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Dyes and Pigments 40 (1999) 243–249

DYES AND PIGMENTS

Kinetic study of reaction of m-(2-sulfatoethyl)sulfonyl aniline and a monochlorotriazinyl dye in aqueous solution

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Received 1 June 1998; accepted 6 July 1998

Abstract

Dye containing two m-(2-sulfatoethyl sulfonyl) anilino groups was synthesized and characterized. The reaction between m-(2-sulfatoethyl sulfonyl) aniline and the monochlorotriazinyl dye has been studied in aqueous solution at various temperatures and pH values, and the rate constants of the reaction determined by the thin layer chromatograph scanning method. The temperature dependence of the rate constants was normal, but an unexpected increase of the rate constant was observed at pH 2.0. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Kinetic study; Reactive dyes; Aqueous solution; TLC double scanning

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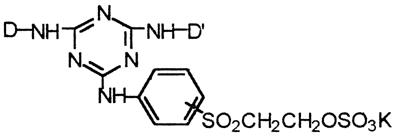
1. Introduction

Reactive dyes containing two 2-sulfatoethyl sulfonyl anilino residues have received much attention recently because of their high fixation yield and good level-dyeing property. We were therefore interested in dyes of the general formula shown below:



in which D is a common chromophore and D′ is a substituted aromatic amino sealed group or a common chromophore with vinylsulfonyl type reactive residues.

The key step of the synthesis of such dyes is the condensation of the monochlorotriazinyl dye with 2-sulfatoethyl sulfonyl aniline. In our previous papers [1,2], we reported the synthetic kinetics of the reaction using model dyes. The results showed that m-(2-sulfatoethyl sulfonyl) aniline was the preferred reactive group. However, in order to simplify the reaction product, these reactions were carried out in non-aqueous media. In this present paper, we report a further study using more practical dyes containing sulfonic acid groups, and the reaction was carried out in an aqueous solution typical of that which occurs in the manufacture process. But in this case, a problem arose that the identification and purification the of dyes were very difficult. Based on our previous work [3], we used an improved dry volume chromatography technique and successfully obtained pure dyes. The rate constants of the reaction at various temperatures and pH values were obtained by the thin layer chromatography

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PII: S0143-7208(98)00059-X

scanning method. As previously reported [3], the poor solubility of the dyes in solutions of low pH limited the range of the pH value studied from 5.0 to 3.0. We therefore selected a chromophore with more sulfonic acid groups to increase the solubility of dye at low pH values, and an unexpectedly large reaction rate was observed at pH 2.0.

2. Results and discussion

2.1. Synthesis and purification of D_1 and D_2

D_1 was obtained by the literature method [4]. D_2 were synthesized by the following route (Scheme 1).

The reaction of D_1 and p-(2-sulfatoethyl sulfonyl) aniline was also investigated, but the determination of the rate constant failed. The quantitative change of D_1 was too small to be examined before the hydrolysis product appeared.

2.2. Standard curve of D_1

The peak areas of the spots obtained are shown in Table 1.

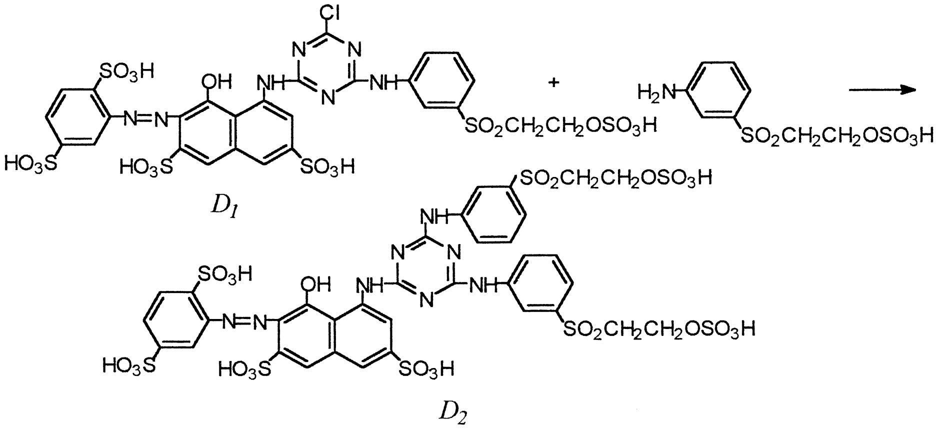
Plots of the peak areas (L) against the corresponding moles (M) are shown in Fig. 1. The regression equation and the correlation coefficient were $L = 0.5434\ M$ and $\gamma = 0.9983$, respectively.

