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Synthesis and properties of acid dyes derived from 7-amino-1-hydroxynaphthalene-3-sulphonic acid

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Abstract

The paper concerns the synthesis of red acid dyes derived from γ-acid and containing one sulphonamide group in the dye molecule. These dyes are designed for dyeing polyamide and wool fibres from weakly acidic dyebaths. The dyes were examined in respect of their application, fastness and spectroscopic characteristics. It was found that the sulphonamide group and substituents present at its nitrogen atom influenced the properties of these dyes. © 1999 Elsevier Science Ltd. All rights reserved.

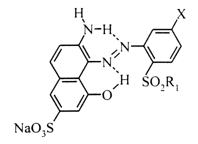
Keywords: Acid dyes; Dyeing polyamide fibres; Dyes derived from γ-acid

1. Introduction

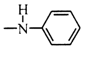
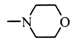
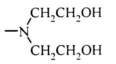
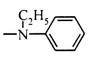
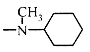
Acid dyes have found wide application in dyeing wool, polyamide fibres and blends of both these fibres [1,2], but they have to meet very high requirements as regards their application and fastness. Considerable attention is paid to the non-toxicity of these dyes and intermediate products used for their synthesis, high light and wet fastness values, high exhaustion degree in weak-acid dyebaths, good levelling power in the case of structural irregularities of polyamide fibres, and capability to form a triple chromatic system.

The present study was focused on monoazo acid dyes derived from γ-acid, and having different orientations of an arylsulphonamide group in relation to the azo bond and different subsituents at the sulphonamide nitrogen atom; γ-acid derivative reds are widely used for dyeing wool and polyamide fibres [3–6].

The structures of the dyes investigated are shown below:



where

	R$_1$	X	Symbol of amine used for the dye synthesis
D – 1		H	A - 1
D – 2		H	A - 2
D – 3	 $-N(CH_2CH_2OH)_2$	H	A - 3
D – 4		H	A - 4
D – 5		H	A – 5

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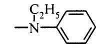
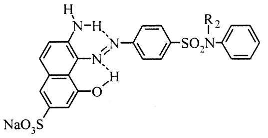
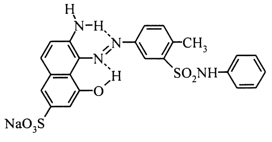
PII: S0143-7208(98)00079-5

D - 6		Cl	A - 6



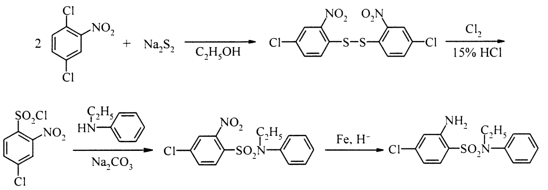
	R_2	
D - 7	H	A - 7
D - 8	C_2H_5	A - 8

D - 9		A - 9

2. Experimental

2.1. Synthesis of arylsulphonamides

Amines A-1 to A-9 were prepared according to the general scheme shown by the example for amine A-6 below.



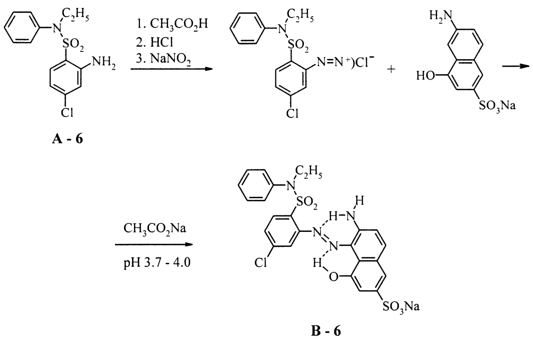
A - 6

2-Nitrobenzenesulphochloride (m.p. = 65–66.5°C), 4-nitrobenzenesulphochloride (m.p. = 70–71°C), 4-chloro-2-nitrobenzenesulphochloride (m.p. = 75.5–76°C) and 4-nitrotoluene-2-sulphochloride (m.p. = 43–46°C) were prepared in accordance with the procedures described in the literature [7,8].

