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# Direct dyes derived from iso- and terephthalic acids

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**Abstract**

The synthesis of symmetrical, direct dyes derived from J and γ acid is described. The dyes were used to dye cotton fabric and their application and spectrophotometric properties were examined, in the case of two dyes (**B1** and **B8**), additional dyeings were carried out with the use of a commercial leveling agent. Spectrophotometric measurements revealed that the disazo dyes possess a strong tendency towards aggregation not only in solution, but also on the substrate, which was confirmed by the remission spectra.
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*Keywords:* Direct dyes; Dyeing fastness; UV–VIS spectroscopy; Standardized spectra; Aggregation; Tere- and isophthalic acids

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## 1. Introduction

Despite their existence for over 100 years, direct dyes continue to be one of the most important groups of dyes for the textile industry [1]. Direct dyes derived from benzidine, owing to their good and very good substantivity towards cellulosic fibers, have gained considerable importance. However, because benzidine is carcinogenic, its use for the production of dyes was forbidden. Another important group of direct dyes includes urea types manufactured by the acylation of aminoazo derivatives with phosgene. This process allows the rapid preparation of valuable dyes, but requires the use of toxic phosgene and hermetic and thus, expensive apparatus.

The problems associated with the synthesis of direct benzidine and urea dyes has resulted in the search for new dyes whose production and use would meet high environmental and safety requirements.

Our studies are focused on the possibilities of using tere- (**I**) and isophthalic (**II**) acid as "bridging groups" for the synthesis of symmetrical direct dyes (Fig. 1).

The aim of the present study was to examine and determine the effects of bridging systems on the spectrophotometric and application properties of symmetrical direct disazo dyes derived from J acid (6-amino-1-hydroxy-3-sulfonic acid) and γ acid (7-amino-1-hydroxy-3-sulfonic acid).

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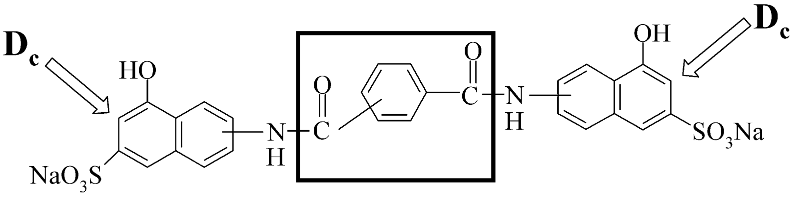


**I, II**

Fig. 1. General formulae of direct disazo dyes derived from J and γ acids.

| Dyes derived from: | | Acid | Disazo component (D$_c$) |
|---|---|---|---|
| J acid | γ acid | | |
| **A1** | **B1** | Terephthalic | Aniline |
| **A2** | **B2** | Terephthalic | *p*-Toluidine |
| **A3** | **B3** | Terephthalic | *p*-Chloroaniline |
| **A4** | **B4** | Terephthalic | *p*-Nitroaniline |
| **A5** | **B5** | Isophthalic | Aniline |
| **A6** | **B6** | Isophthalic | *p*-Toluidine |
| **A7** | **B7** | Isophthalic | *p*-Chloroaniline |
| **A8** | **B8** | Isophthalic | *p*-Nitroaniline |

## 2. Experimental

Symmetrical disazo dyes were prepared as shown in Scheme 1.

### 2.1. *Chlorides of tere- (**I**) and isophthalic (**II**) acids*

0.05 mol of phthalic acid (**I** or **II**) was heated with thionyl chloride (11 ml) in chlorobenzene (250 ml) in the presence of DMF (1 ml) as catalyst [2,3]. The process was carried out at a temperature of 60–70 °C for 6–9 h. Once reaction was terminated, excess thionyl chloride and chlorobenzene (about 180 ml) were distilled off. The obtained acidic chloride, without separation, was immediately used for the acylation of J or γ acid.

### 2.2. *N,N′-bis-(8-hydroxy-6-sulfonyl-nathphalene-2(3)-yl)-phthalamides of tere- (**I**) and isophthalic (**II**) acids*

Acid chloride dissolved in chlorobenzene was added to an aqueous solution of J or γ acid (0.1 mol) at a temperature of 10 °C and at such a rate as to obtain a pH of 6.8–7.2 [4]. The reaction course was controlled by chromatography using Whatman 1 paper with the eluent consisting of pyridine, 20% ammonia and 1% brine (1:1:8).

When the reaction termination was confirmed, the mixture was heated to 50 °C and stirred at this temperature for 30 min after which chlorobenzene was removed by steam distillation. The solution was then cooled, its pH was adjusted to 7.5–7.75 with 10% aq. NaOH and the product was salted out, filtered, washed with brine (pH≈7.7) and dried.

