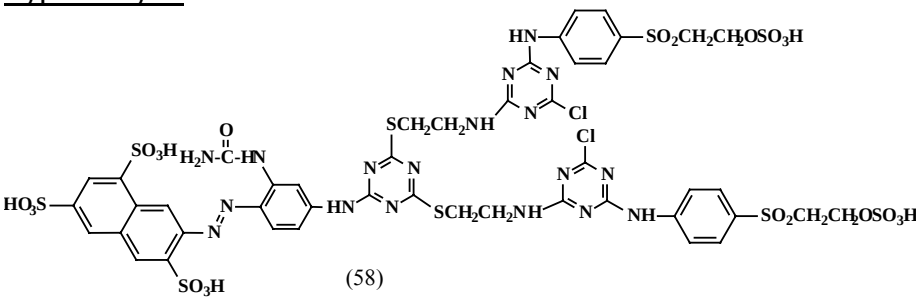
Abstract

ZHAO, MENGNAN. Synthesis and Application of Novel Heterobifunctional Reactive Dyes. (Under the direction of Drs. Harold S. Freeman and C. Brent Smith).

With the goal of improving the performance of traditional dichlorotriazine (DCT) reactive dyes, three types of heterobifunctional reactive dyes were synthesized and evaluated in this study. Type 1 dyes were prepared by a reaction of one equivalent of a DCT-based parent dye with two equivalents of cysteamine followed by two equivalents of cyanuric chloride and *para*-aminobenzenesulfato-ethylsulfone. To make type 2 dyes, cysteine was used instead of cysteamine, and the synthesis of type 3 dyes employed a DCT-based parent dye, and one equivalent of cysteamine, cyanuric chloride, and *para*-aminobenzenesulfato-ethylsulfone.

Type 1 Dyes



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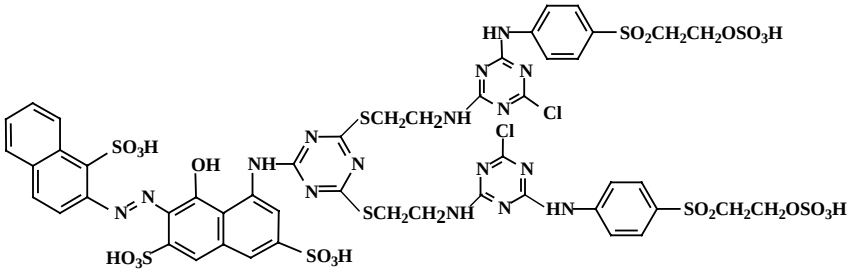

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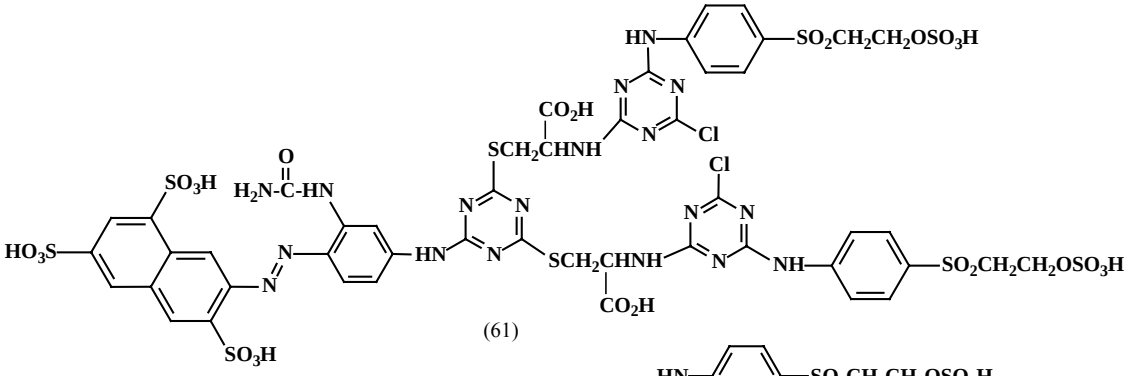
Type 2 Dyes



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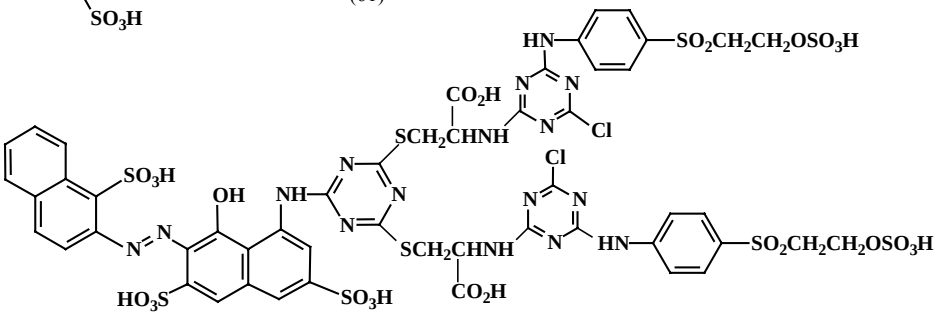

