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Capillary electrophoretic analysis of the reactions of bifunctional reactive dyes under various conditions including a study of the analysis of the traditionally difficult to analyse phthalocyanine dyes

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Abstract

Good analytical techniques for the separation and detection of reactive dyes are necessary not only to monitor residual liquors and effluents but also to aid in optimisation of dye synthesis, purification, formulation and application. HPLC, although generally widely employed, often has difficulty in analysing certain reactive dyes, especially the phthalocyanine-based dyes.

CE analysis of several bifunctional reactive dyes has been carried out with subsequent activation and hydrolysis reactions for a bis-sulfatoethyl sulfone dye, under different pH and temperature conditions, being monitored. A variety of buffers were investigated; the use of acetonitrile in a micellar buffer system proving to be particularly successful.

1. Introduction

In the early studies of dye analysis using capillary electrophoresis (CE) systems the buffers employed were basically just the conventional aqueous buffers such as phosphate, borate and citrate [1–3]. More recently, however, workers have employed micellar buffer systems to analyse a range of dyes and intermediates [4–6] including some selective reactive dyes [4,6].

The work reported on in this paper has been more directly concerned with monitoring the reactions of reactive dyes as they proceed. In the present study the introduction of acetonitrile into the micellar buffer system was found to be beneficial for the analysis of reactive dyes particularly the Procion Turquoise H-A (ICI) (a phthalocyanine-based) dye. This and the actual conditions employed will be discussed in more detail in the relevant sections later in this paper.

Reactive dyes are employed primarily in the coloration of cellulosic materials with which they form covalent bonds. The first commercial bifunctional reactive dye is generally accepted as being Remazol Black B (HOE) which is a bis-sulfatoethyl sulfone dye as illustrated in Fig. 1. The majority of the work reported on in this paper concerns the analysis of this dye and monitoring the activation and subsequent hydrolysis of this dye.

The main and most obvious advantage of bifunctional dyes is the possibility for higher fixation values than with monofunctional dyes. This is because hydrolysis of one of the reactive groups in a bifunctional dye still leaves a dye capable of reacting with the fibre, this is not the

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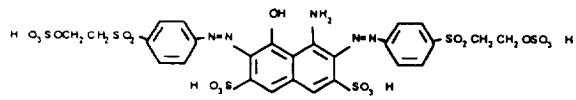

Fig. 1. Structure of Remazol Black B (HOE) dye.

case with monofunctional dyes. This may be demonstrated by looking at the following example where it is hypothetically assumed that the probability of a reactive group (R) being hydrolysed (H) by the end of a set time, such as a dyeing cycle, is 25% (i.e. one in four). Thus, the probability of a reactive group is 75% i.e. three in four. For a bifunctional dye, R–D–R′, there are four possible outcomes:

R–D–R′ (no hydrolysed groups), R–D–H and H–D–R′ (one hydrolysed and one reactive group) and H–D–H (both groups hydrolysed).

Statistically:

R–D–R′	R–D–H	H–D–R′	H–D–H
3/4 × 3/4	3/4 × 1/4	1/4 × 3/4	1/4 × 1/4
9/16	3/16	3/16	1/16

Therefore, there would only be one in sixteen molecules, i.e. 6.25% of dye molecules, which were totally hydrolysed and unable to react with the fibre. Thus instead of having 75% of the dye with a reactive group, as in the case of a monofunctional dye, you now have 93.75% of the dye with at least one reactive group for a bifunctional dye. In this example it is assumed that the hydrolysis of the two reactive groups in the bifunctional dye occurs independently of each other. This simplified example serves to highlight the potential of bifunctional dyes over monofunctional dyes, there are of course many factors which will influence the efficiency of the dye–fibre reaction.

The Remazol Black B dye may be represented as:

$$HO_3S\text{–}O\text{–}CH_2\text{–}CH_2\text{–}SO_2\text{–}D\text{–}SO_2\text{–}CH_2\text{–}CH_2\text{–}O\text{–}SO_3H \quad (A)$$

where D represents the dye chromophore (including the bridging groups between the chromophore and the sulfonyl groups).

