# APPLICATION OF CALORIMETRY TO THE STUDIES ON THE PROCESSES OF DYEING OF FABRIC *

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ABSTRACT

The possibility of the use of direct thermochemical measurements for the determination of the enthalpic characteristics of the most important processes taking place during the dyeing of textile materials by reactive dyes is shown. It is established that the exothermicity of dyeing decreases with the rise in the degree of association of the dye and the degree of filling of the fibre surface by the dye molecules, and with the decrease in the degree of swelling of cellulose. This testifies to the importance of the entropic factor for the dyeing process of cellulose materials by reactive dyes.

INTRODUCTION

Reactive dyes are one of the most important classes of substances for the dyeing of materials made from natural, viscose and polyamide fibres as well as from polyester–cellulose mixtures for colouring the cellulose constituent of the mixture. These dyes are compounds which are soluble in water and contain labile-bonded atoms and groups due to which they are able to participate in a chemical reaction with the functional groups of fibre to form a stable covalent bond between dye and fibre.

Improvement of the technology of dyeing on a scientific basis depends to a great extent on the existence of data on the bonding energies of dyes with fibre. Unfortunately, data on the determination of the energetics of the chemical bonding of the reactive dyes with cellulose materials are very few.

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EXPERIMENTAL

*Materials*

The structure of the dyes studied is represented in Fig. 1 (Reactive Violet 4K). This dye refers to the group of monochlortriazine dyes comprising a reactive group S-triazine cycle with one labile chlorine atom at the carbon atom. The interaction of such dyes with the cellulose fibres proceeds according to the scheme

$$R-Cl + Cell-OH \xrightarrow{OH^-} Cell-O-R + Cl^- + H_2O \qquad (1)$$
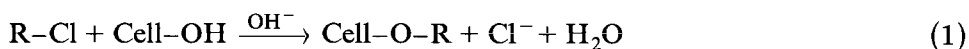
The techniques of purification of this dye [1] implied solution in cold DMF, precipitation by acetone, extraction by ethyl alcohol to remove it from excess chloride ions and drying in vacuo over phosphorus(V) oxide. The water content of the dye thus obtained did not exceed 0.03 wt. %. The dimethylsulfoxide used in this work was purified once by sublimation in vacuo. Its residual water content (below 0.05 %) was taken into account when preparing water–dimethylsulfoxide solutions. The water for the preparation of the solutions was freshly distilled (conductivity did not exceed $2.1 \times 10^{-4}$ S m$^{-1}$).

All the substances used at different stages of the experiment or analysis were classified as "chemically pure".

*Method*

We earlier proposed for the first time a technique for the determination of the energetics of the chemical bonding of dye and fibre using direct thermochemical measurements [2]. For this purpose, a process of the dyeing of fabric by reactive dyes was simulated in a calorimeter with an adiabatic shell [3]; its precision was 0.5%. The calorimeter cell (Fig. 2) was filled with a fresh dyeing solution composed of dye, electrolyte and solvent. A metal ring, 1, on which was wound a sheet of fabric, 2, was also inserted. Thus, the fabric was situated along the perimeter of the calorimetric vessel, 3. Sodium hydroxide solution was placed in a separate ampoule, 4. At the main stage of
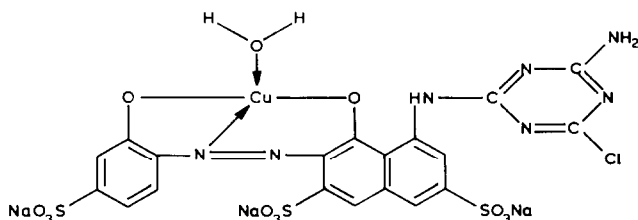


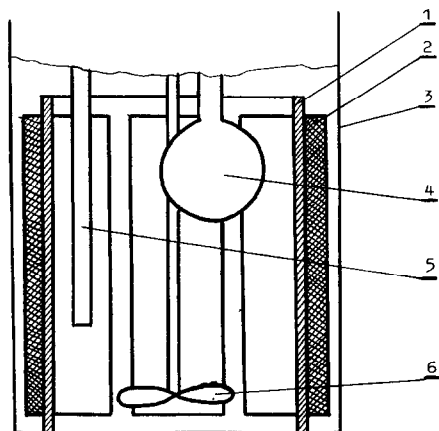Fig. 1. Structural formula of the dye Reactive Violet 4K (R–Cl).

