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The Comparison of the Kinetics of Hydrolysis of Some Reactive Dyes Before and After Purification

Abstract

A dimethylformamide-tetrachloroethylene (DMF/TCE) solvent-nonsolvent mixture was used for the purification of monochloro-s-triazine, monofluoro-s-triazine and bis (monofluoro-s-triazine) reactive dyes. The question is important for dye-house practise in the textile industry, when using reactive dyes for dyeing cotton fabrics and expecting good dye stability after washing. Dye purity was tested by sodium analysis on the basis of the results of the inductively coupled plasma/atomic emission spectroscopy (ICP AES method). The stability of commercial and purified dyes in solutions of pH 7 and pH 12 at 20 °C (60 °C) was investigated by the HPLC method. The pseudo-first-order rate law was used to calculate the rate constants of hydrolysis of dyes in alkaline media. Neutral solutions of all dyes examined at 20 °C remained unchanged after 24 hours. No apparent difference was found between the rates of hydrolysis of all the commercial and purified reactive dyes studied.

Key words: reactive dyes, monochloro-s-triazine, monofluoro-s-triazine, bis (monofluoro-s-triazine), purification, dimethylformamide/tetrachloroethylene (DMF/TCE), hydrolysis, high performance liquid chromatography (HPLC).

Introduction

In comparison to pure dyes, commercial dyes generally contain defined quantities of inorganic salts, buffer salts, and some intermediates or isomeric byproducts of the synthesis.

Scientists either synthesise dyes for basic research [1 - 18], or purify commercial dyes. Several methods are known for purifying direct and acid commercial dyes [19 - 21]. Purification of reactive dyes gives rise to the possibility of hydrolysis during the purification process. In particular reactive dyes, depending on the nature of the reactive system itself and of the influence of the chromogen on it, are prone to hydrolysis. Hydrolysed dye do not form covalent bonds with fibres, and are also not useful for studying fundamental physicochemical phenomena. Some methods for purifying reactive dyes with different reactive systems are also known [22 - 25]; according to those methods, some scientists have purified reactive dyes for their studies [26, 27], while others have used commercial dyes [28 - 31].

The question is important for dye-house practise in the textile industry, when using reactive dyes to dye cotton fabrics, and expecting good dye stability after washing. On the other hand, this problem is also important from the theoretical point of view, in order to answer the question of which method is most appropriate for purifying monochloro-s-triazine, monofluoro-s-triazine, bis(monofluoro-s-triazine) reactive dyes.

The aim of this research was to establish an appropriate method for purifying reactive dyes with different reactive systems.

We studied a mixture of dimethylformamide/tetrachloroethylene (DMF/TCE) sol-vents used for purifying scarlet monochloro-s-triazine (CI Reactive Red 43), monofluoro-s-triazine (CI Reactive Red 183) and bis (monofluoro-s-triazine) (CI Reactive Red 268) dyes. The amount of hydrolysed dye in the parent dye after purification together with the stability of commercial and purified dyes in solutions at pH 7 and pH 12 at 20 °C were determined experimentally by the high performance liquid chromatography (HPLC) method. The stability of pure and commercial monofluoro-s-triazine dye (CI Reactive Red 183) at pH 11 at 60 °C (fixation conditions) was also compared.

Experimental

Materials

CI Reactive Red 43 was supplied by BASF, CI Reactive Red 183 and CI Reactive Red 268 dyes were supplied by Ciba. N,N-dimethylformamide (Merck) and tetrachloroethylene (Fluka Chemie AG) were analytically pure. Buffers of pH 7 and pH 12 (Riedel de Haën AG) were used as media to study the hydrolysis reaction. Acetonitrile (Baker, HPLC grade), tetrabutylammonium bromide (Fluka Chemie AG, 99%), ammonium dihydrogenphosphate (Fluka Chemie AG, 99%), and deionised water were used in the HPLC mobile phase.

The structural schemes and molecular masses of the dyes used for analysis are presented in Figure 1.