The β-sulfatoethyl sulfone (SES) is in fact the precursor of the actual reactive group which is the vinyl sulfone (VS), this is generated under dyeing conditions (typically: pH 11, 50°C). Under these alkaline conditions, in addition to the reaction of the dye with ionised hydroxyl groups of cellulose, there is the potential for hydrolysis of the dye to the fibre-unreactive β-hydroxyethyl sulfone (HES) form of the dye to occur. The major products from the stepwise activation and then hydrolysis of Remazol Black B under alkaline conditions are represented below (structures B–E):

$$HO_3\text{–}S\text{–}O\text{–}CH_2\text{–}CH_2\text{–}SO_2\text{–}D\text{–}SO_2\text{–}CH=CH_2 \quad (B)$$

$$H_2C=CH\text{–}SO_2\text{–}D\text{–}SO_2\text{–}CH=CH_2 \quad (C)$$

$$HO\text{–}CH_2\text{–}CH_2\text{–}SO_2\text{–}D\text{–}SO_2\text{–}CH=CH_2 \quad (D)$$

$$HO\text{–}CH_2\text{–}CH_2\text{–}SO_2\text{–}D\text{–}SO_2\text{–}CH_2\text{–}CH_2\text{–}OH \quad (E)$$

Other products formed under alkaline conditions may include dialkyl ether derivatives where two dye molecules are linked through an ether bond. This type of compound, resulting from the reaction of a HES group from one dye molecule with a VS group of another dye molecule [7], is in equilibrium with the reactants. This means that as more of the VS groups are hydrolysed the concentration of these higher-molecular-mass compounds will start to decrease.

A range of bis-monochlorotriazinyl dyes was successfully introduced by ICI (now known as Zeneca) in the late 1960s and early 1970s under the trade name Procion H-E (ICI) dyes. These were developed to take advantage of the higher fixation values possible with bifunctional dyes. These dyes benefited from having a second triazinyl ring system which enhanced further the substantivity of these dyes, so that in an exhaust dyeing application very high levels of exhaustion, and hence fixation could be achieved [8].

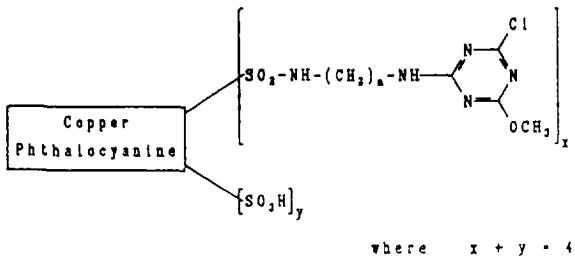

Fig. 2. Representation of the structure of Procion Turquoise H-A.

The second major dye studied as part of this current research was Procion Turquoise H-A (Zeneca) which is based on monochlorotriazinyl reactive groups attached to a copper phthalocyanine chromophore. Due to the complicated synthesis involved in its manufacture this dye is in fact a mixture of related compounds. The basic structure of this dye is outlined in Fig. 2. Analysis of phthalocyanine dyes by HPLC has been largely unsuccessful or unsatisfactory. In this present CE analysis study, by manipulation of buffer composition and pH, it has been possible to obtain some very good separations.

Mixed bifunctional dyes such as those in the Sumifix Supra (NSK) range offer several notable advantages over conventional mono- and bifunctional dyes. The reason for this lays in the difference in reactivity of the two reactive groups, with the VS (generated during dyeing from the SES) reacting typically at 50°C and the monochlorotriazine at 80°C. Thus the dyes are less sensitive to temperature variations during dyeing. Other advantages include minimal sensitivity to alkali and inorganic salts and they are affected less by changes in liquor ratios [9].

In this study the hydrolysis reactions of a selection of model dyes under various pH and temperature conditions were investigated with the aid of CE analysis.

2. Experimental

2.1. Chemicals

The original reactive dyes were of commercial grade (from the manufacturers) and were used without purification. The sodium dodecyl sulfate (SDS) was from Sigma (Poole, UK). The acetonitrile, HPLC grade, was supplied by Vickers Lab. (Burley-in-Wharfdale, UK). All other reagents were analytical grade supplied by BDH (Poole, UK).