Fig. 2. Schematic diagram of the calorimetric cell. 1, metal ring; 2, sheet of fabric (Cell–OH); 3, calorimetric vessel; 4, ampoule containing NaOH; 5, thermistor; 6, stirrer.

the calorimetric experiment the ampoule containing the NaOH solution was broken, the alkali concentration changing from NaOH = 4 m to NaOH = $(3.3-3.5) \times 10^{-2}$ mol kg$^{-1}$ of solvent.

## RESULTS AND DISCUSSION

### The thermodynamic cycle



$$(2)$$
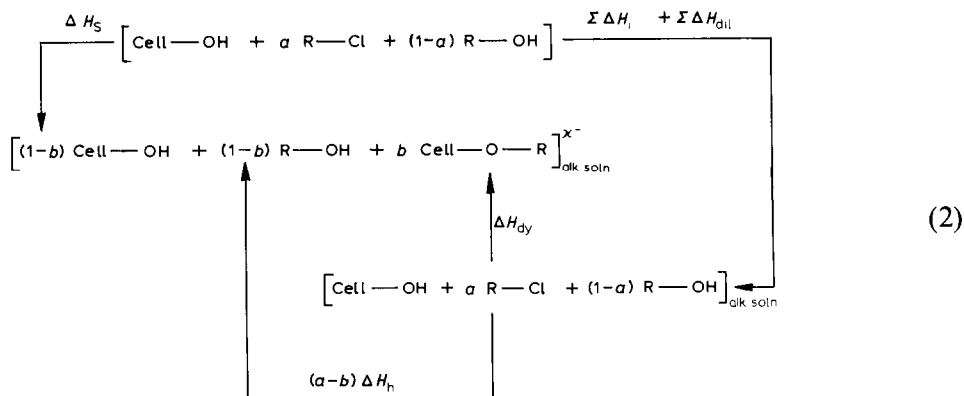
represents the processes occurring after breaking the ampoule of NaOH. In this cycle $a$ is the amount of the reactive form of the dye and $b$ is the amount of the dye which reacts with fibre. The total change in enthalpy ($\Delta H_S$) includes the enthalpy change on ionization of the dye ($\Delta H_{i_{(1)}}$) (process 3) and of the cellulose material ($\Delta H_{i_{(2)}}$) (process 4), on dilution of

the dye, electrolyte and alkali agent ($\Sigma\Delta H_{dil}$), on hydrolysis of the dye ($\Delta H_h$) (process 5) and on dyeing ($\Delta H_{dy}$).

$$R-Cl \overset{OH^-}{\rightleftarrows} R-Cl^- \tag{3}$$

$$\left(R'-NH-R''-Cl + OH^- \rightleftarrows R'-\overline{N}-R''-Cl + H_2O\right)$$

$$Cell + H_2O^- \rightleftarrows Cell-O^- + H_2O \tag{4}$$

$$R-Cl + OH^- \xrightarrow{H_2O} R-OH + Cl^- \tag{5}$$

It follows from the thermodynamic cycle that

$$\Delta H_S = \sum \Delta H_{dil} + \Delta H_{i_{(1)}} + \Delta H_{i_{(2)}} + (a-b)\,\Delta H_h + b\,\Delta H_{dy} \tag{6}$$

Pre-moistening of the fabric in the dye solution made it possible to exclude the thermal effects of diffusion and sorbtion of the dye on the fibre from the total thermal effect. The amounts of dye hydrolysed in the calorimetric experiment ($a$) and covalently bonded to the fibre ($b$) were determined by the methods of potentiometric titration and by colorimetry of the acidic sols [4].