The condensation processes of the arylsulphochlorides with appropriate amines were carried out in a two-phase system viz. water-organic solvent at 40–70°C, using toluene, chlorobenzene and o-dichlorobenzene as solvents [9]. Mostly, a 5% excess of amine in relation to arylsulphochloride was used. The hydrogen chloride resulting from the reaction was neutralized with sodium carbonate, maintaining pH values at 5.5–6.5. Once the process was completed, excess amine was removed by washing the organic layer with dilute sulphuric acid of pH 1.0–1.5. The reaction products, dissolved in organic solvents, without separation, were then reduced with iron in a an aqueous-organic solvent system at 95–97°C. After reduction, amines were extracted with an organic solvent, which was then removed by steam distillation. The reaction products were filtered, washed with water and dried at 50–55°C. The condensation of 2-nitrobenzenesulphochloride with N,N-diethanolamine was carried out in water. The resultant product was reduced by Beschap's method, obtaining amine A-3. The reaction yield, purity and melting point values of the obtained amines are given in Table 1.

2.2. Synthesis of dyes

The synthesis of dyes was carried out according to the following scheme:



Suspensions of the amines A-1, A-2, A-3, A-5 and A-7 in hydrochloric acid containing a phase transfer catalyst were cooled to −5°–0°C and diazotised with a sodium nitrite solution at 0–10°C for 2–3 h.

Amines A-4, A-6 and A-8 were dissolved in acetic acid and after adding hydrochloric acid they were diazotised with sodium nitrite solution.

The obtained diazo compounds were coupled with γ-acid at 0–10°C, maintaining the pH value of the reaction mixture from 2.0 (initial stage) to 3.8–4.0 (final stage) by adding dropwise a 40% solution of sodium acetate. Once the coupling process was completed, the system was alkalised to pH 9.0–10.5 with a 50% aq NaOH. The resultant dyes

Table 1
Some reaction parametrs

Symbol for amine	Yield[a] of reaction	Purity of amine	Melting point (°C)
A-1	79.4	96.9	123–5
A-2	81.7	95.8	116–117.5
A-3	83.4	95.6	Oil
A-4	81.7	95.9	64–5
A-5	83.5	98.0	100.5–101.5
A-6	79.6	96.0	129–132
A-7	88.2	98.2	200–203
A-8	86.7	96.3	134–5
A-9	82.0	97.6	146–7

[a] A total yield of condensation and reduction

were separated by salting out with sodium chloride at 30–60°C; dye yields ranged from 88 to 96%. The coupling process was controlled by chromatography, using Whatman 3 paper and an eluent consisting of pyridine:ammonia:1% brine, 1:1:8 by vol.

The purity of the dyes was determined by HPLC using a Water 996 Photodiode Array Detector and Column Purospher^{R} RP-18e (5 μm), 125–3 nm. Samples were prepared in H_2O HPLC. Condition: linear gradient, injection 10 μl, flow 0.65 ml/min; run time 29.5 min, delay time 13.5 min.

Time (min)	A(%)	B(%)
0–15	40	60
16–30	85	15
31–43	40	60

A = CH_3CN, B = 0.01 m $(C_4H_9)_4N^+Br^-$ in H_2O HPLC.

Quantitative determinations and the R_F coefficients found are given in Table 2.

The max of the dyes were measured in water at concentrations 4×10^{-5} mol/dm^3 and 4×10^{-4} mol/dm^3, as well as in 50% ethanol, at pH from 2 to 12. Measurements were performed with a Spectrophotometer U-3000 (Hitachi). The results are given in Table 3 and shown in Figs. 1 and 2.

The dyes were examined in respect of their exhaustion from the dyebath depending on pH, using 20 miliequivalents of dye (about 1%) per 1 kg of fibre. Dyeings were carried out in a dyeing machine of Roaches Engineering Ltd, using dyebaths with pH 4.0, 5.0 (acetate buffer) and 6.0 (phosphate buffer) at a liquor ratio of 1:20. The dye exhaustion was calculated from formula (1).

