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Benzidine-free direct dyes, amide derivatives of iso- and terephthalic acids

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Abstract

The symmetric diamide derivatives of iso- and terephthalic acids and J acid are described. The spectrophthotometric properties of the dyes in solution and on cotton fabric, their aggregation, pK_a, azo-hydrazone tautomerism and photostability were determined. It was found that amide derivatives of iso- and terephthalic acids influence in a different way at physico-chemical and application properties of dyes in solution and on dyed cotton.

Keywords: Benzidine-free direct dyes; Azo-hydrazone tautomerism; Aggregation; UV–VIS spectroscopy; Basicity constants; Photostability

1. Introduction

As direct dyes used for dyeing cellulosic fibres, benzidine derivatives constituted a large group for many years due to favorable characteristics such as intense colours, hue, bright shades, high substantivity, ease of synthesis and low cost. However, once benzidine was found to be carcinogenic, the production of benzidine dyes was prohibited in many countries. Hence, it became important to replace these dyes with dyes containing harmless aromatic diamines instead of benzidine. An alternative solution was to link two monoazo dyes molecules with bridging grows to provide direct dyes of good functional qualities [1–4].

In this paper with similar properties to those of benzidine derivatives were sought by means of dye syntheses using diamide derivatives of J acid, in which isophthalic and terephthalic acid derivatives were used as connecting compounds. Thus, coupling components were prepared that were used for the preparation of direct, disazo dyes containing components such as aniline, *p*-toluidine, *p*-chloroaniline and *p*-nitroaniline (Table 1).

Physical and chemical properties of the synthesised dyes, their aggregation in solution and in cellulose fibre as well as their azo-hydrazone tautomerism were examined, including pK_a values and the kinetics of light-induced dye decomposition.

2. Experimental

The dye synthesis procedures, spectrophotometric measurement of aqueous dye solutions and examination of functional properties were carried out as described in the previous paper

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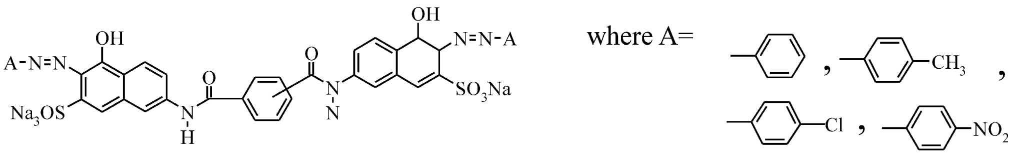
Table 1
Structure of direct dyes derived from iso- and terephthalic acids



B1 - B8

Dye	Acid	Diazo component
B1	Terephthalic	Aniline
B2	Terephthalic	*p*-Toluidine
B3	Terephthalic	*p*-Chloraniline
B4	Terephthalic	*p*-Nitroaniline
B5	Isophthalic	Aniline
B6	Isophthalic	*p*-Toluidine
B7	Isophthalic	*p*-Chloraniline
B8	Isophthalic	*p*-Nitroaniline

[5]. The results obtained were analysed by means of Microcal Origin v. 5.0 (Microsoft Software Inc.). Spectrophotometric measurements were carried out using a Lambda 40 spectrophotometer (Perkin Elmer) fitted with an attachment for remission spectrum analysis (photometric globe).

3. Results and discussion

3.1. Dye aggregation in solution

The dyes under investigation were characterised by the presence of double absorption bands at $\lambda \approx 460–510$ nm, whose appearance can be explained in terms of their vibrational origin [6]. We have found that their intensity depended on dye concentration in solution, which suggest that aggregate may be occurring [7–9]. In this context, it was thus necessary to find out which absorption bands were responsible for absorption of the monomer and which correspond to the aggregate form (dimer). Accordingly, the spectra of aqueous dye solutions of concentrations of 2%, 0.8%, 0.4% and 0.16% were analysed. Standardisation was used to characterise the spectral characteristics of the dyes based on the wavelength ranges ascribed to monomers or dimers [10–12]. The standardisation was performed at the inflexion point of absorption curves (e.g., **B6**—484 nm) or for the value of $\lambda_{\max}$ (e.g., **B8**—474 nm) (Figs. 1 and 2).