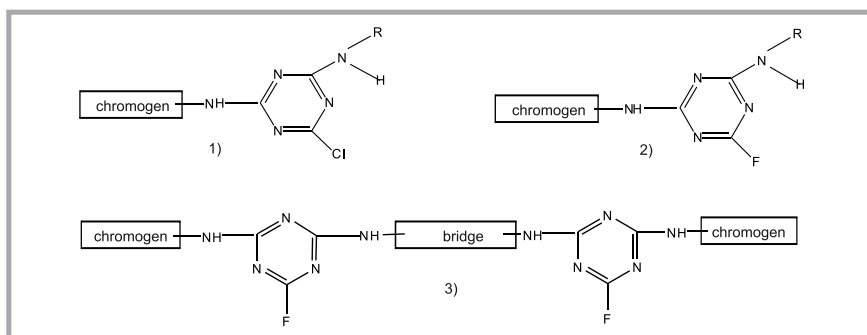


Figure 1. Structural schemes and molecular masses of the dyes used for analysis; 1) Procion Scarlet H-2G (CI Reactive Red 43, $M = 755,8$ g/mol), 2) Cibacron Scarlet F-3G (CI Reactive Red, $M = 713,6$ g/mol), 3) Cibacron Scarlet LS-2G (CI Reactive Red 268, $M = 1333,0$ g/mol).

Buffers used for research:

Buffer pH 12: di-Natriumhydrogenphosphat 99%, $\text{HNa}_2\text{O}_4\text{P}_2\text{H}_2\text{O}$, M_r 177.99 g/mol, p.a. (Fluka BioChemika); Natriumhydroxid, NaOH 98%, M 40.00 g/mol, p.a. (Lachema).

Buffer pH 11: Borsäure, 99.5%, BH_3O_3 , M 61.83 g/mol, p.a. (Fluka Chemika); Natriumhydroxid, NaOH 98%, M 40.00 g/mol, p.a. (Lachema); Kaliumchlorid, 99.5%, KCl, M 74.56 g/mol, p.a. (Fluka Chemika).

Buffer pH 7: di-Natriumhydrogenphosphat 99%, $\text{HNa}_2\text{O}_4\text{P}_2\text{H}_2\text{O}$, M_r 177.99 g/mol, p.a. (Fluka BioChemika); Kaliumhydrogenphosphat, 99%, M 136.1 g/mol, p.a. (TKI Hrastnik).

Method of purification

The method described in the literature [23] was modified only by the temperature of DMF. 15 g of commercial dye was dissolved in 200 ml of dimethylformamide. Next, the temperature was raised to 100 °C for 1 hour. The dye solution was filtered through paper to remove insoluble impurities such as electrolytes and other inorganic salts. 400 ml of tetrachloroethylene was slowly added to the filtrate with continuous stirring. The solution was left in a refrigerator until the following day, when the dye was precipitated. The precipitated dye was then separated by filtration. Recrystallisation was performed twice. The purified dye was dried at room temperature until the following day. Drying was continued in a vacuum drier at 70 °C for 24 hours, and put in a desiccator for 30 min.

Determination of dye purity

Dye purity was tested by sodium analysis. The amount of sodium was determined by the inductively coupled plasma/atomic emission spectroscopy (the ICP AES method).

The method is based on the effect of plasma, which arises when argon gas flows through a field consisting partly of electrically charged particles. Plasma temperatures can be very high, up to 6000-7000 °C. At high temperatures, most elements emit light at characteristic wavelengths.

Hydrolysis kinetics

0.1 g/l solutions of commercial or purified dyes at pHs 7, 11 and 12 were prepared at 20 °C by using the appropriate buffer solution. 10 ml aliquots were withdrawn from the dye solution at 10-minute intervals into a 25 ml volumetric flask. Aliquots of buffer solutions at pH 12 and pH 11 were immediately neutralised to pH 7 with equivalent amounts of dilute 0.1N HCl to prevent further hydrolysis reactions. Next, the aliquots were diluted with bi-distilled water up to the mark. The solution was filtered through 0.45 μm filters. The injected volume of each analysed sample was 20 μl .

