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Short communication

Optimisation of the synthesis of a water-soluble sulfur black dye

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Abstract

A water-soluble sulfur black dye containing carboxylic acid groups was prepared by reducing C.I. Sulfur Black 1 to its leuco form followed by reaction with chloroacetic acid. In conducting this reaction, variables studied included the order of adding reactants, the amount of Na_2S and chloroacetic acid employed, and the time and temperature of the reaction. It was found that the carboxylic acid group content and reaction yield were maximized by controlling the amount of Na_2S and chloroacetic acid employed, and by conducting the reaction for 2 h at 60 °C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfur dye; Water-soluble; Carboxylic acid group; C.I. Sulfur Black 1

1. Introduction

Sulfur dyes are widely used to produce economical black, blue, brown and green shades on cellulosic fibers in medium to heavy depths. It is estimated that about one half of the volume of dye used on cellulosic fibers is due to sulfur dyes, in which case about 80% is the sulfur black dye [1,2].

C.I. Sulfur Black 1 has poor substantivity to cellulosic fibers and has to be converted to the water-soluble leuco form in the present of reducing agent to effect dyeing [3,4]. The traditional reducing agent used in this process is Na_2S, which produces a sulfur-containing effluent and causes adverse effects on the environment. In particular, Na_2S has potential health risks associated with the possible generation of high levels of toxic H_2S upon adding acid to the effluent. The solubilized sulfur black dye cited in the Colour Index is the Bunte salt or the thiosulphuric acid derivative of C.I. Sulfur Black 1.

Recently, a new type of solubilized sulfur dye containing carboxylic acid groups was reported [5]. It was prepared by alkylating the leuco form of sulfur dyes with a 1-halocarboxylic acid. In subsequent studies, we found that this new derivative could be applied to cotton by a pad-steam-fixation process without using a reducing agent, thus preventing the formation of a sulfur-containing effluent in the dyeing step. In the present paper, we report the synthesis of a water-soluble sulfur black dye from C.I. Sulfur Black 1 and chloroacetic acid.

Although the structure of C.I. Sulfur Black 1 has been investigated by a number of workers, it has not yet been established [6]. It is believed to be a mixture of different structures. For C.I. Leuco Sulfur Black 1, which is prepared from the reduction of C.I. Sulfur Black 1 with Na_2S, structures **I–III** have been proposed [5].

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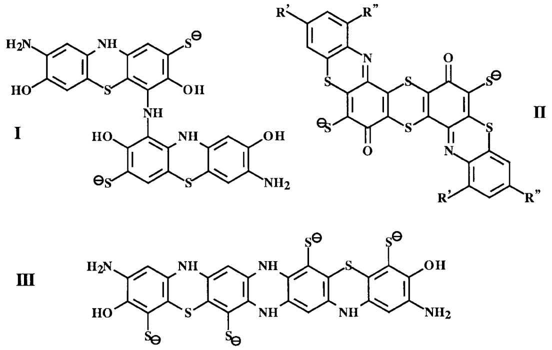

2. Experimental

2.1. Chemicals

Chloroacetic acid, NaOH, and HCl were laboratory grade chemicals. C.I. Sulfur Black 1 and Na_2S were commercial grade products. The C.I. Sulfur Black 1 employed was the powder form and the purity was 69.1%.

2.2. Synthesis of carboxylated sulfur black dye

Chloroacetic acid (40 g) and water (40 ml) were mixed in a 250-ml flask and NaOH (35 ml, 40% w/v) was added slowly at 0 °C with stirring and cooling. Following complete dissolution of chloroacetic acid, C.I. Sulfur Black 1 (50 g) was added and the mixture was stirred and heated. When the temperature reached 60 °C, Na_2S (60 ml, 30% w/v) was added dropwise over 60 min, and the reaction mixture was stirred for 1 h at 60 °C. Afterwards, the reaction mixture was poured into a 500-ml beaker, and the pH was adjusted to 2–3 with 5.9 M HCl. The precipitated dye was collected by filtration, washed with water (1000 ml), and dried at 75–80 °C.