Table 2
Paper chromatography R_F and purity of dyes

Dye no	HPLC Time of retention (min)	HPLC Purity (%)	Paper chromatography (R_F)	Contents of NaCl (%)	Color
D-1	9.220	97.40	0.83	6.9	Red
D-2	4.858	95.95	0.79	8.3	Red
D-3	2.382	95.36	0.82	7.5	Red
D-4	11.183	96.97	0.72	9.3	Bluish red
D-5	11.735	97.36	0.74	8.4	Red
D-6	13.123	98.05	0.75	3.2	Rubine
D-7	8.683	95.37	0.84	10.4	Red
D-8	12.575	95.39	0.57	9.7	Red
D-9	8.663	96.77	0.80	9.8	Scarlet

$$\%E = \frac{C_{s_1} - C_{s_2}}{C_{s_1}} \times 100\% \tag{1}$$

where: C_{s_1} = dye concentration in the dyebath before dyeing,
C_{s_2} = dye concentration in the dyebath after dyeing.

The results are given in Table 4.

Standard affinities of dye to polyamide fibres were calculated, using formula (2):

$$-\Delta\mu^o = RT\ln\frac{[C_f]}{V[C_s]} \tag{2}$$

where: C_f = dye concentration in fibres,
C_s = dye concentration in dyebath,
V = volume of internal phase of fibre, litre/kg; for Nylon 6 this value is 0.08 litre/kg.

The results are listed in Table 3.

Table 3
Molecular weight, spectrophotometric properties and affinities of acid dyes on Nylon 6 (98°C;pH 5.0)

		Spectrophotometry						
		Water				50% ethanol		
		1[a]		2[b]				
Dye	Molecular weight	λ_{max} (nm)	ε_{max} ($dm^3\,mol^{-1}\,cm^{-1}$)	λ_{max} (nm)	ε_{max} ($dm^3\,mol^{-1}\,cm^{-1}$)	λ_{max} (nm)	ε_{max} ($dm^3\,mol^{-1}\,cm^{-1}$)	Affinities $-\Delta\mu$ ($kJ\,mol^{-1}$)
D-1	520	508.6	15 200	509.6	12 600	515.0	16 500	59.4
D-2	514	509.6	15 450	507.4	12 900	514.2	16 350	52.8
D-3	532	508.4	16 500	506.8	14 300	515.4	16 950	45.9
D-4	548	512.8	15 900	513.2	14 000	519.4	16 600	58.9
D-5	540	507.4	15 300	506.0	13 900	513.8	17 000	60.2
D-5	540	507.4	15 300	506.0	13 900	513.8	17 000	60.2
D-6	582.5	517.8	13 500	518.2	11 400	528.0	15 950	63.2
D-7	520	503.4	14 750	501.6	12 400	509.8	20 300	64.9
D-8	548	506.2	14 450	504.4	12 800	512.0	19 300	63.2
D-9	534	497.0	15 150	486.2	14 050	499.6	19 800	62.8

[a] 1,concentration of dye 4×10^{-5} mol/dm^3.
[b] 2,concentration of dye 4×10^{-4} mol/dm^3.

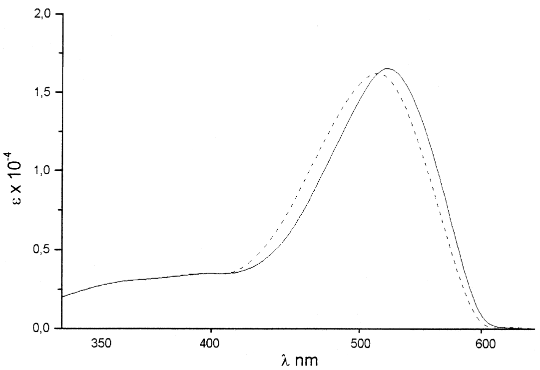


Fig. 1. Absorption spectra of dye D-1 in: 1. (–) Water pH 2–10: ethanol 50:50 by vol.; 2. (- -) Water pH 11–12: ethanol 50:50 by vol.