The thermal effects of ionization and hydrolysis of the dye can be obtained by investigation of the dyeing solutions in the absence of the textile materials. Compared with the method proposed above [2] for the determination of the enthalpies on hydrolysis and ionization of the dye using the heats of solution of a mixture of the reactive and hydrolysed forms of the dye as well as of completely hydrolysed dye, the values noted were obtained by a simpler method [5]. It implies the use of solutions from two batches of the reactive dye with different contents of its reactive form (R–Cl). For this purpose, the dye was predissolved in water or in a water–DMSO mixture in the presence of electrolyte and put into the calorimetric glass. In practice, hydrolysis does not proceed during the initial period [6]. At the main stage of the calorimetric experiment, the ampoule containing sodium hydroxide solution was broken, the alkali concentration changing from NaOH = 4 m to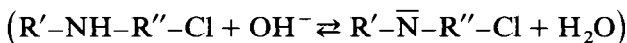 NaOH = $(3.3-3.5) \times 10^{-2}$ mol kg$^{-1}$ of solvent. Here, the total thermal effect is a sum of the constituents

$$q = \sum q_{dil} + q_{i_{(1)}} + aq_h \tag{7}$$

where $\Sigma q_{dil}$ is the thermal effect of the dilution of the alkali, dye solutions, and sodium sulphate, $q_{i_{(1)}}$ is the heat of ionization of the dye, $q_h$ is the thermal effect of the hydrolysis of the dye, and $a$ is the amount of the reactive form of the dye.

Using a dye with a different amount of the reactive form ($a'$) at the same total concentration of the dye, one can write

$$q' = \sum q'_{dil} + q_{i_{(1)}} + a'q_h \tag{8}$$

In agreement with Gess law, subtracting eqn. (8) from eqn. (7), we obtain the thermal effect of the hydrolysis of the reactive form of the dye

$$q_h = \frac{\left(q - \sum q_{dil}\right) - \left(q' - \sum q'_{dil}\right)}{(a - a')} \tag{9}$$

The value of $q_{i_{(1)}}$ is calculated taking into account the heats of dilution from eqn. (7) or eqn. (8). The values of $q_h$ and $q_{1_{(1)}}$ obtained, referred to 1 mol of dye, yield the magnitudes of the enthalpy changes on hydrolysis and ionization of the reactive dye

$$\Delta H_h = \frac{q_h a}{g} M_{rf} \tag{10}$$

$$\Delta H_{i_{(1)}} = \frac{q_{1_{(1)}}}{g} M_{hf} \tag{11}$$

where $g$ is the mass of dye in the calorimetric glass, $M_{rf}$ is the molecular mass of the reactive form of the dye (R–Cl), and $M_{hf}$ is the molecular mass of the hydrolysed form of the dye (R–OH).

To control the accuracy of our method we conducted a parallel determination of the enthalpy changes on hydrolysis and ionization of the dye Reactive Violet 4K in water using completely hydrolysed dye according to ref. 2 and two of its batches with different contents of the reactive form. The magnitudes obtained are shown in Table 1. The data given show a good coincidence under the requirements of experimental precision between the $\Delta H$ values obtained by the different methods.

The enthalpy changes on dyeing are calculated from the thermodynamic cycle (2) and the separately determined thermal effects of dilution ($\sum \Delta H_{dil}$) and ionization of the cellulose material ($\Delta H_{i_{(2)}}$).

The values of the enthalpy change upon dyeing (chemisorption) thus obtained per mole of dye fixed on the fabric at a definite degree of filling of fibre characterize, in a strict sense, the total change taking place in a dyeing system on transition of 1 mol of dye from solution into the fibre phase and include the energy expenditures of the processes of the change in the state of dye, resolution of dye and fibre as well as the chemical interaction between the reactive dye and cellulose.

