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Colorimetric studies of heterocyclic monoazo reactive dyes and their dyeing applications on cotton, silk, and wool fibers

Nikhil M. Parekh · Kalpana C. Maheria

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Abstract Heterocyclic quinazolinone-based hot brand monoazo reactive dyes were obtained by diazotization of 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-one and coupling with a variety of cyanurated coupling components. All the heterocyclic hot brand monoazo reactive dyes were characterized by elemental analysis (C, H, N) and by use of spectroscopic techniques (FT-IR, UV–visible, ^{1}H NMR). Their performance as reactive dyes was assessed on silk, wool, and cotton fabrics. The dyes were found to give a variety of color shades with very good depth and uniformity on the fibers. The fastness of all the dyes on the fibers was moderate to excellent. Colorimetric data (L*, a*, b*, C*, H*, and K/S) of the synthesized dyes were also studied in detail.

Keywords 3-(4-Aminophenyl)-2-phenylquinazolin-4(3*H*)-one · Exhaustion · Fixation · Dyeing · Fastness properties · Colorimetric data

Introduction

Production of reactive dyes with novel structures has recently attracted much attention, and many novel structures useful in commercial application to silk, wool, and cotton, and their blends with other fibers, have been obtained. The success of quinazoline derivatives for production of commercial dyes and pigments, both for natural and man-made fibers, is well known [1]. Reactive dyes are mainly applied to cotton fiber to achieve high wash fastness.

In continuation of our previous work on the development of heterocyclic monoazo compounds, because of their dyeing applications and good fastness

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N. M. Parekh · K. C. Maheria (✉)
Department of Applied Chemistry, S. V. National Institute of Technology,
Surat 395007, Gujarat, India
e-mail: maheria@gmail.com

properties, it seemed appropriate to synthesize a series of hot brand monoazo reactive dyes [2–4]. Because of their strong interaction with the surfaces of many synthetic and natural fabrics, several reactive dyes are used for dyeing wool, cotton, nylon, silk, and modified acrylics [5–16]. It was, therefore, believed to be of interest to synthesize hot brand monoazo reactive dyes based on 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-one by diazotization of 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-one and coupling with a variety of 4-chloroanilino cyanurated naphthalene sulfonic acids. Moreover, introduction of a triazine group to the dye molecule improves the degree of exhaustion and fixation of the dyes studied [17]. These new dyes have been characterized by use of IR and NMR spectroscopy and on the basis of their dyeing properties on cotton, silk, and wool fabrics. On these fabrics the dyes had moderate to very good light fastness and good to excellent washing and rubbing fastness. Colorimetric data (L*, a*, b*, C*, H*, K/S) for the synthesized dyes were also investigated.