2.3. Quantitative change of D_1 by TLC-double scanning

The pH of the buffer used was from 2.0 to 5.0. When the pH was up to 5.0, a spot corresponding to the hydrolysis product appeared after developing. When the pH was below 2.0, it was very difficult to separate the mixture by TLC. To minimise the error, various volumes of samples were spotted and developed according to the reaction rate; resulting data is listed at a note to the table. The developer was n-butanol:ethanol:DMF:acetic acid:water = 25:1:4:1:11.

The experimental data obtained for the reaction rate is shown in Tables 2–8.

On plotting 1/L of D_1 against time (in min) of pH 5.0 at 90°C, a straight line was obtained (Fig. 2). The regression equation and correlation coefficient were $1/L = 0.0028t + 1.7224$ and $\gamma = 0.9967$, respectively.



Scheme 1.

Table 1
Data of standard curve

Mole (10^6)	1.0	2.0	3.0	4.0	5.0	6.0
Peak area	53 977.6	112 745.1	173 855.8	218 799.0	263 420.1	325 225.0

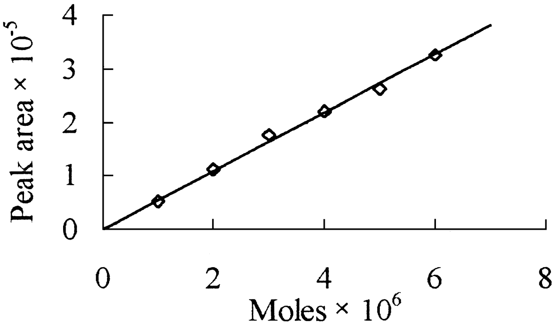


Fig. 1. Standard curve of D_1.

On plotting 1/L of D_1 against time (in min) of pH 4.0 at 90°C, a straight line was obtained (Fig. 3). The regression equation and correlation coefficient were $1/L = 0.0048t + 1.6994$ and $\gamma = 0.9970$, respectively.

On plotting 1/L of D_1 against time (in min) of pH 3.0 at 90°C, a straight line was obtained (Fig. 4). The regression equation and correlation coefficient are $1/L = 0.0069t + 1.1372$ and $\gamma = 0.9990$, respectively.

On plotting 1/L of D_1 against time (in min) of pH 4.0 at 100°C, a straight line was obtained

Table 2
Data for pH 5.0 at 90 ± 1°C

Time (min)	1	10	20	30	40	50	61
Area (L)	58 182.78	57 014.16	56 141.1	55 407.61	54 512.09	53 461.90	52 995.44
1/L (10^5)	1.720	1.754	1.781	1.805	1.834	1.870	1.887

30 μl of mixture was taken out and diluted by 40 μl of water; 1.0 μl of sample was then developed.

Table 3
Data for pH 4.0 at 90 ± 1°C

Time (min)	1	10	20	30	40	50	60
Area (L)	58 603.92	57 155.90	55 632.72	54 710.07	52 650.21	51 412.50	50 477.56
1/L (10^5)	1.706	1.750	1.798	1.828	1.899	1.945	1.981

0.03 ml of sample was taken out and diluted by 0.03 ml water; 1.0 μl of sample was then developed.

Table 4
The data of pH 3.0 at 90 ± 1°C

Time (min)	2	10	20	30	40	50	60
Area (L)	86 630.5	82 745.1	78 342.1	74 634.4	71 048.6	67 768.58	63 987.2
1/L (10^5)	1.154	1.209	1.276	1.340	1.407	1.476	1.563

0.03 ml of sample was taken out and diluted by 0.03 ml water; 2.0 μl of sample was then developed.

Table 5
Data of pH 4.0 at 100 ± 1°C

Time (min)	2	6	10	15	20	25	30
Area (L)	128 260.6	122 449.4	118 299.5	115 801.8	110 864.6	105 695.6	102 016.26
1/L (10^6)	7.797	8.167	8.453	8.635	9.020	9.461	9.802

0.03 ml of sample was taken out and diluted by 0.03 ml water; 2.0 μl of sample was then developed.

(Fig. 5). The regression equation and correlation coefficient are $1/L = 0.0695t + 7.6904$ and $\gamma = 0.9959$, respectively.

On plotting 1/L of D_1 against time (in min) of pH 2.0 at 90°C, a straight line was obtained (Fig. 6). The regression equation and correlation coefficient are $1/L = 1.0806t + 9.9108$ and $\gamma = 0.9973$, respectively.