It was found that not all of the dyes showed a trend towards the decomposition of aggregates (dimers) into monomers due upon dilution. This is exemplified by the spectrum of **B8,** in which the relative ratios of the absorption bands were unchanged upon dilution, which indicates the stability of aggregates [7]. The approximate distribution of monomers and dimers in mixture was determined using the method of deconvolution of absorption bands into Gauss' curves of dye solutions for dye concentrations of 2% (or 0.8%) and 0.16%. Two types of dimers, namely "sandwich" and "head-to-tail", were taken into account [7].

A dependence of monomer content (**M**) on sandwich dimer content, sandwich ($\mathbf{D_I}$) or head-to-tail dimer content ($\mathbf{D_{II}}$) was obtained. The results are given in Table 2, while a graphic illustration of the procedure is shown in Fig. 3 (the sandwich dimer absorbed at lower wavelength and the head-to-tail dimer at higher wavelength [7,13]).

Mixtures of organic solvents with water (50% ethanol and 70% acetone) were used [14,15] as it is known that these solvents display good disaggregating properties, making it possible to

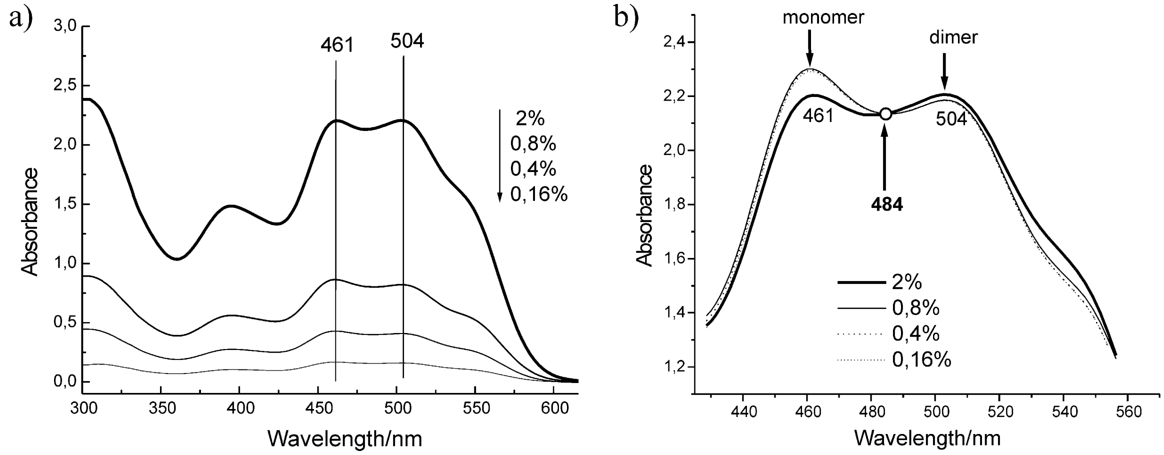


Fig. 1. Exemplary spectrum illustrating the effect of dilution on the aggregation of **B6**: (a) before and (b) after spectrum standardisation at $\lambda = 484$ nm.

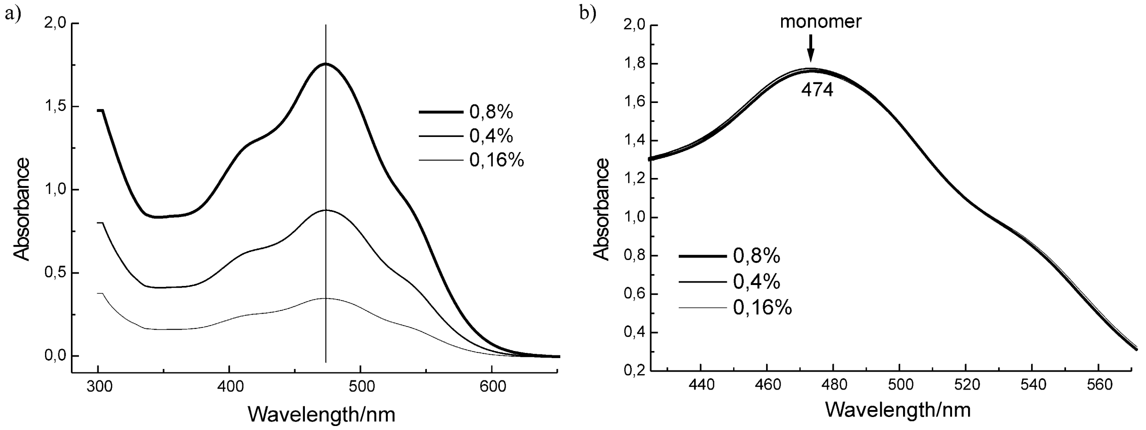


Fig. 2. Exemplary spectrum illustrating the effect of dilution on the aggregation of **B8**: (a) before and (b) after spectrum standardisation at $\lambda = 474$ nm.

confirm the position of the λ_{max} of bands ascribed to the appropriate monomer and dimer forms. Similarly, as in the case of aqueous solution, the absorption bands were subjected to deconvolution into the constituent spectra and the monomer and dimer contents were calculated. The results are given in Table 3.