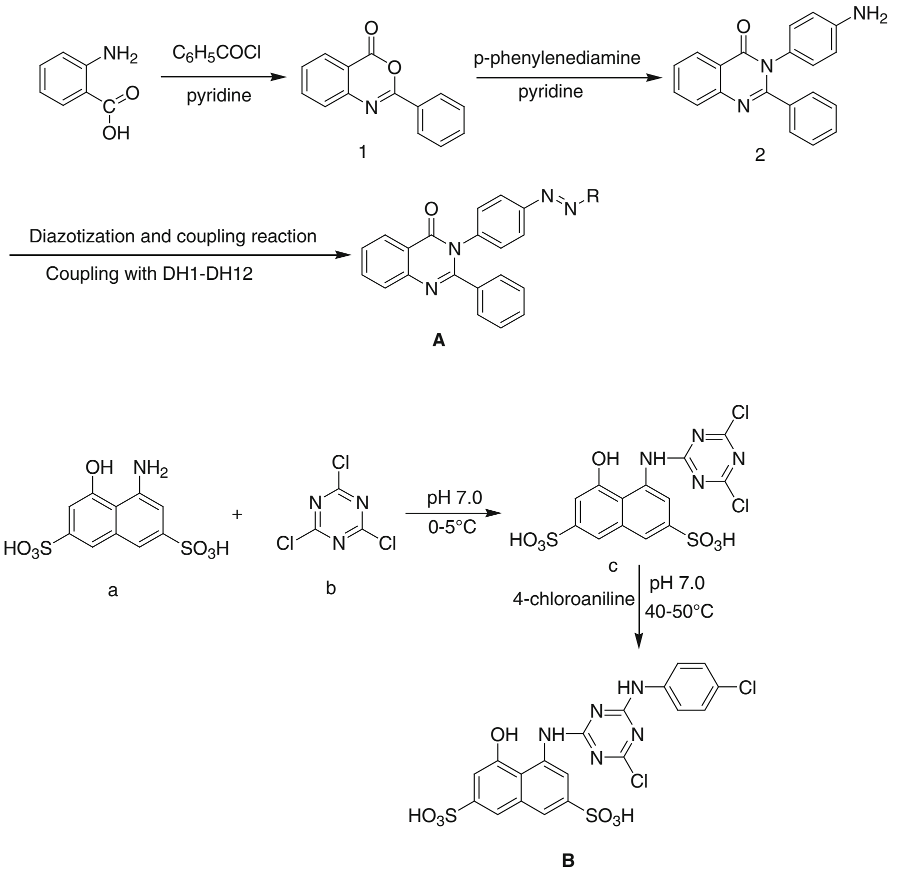
Results and discussion

Chemistry

Synthesis of intermediates and target compounds was accomplished in accordance with the steps illustrated in Scheme 1. Anthranilic acid is converted into 2-phenylbenzo[*d*][1,3]oxazine-4-one by reaction with benzoyl chloride in pyridine as solvent. This was confirmed by the appearance of –C=O group in IR spectrum which contained a band at 1,662 cm^{-1}. 2-Phenyl-benzo[*d*][1,3]oxazine-4-one, on further reaction with *p*-phenylenediamine, afforded 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-one in high yield and purity. This was confirmed by the appearance of an –NH_2 group in IR spectrum, which contained two sharp bands in the region 3,200–3,400 cm^{-1}. This 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-one, on diazotization, and followed by coupling with different cyanurated coupling components yielded quinazolinone-based hot brand monoazo reactive dyes. All the compounds were characterized by IR and ^{1}H NMR spectroscopy, and elemental analysis. The ^{1}H NMR spectra of $\mathbf{D_1}$–$\mathbf{D_{12}}$ contained signals between 5.20 and 5.86 ppm ascribed to the –NH linkage. The singlet at 4.46 ppm was ascribed to the –OH group of the naphthalene ring; the other aromatic protons resonated at 6.78–8.90 ppm as a multiplet. The principle benefit of using quinazoline-based compounds is high yield of the product and fewer steps of the reaction procedure. Simple work up facilitates preparation of starting material.

Dyeing properties

$\mathbf{D_1}$–$\mathbf{D_{12}}$ were applied to silk, wool, and cotton fibers (2 % shade) in accordance with a literature procedure [18]. Variation in the hues of the dyed fabric results from alternation of the coupling components. Remarkable uniformity and brightness after washing indicates good penetration and excellent affinity of these dyes for the fabric.



Scheme 1 Synthesis of quinazolinone-based hot brand monoazo reactive dyes (**D_1**–**D_{12}**). R = different cyanurated coupling components as shown in Table 1

Spectral properties of dyes

Absorption maxima (λ_{max}) of **D_1**–**D_{12}** were recorded in water; the results are listed in Table 1. Introduction of electron-donating or electron-attracting groups at a suitable position in the coupler ring affected the absorption characteristic of the dyes. **D_1** had extended conjugation owing to the presence of lone pairs of electrons on the oxygen atoms of hydroxyl groups. Moreover, the chromophoric group –N=N is attached ortho to the –OH group, causing resonance effects, which in turn increases λ_{max}. Comparison of **D_1** with **D_2** and **D_3** shows that **D_1** has a higher λ_{max} value because of the presence of additional auxochrome (sulfonic groups). The same effect is observed when **D_1** is compared with **D_3** and **D_4** [6].

From the results in Table 1, it is clear that the value of λ_{max} depends on the nature and position of coupling component used. The color change observed for each dye is because of alternation of electrons and the presence of additional substituents. For **D_1** there are more places for alternation of electrons; the presence of –NH and –OH

Table 1 Exhaustion and fixation data for **D_1–D_{12}**

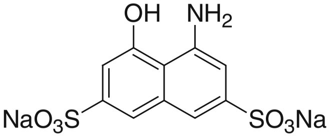
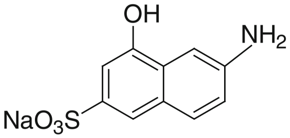
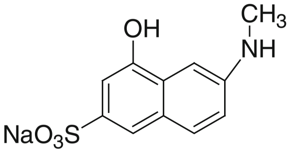
Dye	Shade on dyed fabric	Structure of coupling components	λ_{max} (nm)	% Exhaustion			% Fixation		
				S	W	C	S	W	C
D_1	Purple	 H-acid	546	75.18	70.15	67.00	83.80	89.09	85.82
D_2	Pink	 J-acid	480	74.25	74.00	68.80	85.52	87.83	85.75
D_3	Light pink	 NMJ-acid	492	76.80	70.10	63.93	86.58	86.30	86.04

Table 1 continued

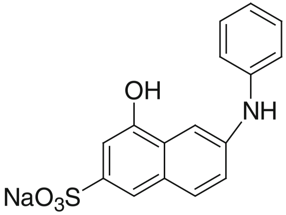
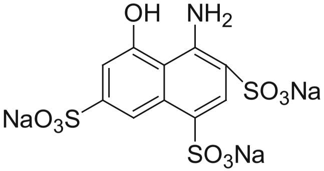
Dye	Shade on dyed fabric	Structure of coupling components	λ_{max} (nm)	% Exhaustion			% Fixation		
				S	W	C	S	W	C
D_4	Light pink	 NPJ-acid	502	77.83	74.28	66.12	84.81	85.49	85.44
D_5	Yellow	 Chicago acid	410	71.85	70.55	62.00	86.29	88.58	85.48

Table 1 continued

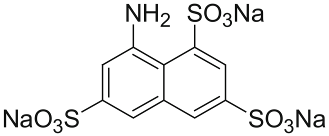
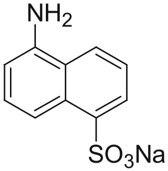
Dye	Shade on dyed fabric	Structure of coupling components	λ_{max} (nm)	% Exhaustion			% Fixation		
				S	W	C	S	W	C
D_6	Brown	 Koch acid	390	68.22	75.20	68.10	87.94	90.36	87.37
D_7	Light brown	 Bronner acid	400	79.40	78.00	69.05	90.05	89.10	87.62