On plotting 1/L of D_1 against time (in min) of pH 2.0 at 80°C, a straight line was obtained (Fig. 7). The regression equation and correlation coefficient are $1/L = 0.5735t + 8.5705$ and $\gamma = 0.9994$, respectively.

On plotting 1/L of D_1 against time (in min) of pH 2.0 at 70°C, a straight line was obtained (Fig. 8). The regression equation and correlation coefficient are $1/L = 0.3468t + 9.5114$ and $\gamma = 0.9959$, respectively.

The rate equation is as our previous report [1,3]; the rate constants of the reaction are shown in Tables 9–11.

Table 6
Data of pH 2.0 at 90 ± 1°C

Time (min)	1	5	10	15	20	25	30
Area (L)	100 077.0	62 820.92	48 579.01	36 113.79	32 164.23	27 391.14	23 718.59
$1/L$ (10^6)	9.972	15.918	20.585	27.690	31.090	36.508	42.161

0.03 ml of sample was taken out and diluted by 0.03 ml water; 2.0 μl of sample was then developed.

Table 7
Data of pH 2.0 at 80 ± 1°C

Time (min)	2	6	10	15	20	25	30
Area (L)	112 879.2	84 598.4	69 682.8	58 409.01	50 361.2	43 492.03	38 780.43
$1/L$ (10^6)	8.859	11.821	14.351	17.121	19.857	22.993	25.786

0.03 ml of sample was taken out and diluted by 0.03 ml water; 2.0 μl of sample was then developed.

Table 8
Data of pH 2.0 at 70 ± 1°C

Time (min)	1	8	15	25	35	45	60
Area (L)	102 539.1	80 380.5	68 926.1	54 708.67	45 463.79	40 303.46	32 961.69
$1/L$ (10^6)	9.752	12.441	14.508	18.279	21.996	24.812	30.340

0.03 ml of sample was taken out and diluted by 0.03 ml water; 2.0 μl of sample was then developed.

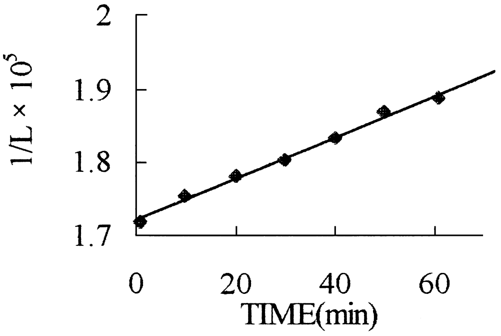


Fig. 2. Plot of 1/L vs time of pH 5.0 at 90 ± 1°C.

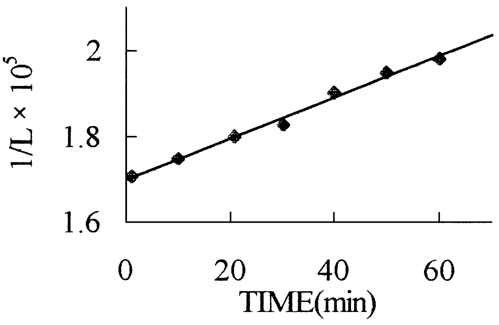


Fig. 3. Plot of 1/L vs time of pH 4.0 at 90 ± 1°C.

The temperature dependence of the reaction at a specific pH is shown to conform to the normal rule (Fig. 10), but higher temperatures may result in a hydrolysis reaction. At the same time, the rate constant rises as pH decreases (Fig. 9). This result can be explained by an acid catalyzed mechanism [3]. But, contrary to our expectation, the rate constant at pH 2.0 increases very significantly.

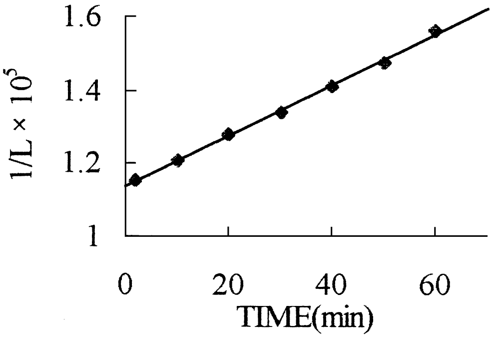


Fig. 4. Plot of 1/L vs time of pH 3.0 at 90 ± 1°C.