In 50% ethanol were more dimer than monomer content in solution. Acetone had a marked effect on the disaggregation of the dye molecules. Dyes **B5**–**B8**, being the derivatives of isophthalic acid, were disaggregated more easily than the analogous derivatives of terephthalic acid, **B1**–**B4.** This may be due to their spatial structure; this aspect will be discussed in a later paper.

3.2. Dye aggregation in dyed woven fabric

The dyes under investigation formed aggregates also in dyed cotton fabric. This was observed for both 1% omf and 2% omf dyeings, with the degree of aggregation being different for different dyeings. Analysis of the 2% dyeings was performed using dyes, **B3** and **B7**, in which *p*-chloroaniline was diazo component. Analysis of the remission spectra before and after washing indicated that dye in the

Table 2
Properties of monomers (M) and dimers (D_I, D_{II}) in **B1**–**B8** (in aqueous solution)

Dye	Dye concentration 2% Property (%)				Dye concentration 0.16% Property (%)			
	D_I (≈480 nm)	M (≈520 nm)	D_{II} (≈560 nm)	α	D_I (≈480 nm)	M (≈520 nm)	D_{II} (≈560 nm)	α
B1	49	29	22	0.41	15	27	57	0.37
B2	30	21	49	0.27	25	27	47	0.37
B3	69	14	17	0.16	5	87	8	6.69
B4	50	24	26	0.32	33	38	29	0.61
B5	53	36	11	0.56	60	14	26	0.16
B6	55	8	37	0.09	51	34	14	0.52
B7	33	52	15	1.08	15	54	31	1.17
B8	52	23	25	0.30	48	23	29	0.30

Ratio of the monomer/dimers equilibrium $\alpha = M/(D_I + D_{II})$ (dimers: D_I—sandwich, D_{II}—head-to-tail).

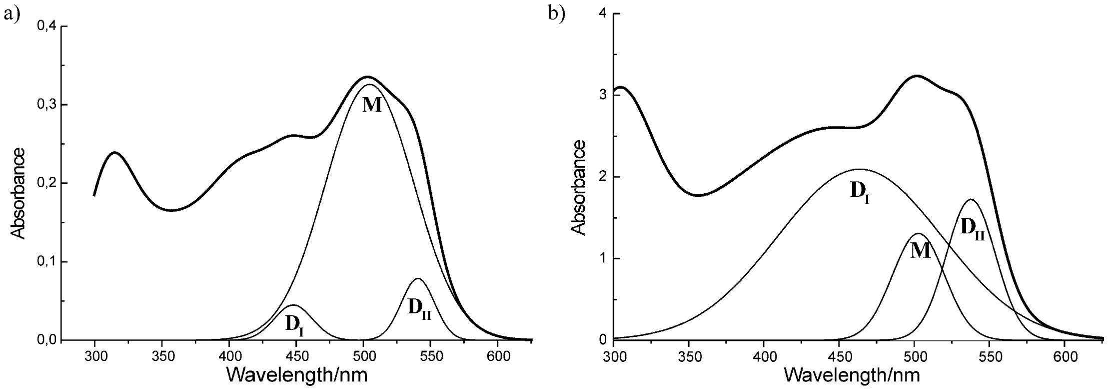


Fig. 3. Exemplary distributions of the spectrum of **B3** resolved into partial spectra (Gauss' curves) for dye solutions of concentration (a) 0.16% and (b) 2%.

form of monomer (M) is faster wash-off from dyed cotton than dimers (D_I, D_{II}) (Fig. 4).