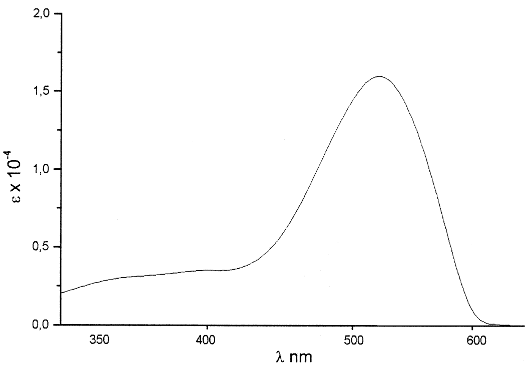


Fig. 2. Absorption spectrum of dye D-4 in water pH 2–12: ethanol 50:50 by vol.

Dye absorption curves were also prepared for polyamide fibres at 60, 80 and 98°C. The absorption curves of dye D-3 in the examined group with the lowest affinity to polyamide fibres are shown in Fig. 3, while those for dye D-7 with the highest affinity to polyamide fibres are shown in Fig. 4.

In order to have a closer look at the effect of dye structure on dye absorption by polyamide fibres, dyeings were carried out within a wide range of dye concentrations from 3 to 60 miliequivalents per 1 kg of fibre. Dyeing conditions: pH 5.0, temperature 98°C, liquor ratio 1:20, time 2 h; dyed fibre: polyamide 6 with a crystallinity degree of 0.49 and amine end groups in the amorphous portion of the fibre amounting to 27.5 miliequivalents.

The dye concentration in fibre (C_f) was calculated as a difference between the concentrations of dye in the dyebath before and (C_{s_1}) after dyeing (C_{s_2}).

Table 4
Relationship between dyebath exhaustion and pH

Dye no	Nylon 6 (pH)			Wool (pH)		
	4.0 (%)	5.0 (%)	6.0 (%)	4.0 (%)	5.0 (%)	6.0 (%)
D-1	99.8	98.4	90.6	99.1	95.0	78.5
D-2	97.2	95.5	84.8	94.6	88.3	54.3
D-3	94.0	87.2	50.0	89.9	69.9	33.8
D-4	99.7	98.2	91.4	99.3	96.6	92.5
D-5	99.8	98.6	92.0	99.4	96.8	83.6
D-6	99.9	99.1	97.7	99.6	99.0	92.5
D-7	99.9	99.3	98.0	99.6	99.2	94.1
D-8	99.9	98.7	97.5	98.5	97.5	94.2
D-9	99.9	99.1	97.8	99.6	99.2	96.0

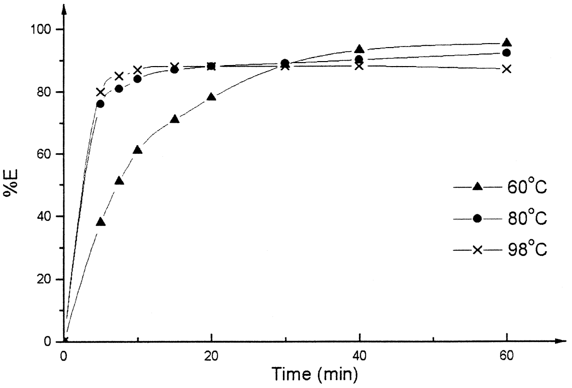


Fig. 3. Absorption curves of dye D-3; dyeing temperature 60, 80, 98°C.

$$C_{\rm f} = C_{s_1} - C_{s_2} \tag{3}$$

Using Kubelka–Munk's equation, the relationship between the concentration of dye in fibre and the depth of dyeing was determined by means of a Datacolor reflection spectrometer.

$$K/S = \frac{(1-R^2)}{2R} = kC_{\rm F} \tag{4}$$

and the relative strength $\frac{(K/S)_x}{(K/S)_{20}}$ of particular dyeings in relation to the standard dyeing where $C_{\rm S} = 20$ miliequivalents per 1 kg of fibre.