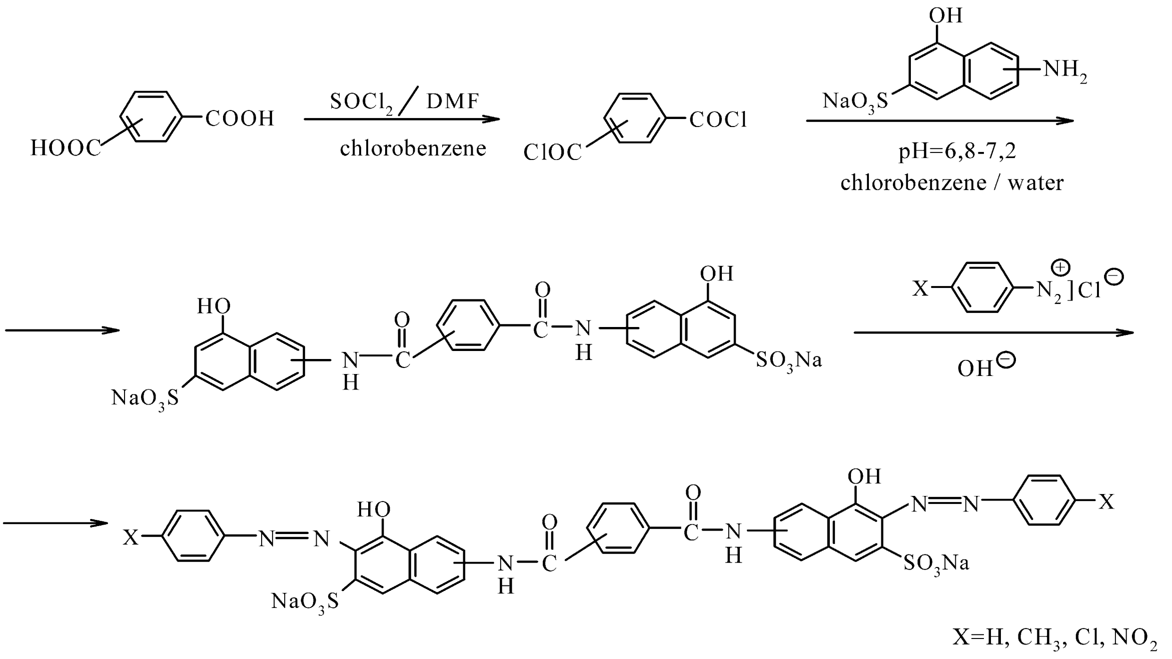
The substrates used for the process, salt content in the products, reaction yield and coefficients $R_f$ of the obtained dicarbamide derivatives of phthalic acids (**I** and **II**) are given in Table 1.

### 2.3. *Synthesis of disazo dyes*

Aniline and its *p*-chloro, *p*-nitro and *p*-methyl substituted derivatives were disazotized in a conventional manner.

Disazo dyes were prepared by coupling the disazotized amines (0.013 mol) with the coupling component (0.005 mol) dissolved in an aqueous solution at pH = 12–12.5 and 10–15 °C [4]. The process was controlled in the usual way. When the reaction termination was confirmed, the dye was salted out using 20% by vol. aq. NaCl, filtered off and dried in air. The purity of the obtained dyes was determined by chromatography and the chlorides content of the final product was determined using a potentiometric method (Tables 2 and 3).

In order to determine the chloride content (in the form of NaCl), a weighed portion of dye (0.25 g) was dissolved in 300–350 ml of distilled water, acidified with 5 ml of 20% $H_2SO_4$ and titrated



**A1-A8, B1-B8**

Scheme 1.

Table 1
Substrates used, reaction yields and coefficients $R_f$ of the dicarbamide derivatives of phthalic acids

| | Chloride | Batch (calculated for γ or J acid) (mole) | Salt content (%) | Yield (%) | $R_f$[a] |
|---|---|---|---|---|---|
| *Derivatives of γ acid* | | | | | |
| Sb1 | terephthaloyl | 0.1 | 12.7 | 81.9 | 0.18 |
| Sb2 | isophthaloyl | | 1.8 | 36.4[b] | 0.28 |
| *Derivatives of J acid* | | | | | |
| Sb3 | terephthaloyl | 0.1 | 32 | 67.0[c] | 0.16 |
| Sb4 | isophthaloyl | | 11.1 | 33.5[c] | 0.41 |

[a] Paper Wh1; eluent: Py:20% $NH_3$:1% brine = 1:1:8.

[b] Additionally purified by dissolution in 2% sodium carbonate, acidification with 30% HCl and salting out.

[c] **Sb3** and **Sb4** were additionally purified by heating at 50-60 °C in a solution at pH = 8–8.5 (30% NaOH).

Table 2
Physical and spectrophotometric properties of direct disazo dyes derived from J acid (**A1**–**A8**)

| Dye | Salt content (%) | Yield (%) | $R_f$[a] | Spectrophotometric determinations[b] | | |
|---|---|---|---|---|---|---|
| | | | | Water | 50% ethanol | 70% acetone |
| | | | | $\lambda_{max}$ (nm) | $\lambda_{max}$ (nm) | $\lambda_{max}$ (nm) |
| **A1** | 9 | 99 | 0.51a | 502 | 495 | 485 |
| **A2** | 30 | 92 | 0.36a | 549 | 487 | 493 |
| **A3** | 26 | 61 | 0.34a | 550 | 511 | 486 |
| **A4** | 3 | 84 | 0.33a | 499 | 494 | 491 |
| **A5** | 2 | 84 | 0.76a | 506 | 486 | 482 |
| **A6** | 4 | 82 | 0.70b | 503 | 494 | 489 |
| **A7** | 7 | 95 | 0.70b | 497 | 485 | 484 |
| **A8** | 13 | 99 | 0.71b | 503 | 489 | 489 |

[a] Paper Wh1; eluent: a—DMF:EtOH:$H_2O$ = 1:1:1; b—MeOH:DMF:$H_2O$ = 3:1:1.