TABLE 1

Enthalpy change upon hydrolysis ($- \Delta H_h$, kJ mol$^{-1}$) and ionization ($- \Delta H_{i_{(1)}}$, kJ mol$^{-1}$) of the dye Reactive Violet 4K in water at 348 K concentration of Na$_2$SO$_4$ = 0.05 mol kg$^{-1}$ solvent.

| Method | $\Delta H_h$ | $\Delta H_{i_{(1)}}$ |
|--------|--------------|----------------------|
| Ref. 2 | 151 ± 5 | 24 ± 1 |
| Ref. 5 | 143 ± 11 | 27 ± 2 |

TABLE 2

Dependence of the enthalpy change on dyeing (kJ $mol^{-1}$) at a corresponding dye concentration (mol $kg^{-1}$ of fabric), $-\Delta H_{dy}/10^3 F$, from water–dimethylsulfoxide solutions with different concentrations of $Na_2SO_4$

| T, K | $X_{DMSO}$, m.f. | Concentration of $Na_2SO_4$, mol $kg^{-1}$ of solvent | | |
| --- | --- | --- | --- | --- |
| | | 0.05 | 0.08 | 0.12 |
| 328 | 0 | $\dfrac{91\pm11}{2.860\pm0.072}$ | $\dfrac{58\pm8}{3.868\pm0.092}$ | $\dfrac{-19\pm5}{5.245\pm0.053}$ |
| | 0.05 | $\dfrac{180\pm23}{1.666\pm0.050}$ | $\dfrac{151\pm21}{2.597\pm0.018}$ | $\dfrac{90\pm12}{3.768\pm0.027}$ |
| | 0.1 | $\dfrac{186\pm27}{1.769\pm0.008}$ | $\dfrac{153\pm23}{2.548\pm0.009}$ | $\dfrac{33\pm8}{2.823\pm0.139}$ |
| 348 | 0 | $\dfrac{149\pm25}{2.185\pm0.085}$ | $\dfrac{147\pm29\ ^a}{0.572\pm0.038}$ | |
| | | | $\dfrac{70\pm14}{3.012\pm0.115}$ | $\dfrac{-71\pm19}{4.195\pm0.160}$ |
| | | | $\dfrac{57\pm14\ ^b}{1.199\pm0.068}$ | |
| | 0.05 | $\dfrac{208\pm26}{2.701\pm0.160}$ | $\dfrac{147\pm27}{3.166\pm0.202}$ | $\dfrac{98\pm16}{5.273\pm0.331}$ |
| | 0.1 | $\dfrac{281\pm27}{1.243\pm0.050}$ | $\dfrac{159\pm26}{1.624\pm0.015}$ | $\dfrac{109\pm20}{2.117\pm0.055}$ |

[a] Dye concentration = $2.5\times10^{-3}$ mol $kg^{-1}$ of solvent.
[b] Dye concentration = $7.5\times10^{-3}$ mol $kg^{-1}$ of solvent.

To demonstrate the possibilities of the quantitative evaluation of the influence of the solvent on the processes taking place during the dyeing of textile materials by reactive dyes, we give the data on the determination of the enthalpy changes for the dyeing of cellulose material in water and in water–DMSO mixtures containing 0.05 and 0.1 mole fraction of the latter (Table 2). The ionicity of the medium was created by the introduction of sodium sulphate at concentrations of 0.05, 0.08, and 0.12 mol kg $^{-1}$ of solvent. The concentration of dye was $5\times10^{-3}$ mol $kg^{-1}$ of solvent.

Separately determined values of $\Delta H_h$, $\Delta H_{i_{(1)}}$ and $q_{(2)}$ which are necessary for the calculation of $\Delta H_{dy}$ are given in Tables 3 and 4.

It follows from the data of Table 2 that the exothermicity of dyeing decreases with increase in the inorganic electrolyte concentration and amount of dye in the dye bath. This is connected with the increase in the endothermic contribution from breakdown of the association of the reactive dye particles sorbed on the fabric, on the decrease in their dispersion in the process of the interaction between dye and cellulose [6], and with the energy distribution of the adsorption centres [7]. Of interest is the transition of the