High performance liquid chromatography (HPLC) analysis

Analysis was carried out at room temperature using HPLC (Thermo Separation Products), with a C-18 ion pair reverse-phase column (ODS Hypersil 5 μm , Thermo Hypersil-Keystone). Isocratic elution was used with 40 parts of solvent A (100% acetonitrile containing 0.025 M tetrabutylammonium bromide as an ion pairing agent) and 60 parts of solvent B (30 parts of A and 70 parts of deionised water containing 0.05 M ammonium dihydrogenphosphate) as a mobile phase [28]. With the flow rate of the mobile phase at 1 ml/min, 20 μl of neutralised dye solution was injected. Separated active and hydrolysed dyes, eluted from the column, were detected at 500 nm.

The results of the constants of the rate of dye hydrolysis are the mean values of the two measurements.

Results and discussion

The method of purification according to Chavan was used to purify three commercial scarlet reactive dyes with different reactive systems [23]. This method provides a simple technique for purifying anionic dyes. The inorganic salts are insoluble in DMF, and the dyes after recrystallisation are free from inorganic impurities. One of the criteria for establishing the purity of dyes is to determine the amount of sodium by the ICP AES method. Purification was conducted twice. The results of sodium content in the dye according to an ICP AES analysis of the CI: RR 43, CI: RR 183 and CI: RRE 268 commercial dyes and the twice-purified dyes are shown in Table 1.

The percent of sodium shows that after the second treatment in DMF/TCE, the dyes are practically free of inorganic salts. The purity levels of CI: RR 43, CI: RR 268 and CI: RRE 183 was 93.4%, 91.3% and 100%.

The amounts of hydrolysed dye in the parent dye after the DMF/TCE treatment as identified by HPLC were 0.9%, 4.5%, and 3.7% for CI: RR 43, CI: RR 183 and CI: RRE 268 respectively. DMF/TCE seems quite an appropriate solvent/nonsolvent mixture for the purification of treated reactive dyes. The mixture had no apparent influence on the hydrolysis of the dyes.

The stability of 0.1 g/l solutions of commercial and purified dyes at pH 7 at 20 °C was determined by HPLC. The necessary corrections of peak areas of active forms were made according to the correlation of peak areas of different concentrations of the pure dye. No hydrolysis reaction takes place within 24 hours with either the commercial or the purified dyes. These findings are important in everyday dye-house practise in preparing dyeing solutions and printing pastes with monochloro-s-triazine, monofluoro-s-triazine and bis (monofluoro-s-triazine) reactive dyes.

Experimental data using HPLC was used to compare the stability of solutions of commercial and purified dyes at pH 12 at 20 °C. The pseudo-first-order reaction was used to calculate the kinetics of

hydrolysis from the experimental data, in accordance with the great excess of hydroxide anions in pH 12 buffer solution.

The overall rate of disappearance of the reactant (active form of dye A) at a constant temperature was determined by Equation (1) [32]:

$$-\frac{d[A]}{dt} = k \cdot [A] \quad (1)$$

The reaction rates of the hydrolysis of CI Reactive Red 43, CI Reactive Red 183 and CI Reactive Red 268 were determined by plotting $\ln[A]_0/[A]_t$ against reaction time at 20 °C (60 °C). Straight lines were obtained, and the slopes corresponded to the reaction rate constants (k). The values of the rate constants are given in Table 2.

The results indicate that there is no difference in the rate constants of hydrolysis for commercial and purified CI Reactive Red 43 dye. Hydrolysis of this monochloro-s-triazine dye at 20 °C is very low.

CI Reactive Red 183 dye hydrolyses approximately 40 times faster than CI Reactive Red 43 dye, and the results further show that the rate of hydrolysis of the purified form of CI Reactive Red 183 is much the same as that for its commercial form.