Table 1 continued

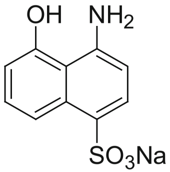
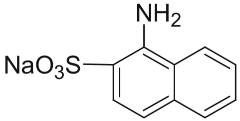
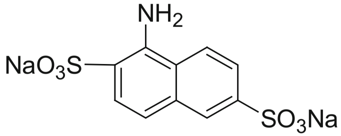
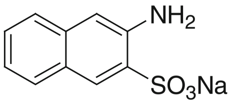
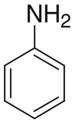
Dye	Shade on dyed fabric	Structure of coupling components	λ_{max} (nm)	% Exhaustion			% Fixation		
				S	W	C	S	W	C
D₈	Yellow	 K-acid	417	69.82	71.80	76.25	84.02	91.23	85.90
D₉	Light yellow	 Tobias acid	420	70.25	77.15	68.22	86.83	84.25	85.74

Table 1 continued

Dye	Shade on dyed fabric	Structure of coupling components	λ_{max} (nm)	% Exhaustion			% Fixation		
				S	W	C	S	W	C
D_{10}	Yellow	 ST acid	417	66.45	72.00	70.80	91.05	87.50	86.86
D_{11}	Pink	 Peri acid	497	73.95	67.65	74.15	83.16	89.40	83.61
D_{12}	Light yellow	 Metanilic acid	400	73.20	75.85	70.85	84.69	86.35	81.86

S silk, *W* wool, *C* cotton

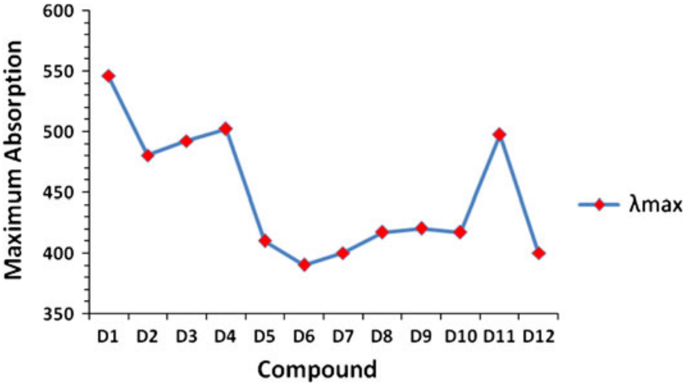


Fig. 1 Absorption maxima (λ_{max} nm) of $\mathbf{D_1}$–$\mathbf{D_{12}}$

groups also contributes to the increase of λ_{max} (546 nm). For $\mathbf{D_2}$, $\mathbf{D_3}$, $\mathbf{D_4}$, $\mathbf{D_7}$, and $\mathbf{D_9}$–$\mathbf{D_{12}}$ the effect is slightly lower because of fewer electrons and, thus, λ_{max} values for all these dyes are lower than for $\mathbf{D_1}$. For $\mathbf{D_5}$, $\mathbf{D_6}$, and $\mathbf{D_8}$, the substituents are same as for $\mathbf{D_1}$ but alternation of electrons is rapid because of the vicinity of the –NH and –SO_3Na groups; therefore, neutralization of electrons takes place rapidly [6]. The dyes' absorption maxima are plotted in Fig. 1.

The magnitude of bathochromic shift depends on the nature of substituents at the terminal amino group [2]. Such bathochromic shifts have been observed for J-acid, N-methyl-J-acid, and N-phenyl-J-acid. $\mathbf{D_2}$ has λ_{max} at 480 nm and $\mathbf{D_3}$ has λ_{max} at 492 nm. Thus, there is a bathochromic shift of 12 nm in the λ_{max} value of $\mathbf{D_3}$ because of the presence of –CH_3. Similarly, $\mathbf{D_4}$ has λ_{max} 502 nm; thus, there is a bathochromic shift of 10 nm in the λ_{max} of $\mathbf{D_3}$ because of the presence of the –C_6H_5 ring, which increases λ_{max} by extending the conjugation by resonance. Combinations of chromophores and auxochromes behave as new chromospheres, leading to extended conjugation involving the lone pair of electrons on the nitrogen atom, resulting in increased λ_{max} values [6].

Exhaustion and fixation study

Percentage exhaustion and fixation data for $\mathbf{D_1}$–$\mathbf{D_{12}}$ were determined by known methods [19]; again the results are summarized in Table 1. Percentage exhaustion for 2 % dyeing on silk ranges from 66 to 80 %; maximum exhaustion is 79.40 % for $\mathbf{D_7}$ and minimum exhaustion is 66.45 % for $\mathbf{D_{10}}$. For wool, percentage exhaustion ranges from 67 to 78 %; maximum exhaustion is 78.00 % for $\mathbf{D_7}$ and minimum exhaustion is 67.65 % for $\mathbf{D_{11}}$. For cotton, percentage exhaustion ranges from 62 to 77 %; maximum exhaustion is 76.25 % for $\mathbf{D_8}$ and minimum exhaustion is 62.00 % for $\mathbf{D_5}$.