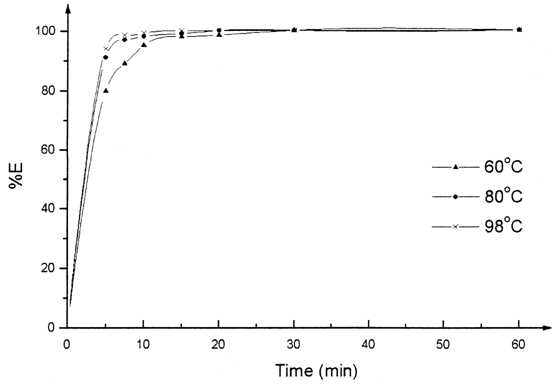


Fig. 4. Absorption curves of dye D-7, dyeing temperature 60, 80, 98°C.

$$\frac{C_{f_x}}{C_{f_{20}}} = \frac{(K/S)_x}{(K/S)_{20}} \tag{5}$$

C_{f_x} was calculated from Eq. (5):

$$C_{f_x} = \frac{(K/S)_x}{(K/S)_{20}} \times C_{f_{20}} \tag{6}$$

The results obtained for selected dyes are given in Table 5.

The dyeings of polyamide 6 to a depth of 1/1 standard depth were used for testing colour fastness to water, acid and alkaline perspiration, dry and wet rubbing and washing at 40°C. The light fastness measurements were carried out by means of a Xenotest 150S apparatus (Heraus, Hanau). The results are listed in Table 6.

2.3. Typical example of syntheses

2.3.1. 4-chloro-2-nitro-N-ethyl-N-phenylbenzenesulphonamide

To a mixture containing 90 g (0.35 mole) of 4-chloro-2-nitrobenzenesulphochloride dissolved in 110 cm^3 of o-dichlorobenzene and 15 cm^3 of water, 45 g (0.37 mole) of N-ethylamine was added dropwise with vigorous stirring for 1 h. The temperature was maintained at 40–45°C and the pH at 5.5–6.5 through adding drops of 20% aq sodium carbonate. After adding the whole quantity of amine, the reaction mixture was maintained at 40–45°C and pH 6.0–6.5 for another hour. Once the pH value was stabilised, the mixture was

Table 5
Relationship between dye concentration in the bath (C_{s_1}) and dye concentration on the fibre (C_f). Relative strength of dyeing $\left(\frac{(K/S)_x}{(K/S)_{20}}\right)$

Dye no.	C_{s_1} (mEq/1 kg of fibre)	C_f (mEq/1 kg of fibre)	$\frac{K/S)_x}{(K/S)_{20}}$	C_{f_x} (mEq/1 kg of fibre)	$C_f - C_{f_x}$ (mEq/1 kg of fibre)
D-3	3.0	2.781	0.162	2.826	−0.045
	8.0	7.422	0.428	7.467	−0.045
	14.0	12.653	0.728	12.703	−0.050
	20.0	17.446	1.0	17.446	–
	30.0	22.902	1.030	22.734	0.168
	40.0	27.235	1.494	26.064	1.171
	60.0	36.024	1.584	27.634	8.400
D-4	3.0	2.896	0.146	2.974	0.022
	8.0	7.874	0.401	7.879	−0.005
	14.0	13.811	0.0698	13.714	0.097
	20.0	19.648	1.0	19.648	–
	30.0	28.589	1.304	25.621	2.968
	40.0	35.394	1.416	27.822	7.572
	60.0	40.569	1.484	29.157	11.412
D-7	3.0	2.955	0.148	2.940	0.015
	8.0	7.946	0.399	7.927	0.019
	14.0	13.920	0.701	13.927	−0.007
	20.0	19.867	1.0	19.867	–
	30.0	29.691	1.369	27.198	2.483
	40.0	39.237	1.595	31.688	7.549
	60.0	51.656	1.721	34.191	17.465
D-9	3.0	2.968	0.151	2.992	−0.024
	8.0	7.923	0.405	8.026	−0.103
	14.0	13.888	0.699	13.852	0.036
	20.0	19.817	1.0	19.817	–
	30.0	29.495	1.187	23.522	5.973
	40.0	37.710	1.289	25.544	12.166
	60.0	44.621	1.449	28.715	15.906