[b] There is cited a band with a higher intensity.

Table 3
Physical and spectrophotometric properties of direct disazo dyes derived from $\gamma$ acid (**B1**–**B8**)

| Dye | Salt content (%) | Yield (%) | $R_f$ | Spectrophotometric determinations[a] | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Water | | 50% ethanol | | 70% acetone | |
| | | | | $\lambda_{max}$ (nm) | $\epsilon_{max}\times10^{-3}$ ($dm^3$/cm×mole) | $\lambda_{max}$ (nm) | $\varepsilon_{max}\times10^{-3}$ ($dm^3$/cm×mole) | $\lambda_{max}$ (nm) | $\varepsilon_{max}\times10^{-3}$ ($dm^3$/cm×mole) |
| **B1** | 19 | 99 | 0.83a | 515 | 28.0 | 503 | 31.0 | 504 | 30.8 |
| **B2** | 19 | 96 | 0.76a | 566 | 41.0 | 509 | 37.0 | 508 | 37.8 |
| **B3** | 10 | 97 | 0.74a | 524 | 34.3 | 511 | 34.7 | 506 | 35.7 |
| **B4** | 12 | 97 | 0.78a | 519 | 25.1 | 505 | 43.5 | 501 | 43.2 |
| **B5** | 3 | 88 | 0.70a | 511 | 27.8 | 503 | 39.7 | 503 | 40.0 |
| **B6** | 38 | 63 | 0.67b | 517 | 25.8 | 507 | 33.3 | 507 | 34.8 |
| **B7** | 15 | 52 | 0.66c | 511 | 19.7 | 505 | 30.1 | 503 | 31.9 |
| **B8** | 12 | 80 | 0.63c | 505 | 24.0 | 503 | 31.9 | 503 | 48.9 |

Paper Wh1; eluent: a—DMF: EtOH: $H_2O$ = 1:1:1; b—MeOH: DMF: $H_2O$ = 3:1:1; c—MeOH: DMF : $H_2O$ = 3:2:1.

[a] There is cited a band with a higher intensity.

with 0.1N $AgNO_3$ against a silver electrode. The NaCl content in the direct dyes was calculated using Eq. (1) [5]:

$$\%\text{NaCl} = \frac{M \times N \times V}{m \times 1000} \times 100\% \qquad (1)$$

where: $M$—molal mass of sodium chloride (58.4g/mol); $N$—normality of $AgNO_3$ solution (0.1N); $V$—quantity (ml) of $AgNO_3$ solution read from the titration curve at the titration drop; $m$—dye mass (g).

## 2.4. Spectrophotometric measurements

The synthesised direct dyes were subjected to spectrophotometric measurements in water, 50% ethanol and 70% acetone. The spectra of disazo dyes were taken by means of a Specord M-40 (Carl-Zeiss Jena) spectrophotometer, using the following concentrations of dyes: **B1–B8** $2.79\times10^{-5}$–$7.36\times10^{-5}$ mol/l, while dyes **A1**–**A8** were used in the form of saturated solutions in appropriate solvents. The results of measurements are given in Tables 2 and 3.

## 2.5. Dyeing of woven cotton fabric

Conventional bleached and mercerised woven cotton fabric was used. The dyeings were performed in a Roaches-Rotec apparatus with temperature accuracy of ±1 °C. The dyeing process was carried out in a dyebath with a liquor ratio of 1:30, containing 25 mg of 100% dye (1% omf dyeing) or 50 mg of 100% dye (2% omf dyeing) added in a 10% solution of $Na_2SO_4\times10H_2O$. The dyeing method is shown in Fig. 2.

After 1 h of dyeing, Glauber's salt was added to the dyebath to increase the dye absorption by cellulose fibers [6] (Fig. 3).

Dyeings produced using dyes **B1** and **B8** were carried out also with the addition of a leveling agent (Albegal B): 2% omf dyeings with **B1 (B1-alb)** and **B8 (B8-alb)**.

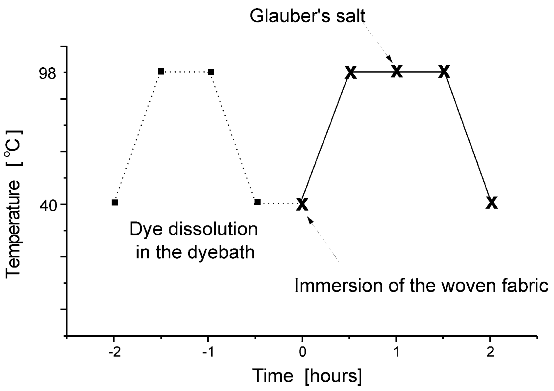


Fig. 2. Dyeing method.