Percentage fixation for 2 % dyeing on silk ranges from 83 to 92 %; maximum fixation is 91.05 % for $\mathbf{D_{10}}$ and minimum fixation is 83.16 % for $\mathbf{D_{11}}$. For wool, percentage fixation ranges from 84 to 92 %; maximum fixation is 91.23 % for $\mathbf{D_8}$ and minimum fixation is 84.25 % for $\mathbf{D_9}$. For cotton, percentage fixation ranges

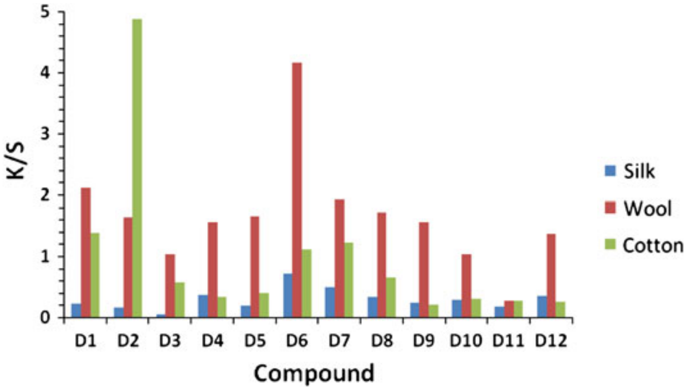


Fig. 2 K/S value of synthesized dyes ($\mathbf{D_1}$–$\mathbf{D_{12}}$)

from 81 to 88 %; maximum fixation is 87.62 % for $\mathbf{D_7}$ and minimum fixation is 81.86 % for $\mathbf{D_{12}}$. The data are summarized in Table 1, from which it is apparent exhaustion and fixation values are very good. This is because diffusion of the dye molecule within the fabric is rapid.

Fastness properties

The light, wash, and rubbing fastness properties of $\mathbf{D_1}$–$\mathbf{D_{12}}$ were determined by a known method [20]; the results are summarized in Table 2. It is apparent from the table that light fastness of all the dyes was in the range 3–5 for all three fabrics, which shows light fastness is moderate to good. The wash fastness for all the dyes was in the range 3–5 for all three fabrics, which shows wash fastness is good to excellent. The rubbing (dry and wet) fastness of all the dyes was in the range 3–5 for all three fabrics which shows rubbing fastness is good to excellent.

Colorimetric data for $\mathbf{D_1}$–$\mathbf{D_{12}}$

The color of a dye on silk, wool, and cotton is expressed in terms of CIE lab values (Table 3). The CIE lab coordinates measured were: Lightness (L*), Chroma (C*), hue angle from 0° to 360° (H), a* value representing the degree of redness (positive) and greenness (negative), and b* representing the degree of yellowness (positive) and blueness (negative). A reflectance spectrophotometer was used for colorimetric measurements on dyed samples. K/S values given by the reflectance spectrophotometer are calculated at λ_{max} and are directly correlated with the dye concentration on the substrate according to the Kubelka–Munk equation [21], $K/S = (1-R)^2/2R$, where K is absorbance coefficient, S is scattering coefficient, and R is reflectance ratio.

The color coordinates (Table 3) indicate the dyes have high affinity for silk, wool, and cotton. From the results listed in Table 3 it is apparent that, for silk, the dyeing achieved by use of dye $\mathbf{D_1}$ was redder (lower a* value), brighter (lower C*), and darker (higher L* value) than that achieved by use of dye $\mathbf{D_2}$, and the dyeing

Table 2 Fastness properties of heterocyclic monoazo reactive dyes

Dye	Light fastness			Wash fastness			Rubbing fastness					
							Dry			Wet		
	S	W	C	S	W	C	S	W	C	S	W	C
$\mathbf{D_1}$	3–4	4	5	4–5	3–4	5	5	4–5	4	5	4–5	4
$\mathbf{D_2}$	4	5	4	3–4	4	4	4–5	4	4–5	4	4	4–5
$\mathbf{D_3}$	4–5	4–5	5–6	4	4–5	4–5	3	3–4	4	3–4	3	3
$\mathbf{D_4}$	5	3–4	4–5	4–5	3	4	3–4	5	5	4	4–5	3–4
$\mathbf{D_5}$	3–4	5–6	5	5	3–4	3–4	4	4–5	3–4	4–5	3–4	3–4
$\mathbf{D_6}$	4	5–6	5–6	4–5	4	3–4	5	5	4–5	4	4	4
$\mathbf{D_7}$	5	5	5	3	4–5	4	4–5	4–5	4	3–4	4–5	5
$\mathbf{D_8}$	5	4–5	4–5	3–4	4	4–5	3	5	4	3–4	4	4–5
$\mathbf{D_9}$	4–5	5	4	4	4–5	4	3–4	4	3–4	4–5	4	4
$\mathbf{D_{10}}$	4–5	5	4	4	4–5	4	3–4	4	3–4	4–5	4	4
$\mathbf{D_{11}}$	4–5	5	4	4	4–5	4	3–4	4	3–4	4–5	4	4
$\mathbf{D_{12}}$	4	5	5	4–5	4	3–4	4	3–4	4	4	3–4	3–4