Table 6
Fastness properties of acid dyes

Dye no.	Water			Washing			Perspiration						Rubbing		Light-fastness			
							Alkaline			Acid					Polyamide		Wool	
	1	2	3	1	2	3	1	2	3	1	2	3	Dry	Wet	1/1	1/3	1/1	1/3
D-1	4-5	3-4	4-5	4	4-5	5	4-5	3	4-5 ←	5	3-4	4-5	5	5	6	5	6	5-6
D-2	5	3	4-5	4-5	4-5	5	4-5	3	4-5	5	3	4	5	5	6	5-6	6	5-6
D-3	4-5	2-3	4-5	4-5	5	5	4-5	2-3	3-4	5	2	3-4	5	5	6-7	6	6	6
D-4	5	3-4	4-5	4-5	4-5	5	4-5	3-4	4-5	4-5	3-4	4-5	5	5	6	5-6	6	5-6
D-5	5	3-4	4-5	4-5	4-5	5	4-5	3-4	4-5	4-5	3-4	4-5	5	5	6	5-6	6	6
D-6	5	4	4-5	4-5	4-5	5	4-5	4	5	5	4	4-5	5	5	6-7	6	6-7	6
D-7	5	4-5	5	3-4 ←	5	5	4	4	5	5	4-5	5	5	5	5-6	5	5-6	5
D-8	5	4-5	5	4-5	5	5	5	4-5	5	5	4-5	5	5	5	5	4-5	5-6	5
D-9	4-5	4-5	5	4-5 ←	5	5	5	4-5	5	5	4-5	5	5	5	5-6	5	5-6	5

1.Change of shade of dyed farbic; 2. Staining of nylon; 3. Staining of wool.
←Hypsochromic effect.

heated up to 65–70°C and then this temperature was maintained for the next hour. After this time, no arylbenzenesulphochloride was found by thin layer chromatography (Silufol plates UV_{254}; eluent: toluene).

To the reaction mixture at 60–65°C, a 4% solution of sulphuric acid was added dropwise to obtain pH 1.0–1.5 and after intensive stirring for 10 min, the top aqueous layer was separated. To the organic layer, 500 cm^3 of water was added, the whole was heated up to 60–65°C and acidified with 40% sulphuric acid to pH 1.0–1.5; it was then intensively stirred for 10 min and the top aqueous layer was separated. The washing operation was repeated three times until no N-ethylamine was found in the organic layer (TLC).

*2.4. 2-amino-4-chloro-*N*-ethyl-*N*-phenylbenzenesulphonamide*

To 100 cm^3 of water containing 60 g of Fe and 5 g of CH_3COOH at 95–97°C, a hot solution of 0.35 mole of 4-chloro-2-nitro-*N*-ethyl-*N*-phenylbenzenesulphonamide in 110 cm^3 of dichloro benzene was added dropwise with intensive stirring. The mixture was maintained at the boil for about 6 h until no nitro-compound remained (TLC). The mixture was cooled to 75–80°C, 6.5 g of Na_2CO_3 was added and it was reheated up to 85–90°C and stirred at this temperature for about 15 min. Stirring was then stopped and the organic layer was decanted. To the postreduction sludge, the next o-dichlorobenzene layer was added and the whole was heated at the boil for 0.5 h. The flask content was then cooled to 80°C and the organic layer was decanted. This operation was repeated twice. About 500 cm^3 of the organic layer was collected. To the organic layer at 70°C, 2 g of celite and 2 g of active carbon was added and the whole was filtered off. Water was then added to the organic layer and o-dichlorobenzene was removed from the product by vacuum steam distillation at a temperature of about 70°C. The resultant product was filtered off and washed with water. After drying, it contained 89.8 g of amine with a purity of 96.0% and m.p. 129–132°C. The total yield of condensation and reduction was 79.6%.

2.5. Synthesis of dye B-6

First 15.53 g (0.05 mole) of 2-amino-4-chloro-*N*-ethyl-*N*-phenylbenzenesulphonamide and 0.7 g of TBMAC (tributylmethylammonium chloride) was made into a paste in 15 cm^3 of acetic acid and 17.5 cm^3 of 32% hydrochloric acid. The resultant mixture was cooled down with ice to 0°C and 3.5 g of sodium nitrite dissolved in 10 cm^3 of water was added dropwise over 2 min. The diazotisation process was carried out at 5–10°C for 3 h, adding ice to control the temperature and maintaining a slight excess of sodium nitrite. After 3 h, excess nitrite was removed by adding 0.1 g of sulphamic acid.