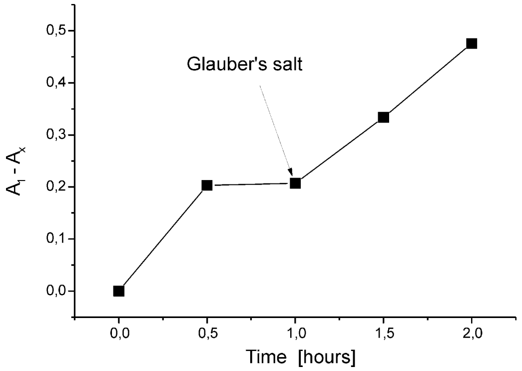


Fig. 3. Absorption curve of dye **B7** in a 1% dyebath. $A_1$—absorbance of the dye solution before dyeing; $A_x$—absorbance of the dye solution after 0.5, 1, 1.5 and 2 h.

The degree of dye exhaustion ($E$) was determined by spectrophotometry, measuring dye concentrations in the dyebath before ($C_1$) and after ($C_2$) dyeing [7] using Eq. (2):

$$E = \frac{A_1 - A_2}{A_1} \times 100\% \qquad (2)$$

where: $A_1$, $A_2$— the absorbances of the dye solutions before and after dyeing, respectively.

The results obtained are given in Tables 4–7.

### 2.6. Determination of fastness to rubbing and wet treatments

The dyed fabrics were evaluated using a standard procedure: fastness to water according to ISO 105-E01, fastness to perspiration according to ISO 105-E04, fastness to rubbing according to ISO 105-X12, fastness to washing according to ISO 105-C01. The change in shade and staining of adjacent undyed fabrics were assessed using grey scales 1 (poor)–5 (excellent). The results obtained are given in Tables 4–7.

### 2.7. Determination of fastness to light

Fastness to light of dyed fabrics was performed according to ISO 105-B02, using a Xenotest 150S (Heraus-Hanau) apparatus. Colour change was estimated against the blue wool standard scale 1

Table 4
Dyeing and fastness properties of dyes **A1**–**A8** (1% omf dyeings)

| Dye | Degree of dye exhaustion (%) | Degree of dye combination (%) | Rubbing | | Water | | | Washing | | | Perspiration | | | | | | Light fastness |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Alkaline | | | Acidic | | | |
| | | | Dry | Wet | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | |
| | | | | | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | |
| **A1** | 78 | – | 5 | 4/5 | 4/5 | 5 | 5 | 3/4 | 5 | 5 | 4/5 | 5 | 5 | 4/5 | 5 | 5 | 3/4 |
| **A2** | 34 | 90.1 | 5 | 4/5 | 4/5 | 5 | 5 | 4/5 | 5 | 5 | 4/5 | 5 | 5 | 4/5 | 5 | 5 | 3 |
| **A3** | 68 | – | 5 | 4 | 3 | 5 | 4/5 | 3 | 5 | 5 | 3 | 5 | 4/5 | 4 | 5 | 4/5 | 3/4 |
| **A4** | 51 | 99.2 | 5 | 4/5 | 3/4 | 5 | 4/5 | 3 | 5 | 5 | 3/4 | 5 | 5 | 4 | 5 | 5 | 3 |
| **A5** | 78 | 98.6 | 5 | 4 | 4/5 | 5 | 5 | 3/4 | 5 | 5 | 4 | 5 | 5 | 4/5 | 5 | 5 | 3/4 |
| **A6** | 54 | 96.1 | 5 | 4/5 | 4 | 5 | 5 | 3/4 | 5 | 5 | 4 | 5 | 5 | 4 | 5 | 4/5 | 3 |
| **A7** | 38 | 96.9 | 5 | 4/5 | 4 | 5 | 5 | 3/4 | 5 | 5 | 4 | 5 | 5 | 4/5 | 5 | 5 | 3 |
| **A8** | 64 | 90.4 | 5 | 4/5 | 4 | 5 | 5 | 3/4 | 4 | 5 | 4 | 5 | 5 | 4/5 | 4 | 5 | 3 |

Table 5
Dyeing and fastness properties of dyes **A1–A8** (2% omf dyeings)

| Dye | Degree of dye exhaustion (%) | Degree of dye combination (%) | | | | | | | | | Perspiration | | | | | | Light fastness |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Rubbing | | Water | | | Washing | | | Alkaline | | | Acidic | | | |
| | | | Dry | Wet | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | |
| | | | | | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | |
| *A1* | 49 | – | 5 | 4/5 | 4/5 | 5 | 5 | 3 | 5 | 5 | 4 | 5 | 5 | 4/5 | 5 | 5 | 3/4 |
| **A2** | [a] | 97.3 | 5 | 4/5 | 3/4 | 5 | 4/5 | 3 | 4 | 5 | 3 | 5 | 5 | 4 | 5 | 4/5 | 3 |
| **A3** | 28 | – | 5 | 4 | 3 | 5 | 4 | 4 | 5 | 5 | 2/3 | 5 | 4/5 | 3 | 5 | 4 | 3/4 |
| **A4** | 15 | 97.1 | 5 | 4/5 | 3 | 5 | 4/5 | 3 | 5 | 5 | 2/3 | 5 | 4/5 | 3/4 | 5 | 4 | 3/4 |
| **A5** | 63 | 96.4 | 5 | 4/5 | 3 | 5 | 4/5 | 3 | 5 | 5 | 3 | 5 | 4/5 | 4/5 | 5 | 4/5 | 3/4 |
| **A6** | 22 | 97.0 | 5 | 4/5 | 2/3 | 5 | 4/5 | 3 | 5 | 5 | 3/4 | 5 | 4/5 | 3/4 | 5 | 4/5 | 3/4 |
| **A7** | 25 | – | 5 | 4/5 | 3/4 | 5 | 4/5 | 3 | 4 | 5 | 3 | 5 | 4/5 | 3/4 | 5 | 4/5 | 3/4 |
| **A8** | 32 | 94.4 | 5 | 4/5 | 3/4 | 5 | 4 | 3 | 4 | 5 | 3 | 5 | 4/5 | 3/4 | 5 | 5 | 3 |

[a] Saturated solution (a strong dye aggregation in the dyebath).