Light fastness: *1* poor; *2* slight; *3* moderate; *4* fair; *5* good; 6 very good
Wash and rubbing fastness: *1* poor; *2* fair; *3* good; *4* very good; *5* excellent
S silk, *W* wool, *C* cotton

achieved by use of dye $\mathbf{D_3}$ was greener, duller, and lighter than that achieved by use of dye $\mathbf{D_1}$. Dyeing achieved by use of dye $\mathbf{D_6}$ was redder, brighter, and darker than that achieved by use of dye $\mathbf{D_5}$. Dyeing achieved by use of dye $\mathbf{D_{10}}$ was redder, brighter, and darker than that achieved by use of dye $\mathbf{D_9}$, and dyeing achieved by use of dye $\mathbf{D_{12}}$ was greener, duller, and lighter than that achieved by use of dye $\mathbf{D_{11}}$. Dye $\mathbf{D_6}$ had the highest value of color strength (K/S) of 0.72. The K/S value for silk was found to be in the order:

$$D_6 > D_7 > D_4 > D_{12} > D_8 > D_{10} > D_9 > D_1 > D_5 > D_{11} > D_2 > D_3$$

From the results in Table 3 it is apparent that, for wool, dyeing achieved by use of dye $\mathbf{D_1}$ was redder, duller, and darker than that achieved by use of dye $\mathbf{D_2}$ whereas dyeing achieved by use of dye $\mathbf{D_3}$ was greener, brighter, and lighter than that achieved by use of dye $\mathbf{D_1}$. Dyeing achieved by use of dye $\mathbf{D_6}$ was redder, brighter, and darker than that achieved by use of dye $\mathbf{D_5}$. Dyeing achieved by use of dye $\mathbf{D_{10}}$ was greener, duller, and lighter than that achieved by use of dye $\mathbf{D_9}$. Dyeing achieved by use of dye $\mathbf{D_{12}}$ was greener, duller, and lighter than that achieved by use of dye $\mathbf{D_{11}}$. Dye $\mathbf{D_6}$ had the highest value of color strength (K/S) of 4.16. The K/S value for wool was found to be in the order:

$$D_6 > D_1 > D_7 > D_8 > D_5 > D_2 > D_4 > D_8 > D_{12} > D_3 > D_9 > D_{11}$$

From the results listed in Table 3 it is apparent that, for cotton, dyeing achieved by use of dye $\mathbf{D_1}$ was greener, duller, and lighter than that achieved by use of dye $\mathbf{D_2}$ whereas dyeing achieved by use of dye $\mathbf{D_3}$ was redder, brighter, and lighter than that achieved by use of dye $\mathbf{D_1}$. Dyeing achieved by use of dye $\mathbf{D_6}$ was redder, brighter,

Table 3 Colorimetric data for heterocyclic monoazo reactive dyes

Dye	L*			a*			b*			C*			H*			K/S		
	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C	S	W	C
D_1	79.66	52.84	57.98	9.40	21.35	17.67	2.88	1.09	−3.61	9.83	21.38	18.04	17.07	2.91	348.46	0.23	2.12	1.39
D_2	83.10	59.80	43.14	7.81	23.68	24.80	3.00	10.19	0.38	8.37	25.78	24.80	21.00	23.28	0.87	0.16	1.64	4.88
D_3	84.28	66.76	72.59	6.38	19.90	18.69	4.37	11.32	3.84	7.73	22.89	19.08	34.37	29.64	11.63	0.05	1.03	0.57
D_4	79.12	65.89	77.57	9.93	22.61	14.74	13.39	17.66	2.21	16.67	28.69	14.91	53.46	37.99	8.54	0.36	1.56	0.33
D_5	87.08	74.64	72.16	1.10	5.01	9.73	5.94	23.12	7.50	6.04	23.66	12.29	79.48	77.78	37.63	0.20	1.65	0.40
D_6	83.02	61.49	70.71	3.23	17.31	10.37	14.15	29.29	12.37	14.52	34.02	16.14	77.16	59.42	50.02	0.72	4.16	1.12
D_7	79.14	67.22	63.75	8.45	16.03	11.52	4.61	22.66	4.19	9.63	27.76	12.25	28.64	54.73	20.00	0.50	1.92	1.23
D_8	85.78	56.18	74.73	1.13	18.75	10.16	10.85	6.65	13.57	10.91	19.90	16.95	84.06	19.52	53.19	0.34	1.72	0.66
D_9	85.67	68.63	82.02	1.26	14.75	9.30	8.33	26.25	4.77	8.43	30.11	10.45	81.39	60.67	27.13	0.24	1.56	0.21
D_{10}	84.00	73.81	79.03	1.70	6.07	9.31	9.01	18.20	5.56	9.17	19.18	10.85	79.32	71.55	30.85	0.29	1.03	0.30
D_{11}	83.19	68.27	78.60	3.90	11.83	9.84	9.37	19.83	5.25	10.15	23.09	11.16	67.37	59.17	28.10	0.17	0.28	0.27
D_{12}	85.40	77.32	82.74	0.73	2.03	8.43	8.40	17.65	4.52	8.43	17.76	9.57	85.03	83.44	28.22	0.35	1.36	0.26

S silk, *W* wool, *C* cotton

and darker than that achieved by use of dye $\mathbf{D_5}$. Dyeing achieved by use of dye $\mathbf{D_{10}}$ was redder, brighter and darker than that achieved by use of dye $\mathbf{D_9}$, and dyeing achieved by use of dye $\mathbf{D_{12}}$ was greener, duller, and lighter than that achieved by use of dye $\mathbf{D_{11}}$. Dye $\mathbf{D_2}$ had the highest value of color strength (K/S) of 4.88. The K/S value for cotton was found to be in the order:

$$D_2 > D_1 > D_7 > D_6 > D_8 > D_3 > D_5 > D_4 > D_{10} > D_{11} > D_{12} > D_9$$

The dyes' K/S values are plotted in Fig. 2.