2.2. Analysis

A Dionex CE system, CES1, (Dionex, Sunnyvale, CA, USA) was employed for all analyses. An uncoated fused-silica capillary of 59 cm total length × 75 μm I.D. was used. A variety of buffers were investigated with the following buffer composition being particularly good with the selection of dyes employed in this study: 10 m*M* SDS [$CH_3(CH_2)_{11}SO_3^-Na^+$], 10 m*M* sodium tetraborate ($Na_2B_4O_7 \cdot 10H_2O$) and 6 m*M* potassium dihydrogenphosphate (KH_2PO_4) which was made up in acetonitrile–deionised water (1:9, v/v), to give a final pH of pH 9.0. A hydrodynamic injection method was employed with the samples being raised to 50 mm for 10 s. The analyses were run in the constant current mode, generally set at 25 μA (requiring an average voltage of 11 kV). Detection was by an on-line UV–Vis detector positioned at the cathode. The detection wavelength was generally set at the λ_{max} for each dye (Remazol Black B = 597 nm and Procion Turquoise H-A = 666 nm). The AI 450 software (Dionex) was used for peak integration/analysis.

2.3. Remazol Black B activation/hydrolysis investigations

The pH of a fresh solution of Remazol Black B (1.0 g/l) was adjusted by addition of sodium hydroxide solution (concentration varied depending on the pH value required). The dye solution, in a sealed vessel was then placed in a water bath at the required temperature. Small samples were taken for analysis after various time intervals. The temperatures investigated were 32, 45, 61 and 75°C. The pH values investigated were 8, 9, 10 and 11.

3. Results

3.1. Bifunctional SES reactive dye

The main dye analysed in this section was Remazol Black B, a bifunctional reactive dye containing two SES groups per molecule. These results highlight how CE analysis has been utilised to study the reactions of compounds of this type. The selected electropherograms included give an indication of the type of results which were achieved.

Using a micellar buffer system, as previously described in the *Analysis* section, the five major components present/formed under alkaline conditions could be separated and identified. These are labelled (A–E) in the electropherogram displayed in Fig. 3.

The SES groups were converted into the VS form of the dye, the actual reactive form of the dye, by increasing the pH value and/or temperature of the dye solution. Fig. 4 shows a typical example of the CE analysis of a partially activated Remazol Black B dye solution. The actual sample in Fig. 4 was from a dye solution after 30 min at 61°C, pH 9. The conversion to the divinyl sulfone derivative occurring via the monosulfatoethyl sulfone monovinyl sulfone derivative. Under increasingly more severe conditions the divinyl sulfone derivative was hydrolysed to the dihydroxyethyl sulfone derivative via the monovinyl sulfone monohydroxyethyl sulfone derivative. Fig. 5 is of a largely hydrolysed Remazol Black B dye solution.

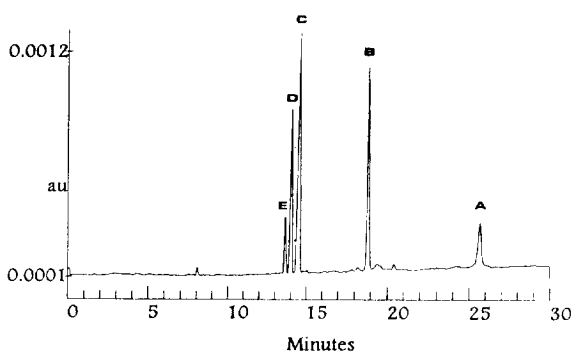

Fig. 3. Electropherogram of Remazol Black B and associated forms (from combined sample of dye solution after 300 min at 32°C, pH 8 with dye solution neutralised after 60 min at 75°C, pH 11). Analysis conditions as described in the *Analysis* section.

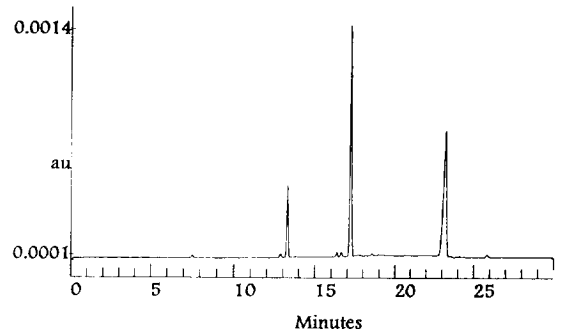

Fig. 4. Electropherogram of partially activated Remazol Black B (dye solution after 30 min at 61°C, pH 9). Analysis conditions as described in the *Analysis* section.