Table 6
Dyeing and fastness properties of dyes **B1-B8** (1% omf dyeings)

| Dye | Degree of dye exhaustion (%) | Degree of dye combination (%) | | | | | | | | | Perspiration | | | | | | Light fastness |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Rubbing | | Water | | | Washing | | | Alkaline | | | Acidic | | | |
| | | | Dry | Wet | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | |
| | | | | | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | |
| **B1** | 77 | 92.7 | 5 | 5 | 5 | 3 | 4 | 4 | 2/3 | 5 | 4 | 2/3 | 4 | 4 | 3 | 3/4 | 2 |
| **B2** | 23[a] | 89.1 | 5 | 5 | 5 | 4 | 4/5 | 4 | 3/4 | 5 | 5 | 2/3 | 4/5 | 4 | 3/4 | 4 | 2 |
| **B3** | 38[a] | 84.2 | 5 | 5 | 5 | 3/4 | 4/5 | 4 | 3/4 | 5 | 5 | 3/4 | 4/5 | 5 | 4 | 4/5 | 2 |
| **B4** | 38[a] | 85.2 | 5 | 5 | 5 | 4 | 5 | 4 | 4/5 | 5 | 5 | 4 | 5 | 5 | 4/5 | 4/5 | 1/2 |
| **B5** | 72 | 88.5 | 5 | 5 | 5 | 3/4 | 4 | 2 | 3/4 | 5 | 5 | 2 | 4 | 4 | 3 | 4 | 2 |
| **B6** | 79 | 94.0 | 5 | 4/5 | 4 | 2 | 2/3 | 3 | 3/4 | 5 | 4 | 2 | 4 | 4 | 2 | 2/3 | 2 |
| **B7** | 62[a] | 84.5 | 5 | 4/5 | 5 | 2/3 | 3 | 4 | 4 | 5 | 4 | 2 | 4/5 | 4 | 3 | 3 | 2 |
| **B8** | 32[a] | 74.8 | 5 | 5 | 5 | 4 | 5 | 4 | 4/5 | 5 | 5 | 4 | 4/5 | 5 | 4/5 | 4/5 | 1/2 |

[a] Saturated solution.

(poor)–8 (excellent). The results obtained are given in Tables 4–7.

## 3. Discussion of results

The studies resulted in several dyes derived from J and $\gamma$ acids, which where at oranges and red hues, respectively. The chosen method of acid chloride synthesis in an organic solvent (chlorobenzene) allows one to prepare products in a simple way, preventing also their partial decomposition. The selected method for the synthesis of disazo dyes is simple and makes it possible to prepare dyes in high yield.

### 3.1. Spectrophotometric analysis

Spectrophotometric measurement showed that the spectra of the disazo dyes possess two clearly visible absorption peaks whose intensity changes with the polarity of solvent (Fig. 4). This is probably due to the aggregation of the dyes.

A strongly polar solvent such as water [Dimroth's constant $E_T(30) = 63.1$ kcal/mol [8] considerably affected the spectra of the dyes under investigation. The dyes derived from $\gamma$ acid, derivatives of terephthalic acid (**B1**–**B4**), exhibited a bathochromic shift in relation to the bands of dyes derived from isophthalic acid (**B5**–**B8**) (a shift at 4–49 nm), while in the case of dyes derived from J acid, an opposite effect was observed, i.e., the absorption bands of dyes derived from terephthalic acid (**A1**–**A4**) shifted hypsochromically in relation to dyes derived from isophthalic acid (**A5**–**A8**) (a shift at 4–53 nm, with the exception of dyes, in which *p*-chloroaniline was used as a diazo component). This confirms the existence of conjugation between two parts of dye, despite the fact that two amide groups are present in the dyes and which should not permit conjugation.

The replacement of water with a water–organic solvent system brings about changes in the position of $\lambda_{max}$. Basic absorption bands of dyes derived from terephthalic acid (**I**) are more bathochromic shifted in relation to those of dyes derived from isophthalic acid (**II**), in the case of derivatives of both J and $\gamma$ acids. The replacement

