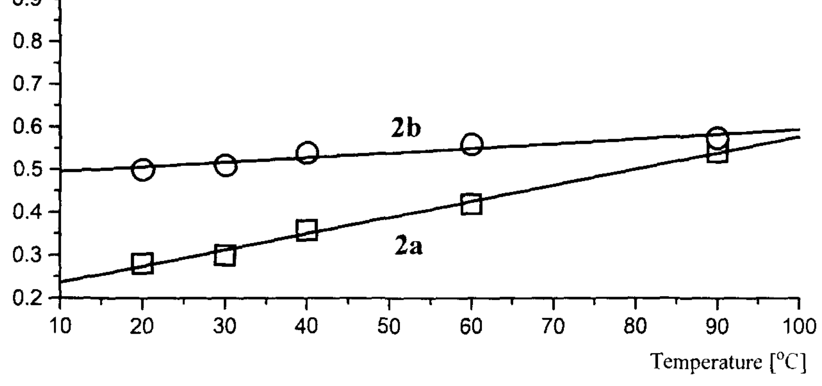


Fig. 2. Relationship between absorbance *A* of dye **2a** and **2b** and temperature *t*.

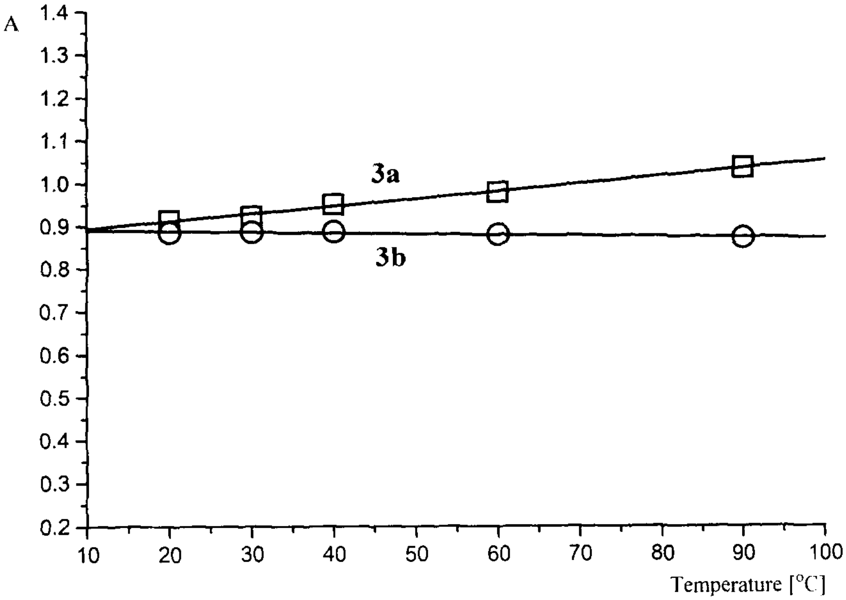


Fig. 3. Relationship between absorbance *A* of dye **3a** and **3b** and temperature *t*.

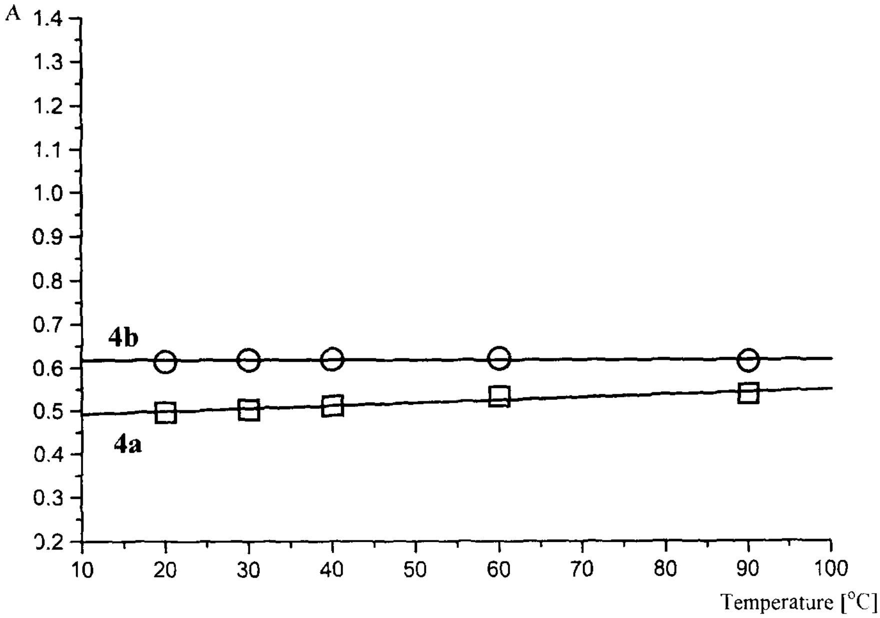


Fig. 4. Relationship between absorbance *A* of dye **4a** and **4b** and temperature *t*.

$$K_{\mathrm{d}} = \frac{(A_a - A_{20}) \times 10}{(t_a - 20) : 10} \tag{2}$$

where A_{20} = absorbance at 20°C,

A_a = absorbance at the point of the intersection of the two linear segments,

t_a = temperature at the point of the intersection of the two linear segments or 90°C.