Conclusion

In the work discussed in this paper we performed detailed studies on quinazolinone based heterocyclic monoazo reactive dyes and their applications. Purple, pink, brown, and yellow shades were obtained on fibers. Characterization of the synthesized dyes was in agreement with expected values. The excellent exhaustion and fixation of these dyes indicates they have good solubility and good affinity for the fabric. Dyes $\mathbf{D_7}$ and $\mathbf{D_8}$ have good light fastness properties on silk whereas $\mathbf{D_5}$ and $\mathbf{D_6}$ have very good light fastness properties on wool and $\mathbf{D_3}$ and $\mathbf{D_6}$ have very good light fastness properties on cotton. The light fastness of all the dyes was moderate to very good. Dyes $\mathbf{D_1}$, $\mathbf{D_4}$, $\mathbf{D_5}$, $\mathbf{D_6}$, and $\mathbf{D_{12}}$ have excellent wash fastness properties on silk whereas $\mathbf{D_3}$, $\mathbf{D_7}$, $\mathbf{D_9}$, $\mathbf{D_{10}}$, and $\mathbf{D_{11}}$ have excellent wash fastness properties on wool. $\mathbf{D_1}$, $\mathbf{D_3}$, and $\mathbf{D_8}$ have excellent wash fastness properties on cotton. Dyes $\mathbf{D_1}$, $\mathbf{D_2}$, $\mathbf{D_6}$, and $\mathbf{D_7}$ (dry) and $\mathbf{D_1}$, $\mathbf{D_5}$, $\mathbf{D_9}$, $\mathbf{D_{10}}$, and $\mathbf{D_{11}}$ (wet) have excellent rubbing fastness properties on silk whereas $\mathbf{D_1}$, $\mathbf{D_4}$, $\mathbf{D_5}$, $\mathbf{D_6}$, $\mathbf{D_7}$, and $\mathbf{D_8}$ (dry) and $\mathbf{D_1}$, $\mathbf{D_4}$ and $\mathbf{D_7}$ (wet) have excellent rubbing fastness properties on wool. Dyes, $\mathbf{D_2}$, $\mathbf{D_4}$, and $\mathbf{D_6}$ (dry) and $\mathbf{D_2}$, $\mathbf{D_7}$, and $\mathbf{D_8}$ (wet) have excellent rubbing fastness properties on cotton. The wash and rubbing fastness studies of all the dyes show that wash and rubbing fastness are good to excellent. Dyes $\mathbf{D_6}$, $\mathbf{D_6}$, and $\mathbf{D_2}$ have the highest value of color strength for silk, wool, and cotton, respectively, which indicates that dyes $\mathbf{D_6}$, $\mathbf{D_6}$, and $\mathbf{D_2}$ have good affinity for silk, wool, and cotton, respectively. In this case, cotton, for which color strength is highest, has a higher K/S value than wool and silk because of the high substantivity of the dyes for cotton. The color coordinates indicate the dyes have good affinity for silk, wool, and cotton.

Experimental

Materials and methods

All chemicals were of analytical grade and used as received. All melting points were determined on a PMP-DM scientific melting point apparatus and are uncorrected. The purity of all dyes were determined by thin-layer chromatography (TLC) [22] on silica gel-G coated Al foil plates (0.5 mm thickness; Merck). Infrared spectra were recorded on a Shimadzu FT-IR 8400S model using KBr pellets. ^{1}H NMR spectra were acquired on a Varian 400 MHz model spectrophotometer using DMSO as solvent and TMS as internal reference (chemical shifts in δ, ppm). Elemental analysis of C, H, and N was performed with a Carlo Erba 1108 instrument. Light fastness was assessed in accordance with BS 1006-1978 [23]. The rubbing fastness test was performed with a crockmeter (Atlas) in accordance with AATCC-1961 [24] and the wash fastness test was in accordance with IS 765-1979 (Indian standard ISO, 1979) [25]. Colorimetric data (L*, a*, b*, C*, H*, K/S) were recorded with a Gretag Macbeth CE: 7000 reflectance spectrophotometer.

Synthesis of 2-phenylbenzo[d]1,3]oxazine-4-one

2-Phenylbenzo[*d*][1,3]oxazine-4-one was prepared in accordance with a reported procedure [26].

Synthesis of 3-(4-Aminophenyl)-2-phenyl-3H-quinazolin-4-one

3-(4-Aminophenyl)-2-phenyl-3*H*-quinazolin-4-one was prepared in accordance with a reported procedure [27, 28].

Diazotization and coupling procedure

Concentrated HCl was added to a well stirred suspension of 3-(4-aminophenyl)-2-phenylquinazolin-4(3*H*)-one (0.0048 mol) in water and the mixture was heated to 70 °C and maintained at that temperature until a clear solution was obtained. After cooling to 0–5 °C in an ice-bath, an aqueous solution of sodium nitrite (0.66 g) in water was added dropwise over a period of 30 min with continuous stirring. The reaction was stirred at a temperature below 5 °C for approximately 1 h. Excess of nitrous acid was tested by use of starch–iodide paper and was removed by adding required amount of sulfamic acid solution (10 %). The clear diazonium salt solution (A) thus obtained was used immediately in the coupling reaction.