Table 7
Dyeing and fastness properties of dyes **B1**–**B8** (2% omf dyeings)

| Dye | Degree of dye exhaustion (%) | Degree of dye combination (%) | Rubbing | | Water | | | Washing | | | Perspiration | | | | | | Light fastness |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | Alkaline | | | Acidic | | | |
| | | | Dry | Wet | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | Alternation | Staining | | |
| | | | | | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | | Cotton | Wool | |
| **B1** | 56 | 92.7 | 5 | 5 | 5 | 2/3 | 4 | 4 | 2/3 | 5 | 4 | 2/3 | 3/4 | 4 | 2/3 | 3 | 2 |
| **B2** | 25[a] | 85.7 | 5 | 5 | 4 | 3/4 | 4 | 4 | 3/4 | 5 | 4 | 2/3 | 4 | 4 | 3 | 4 | 2 |
| **B3** | [b] | 80.7 | 5 | 4/5 | 4 | 3/4 | 4/5 | 4 | 3/4 | 5 | 4 | 3 | 4/5 | 5 | 3/4 | 4/5 | 2 |
| **B4** | [b] | 83.6 | 5 | 4/5 | 5 | 4 | 4/5 | 4 | 4/5 | 5 | 5 | 3/4 | 4/5 | 5 | 4/5 | 4/5 | 1/2 |
| **B5** | 69 | 89.1 | 5 | 4/5 | 4 | 3/4 | 4 | 4 | 3/4 | 5 | 5 | 2 | 4 | 5 | 2/3 | 4 | 2 |
| **B6** | 53 | 92.3 | 5 | 4/5 | 3 | 1/2 | 2/3 | 3 | 3 | 5 | 4 | 1/2 | 3/4 | 4 | 1/2 | 2 | 2 |
| **B7** | 36[a] | 89.4 | 5 | 4/5 | 3 | 2 | 2/3 | 3 | 4 | 5 | 4 | 1/2 | 3/4 | 4 | 2/3 | 2/3 | 2 |
| **B8** | [b] | 85.6 | 5 | 5 | 4 | 3/4 | 4 | 4 | 4 | 5 | 4 | 3 | 4/5 | 5 | 4 | 4/5 | 1/2 |

[a] Saturated solution.

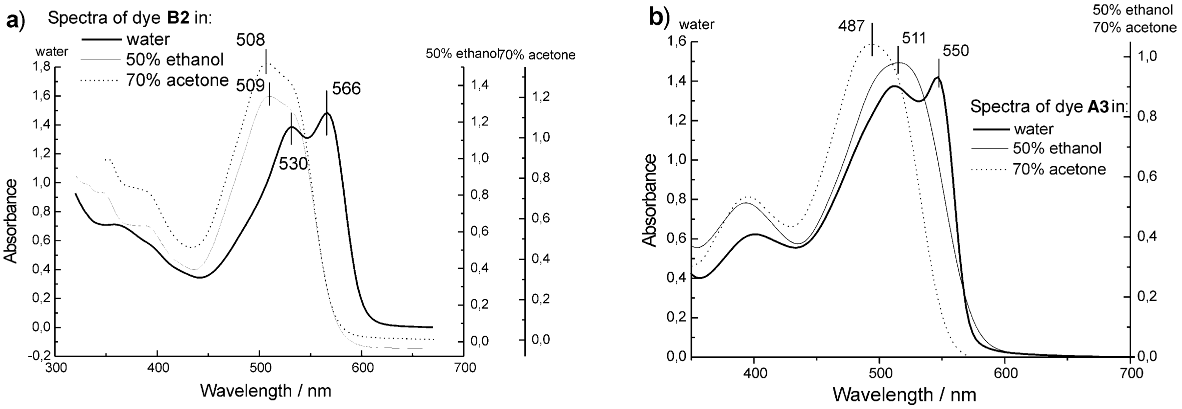


Fig. 4. Examples of spectral characteristics of dyes (a) **B2** and (b) **A3** in various solvents.

of the solvent consisting of 50% ethanol with 70% acetone does not affect the positions of spectra of dyes derived from isophthalic acid (**II**), while in the case of dyes derived from terephthalic acid (**I**) the shift is several nm (dyes **B1**–**B8**). In the case of dyes derived from J acid (**A1**–**A8**) the difference in shifts is higher, amounting even to 25 nm. This effect of the solvent on the spectra of the dyes **B1**–**B8** in mixed solvents may give rise to the presence of a strong intramolecular hydrogen bond in these compounds [9–13]. In addition, 50% ethanol and 70% acetone have the same polarity ($E_T(30)$ for 50% ethanol is 55.1 kcal/mol and that for 70% acetone is 55.2 kcal/mol [8,14]) and thus they will similarly affect the shape of the spectra and the position of $\lambda_{max}$. The spectrophotometric properties of the dyes are also affected by the selective solvation of the dye molecules by the solvent to form flat or three-dimensional structures [13,15–17].

Comparing the values of $\varepsilon_{max}$ of the dyes derived from $\gamma$ acid (**B1**–**B8**), one can notice that the derivatives of terephthalic acid (**B1**–**B4**) have slightly lower $\varepsilon_{max}$ values than the corresponding dyes derived from isophthalic acid (**B5**–**B8**). The extinction coefficient ranges from 24 000 to 48 900 $dm^3/cm \times mol$ with the exception of **B7** in water ($\varepsilon_{max} = 19\ 700\ dm^3/cm \times mol$). In addition, the values of $\varepsilon_{max}$ of most dyes dissolved in 50% ethanol and 70% acetone are comparable (exception: **B8**) and higher than those of the dyes dissolved in water (exception: **B2**), which results from their capabilities to disaggregate.