Then 12.8 g of γ-acid was dissolved in 100 cm^3 of water and 2.1 g of NaOH in the form of 50% aq. solution (pH 7.5–8.0). Ice was added to cool down to 0°C and 5 cm^3 of 32% hydrochloric acid adjust the pH to 2.2–2.5. To the freshly precipitated suspension of γ-acid, the diazo-liquor was added dropwise for 30 min, maintaining the temperature at 3–5°C. Then, 40% sodium acetate solution was added dropwise for 1 h, raising the pH to 2.5. The mixture was stirred for 2 h at 0–5°C at pH 2.0–2.5. During the next hour, the pH was raised to 3.7–3.8 by adding dropwise 120 cm^3 of 10% aq. sodium carbonate. It was then stirred overnight, allowing the temperature to rise to 20–25°C. The pH of the reaction mixture was the raised to 9.5–10.0 by adding dropwise 50% aq sodium hydroxide (20 g NaOH). The mixture was heated up to 65°C and this temperature maintained for about 1 h. After cooling to 55°C, the dye was filtered off and washed twice with 1% brine alkalised with sodium hydroxide solution to pH 10.5. The obtained dye paste weighed 45 g, while the quantity of dye after drying was 28 g. The total yield of the diazotisation and coupling processes was 93%.

The remaining dyes were prepared in the same way.

3. Results and discussion

The condensation of nitrobenzenesulphochlorides with amines in the two-phase system of water–organic solvent was an important stage of the synthesis. The use of an organic solvent immiscible with water made it possible to decrease the quantity of amine used for the condensation (only a 5% excess of amine) and to protect the sulphochlorides against hydrolysis, which consequently increased the yield of the condensation. The arylnitro-compounds dissolved in an organic solvent were reduced with iron by Beschamp's method. The use of this procedure made it possible to prepare the desired amines in high yield and purity.

Diazotisation of the amines with sodium nitrite was carried out in the hydrochloric acid system with an addition of phase transfer catalyst such as tributylmethylammonium chloride. Diazotisation of amines whose hydrochlorides were hardly soluble in hydrochloric acid was carried out with sodium nitrite using an acetic acid-hydrochloric acid system. The coupling of the diazotised amines with γ-acid ortho to the amino group was performed in aqueous medium at a precisely specified pH value (acetic acid–sodium acetate buffer). This allowed one to considerably reduce the quantity of products coupled in the ortho position in relation to the hydroxyl group of γ-acid. In order to remove impurities, the dyes were separated from the strong alkaline medium. Such a procedure made it possible to prepare dyes with a high purity (HPLC).

Spectrophotometric measurements carried out in 50% ethanol and water showed the effect of the sulphonamide group on λ_{max}, molar absorption and aggregation. The dyes met Lambert–Beer's law in 50% ethanol within the concentration range from 2×10^{-6} mol/dm^3 to 4×10^{-4} mol/dm^3. All the examined dyes showed one absorption band, while λ_{max} and molar absorption depended on the nature of substituents and their position in the aryl ring of the amine. Some effect was also shown by substituents on the nitrogen or the sulphonamide group. Within the examined dyes, pressure of the sulphonamide group in position 2 relative to the azo link resulted in a considerable decrease in molar absorption, with the absorption band also broadening, e.g. the difference in molar absorption between dye D-7 and D-1 is 23%, which is due to steric disturbance of the system. The 2-aminoarylsulphonamide substituted dyes showed a bathochromic effect in relation to the isomeric 4-aminoarylsulphonamide derivatives. The differences in the absorption of energy quantum between dyes D-7 and D-1 was 2.3 kJ mol^{-1}, and that between D-8 and D-4 was 3.3 kJ mol^{-1}. The sulphonamide group ortho position to the azo bond probably participates in spatial conjugation with the dye chromophore group. A bathochromic effect was also brought about by the chlorine atom. For dye D-6 in comparison to D-4 it, amounts to 8.6 nm (3.8 kJ mol^{-1}). Spectroscopic measurements in 50% ethanol within a wide pH range from 2 to 12 showed a high stability of dyes substituted twice at the sulphonamide nitrogen atom, such as D-2, D-3, D-4, D-5, D-6 and D-8 (Fig. 2). On the other hand, in dyes D-1, D-7 and D-9, the sulphonamide group is ionised at pH over 10 and the spectrum is shifted in a hypsochromic way (Fig. 1). Lambert-Beer's law for the examined dyes in water is not satisfied; with increase in the dye concentration, its molar absorption decreases. Dyes with sulphonamide groups ortho to the azo bond are aggregated to a lesser percentage extent.