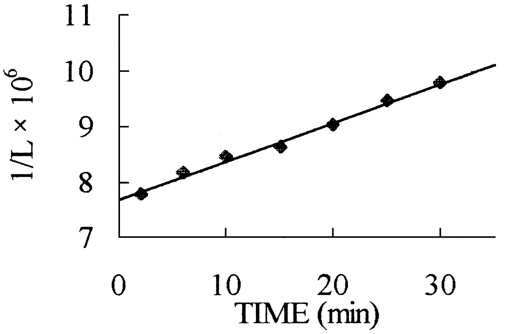


Fig. 5. Plot of 1/L vs time of pH 4.0 at 100°C.

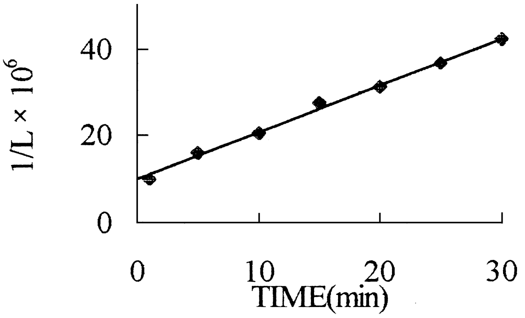


Fig. 6. Plot of 1/L vs time of pH 2.0 at 90 ± 1°C.

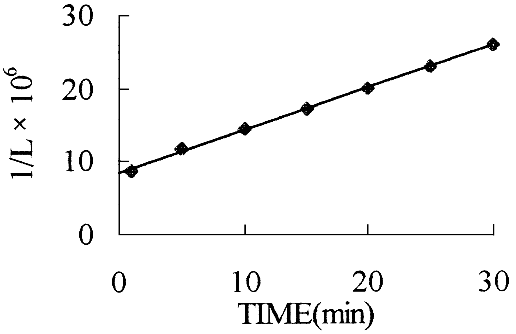


Fig. 7. Plot of 1/L vs time of pH 2.0 at 80 ± 1°C.

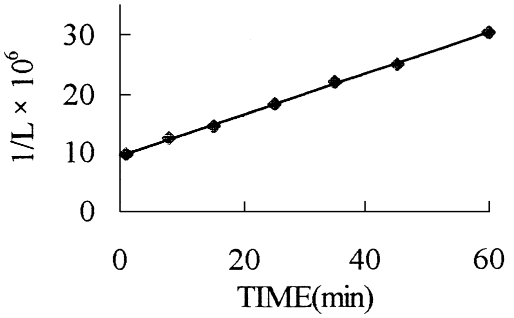


Fig. 8. Plot of 1/L vs time of pH 2.0 at 70 ± 1°C.

Table 9
Reaction rate constant at 90 ± 1°C

pH value	5.0	4.0	3.0	2.0
Rate constant	0.2845	0.4236	0.9101	16.3550

Table 10
Reaction rate constants at pH 2.0

Temperature (°C)	70	80	90
Rate constant	5.4693	10.0374	16.3550

Table 11
Reaction rate constants at pH 4.0

Temperature (°C)	90	100
Rate constant	0.4236	1.3556

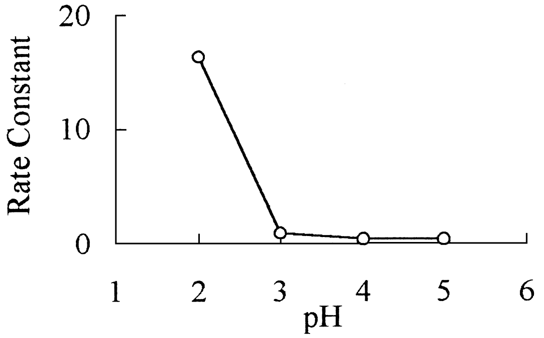


Fig. 9. pH dependence of rate constant.

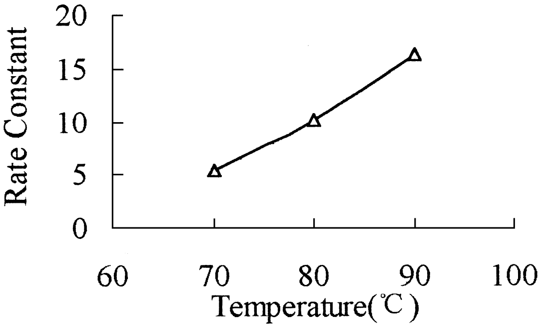


Fig. 10. Temperature dependence of rate constant.