When dye solutions were kept under moderately mild alkaline conditions for prolonged periods of time some interesting CE results were obtained; for example Fig. 6 shows an electropherogram of a Remazol Black B dye solution after 116 h at 75°C, pH 9. Some of the various compounds eluted between 16 and 23 min were thought to be due to dialkyl ether derivatives formed from the reaction of a HES group of one dye molecule reacting with a VS grouping of another dye molecule.

The rates of activation and hydrolysis of Remazol Black B dye solutions under various pH and temperature conditions were successfully

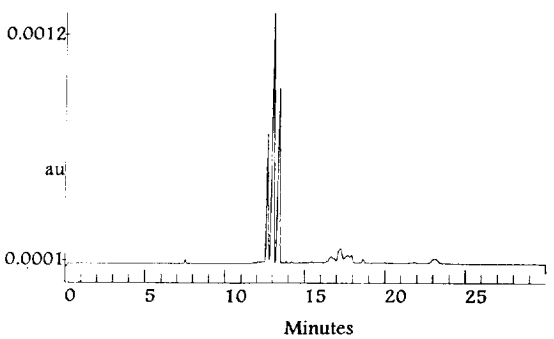

Fig. 5. Electropherogram of largely hydrolysed Remazol Black B (dye solution after 330 min at 61°C, pH 11). Analysis conditions as described in the *Analysis* section.

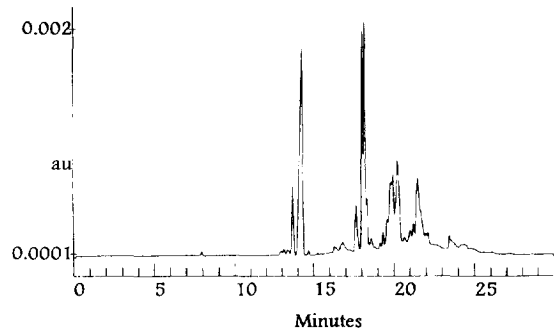

Fig. 6. Electropherogram of Remazol Black B dye solution after 116 h at 75°C, pH 9. Analysis conditions as described in the *Analysis* section.

investigated by CE analysis employing a micellar buffer system containing 10% (v/v) acetonitrile. The results were largely as expected. By plotting the % peak area (which was proportional to concentration) for each component against time of "reaction" then it was possible to graphically represent the rate of both activation and hydrolysis. A selection of the data obtained is presented in Tables 1–4. Tables 1–3 give an indication of how the speed of the conversion of the original dye to the divinyl sulfone form, via the monosulfatoethyl sulfone monovinyl sulfone, was dependent on both the pH of the solution and the temperature. From all the results obtained the pH value was of greater significance than the temperature employed during this study. Table 4 gives an indication of the speed of hydrolysis of the dye solution at 61°C, pH 11.

Table 1
Data illustrating the activation of Remazol Black B at 32°C, pH 8

Time (min)	Percentage composition based on peak area			
	SES–SES	VS–SES	VS–VS	VS–HES
0	92	6	0	0
90	75.6	19.6	2	0
195	70	23.7	2.2	0.4
1 230	43	43	10.5	0.8
1 545	39	44.6	12.1	0.8
10 080	7.1	39.7	50	1.2

Table 2
Data illustrating the activation of Remazol Black B at 61°C, pH 9

Time (min)	Percentage composition based on peak area			
	SES–SES	VS–SES	VS–VS	VS–HES
0	92	6	0	0
30	48.6	42.6	11.8	0.4
60	36.1	46	17.9	0.5
90	28.2	46.4	24.5	0.9
120	22.2	45.8	31	1
360	11	39.3	48.7	1.1

3.2. Phthalocyanine-based chlorotriazinyl reactive dye

An initial attempt to separate the different phthalocyanine-based dye components present in a commercial sample of Procion Turquoise H-A (ICI) by CE utilised a successful buffer from an entirely different project (by the author, at Leeds) and was as described in the method at the start of this section but with 20 m*M* SDS instead of 10 m*M* (current 30 μA). This analysis showed a number of coloured components to be present but they were not baseline resolved, instead all migrating and being detected as a spiked hump between about 13 min and 26 min. Greater resolution was achieved when the buffer contained 10 m*M* SDS. A further increase in resolution was obtained when acetonitrile was employed in the buffer as a co-solvent with water