2.3. Analysis of carboxylic acid group content

The carboxylic acid group content in the carboxylated dye was determined by direct titration. NaOH (0.4652 M, 20 ml) and distilled water (50 ml) were added to 1 g dye in a 200-ml beaker, and the mixture was stirred until the dye dissolved completely. The resultant dye solution was titrated with HCl (0.4838 M) until pH 7.1–7.3 was measured on a pH meter. The equation employed to determine the carboxylic acid group content was Eq. (1):

$$\text{–COOH content} = (20 \times 0.4652 - 0.4838 \times V) \times 100\ \text{mmol}/100\ \text{g dye} \quad (1)$$

2.4. Absorption curve

Carboxylated dye (0.1 g) was dissolved in distilled water (250 ml) maintaining pH 7.1–7.3, and then the solution was diluted to 1/20th of its concentration. The optical density of the dye solution was measured in the 410–700 nm region using a model 721-100 visible spectrophotometer from Shanghai Analytical Instruments Company.

3. Results and discussion

The reaction between the leuco sulfur black dye and 1-chloroacetic acid introduces carboxylmethyl groups [Eq. (2)]. We found that the mode of combining the reactants, the amount of 1-chloroacetic acid and Na_2S, and the reaction temperature and time affected the reaction yield and carboxyl group content of the resultant black dye.

$$\underset{\text{(C.I. Sulfur Black 1)}}{\text{Dye-S-S-Dye}} \xrightarrow{Na_2S} \underset{\text{(leuco form)}}{\text{2Dye-S-Na}} \xrightarrow{ClCH_2CO_2Na} \underset{\text{(water-soluble sulfur black)}}{\text{2Dye-S-CH}_2\text{Co}_2\text{Na}} \quad (2)$$

3.1. Effects of combination sequences

Experiments conducted in which the method of adding Na_2S and 1-chloroacetic acid to the parent dye was varied included the following:

1. C.I. Sulfur Black 1 was reduced to the leuco form by Na_2S (aq.) and then sodium chloroacetate (aq.) was added.
2. Na_2S (aq.) and sodium chloroacetate (aq.) were added sequentially to C.I. Sulfur Black 1 in portions.

3. Na_2S (aq.) was added in three portions to a mixture of sodium chloroacetate (aq.) and C.I. Sulfur Black 1.
4. Na_2S (aq.) was added dropwise to a mixture of sodium chloroacetate (aq.) and C.I. Sulfur Black 1.

The reactions were carried out at 60° C for 2 h and the ratio (w/w) of C.I. Sulfur Black 1, 1-chloroacetic acid and Na_2S was 1:1:0.8. The results of these experiments are shown in Table 1.

It can be seen from Table 1 that the carboxylic acid group content and the reaction yields were higher from Method 4 than from Methods 1–3. It is well known that leuco sulfur dyes are easily oxidized in air to insoluble sulfur dyes, and that the latter cannot react with 1-chloroacetic acid. In the preparation of carboxylated dye via Method 4, reduction of the parent dye to its leuco form and reaction with 1-chloroacetic acid, took place simultaneously. As a result, oxidation of the leuco sulfur dye was circumvented, and the carboxylic acid group content and reaction yield were maximized. In carrying out the experiments that followed, Method 4 was used.

3.2. *Effects of the amount of Na_2S*

The effects of the amount of Na_2S on carboxylic acid group content are summarized in Fig. 1. It is clear that the carboxylic acid group content first increased upon increasing the ratio of Na_2S to C.I. Sulfur Black 1 from 0.26 to 0.39, and then decreased. At weight ratios lower than 0.39, the amount of Na_2S was insufficient to achieve complete reduction of the parent dye, and at ratios higher than 0.39 the effectiveness of the reaction sequence decreased due to competition between the desired alkylation step and hydrolysis of chloroacetate. In addition, a side reaction between Na_2S with sodium chloroacetate occured at higher amounts of Na_2S. In essence, an improvement in the reaction yield could not be achieved by varying the amount of Na_2S.

3.3. *Effects of the amount of 1-chloroacetic acid*

A summary of the results of experiments in this area is shown in Fig. 2. It can be seen that holding the amount of Na_2S constant and increasing the weight ratio of 1-cloroacetic acid to C.I. Sulfur Black 1 from 0.2 to 0.8 resulted in an increase in carboxylic acid group content and an increase in reaction yield.

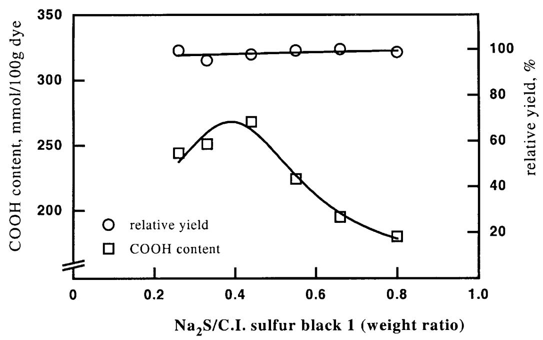

Fig. 1. Relationship between the amount of Na_2S and the carboxylic acid group content and relative yield.