Bifunctional CI: RRE 268 dye was hydrolysed in two steps. The rate of hydrolysis was determined as the disappearance of an active bifunctional form at pH 12 at 20 °C. The rate of hydrolysis of purified CI Reactive Red 268 is practically the same as that of the commercial dye.

Taking into account the maximum error between measurements of $\pm 5\%$, the results of the rates of hydrolysis are practically the same.

As there was a negligible difference between the hydrolysis rates of the pure and commercial forms of reactive dyes in a buffer solution of pH 12 at 20 °C, we chose to repeat the hydrolysis experiments in a buffer solution of pH 11 at

Table 3. Rate constants k (in min^{-1}) for CI: RR 183 at 60 °C at pH 11, calculated without zero point; max. error $\pm 5\%$.

Commercial	Purified	Purified form + sodium sulphate
$8.69 \cdot 10^{-2}$	$7.68 \cdot 10^{-2}$	$8.02 \cdot 10^{-2}$

Table 1. Percent of sodium in commercial and purified dye.

Dye	No. of SO_3Na	Mol. Wt., g/mol	Sodium, %		Purity, %
			Theor.	Exptl.	
CI Reactive Red 43	2	755.8	6.1	6.5	93.4
CI Reactive Red 183	2	713.6	6.5	6.5	100.0
CI Reactive Red 268	4	1333.0	6.9	7.5	91.3

Table 2. Rate constants k (in min^{-1}) at 20 °C at pH 12 for CI: RR 43, CI: RR 183 and CI: RRE 268; max. error $\pm 5\%$.

DYE	Commercial	Purified
CI: Reactive Red 43	$5.123 \cdot 10^{-5}$	$5.164 \cdot 10^{-5}$
CI: Reactive Red 183	$1.958 \cdot 10^{-3}$	$2.103 \cdot 10^{-3}$
CI: Reactive Red E 268	$1.475 \cdot 10^{-3}$	$1.513 \cdot 10^{-3}$