TABLE 3

Dependence of the enthalpy change vs. concentration of $Na_2SO_4$ on hydrolysis ($-\Delta H_h$, kJ $mol^{-1}$) and ionization ($-\Delta H_{(1)}$, kJ $mol^{-1}$)

| $T$, K | $X_{DMSO}$, m.f. | Concentration of $Na_2SO_4$, mol $kg^{-1}$ of solvent | | |
|---|---|---|---|---|
| | | 0.05 | 0.08 | 0.12 |
| $-\Delta H_h$ | | | | |
| 328 | 0 | 76± 6 | 71± 8 | 42± 7 |
| | 0.05 | 143± 9 | 107±11 | 74± 9 |
| | 0.1 | 105±11 | 99±10 | 106±15 |
| 348 | 0 | 143±11 | 93±10 | 68± 7 |
| | 0.05 | 50± 4 | 49± 5 | 56± 7 |
| | 0.1 | 40± 4 | 37± 4 | 33± 5 |
| $-\Delta H_{(1)}$ | | | | |
| 328 | 0 | 7.7± 0.1 | 8.4± 0.2 | 9.6± 0.2 |
| | 0.05 | 11.3± 0.1 | 11.5± 0.2 | 10.6± 0.1 |
| | 0.1 | 14.8± 0.3 | 12.9± 0.2 | 11.9± 0.1 |
| 348 | 0 | 27± 2 | 53± 6 | 59± 7 |
| | 0.05 | 66± 6 | 73± 7 | 71± 9 |
| | 0.1 | 91± 9 | 93±10 | 99±14 |

$\Delta H_{dy}$ dependence on the concentration of $Na_2SO_4$ in water at $Na_2SO_4 = 0.12$ mol $kg^{-1}$ into the endothermic region. The increase in the degree of fixation of the dye on the increase in sulphate concentration up to 0.12 mol $kg^{-1}$ testifies to a significant role of the entropic factor in the dyeing process. In this case, the effect of the disordering of the system due to the release of solvent molecules during the chemical interaction between the dye and the fibre material prevails over the ordering effect which is the result of the dye molecules entering an oriented state on fixation. In this case, the entropy of the system increases.

TABLE 4

Thermal effect of the interaction of alkali with cellulose material ($-q_{(2)}$, J $g^{-1}$ of fabric)

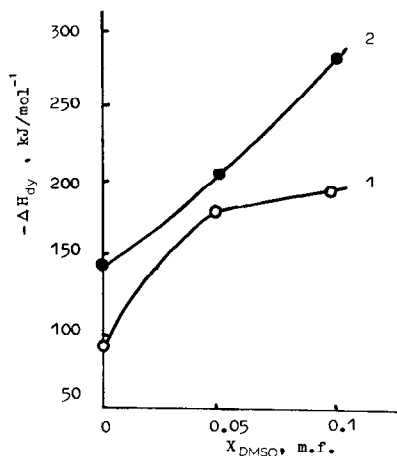| $T$, K | $X_{DMSO}$, m.f. | Concentration of $Na_2SO_4$, mol $kg^{-1}$ of solvent | | |
|---|---|---|---|---|
| | | 0.05 | 0.08 | 0.12 |
| 328 | 0 | 0.55±0.03 | 0.73±0.02 | 1.06±0.05 |
| | 0.05 | 1.44±0.03 | 1.48±0.03 | 1.41±0.03 |
| | 0.1 | 1.96±0.01 | 2.32±0.07 | 2.37±0.02 |
| 348 | 0 | 1.04±0.02 | 1.37±0.03 | 0.45±0.01 |
| | 0.05 | 1.18±0.01 | 1.42±0.02 | 1.07±0.01 |
| | 0.1 | 1.48±0.04 | 1.67±0.02 | 2.10±0.05 |

Fig. 3. Dependence of $\Delta H_{dy}$ on DMSO content at 1, 328 K and 2, 348 K. Concentration of $Na_2SO_4$ was 0.05 mol kg$^{-1}$ of solvent.

The introduction of DMSO causes an increase in the exothermicity of dyeing for solutions diluted with respect to sodium sulphate (Fig. 3). This is connected with the increase in the number of the adsorbtion centres caused by the increase in the degree of swelling of the fibrous material due to the addition of DMSO to the dyeing solution [8].

The decrease in the exothermicity of dyeing with decreasing temperature (Fig. 3) testifies to the decrease in dispersion of dye particles sorbed on the fabric [6].

Thus, the technique described allows the change in the enthalpic characteristics of the most important processes proceeding during the dyeing of textile materials by reactive dyes to be determined and the influence of solvent on the processes observed to be characterized.

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