The dye application evaluations shouwed high exhaustion of the dyes by polyamide and wool fibres from dyebaths with pH 4.0 and 5.0, and for some dyes also at pH 6.0. Only dye D-3 containing electrophilic substituents at the nitrogen atom in the sulphonamide group showed lower affinities to wool and polyamide fibres. In this case, solvophobic interactions of the dye are intensified, while the hydrophobic interactions with fibres are depressed [10]. There is also some significant effect of the dye molecular structure. The dyes with sulphonamide groups in the *para* or *meta* position in relation to the azo bond showed higher affinities to polyamide fibres in comparison to isomeric dyes containing sulphonamide groups in position 2. The difference between dye D-7 and D-1 was 5.5 kJ mol^{-1}, while that between dyes D-8 and D-4 was 4.3 kJ mol^{-1}. Also the hydrophobic chlorine atom present in dye D-6 increases its affinity in comparison to dye D-4 by 4.3 kJ mol^{-1}. The dyes with higher affinities to polyamide fibres are characterised by a higher dyeing rate (compare Figs. 3 and 4). Despite the high rate of dye exhaustion from the dyebath, the examined group of dyes show good levelling power against the structural irregularities of fibres. The increase in the dye affinity is accompanied by improved wet fastness. Within the examined dyes, the highest wet fastness values were shown by dyes from D-6 to D-9.

In the case of dyes D-1, D-7 and D-9 (derivatives of monosubstituted sulphonamides), the shade of the dyed fibres is subject to a hypsochromic effect with strongly alkaline washing and with perspiration. The spectroscopic measurements indicate ionisation of the sulphonamide group.

Examination of dye absorption by polyamide fibres showed that at dye concentrations in dyebaths below the quantity of amino end groups present in the amorphous regions of the fibres, the dyes under investigation are almost quantitatively exhausted by polyamide fibres, with the exception of dye D-3, which has the lowest affinity to polyamide fibres. The relative color strength is proportional to the dye quantity in the fibres. Within this concentration range, the obtained acid dyes are combined with the amine groups of polyamide fibres through ionic forces. At higher dye concentrations in dyebaths, the dye absorption by fibre depends on the dye concentration as well as on the dye molecular structure. The obtained dyes show an overdyeing effect which increases with the affinity of the given dye to polyamide fibres. Thus, the dye structure affects the dye absorption and the differences between dyes in this respect are considerable (Table 5). Dyes with sterically developed molecules (sulphonamide groups in the ortho position) show a lower overdyeing effect than the isomeric dyes with sulphonamide groups in the para position in relation to the azo bond. The relative color strength is not proportional to the amount of dye in the fibres. This confirms the assumption about the aggregation of these dyes in polyamide fibres [11]. It is of interest that the dyes with a higher aggregation in water, such as D-6 to D-9, show a higher overdyeing effect of polyamide fibres, and consequently a higher aggregation in fibres.

The dyes are generally characterised by a good fastness to light. Somewhat better fastness to light is shown by the 2-sulphonamido derivatives. The sulphonamide group in the ortho position to the azo bond probably decreases excited state reactivity through dispersion of the absorbed energy of the molecule.

4. Conclusion

Some valuable acid reds were synthesised, constituting derivatives of γ-acid which contain one sulphoamide group in the ortho, meta and para positions in relation to the azo bond. The obtained dyes may be used for dyeing polyamide fibres, wool and polyamide-wool blends from weakly acid dyebaths. The dyes show a very good levelling power on polyamide fibres. The position of the sulphonamide group influences the dye affinity to polyamide fibres. The 4-sulphonamido derivatives of have higher affinities to the polyamide fibres than those of the isomeric 2-sulphonamido derivatives. The latter dyes show a slightly higher fastness to light.

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