Table 1
Effects of reactant combinations on the carboxylic acid group content and relative yield

Experiment no.	Crude yield[c] (%)	$\varepsilon_{ave}\times10^{-4}$ (cm^2/g)[a]	Relative yield[b] (%)	Carboxyl group content (mmol COOH/100 g dye)
1	86.0	1.227	63.5	134
2	100.0	1.221	73.5	151
3	92.4	1.531	85.2	167
4	93.1	1.763	98.8	180

[a] ε_{ave} is the average extinction coefficient for the carboxylated dye.

[b] Relative yield = $(\varepsilon_{ave}\times\text{crude yield})/(\varepsilon_{ave}\times\text{crude yield})_r$, where r represents the carboxylated dye in which the weight ratio of Na_2S to C.I. Sulfur Black 1 was 0.66.

[c] Crude yield is the weight ratio of carboxylated dye obtained to parent dye (C.I. Sulfur Black 1).

Table 2
Effects of reaction temperature on the carboxylic acid group content and relative yield[a]

Experiment no.	Temperature (°C)	Crude yield (%)	$\varepsilon_{ave}\times 10^{-4}$ (cm^2/g)	Relative yield (%)[b]	Carboxyl group content (mmol COOH/100 g dye)
1	45	92.0	1.374	76.1	227
2	60	104.1	1.563	97.8	265
3	85	95.1	1.272	72.8	246

[a] Weight ratio of C.I. Sulfur Black 1:Na_2S:chloroacetic acid = 1:0.4:0.8.
[b] Relative yield = (ε_{ave}×crude yield)/(ε_{ave}×crude yield)$_r$, where r represents the carboxylated dye in which the weight ratio of Na_2S to C.I. Sulfur Black 1 was 0.66.

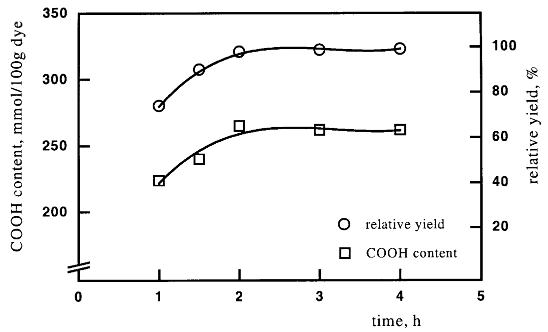

Fig. 2. Relationship between the amount of chloroacetic acid and the carboxylic acid group content and relative yield.

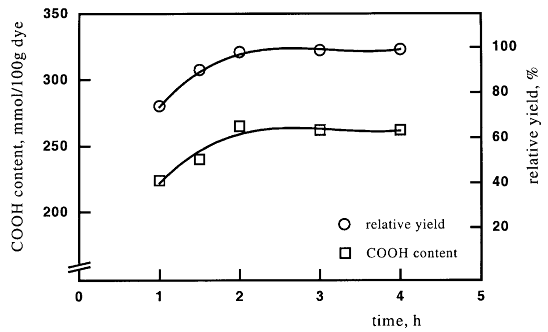

Fig. 3. Relationship between the reaction time and the carboxylic acid group content and relative yield.

3.4. Effects of reaction temperature

The dependence of carboxylic acid group content and yield on the reaction temperature is summarised in Table 2. Increasing the reaction temperature to 60°C gave an increase in carboxylic acid group content and reaction yield. Increasing the temperature to 80°C led to dye having a lower carboxylic acid group content and a lower yield. This decrease was attributed to the hydrolysis of the sodium chloroacetate to sodium hydroxylacetate.

3.5. Effects of reaction time

The relationships between reaction time and carboxylic acid group content and reaction yield, at constant Na_2S and chloroacetic acid, at 60°C, and at different reaction times are shown in Fig. 3. It is clear that carboxylic acid group content and reaction yield reached a maximum at 2 h.

4. Conclusions

Water-soluble sulfur black dye containing carboxylic acid groups can be prepared by reducing C.I. Sulfur Black 1 to its leuco form and reacting the leuco intermediate with chloroacetic acid. Variables affecting this process include the order of adding the reactants, the ratio of the reactants, and the time and temperature of the reaction. It is clear that the carboxylic acid group content and product yield are maximized by controlling the amounts of Na_2S and chloroacetic acid, and by conducting the reaction for 2 h at 60 °C.

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