Table 3
Data illustrating the activation of Remazol Black B at 32°C, pH 11

Time (min)	Percentage composition based on peak area			
	SES–SES	VS–SES	VS–VS	VS–HES
0	92	6	0	0
5	6.5	37	53	1
15	0	1.4	94.5	1.8
30	0	1.2	96.9	1.9
60	0	1.3	97	1.7
90	0	1.3	96.3	2.4

Table 4
Data illustrating the activation and hydrolysis of Remazol Black B at 61°C, pH 11

Time (min)	Percentage composition based on peak area				
	SES–SES	VS–SES	VS–VS	VS–HES	HES–HES
0	92	6	0	0	0
15	3	1.8	95	3.2	0
30	4.5	6	80	5.3	0
60	2	2.7	74.8	9.1	0.5
90	2	1	70.5	11.2	8
330	0	0	30.4	47.3	18.4
1230	0	0	2.3	22.6	58
1470	0	0	1.6	18.3	61.7
2760	0	0	0	10.4	73.2
3960	0	0	0	0	91.8
4080	0	0	0	0	93.4

(25/75) —an example of the results achieved, with a controlled current of 25 μA, is displayed as Fig. 7. This electropherogram clearly showed that the Procion Turquoise H-A was indeed a mixture containing a high number (>12) of coloured components (detection at 666 nm); unfortunately a rather long analysis run time was required for this separation.

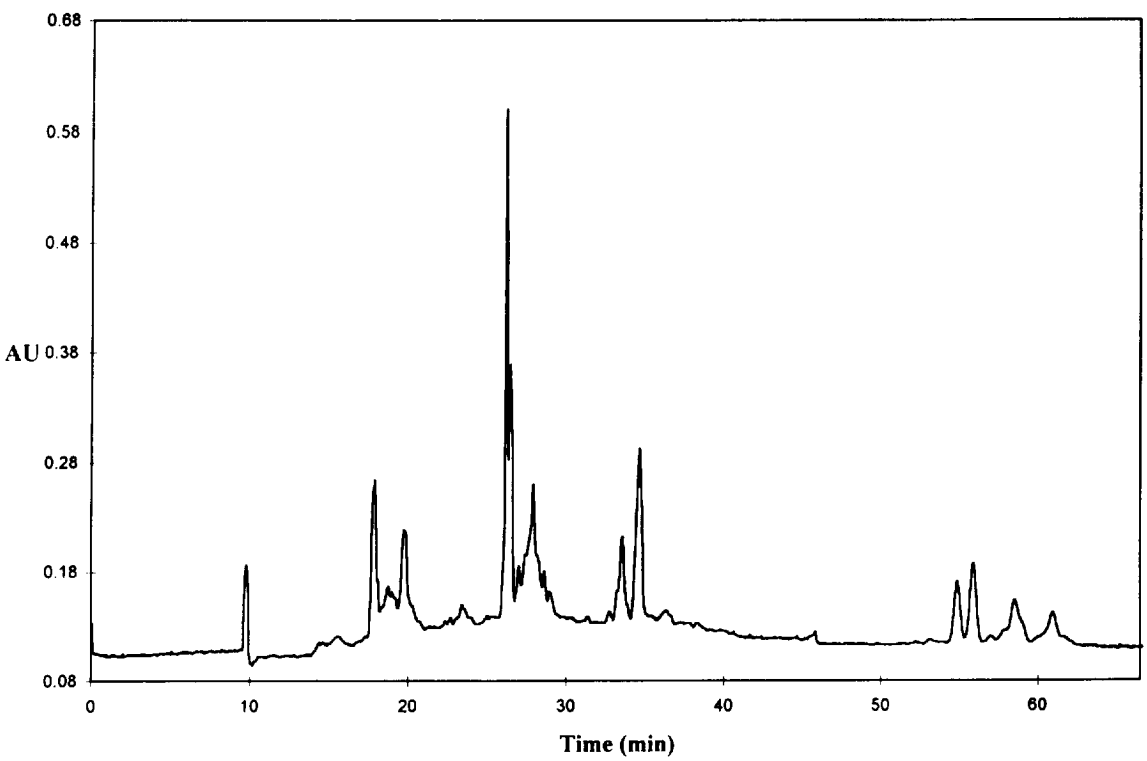

Fig. 7. Electropherogram of Procion Turquoise H-A. Buffer: acetonitrile–deionised water (25:75). Other additives and conditions as described in the *Analysis* section.