The influence of dye concentration on aggregation is shown by the increase in absorbance of the dimer D_{II}, and the simultaneous decrease in the absorption of the monomer M. Spectral analysis after standardisation for $\lambda = 504$ nm (**B3**) illustrates this phenomenon. It is known that removed from dyed fabric more rapidly than the rate of their aggregation in intermicellar fibre spaces. This is shown by the relative decrease in the absorbance of dimer. Molecules in the aggregated form are more strongly combined with fibres through hydrogen bonds, which results in increased fastness to washing [16].

Table 3
Properties of monomer and dimer in dyes **B1**–**B8** (in 50% ethanol and 70% acetone)

Dye	Ethanol 50% Property (%)				Acetone 70% Property (%)			
	D_I	M	D_{II}	α	D_I	M	D_{II}	α
B1	32	13	55	0.15	26	56	18	1.27
B2	38	8	53	0.09	23	46	30	0.85
B3	63	23	13	0.30	28	39	33	0.64
B4	26	12	62	0.14	–	96	4	24.0[a]
B5	46	5	49	0.05	18	66	16	1.94
B6	37	7	56	0.07	32	54	13	1.17
B7	44	10	46	0.11	20	70	10	2.33
B8	21	7	72	0.07	–	88	12	7.33[a]

Ratio of the monomer/dimers equilibrium $\alpha = M/(D_I + D_{II})$.

[a] $\alpha = M/D_{II}$ (D_I—sandwich, D_{II}—head-to-tail).

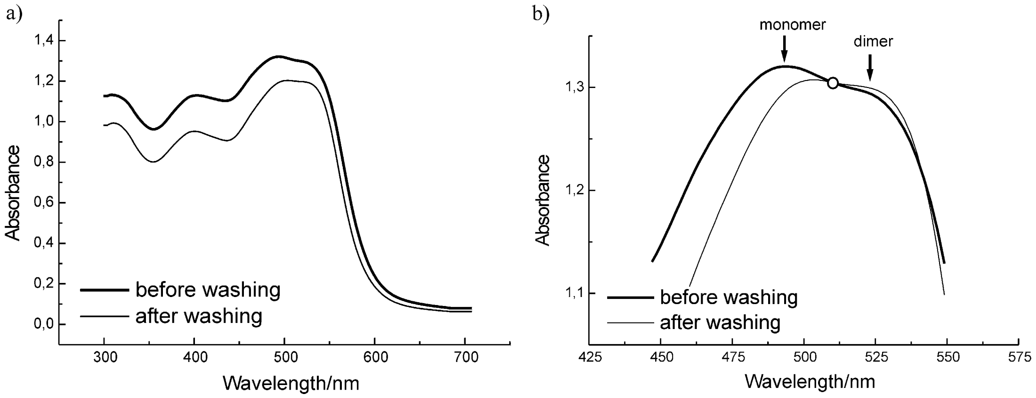


Fig. 4. Remission spectra of **B3** before and after washing for 2% omf dyeings: (a) before and (b) after spectrum standardisation at $\lambda = 504$ nm.

3.3. *Azo-hydrazone tautomerism*

It is well known that the equilibrium between the azo and hydrazone forms of *o*-hydroxyazo dyes is considerably affected by the type of solvent used in the spectral measurement of direct dyes [7,17–19]. This is associated with both selective solvation, which is dependent on the dye structure, and the dye's ability to generate intermolecular hydrogen bonds. The dyes appear to be mostly in the hydrazone form, the amount of which increases in relation to the azo form with increase in solvent polarity [17,18,20–22].

To determine the ratio of the two tautomers, the band deconvolution procedure was used as for the determination of the monomer/dimer equilibrium. The results are given in Table 4.

Table 4
Properties of azo and hydrazone forms in mixture, in water and 70% acetone

Dye	Property (%)			
	Water		70% acetone	
	Azo	Hydrazone	Azo	Hydrazone
B1	0.27	0.73	0.32	0.68
B2	0.24	0.76	0.32	0.68
B3	0.27	0.73	0.37	0.63
B4	0.36	0.64	0.37	0.63
B5	0.15	0.85	0.39	0.61
B6	0.18	0.82	0.57	0.43
B7	0.23	0.77	0.56	0.44
B8	0.26	0.74	0.73	0.27

In both water and 70% acetone, there is favour at the hydrazone form a tautomeric [azo/hydrazo] equilibrium was realised for **B1**–**B8**. In 70% acetone, the proporties of the azo form increased in comparison to the analogous spectra in water, while for **B6**–**B8,** the derivatives of isophthalic acid, the azo form predominated.