Cyanuric chloride (0.01 mol) was stirred in acetone at a temperature below 5 °C for 1 h. A neutral solution of H-acid (0.01 mol) in an aqueous sodium carbonate solution (10 % *w*/*v*) was then added in small amounts in approximately 1 h. The pH was maintained neutral by simultaneous addition of sodium carbonate solution (1 % *w*/*v*). The reaction mass was stirred at 0–5 °C for a further 4 h when a clear solution was obtained. The resulting solution was used for condensation reaction with 4-chloroaniline. The temperature of an ice-cooled, well stirred solution of cyanurated H-acid was gradually increased to 45 °C for 30 min. To this cyanurated H-acid, 4-chloroaniline (1.73 g, 0.01 mol) was added dropwise at the same temperature, during a period of 30 min, maintaining the neutral pH by simultaneous addition of sodium bicarbonate (1 % *w*/*v*). After addition was complete, stirring was continued for a further 3 h. The 4-chloroanilino cyanurated H-acid solution (B) thus obtained was subsequently used for further coupling reaction.

To an ice-cold and well stirred solution of 4-chloroanilino cyanurated H-acid (d) (0.01 mol) a freshly prepared diazo solution (0.005 mol) was added dropwise over a period of 10–15 min. The pH was maintained at 7.5–8.5 by simultaneous addition of sodium carbonate solution (10 % *w*/*v*). During coupling a purple solution was formed. Stirring was continued for a further 3–4 h, maintaining the temperature below 5 °C. The reaction mixture was heated to 60 °C and sodium chloride (12 g) was added until the purple colored dye was precipitated. The mixture was stirred for approximately 1 h, filtered, and the residue was washed with a small amount of sodium chloride solution (5 % *w*/*v*). The solid was then dried at 80–90 °C and extracted with DMF. The dye was precipitated by diluting the DMF extract with excess chloroform. A violet dye (**D$_1$**) was then isolated by filtration, washed with chloroform, and dried at 60 °C. By following this procedure, the other reactive dyes **D$_2$**–**D$_{12}$** were synthesized by use of the 4-chloro anilino cyanurated coupling components J-acid, NMJ-acid, NPJ-acid, Chicago acid, Koch acid, Bronner acid, K-acid, Tobias acid, Sulfo Tobias acid, Peri acid, and Metanilic acid (Table 1).

*Dye **D$_1$** (4-chloro anilino cyanurated H acid)* Yield: 79 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,474–3,242 (O–H and NH), 3,076 (C–H), 1,650 (C=O), 1,558, 1,309, 848 (C–N), 1,629 (N=N), 1,197, 1,053 (S=O, asym. and sym.), 754 (C–Cl); ^{1}H NMR (400 MHz, DMSO-*d*$_6$): $\delta = 4.46$ (1H, s, –OH), 5.80 (1H, s, –NH), 6.30 (1H, s, –NH), 7.18–8.41 (20H, m, Ar–H); Anal. Calcd. For $C_{39}H_{23}Cl_2N_9Na_2O_8S_2$: C, 50.55; H, 2.50; N, 13.60. Found: C, 50.49; H, 2.44; N, 13.56.

*Dye **D$_2$** (4-chloro anilino cyanurated J acid)* Yield 82 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,470–3,244 (O–H and NH), 3,078 (C–H), 1,650 (C=O), 1,560, 1,308, 844 (C–N), 1,632 (N=N), 1,189, 1,056 (S=O, asym. and sym.), 752 (C–Cl); ^{1}H NMR (400 MHz, DMSO-*d*$_6$): $\delta = 4.48$ (1H, s, –OH), 5.80 (2H, s, –NH), 6.78–8.41 (21H, m, Ar–H); Anal. Calcd. for $C_{39}H_{24}Cl_2N_9NaO_5S$: C, 56.80; H, 2.93; N, 15.29. Found: C, 56.77; H, 3.00; N, 15.36.

*Dye **D$_3$** (4-chloro anilino cyanurated NMJ acid)* Yield: 74 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,470–3,258 (O–H and NH), 3,076 (C–H), 1,652 (C=O), 1,556, 1,309, 842 (C–N), 1,630 (N=N), 1,197, 1,054 (S=O, asym. and sym.), 759 (C–Cl); ^{1}H NMR (400 MHz, DMSO-*d*$_6$): $\delta = 3.48$ (1H, s –CH_3), 4.46 (1H, s, –OH), 5.80 (1H, s, –NH), 6.78–8.41 (21H, m, Ar–H); Anal. Calcd. For $C_{40}H_{26}Cl_2N_9NaO_5S$: C, 57.29; H, 3.12; N, 15.03. Found: C, 57.22; H, 3.19; N, 15.10.

*Dye **D$_4$** (4-chloro anilino cyanurated NPJ acid)* Yield: 81 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,480–3,252 (O–H and NH), 3,066 (C–H), 1,658 (C=O), 1,564, 1,307, 848 (C–N), 1,634 (N=N), 1,198, 1,054 (S=O, asym. and sym.), 756 (C–Cl); ^{1}H NMR (400 MHz, DMSO-*d*$_6$): $\delta = 4.46$ (1H, s, –OH), 5.84 (1H, s, –NH), 6.78–8.41 (26H, m, Ar–H); Anal. Calcd. for $C_{45}H_{28}Cl_2N_9NaO_5S$: C, 60.01; H, 3.13; N, 14.00. Found: C, 60.10; H, 3.19; N, 14.07.