By decreasing the acetonitrile content of the buffer to 10% a much shorter analysis time was achieved but with a reduction in the resolution obtained. This buffer (as described in the Experimental section) was employed to obtain the results shown in Figs. 8 and 9.

The electropherogram for the dye solution at pH 7 was the same as that obtained when the dye solution was adjusted to pH 11 prior to analysis. Fig. 8 shows the result for the analysis of the fresh dye solution at pH 11. On heating the dye solution, at pH 11, to 80°C for 1 h a significantly different electropherogram (Fig. 9) was obtained with the loss and addition of a number of peaks. These results gave evidence for the hydrolysis of dyes containing reactive chlorotriazinyl groups (peaks not present in Fig. 9) to dyes with the fibre-unreactive hydroxytriazinyl analogues (new peaks in Fig. 9).

The electropherograms displayed in this subsection demonstrated the potential of CE to analyse and aid in the study of this dye and dyes of this type based on a phthalocyanine chromophore. A full study and interpretation of the results for phthalocyanine dyes has still to be undertaken.

3.3. Mixed bifunctional reactive dyes

A number of mixed bifunctional reactive dyes have been successfully analysed using buffer systems very similar to or the same as those already described in this paper. The Sumifix Supra dyes contain both a SES reactive moiety and a monochlorotriazine reactive grouping. Reactions, including hydrolysis, of these different groups were distinguished and monitored —this forming part of some continuing research work at the Colour Chemistry and Dyeing Department, University of Leeds.

4. Conclusions

A variety of bifunctional reactive dyes were successfully analysed by micellar electrokinetic