3.4. *Values of pK_a*

The ease of ionisation of the –OH groups in dyes derived from J acid influences the colour fastness of dyed cellulosic fibres, especially fastness to washing [15,23,24]. Determination of the acid-base equilibrium constant, pK_a, was carried out in alkaline, aqueous 50% ethanol solutions at various pH values. As a result of absorption curve superposition, the position of the isosbestic point was determined and the analytical wavelength was found [25–27]. The values of pK_a were then calculated from the dependence $\log A = f(\text{pH})$ (Table 5).

The ionised form of the dye absorbs at shorter wavelength than the non-ionised form and it is assumed that this is the ionised azo form [28] (Fig. 5). Exceptions were **B4** and **B8** ($R = NO_2$), in

Table 5
pK_a values of **B1**–**B8**

Dye	**B1**	**B2**	**B3**	**B4**	**B5**	**B6**	**B7**	**B8**
pK_a	–	11.3	10.5	11.6	13.8	–	14.3	14.1

which the absorption maxima of the ionised forms were shifted bathochromically in relation to the absorption of the hydrazone form. This range is ascribed to the absorption of the ionised hydrazone form [28].

Over the particular pH range examined (8–13) the correlation coefficient of the straight line log $A = f(\mathrm{pH})$, R was low and ranged from 0.63 to 0.83. Hence the accuracy of the determination of pK_a was low. Fig. 5b shows that two different lines were obtained below and above 12; these two straight lines clearly have different slopes. In this connection, the determinations were carried out for two pH ranges, one within which low changes in absorbance were observed (pH = 7–12.5) and another where the absorbance changes were high (pH > 12.5) indicating dye ionisation and dye transfer into the anion form. The procedure used allowed the pK_a determination accuracy to be satisfactory (Fig. 5). The type of bringing group influences considerably the colour fastness to alkaline media. The derivatives of terephthalic acid are easily ionised. Analogous dyes derived from isophthalic acid have pK_a values higher by almost 3 units than those of the derivatives of terephthalic acid.

3.5. Measurement of the dye photostability

The photostability of the dyes under investigation was determined by measuring the changes in absorbance after 0, 2, 6, 10, 18 and 26 h of exposure of dyed woven fabric (1% and 2% omf) samples under standard conditions in a Xenotest 150S apparatus (Heraus-Hanau) (Fig. 6).

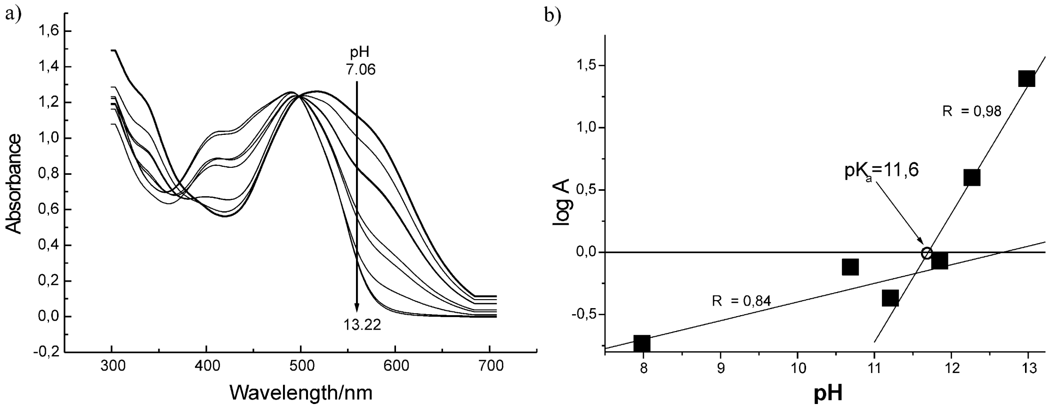


Fig. 5. Determination of analytical wavelength (567 nm) for **B4** (a) and the calculation of pK_a from log A as a function at pH (b) (R—correlation coefficient).