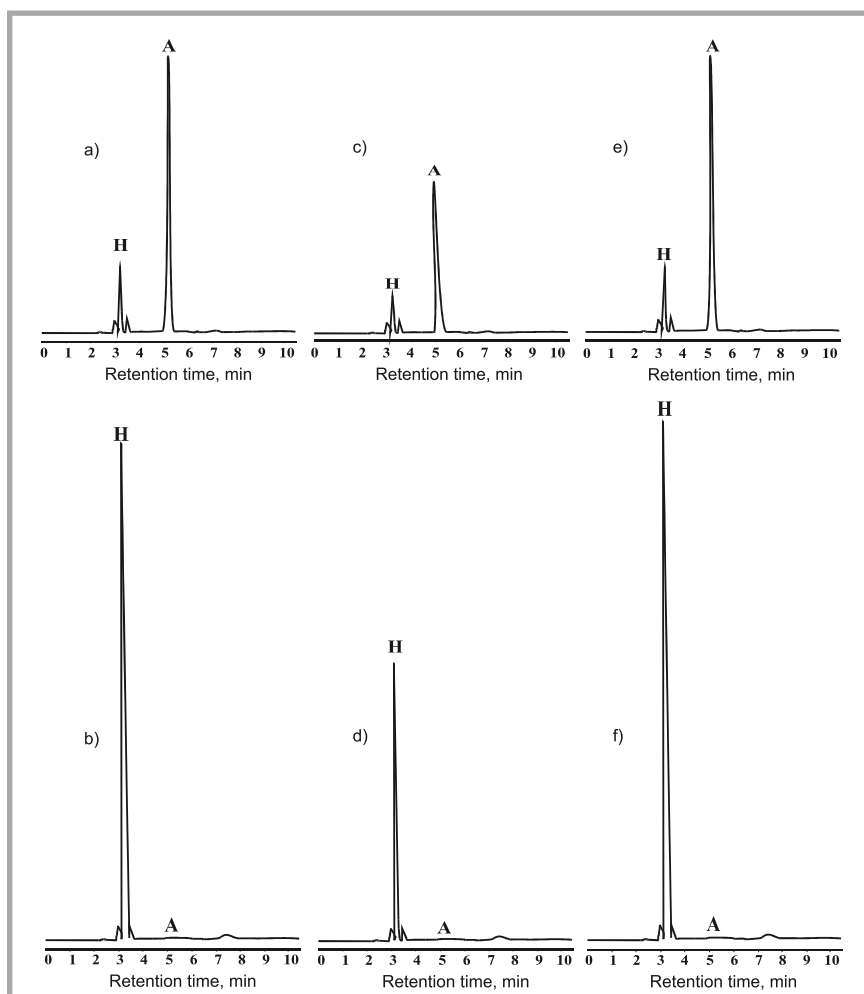


Figure 2. HPLC chromatograms of C.I. Reactive Red 183 dye at the beginning and after one hour at pH 11 at 60 °C: a) purified dye at the beginning, b) purified dye after one hour; c) purified dye + electrolyte at the beginning, d) purified dye + electrolyte after one hour; e) commercial dye at the beginning, f) commercial dye after one hour.

60 °C for CI Reactive Red 183. These parameters for the pH media and temperature are appropriate for the fixation of this dye with cellulose fibres. The rate of hydrolysis of purified & commercial dyes, and a mixture of purified dye (60%) and electrolyte (40% Na_2SO_4), were tested at pH 11 at 60 °C. However, the results collected in Table 3 do not show any signifi-

cant difference (the maximum error between measurements being $\pm 5\%$) in the rate of hydrolysis of the individual dyes.

Figure 2 shows HPLC chromatograms of CI Reactive Red 183 which is purified, purified with sodium sulphate and commercially made in a pH 11 solution at 60 °C.

Conclusions

The results of the research show the following:

1. a DMF/TCE solvent/nonsolvent system is an appropriate system for the purification of used scarlet reactive dyes;
2. the content of hydrolysed dye, checked by HPLC, in purified CI Reactive Red 43 is 0.9%, in purified CI Reactive Red 183 4.5% and in purified CI Reactive Red 268 is 3.7%;
3. the calculated purity of dyes obtained from the results of ICP AES of dyes on the content of sodium is 93.4% (CI Reactive Red 43), 100% (CI Reactive Red 183) and 91.3% (CI Reactive Red 268). From the theoretical point of view, an evaluation of the concentration of reactive dyes in different solutions of commercial dyes using pure dye is important. The calibration curves made by purified reactive dyes are of particular importance for the exactness of measurements and for determining their physicochemical properties;
4. no transformation of active to hydrolysed dye (HPLC, all dyes) takes place in a pH 7 solution at 20 °C. This result is useful in laboratory practise, and also in industry for everyday preparation of solutions of reactive dyes or printing pastes used for dyeing and printing of cotton textiles. Under these conditions, good wet fastness of dyed textiles are expected;
5. the rates of hydrolysis (as checked by HPLC) of commercial and purified CI Reactive Red 43, CI Reactive red 183 and CI Reactive Red 268 in solution pH 12 at 20 °C are the same,
6. the rates of hydrolysis (as checked by HPLC) of commercial, purified and purified CI Reactive Red 183 with sodium sulphate in solution pH 11 at 60 °C are practically the same, taking into account the maximum error between measurements $\pm 5\%$;
7. the rate of hydrolysis in solution at 20 °C at pH 12 (checked by HPLC) of CI Reactive Red 183 (monofluoro-s-triazine) is 40 times higher than that of CI Reactive Red 43 (monochloro-s-triazine); and
8. bis(monofluoro-s-triazine) dye in solution at 20 °C at pH 12 is less prone to hydrolysis (checked by HPLC) than monofluoro-s-triazine dye.

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