*Dye **D$_5$** (4-chloro anilino cyanurated Chicago acid)* Yield: 80 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,474–3,242 (O–H and NH), 3,076 (C–H), 1,650 (C=O), 1,558, 1,309, 848 (C–N), 1,629 (N=N), 1,197, 1,053 (S=O, asym. and sym.), 754 (C–Cl);

^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 4.46$ (1H, s, –OH), 5.80 (1H, s, –NH), 6.30 (1H, s, –NH), 7.18–8.41 (20H, m, Ar–H); Anal. Calcd. for $C_{39}H_{23}Cl_2N_9Na_2O_8S_2$: C, 50.55; H, 2.50; N, 13.60. Found: C, 50.52; H, 2.44; N, 13.49.

*Dye **D₆** (4-chloro anilino cyanurated koch acid)* Yield: 89 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,464–3,272 (O–H and NH), 3,074 (C–H), 1,658 (C=O), 1,562, 1,305, 842 (C–N), 1,628 (N=N), 1,197, 1,053 (S=O, asym. and sym.), 768 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 5.80$ (1H, s, –NH), 6.30 (1H, s, –NH), 7.18–8.84 (20H, m, Ar–H); Anal. Calcd. for $C_{39}H_{22}Cl_2N_9Na_3O_{10}S_3$: C, 46.25; H, 2.19; N, 12.45. Found: C, 46.18; H, 2.24; N, 12.39.

*Dye **D_7** (4-chloro anilino cyanurated bronner acid)* Yield: 89 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,480–3,254 (O–H and NH), 3,076 (C–H), 1,660 (C=O), 1,558, 1,310, 848 (C–N), 1,629 (N=N), 1,197, 1,056 (S=O, asym. and sym.), 752 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 5.80$ (2H, s, –NH), 6.78–8.41 (22H, m, Ar–H); Anal. Calcd. for $C_{39}H_{24}Cl_2N_9NaO_4S$: C, 57.93; H, 2.99; N, 15.59. Found: C, 57.84; H, 2.88; N, 15.62.

*Dye **D_8** (4-chloro anilino cyanurated K acid)* Yield: 78 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,474–3,242 (O–H and NH), 3,076 (C–H), 1,650 (C=O), 1,558, 1,309, 848 (C–N), 1,629 (N=N), 1,197, 1,053 (S=O, asym. and sym.), 754 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 5.80$ (2H, s, –NH), 6.78–8.41 (22H, m, Ar–H); Anal. Calcd. for $C_{39}H_{24}Cl_2N_9NaO_4S$: C, 57.93; H, 2.99; N, 15.59. Found: C, 57.88; H, 2.87; N, 15.64.

*Dye **D_9** (4-chloro anilino cyanurated Tobias acid)* Yield: 79 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,468–3,242 (O–H and NH), 3,079 (C–H), 1,666 (C=O), 1,560, 1,310, 848 (C–N), 1,629 (N=N), 1,197, 1,056 (S=O, asym. and sym.), 754 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 5.22$ (1H, s, –NH), 5.72 (1H, s, –NH), 7.18–8.41 (23H, m, Ar–H); Anal. Calcd. for $C_{39}H_{25}Cl_2N_9O$: C, 66.29; H, 3.57; N, 17.84. Found: C, 66.22; H, 3.54; N, 17.90.

*Dye **D_{10}** (4-chloro anilino cyanurated sulfo Tobias acid)* Yield: 80 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,476–3,242 (O–H and NH), 3,085 (C–H), 1,650 (C=O), 1,558, 1,309, 846 (C–N), 1,634 (N=N), 1,197, 1,053 (S=O, asym. and sym.), 752 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 5.80$ (2H, s, –NH), 7.18–8.50 (22H, m, Ar–H); Anal. Calcd. for $C_{39}H_{24}Cl_2N_9NaO_4S$: C, 57.93; H, 2.99; N, 15.59. Found: C, 57.88; H, 2.85; N, 15.64.

*Dye **D_{11}** (4-chloro anilino cyanurated peri acid)* Yield: 85 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,476–3,254 (O–H and NH), 3,070 (C–H), 1,662 (C=O), 1,560, 1,309, 850 (C–N), 1,629 (N=N), 1,197, 1,053 (S=O, asym. and sym.), 760 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 4.46$ (1H, s, –OH), 5.80 (2H, s, –NH), 7.15–8.41 (21H, m, Ar–H); Anal. Calcd. for $C_{39}H_{24}Cl_2N_9NaO_4S$: C, 57.93; H,2.99; N, 15.59. Found: C, 57.82; H, 3.10; N, 15.46.

Dye ***D***$_{12}$ *(4-chloro anilino cyanurated metanilic acid)* Yield: 89 %; m.p. >300 °C; IR (KBr) cm^{-1}: 3,472–3,268 (O–H and NH), 3,082 (C–H), 1,658 (C=O), 1,566, 1,314, 848 (C–N), 1,638 (N=N), 1,197, 1,056 (S=O, asym. and sym.), 752 (C–Cl); ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 5.80$ (2H, s, –NH), 7.18–8.50 (20H, m, Ar–H); Anal. Calcd. for $C_{35}H_{22}Cl_2N_9NaO_4S$: C, 55.42; H, 2.92; N, 16.62. Found: C, 55.12; H, 2.84; N, 16.50.

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