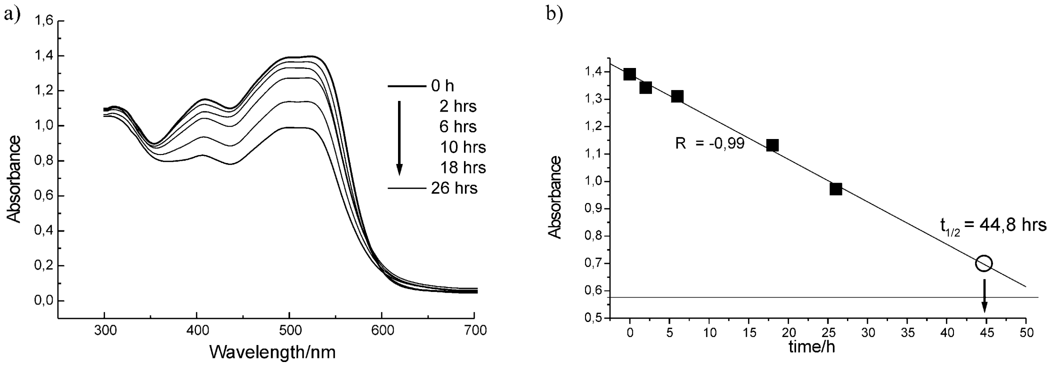


Fig. 6. Changes in absorbance of **B5** during exposure (2% omf dyeing) (a) and an example of the determination of dye decomposition half-time, $t_{1/2}$ (b). Analytical wavelength $\lambda = 524$ nm, R—correlation coefficient.

Table 6
Dye decomposition half-time, $t_{1/2}$

Dye	$t_{1/2}$ (h)	
	1% omf	2% omf
B1	41.0	45.2
B2	29.7	31.3
B3	32.9	38.0
B4	32.4	36.9
B5	34.6	44.8
B6	35.2	36.6
B7	34.0	35.9
B8	25.9	27.3

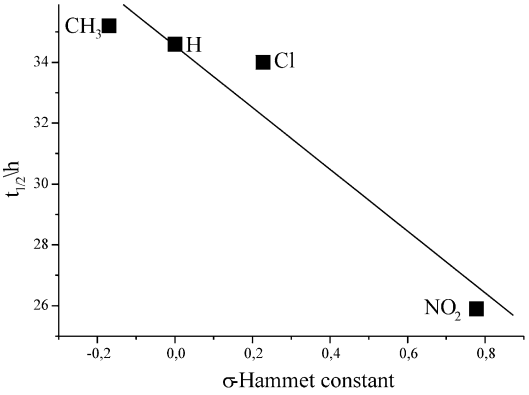


Fig. 7. Dependence of $t_{1/2}$ of **B5**–**B8** on Hammett's σ constant [18] (correlation coefficient $R = 0.960$).

The extrapolated value of $t_{1/2}$ from the dependence $A = f(t)$ for $A_{1/2}$ was assumed as a measure of dye fastness to light; the results are given in Table 6.

Analysis of the results obtained makes it difficult to draw definite conclusions about the effects of substituents in the diazo component on the light fastness of the dyes. The relationships found experimentally vary and even the presence of chlorine (e.g., dyes **B3**, **B7**) in the dye molecule failed to increase fastness to light.

For 1% omf dyeings with dyes **B5**–**B8** (i.e. the derivatives of terephthalic acid), one can determine the dependence of decomposition half-time on Hammett's σ constants of substituent R in the diazo component (Fig. 7) [29–31]. The negative values mean that photodegradation occurres during the photo-oxidation process.

4. Conclusions

Spectral analysis has shown that the used dyes were strongly aggregated in aqueous solution. Measurements performed in 70% aqueous acetone solution made it possible to determine the positions of the absorption bands responsible for monomer and dimer absorptions.

Dilution of the dye solutions induced the decomposition dimer on monomers (**B2**, **B4**, **B6**, **B7**) or a change in the dimer proportion (**B1**, **B3**, **B5**, **B8**).

The type of bringing groups used determines the kind of decomposition; in the case at the derivatives of terephthalic acid, the predominant mechanism of decomposition is that of dimers into monomers, while in the isophthalic acid derivatives, one can observe first the decomposition of one of the dimers, which results in the change in the ratio of dimers to monomer. The weakest aggregation in water was shown by **B3** and **B7**, derivatives of *p*-chloroaniline.

In dyes dissolved in 70% acetone, the monomer form predominates. This solvent probably forms competitive hydrogen bonds with the dye molecules, making their intermolecular aggregation difficult. The dyes examined also form aggregates in dyed cotton fabric.