The measurement was repeated after 24 h when the solution was cooled and the absorbance was found to be the same at 20°C (A_{20}).

RESULTS AND DISCUSSION

Four imidazolone dyes **1–4a** were examined and their properties were compared with those of analogous compounds **1–4b** containing no imidazolone residue.

Table 1 shows the values of the exhaustion degrees of the dyes determined under conditions used in a previous investigation.[3] In the case of dyes **1**, **2** and **4**, the imidazolone dyes **a** are characterized by a higher degree of exhaustion than that of dyes **b** containing no imidazolone residue. On the other hand, dye **3a**, despite the presence of the imidazolone residue, shows a lower affinity than that of dye **3b**.

In order to examine the possibility of deaggregation of the dyes during heating in the dyebath, solutions of the dyes were spectrophotometrically

TABLE 1

Properties of dyes **1–4**

Dye	Exhaustion E (%)	$\lambda_{\max}$ (nm)			Deaggregation constants K_{d}
		H_2O		EtOH	
		20°C	90°C		
1a	67.1	479	505	503	1.21*; 0.005**
1b	33.5	479	480	477	0.00
2a	59.9	504	502	498	0.29
2b	23.3	497	500	518	0.10
3a	27.4	484.5	484.5	482	0.14
3b	48.3	487.5	488.3	485	0.11
4a	77.1	504	502	500	0.00
4b	59.3	500	504	500	0.00

*K_{d} measured by increase of temperature from 20 to 50°C.

**K_{d} measured by increase of temperature from 50 to 90°C.

measured at various temperatures, using a dye concentration similar to that used in the dyebath.

Measurements were carried out in thermostated cells, raising the temperature gradually from 20 to 90°C. The plots of absorbance A vs temperature t (Figs 1–4) clearly show that only some of the dyes can be deaggregated under dyeing conditions during heating of their solutions over 90°C, and that they can form aggregates again at 40–60°C. A typical example of considerable aggregation and deaggregation is dye **1a**. Owing to its complete deaggregation above 60°C, this dye diffuses readily into the fibre and forms stable aggregates combined with the fibre after recooling. As a result, its degree of exhaustion is twice as high as that of the analogous dye containing no imidazolone residue. Dye **2a** is gradually deaggregated within the whole temperature range from 20 to 90°C, and this factor also provides the possibility of its exhaustion being twice as high as that of the dye **2b** with no imidazolone group. In the case of dyes **3a** and **3b** almost no deaggregation is observed as the temperature is raised and therefore dye **3a**, with a more developed and probably non-planar molecule, is exhausted from the bath to only a very low extent (below 30%). Dyes **4a** and **4b** are also not deaggregated under the conditions used, but both the dyes show quite a high degree of exhaustion due to their sufficiently large molecules. At the same time dye **4a** shows somewhat higher affinity, probably due to possible dye–fibre interaction through hydrogen bonds of the imidazolone residues.

The presence or absence of deaggregation is also confirmed by the changes in λ_{max} of the dye solutions during their heating; relevant data are given in Table 1. Different λ_{max} values of aqueous and ethanolic solutions of the same dyes were also observed. The absorbance of the aqueous and ethanolic solutions measured at 20°C is considerably higher only in the case of ethanol solution of dyes **1a** and **3a**, which testifies to their deaggregation in ethanol. The remaining dyes show no differences in the absorbance of ethanol and aqueous solutions, indicating the absence of aggregation under the experimental conditions used.

CONCLUSION

Based on the presented findings, a more detailed hypothetical mechanism than the one reported previously[1–3] can be proposed to explain the causes of the increased affinities of some imidazolone dyes for cellulose. It is concluded that imidazolone dyes are deaggregated mostly at elevated temperature, diffuse into fibres in the form of monomolecules, and after being cooled down to at least 60°C, they reaggregate and only in this aggregated form are they durably combined with fibres. The degree of dye exhaustion from the dyebath, however, is also affected by other well known factors such as molecular size, linearity and planarity. These make possible a durable dye–fibre interaction independent of the presence of the imide arrangement in the dye molecule, which is thus only an additional factor which increases the dye affinity for cellulose.

The location of the imidazolone moiety in the dye molecule has a considerable advantageous effect on the ability of the dyes to aggregation and deaggregation in solution under the influence of increasing temperature only in the case of direct conjugation of this moiety with the chromophore system. When the imidazolone residue is isolated from the chromophore, dyeing properties are determined mainly by structural features of the dye molecule, while the presence of the imidazolone system is only an additional factor which increases the affinity to a slight extent.

REFERENCES

1. Szadowski, J. & Niewiadomski, Z., *Dyes and Pigments*, **21** (1993) 123.
2. Niewiadomski, Z., Szadowski, J. & Boruszczak, Z., *Barwniki, Śr. Pom.*, **37**(4) (1993) 1.
3. Szadowski, J. & Niewiadomski, Z., *Melliand Textilber.*, **76** (1995) 1096.
4. Niewiadomski, Z. & Szadowski, J., *Barwniki, Śr. Pom.*, **40** (1996), 55.
5. Alberti, G. & de Giorgi, M. R., *Ann. Chim. (Rome)*, **73** (1983) 57.
6. Ackermann, H. & Dussy, P., *Helv. Chim. Acta*, **45** (1962) 1683.
7. Weatherall, I. *Amer. Dyest. Rep.* (1992), 43.