### 3.2. Application properties

The dyes were used to dye cotton fabric and their application and spectrophotometric properties were examined. The results are given in Tables 2–7. The dyeing process was preceded by a preliminary dissolution of the dyes in the dyebath due to their strong tendency towards aggregation as was it shown in Fig. 2.

The examined dyes showed a strong tendency towards aggregation in the dyebath, which, in some cases it made impossible to determine the degree of dye exhaustion from the dyebath using a spectrophotometric method (e.g., **A2**, **B3**, **B4**, **B8** and **B8-alb**).

Clear differences were also observed in the case of 1% omf and 2% omf dyeings; in the case of 2% omf dyeings, the rate of dye absorption drops considerably as a result of it aggregation in solution.

According to literature, the degree of exhaustion of direct dyes amounts to 60–80% and sometimes even lower [18–20]. Some of the dyes derived from $\gamma$ acid examined by (**B1**, **B5**–**B7**) displayed dye exhaustion within this range. Of the J derivatives acid, only dyes **A1** and **A5** showed an adequate solubility and degree of exhaustion under normal dyeing conditions.

### 3.3. Dyeing with the use of a leveling agent

In the case of dyes **B1** and **B8**, additional dyeings were carried out with the use of the commercial leveling agent Albegal B whose function is to change dye–dye associates into dye-leveling agent associates which cannot penetrate the dyed fiber [21–23]; during dyeing the latter release particular dye molecules which diffuse into fibers [24].

Dyeing in the presence of Albegal B, facilitated the decomposition of dye aggregates (dye dimers) and on the other hand brings about a decrease in the extent of dye exhaustion of about twice lower than that achieved without the disaggregating agent. This may result either from the partial combination of the dye and the leveling agent to form a water-insoluble complex or from the formation of a larger and more hydrophilic complex (dye-leveling agent) which keeps the dye in the dyebath [21,22] (Fig. 5b).

To illustrate more precisely the changes taking place and the relation between the dye monomer and dimer, the spectra of dyes in the dyebath were standardized for the wavelength $\lambda = 535$ nm (Fig. 5) [25–28].

Slight differences were also observed in the dye absorption curves after the addition of electrolyte (Glauber's salt) (Fig. 6). The addition of electrolyte to the solution of **B1-alb** increased the degree of dye exhaustion at 98 °C, but also reduced dye adsorption during the cooling of dyebath since this addition lowers the solubility of the dyes at a given temperature, intensifying the ionic character of water and facilitating the stabilization of dye aggregates [29].

The addition of Albegal B considerably reduced the rate of dye uptake (Fig. 6) and, consequently, the degree of dye exhaustion under the standard dyeing conditions used was only about 50%.

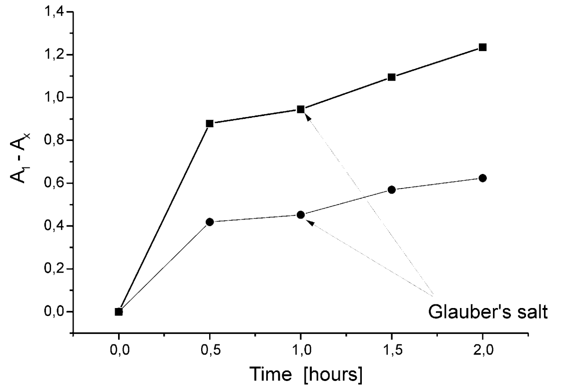


Fig. 6. Absorption curves of dye **B1** in the 2% dyebath without (—■—) and with the addition of Albegal B (—●—).

### *3.4. Analysis of remission spectra of 1% omf and 2% omf dyeings on cotton fabrics*

The analysis of remission spectra shows that the dyes, as observed in solution, formed aggregates on the substrate. The remission spectra of dyeings obtained with the dyes derived from γ acid (**B1**–**B8**) show that in the case of 1% omf dyeings, the highest amount of dye was washed out from cotton fabric dyed with the derivatives of isophthalic acid (**II**), with the loss to 11.5–25% (exception dye **B6**). In the case of 2% omf dyeings, the dyes derived from terephthalic acid (**I**) were washed out to a

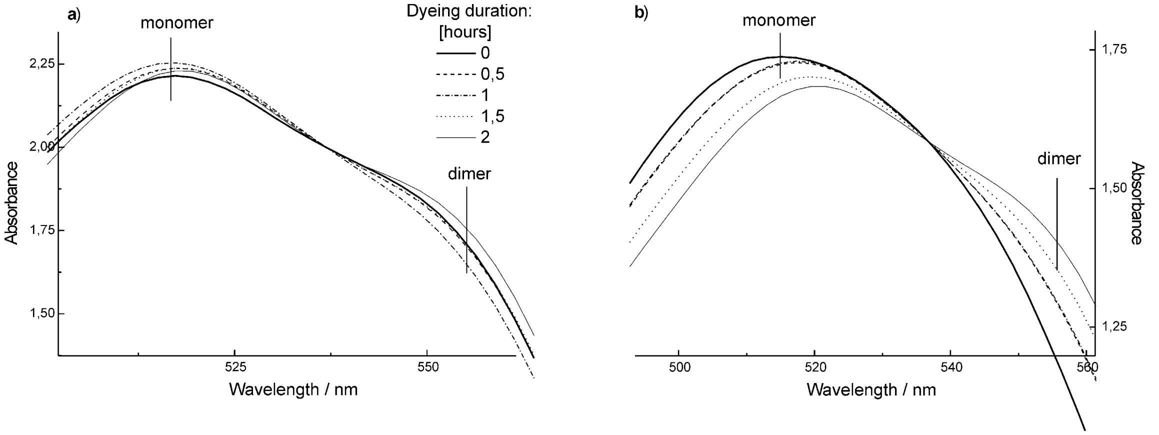


Fig. 5. Standardized spectra of dye **B1** in 2% dyebath (a) without the leveling agent, (b) with the leveling agent (Albegal B).