An increase in solvent polarity causes an increase in the hydrazone form content. Spectra in water indicate a shift in the azo-hydrazone equilibrium towards the formation of the azo form, with this effect being the most intensive in 70% acetone (from 5 to 49%). The derivatives of isophthalic acid (**B5–B8)** appear in water mostly in the hydrazone form, while in 70% acetone they are in the azo form. These findings are reversed for derivatives of terephthalic acid (**B1**–**B4**).

The pK_a of the obtained dyes were found to range from 11.3 to 12.6 for the dyes derived from terephthalic acid and from 13.8 to 14.3 for the dyes derived from isophthalic acid. The high pK_a values indicate that dyes **B5**–**B8** are resistant to alkaline media.

The aggregation of the dyes increases the half-time of dye decomposition, $t_{1/2}$. The differences are rather low, from 5 to 18%, and the changes are unsystematic and difficult to interpret.

From the dependence of $t_{1/2}$ on Hammett's σ constants of the substituents in the diazo component, $t_{1/2}=f(\sigma)$, it follows that dye photodegradation takes place in the photo-oxidation process.

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References

[1] Szadowski J, Niewiadomski Z, Wojciechowski K. Dyes and Pigments 2001;50:87.

[2] Blus K, Wojciechowski K. XLIV Congress PTChem and SITPChem, Katowice, 9–13 September 2001.

[3] Wojciechowski K, VII Congress "Colorchem'2000", Szpindleruv Mlyn (CSR), 14–18 May 2000.

[4] Wojciechowski K, II Congress "Textile Chemistry—2000", Ivanovo, 19–21 September 2000 [in Russian].

[5] Wojciechowski K., Wyrêbak A., Gumulak J., Dyes and Pigments 2003;56:

[6] Antonov S, Stoyanov S. Dyes and Pigments 1995; 28:31.

[7] Coates E. J Soc Dyers Colourists 1969;85:355.

[8] Shore J. Colorant and axiliaries, vol. I. Rochester: Society of Dyers and Colourists; 1990.

[9] Dakiky M, Kanan K, Khamis K. Dyes and Pigments 1999;41:199.

[10] Hsieh BR, Desilets D, Kazmaier PM. Dyes and Pigments 1990;14:165.

[11] Ferreira LFV, Freixo MR, Garcia AR. J Chem Soc Faraday Trans 1992;88:15.

[12] Oliveira AS, Ferreira LF, Worrall DR, Wilkinson F. J Chem Soc Faraday Trans 1996;92:4809.

[13] Monahan AR, Bloosey DF. J Phys Chem 1970;74:4014.

[14] Staab HA. Einführung in die theoretische organische chemie [Polish trans.]. Warszawa: PWN; 1966.

[15] Gronowska J. Podstawy fizykochemii barwników. Toruñ: Uniwersytet im. Mikołaja Kopernika; 1982.

[16] Babko AK, Pilipienko AJ. Fotometriczeskij analiz [Polish translation]. Warszawa: WNT; 1972.

[17] Kuder JE. Tetrahedron 1972;28:1973.

[18] Ball P, Nicols CH. Dyes and Pigments 1982;3:5.

[19] Zollinger H. Color chemistry. Weinheim: VCH; 1991.

[20] Kelemen J. Dyes & Pigments 1981;2:73.

[21] Reeves RL, Skaiser R. J Org Chem 1970;35:3670.

[22] Stoyanov S, Antonov L. Dyes and Pigments 1995;27:133.

[23] Buchowski H, Skulski L. Metody fizyczne w chemii. Łódź: Uniwersytet Łódzki; 1971.

[24] Wojciechowski K, Szadowski J. Dyes and Pigments 2000; 44:137.

[25] Bernstein IJ, Kaminski JL. Spektrofotometiczeskij analiz w organiczeskoj chimii [Russian translation]. Chimija: Leningrad; 1975.

[26] Albert A, Searjeant E. Ionisation constants of acid and bases [Russian translation]. Moskwa: Izd Chimija; 1964.

[27] Perkampus HH. Uv–vis spectroscopy and its application. Berlin: Springer-Verlag; 1992.

[28] Fabian J, Hartman H. Light absorption of organic colorants. Berlin: Springer Verlag; 1980.

[29] Giles HR, McKey RB. Text Res J 1963;34:528.

[30] Chipalkatti HR, Dasai NF, Giles CH, Macauly N. J Soc Dyers Col 1954;70:487.

[31] Cummings JW, Giles CH, McEachran AE. J Soc Dyers Colourists 1956;72:373.