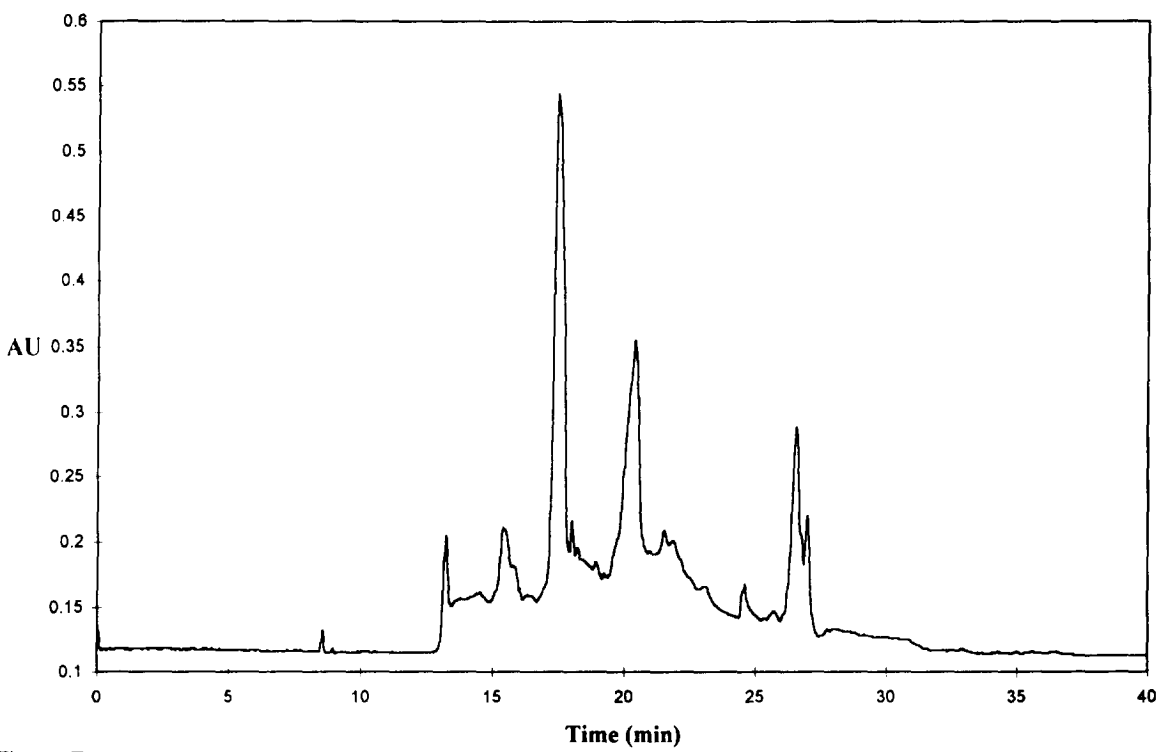

Fig. 8. Electropherogram of Procion Turquoise H-A at pH 11. Analysis conditions as described in the *Analysis* section.

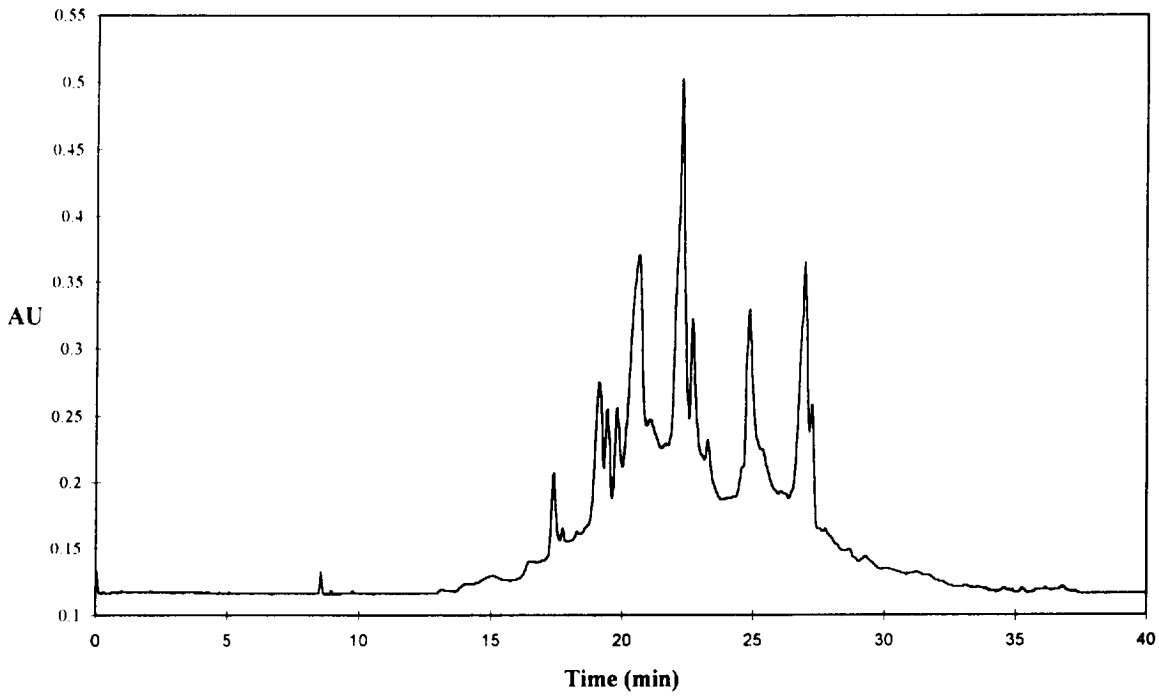

Fig. 9. Electropherogram of Procion Turquoise H-A dye solution at pH 11 after heating to 80°C for 1 h. Analysis conditions as described in the *Analysis* section.

capillary chromatography. The employment of acetonitrile at a ratio of 1:9 with the aqueous buffer generally improved the resolution of the different components in the samples. Examples of the potential applications of buffer systems of this type include: checking the purity of reactive dye samples; monitoring the reactions plus rate of reactions (kinetic studies) of reactive dyes with nucleophiles; analysing coloured effluents; investigating components in residual dye baths; investigating the breakdown of reactive dyes and the identity of breakdown species from effluent treatment processes.

Acknowledgement

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