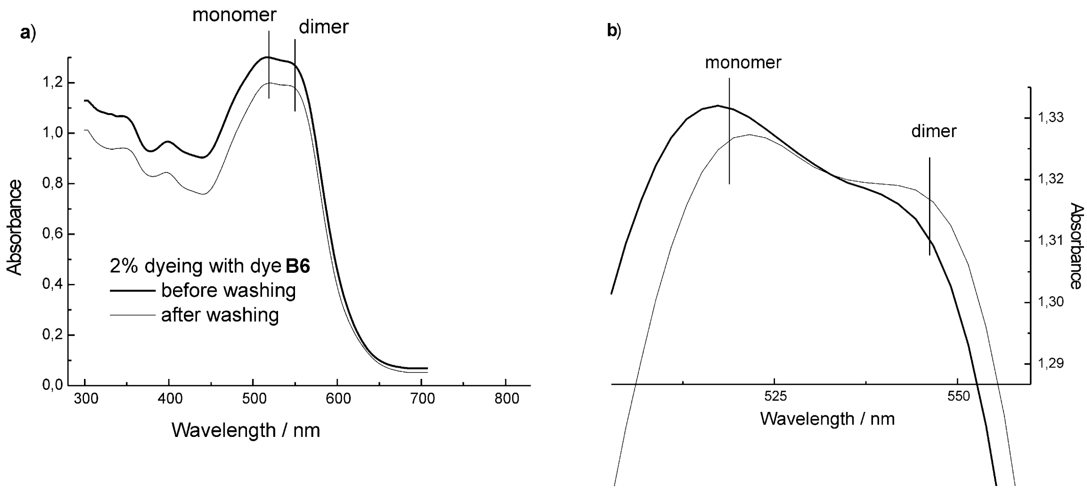


Fig. 7. Remission spectra of 2% omf dyeing with dye **B6** (a) before and (b) after the standardization.

higher extent, with the loss amounting to 16.4–19% (exception **B1**).

Standardization of the spectra of the dyeings before and after washing showed that in some cases (1% omf dyeings with **B5, B6** and **B7**, 2% omf dyeings with **A1, A3, A7** and **B6**) the monomer absorbance on the washed fabric decreased, but that of the dimer increased, which means that during dyeing a dye dimer was formed (Fig. 7).

### *3.5. Fastness results*

The light fastness of the dyes derived from J acid are moderate and close to those of similar dyes cited in the Colour Index [30] (all fastness were determined at intensity of dyeings 1/1) . The use of the derivatives of iso- (**II**) and terephthalic (**I**) acids as "bridging groups" makes it possible to obtain dyes with fastness values slightly higher than those of urea dyes with a similar structure, with the differences amounting to 1–1.5 units in the 8-degree scale.

Lower light fastness values are shown by the dyeing with dyes **B1**–**B8** derived from γ acid. The lowest light fastness was displayed by dyes **B4** and **B8.**

The dyes show very good fastness to dry rubbing, but slightly worse fastness to wet rubbing, especially dyeings achieved with dyes **A1**–**A8**, which may result from a superficial combination between the dye and fiber. The effect of aggregation is particularly visible on 2% omf dyeings.

The fastness to wet treatments are at very different levels. The highest values of fastness to wet treatments among the dyeings with the dyes derived from J acid are shown by the dyes being the isophthalic acid derivatives; they are higher than those of analogous dyeings with the dyes derived from γ acid. The preliminary treatment with the leveling agent Albegal B has no significant effect on dyeing quality.

The obtained dyes show good fastness to water and washing, but not too high fastness to perspiration, especially alkaline perspiration.

## 4. Conclusions

In the case of dyes **B1**–**B8**, in aqueous solution, the derivatives of terephthalic acid (**I**) exhibited a bathochromic shift in relation to the derivatives of isophthalic acid (**II**), this being opposite to that found in the case of the dyes derived from J acid (**A1**–**A8**). This effect was not observed in mixed solvents, probably due to aggregation of the dyes in aqueous solution. Mixed solvents such as 50% ethanol and 70% acetone facilitated the disaggregation of the dyes and a change in the relative extents of dimerisation and monomerisation.

The type of the "bridging group" used affects $\lambda_{max}$ only to a slight extent, which indicates the transition of conjugation by the diamide system. These changes are, however, of an accidental character and are difficult to interpret.

Based on the performed examination and measurements, one can state that the obtained dyes, owing to their properties, can replace urea dyes with similar structures. Their practical properties such as light fastness, especially those of the derivatives of J acid are higher then those of the latter dyes. The type of the " bridging group" used in the dye synthesis plays also an important part, with the best effect being obtained with the derivatives of isophthalic acid.

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