Even at a lower temperature (70°C), the rate constant is still quite greater than that at other pH values at 90°C. This observation offers us a way to optimize the reaction conditions to minimise the hydrolysis of the 2-sulfatoethyl sulfonyl group. Although the 2-sulfatoethyl sulfonyl group is relatively stable in acidic solution, it is still unavoidable to prevent hydrolysis in practical synthesis. Therefore, whilst lower temperature and pH give high yield of the dyes, at low pH value, the problem of precipitation of dyes with less sulfonic acid groups still needs to be resolved.

3. Experimental section

The TLC double wavelength scanning was measured on a Shumidazu CS-930 double scanner; elemental analysis was determined on an MA-1106 instrument.

3.1. Preparation and purification of dyes

3.1.1. Synthesis and purification of D_1

Two grams (0.011 mol) of cyanuric chloride and 25 g of ice were mixed and stirred for 0.5 h and then a 20% solution of H-acid 17.1 ml (0.01 mol) was added, pH raised to 3–4 and reaction continued at 0–3°C for 5 h. Subsequently, 0.01 mol of the diazoium salt of 2-aminobenzene-1,5-di-sulfonic acid was poured into the reaction mixture and the pH adjusted to 5.5 with 20% aq. sodium carbonate at 8–10°C. When the diazonium salt had fully reacted, 0.011 mol of m-(2-sulfatoethyl sulfonyl)aniline was added and the liquor stirred at 25–30°C for 10 h. The crude dye D_1 was obtained.

The crude dye D_1 was then dissolved in water, precipitated by potassium chloride and filtered. The filtrate was dissolved in water again, and the above process was repeated several times until the dye gave a single spot on TLC. The dye thus obtained was dried in a vacuum desiccator with P_2O_5. The dye was then further purified twice by dry volume chromatography as previously reported [3], the developer was n-butanol:ethanol:DMF: acetic acid:water = 30:1:4:1:11 and the eluent was mixed with ethanol to precipitate the dye which was filtered off to give pure dye D_1.

Both D_1 and D_2 contained water of crystallization; these were treated as our previous reported [3,5].

Anal. Calcd. for D_1: C, 29.18; H, 3.35; N, 8.82. Found: C, 28.88; H, 3.20; N, 9.20.

3.1.2. Synthesis and purification of D_2

D_2 was prepared according to Scheme 2.

Solution of D_1 (0.01 mol) and 0.011 mol of a 20% solution of m-(2-sulfatoethyl sulfonyl) aniline were mixed with pH being adjusted to 5.5. The mixture was refluxed for 1 h to give crude dye D_2.

The crude dye D_2 was purified by dry volume chromatography [3], but the mobile phase was developed from top to bottom to shorten the experiment time. The developer was n-butanol:ethanol:DMF:acetic acid:water = 25:1:4:1:11. The dye thus obtained was mixed with acetic potassium and filtered off. This process was repeated. The filtrate was washed by ethanol until the AgCl test showed a negative result. The pure dye was dried with P_2O_5 under vacuum.

Anal. Calcd. for D_1: C, 26.08; H, 2.75; N, 7.69. Found: C, 25.81; H, 2.44; N, 7.33.

3.2. Kinetic Study

3.2.1. Standard curve of D_1

A standard solution of the dye in water at a concentration of 2×10^{-5} mol/liter was prepared. Aliquot portions of this solution were further diluted to give a series of solutions. The samples were applied to the chromatographic plate, developed and scanned. The developer was n-butanol:ethanol:DMF:acetic acid:water = 30:1:4:1:11.

3.2.2. Determination of the quantitative change of model D_1 by TLC-double scanning

D_1 (0.02 mmol) in 1 ml of pH 5.0 buffer was heated to 90°C in a super thermostat, and 0.5 ml of 4×10^{-5} mol/liter of solution of m-(2-sulfatoethyl sulfonyl)aniline was added. Samples were taken out and diluted by water immediately at various time intervals. A specific volume of the diluted sample was spotted onto a thin-layer plate, developed and scanned, and the peak area (L), and 1/L vs time, were thus obtained.

4. Conclusion

The reaction of monochlorotriazinyl dyes and m-(2-sulfatoethyl sulfonyl)aniline in aqueous solution at various temperatures and pH values was studied kinetically. The dyes were purified by dry volume chromatography and confirmed by elemental analysis. The rate constants of reactions were determined by the TLC scanning method. The temperature dependence of rate constant was normal, but a dramatic increase of the reaction rate at pH 2.0 was observed. The result supplies a clue to optimize the condition of this reaction, which is essential to improve the dye yield.

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