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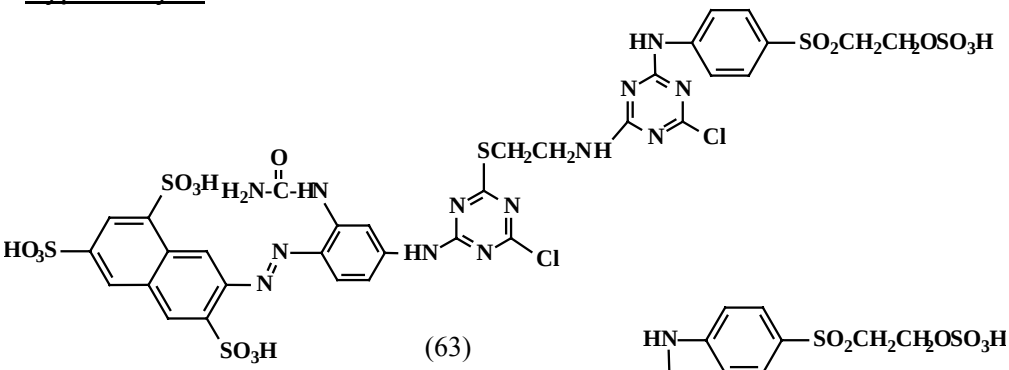
Type 3 Dyes



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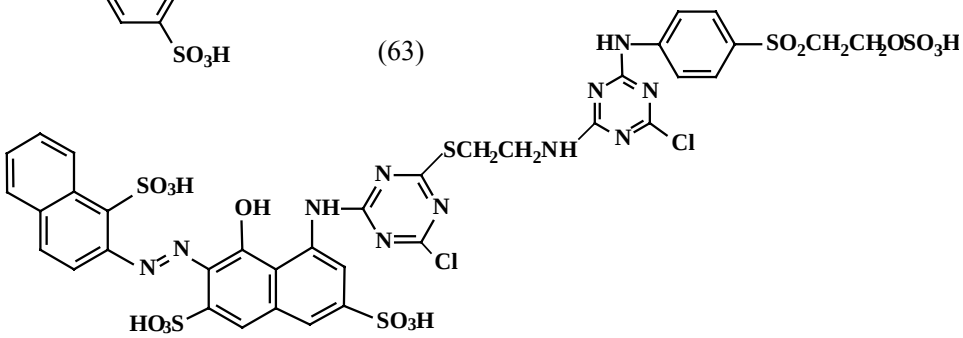

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The visible absorption spectra of the new reactive dyes showed a 7-17 nm increase in λ_{max} compared to parent dichlorotriazine dyes. The structures of new dyes were supported by data from ESI mass spectrometry and results from HPLC analysis indicated that isomeric structures had formed, in which the reaction of cysteamine/cysteine simultaneously occurred at the $–NH_2$ and –SH groups.

The application properties of the new dyes on cotton fabric were compared with those of the DCT-based commercial dyes. The results indicated that type 1 and type 3 dyes, which are derived from cysteamine, gave higher exhaustion levels and K/S values than the corresponding commercial dyes. Of these two new types, type 3 dyes performed better. Type 2 dyes, which are based on cysteine, did not have a good affinity for cotton. It is believed that the presence of a carboxyl group on the linking moiety distorts the geometry of the dye structure, giving an irregular molecular shape.

The results of percent fixation studies showed that type 1 and type 3 dyes can be applied at a lower salt level (40g/L) than the commercial dyes and simultaneously give higher fixation and better leveling. Similarly, it was found that the fastness properties of type 1 and type 3 dyes are not adversely affected by modification of the commercial dyes.

The above mentioned results suggest that the new dyes can be used to produce standard depths using less dye and salt, giving the potential to reduce color and chloride in reactive dye wastewater.

SYNTHESIS AND APPLICATION OF NOVEL HETEROBIFUNCTIONAL REACTIVE DYES

BY

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Biography

Mengnan Zhao was born on October 28, 1976, in Tianjin, China, and graduated in 1995 from Tianjin Dishiqi High School. Mengnan graduated with a Bachelor of Science degree in Polymer Science in July 1999 from Tianjin Institute of Textile Science and Technology. She then worked at China National Institute of Garment Inspection for three years. In August 2004, she enrolled in the Master of Science degree program in textile chemistry at North Carolina State University.

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The author would like to thank Dr. Harold Freeman and Dr. Brent Smith for their guidance and constant support throughout this work. She thanks Dr. Malgorzata Szymczyk for her help with synthesis and Kangqin Chen, her laboratory peer and friend, for help with HPLC analysis. She would also like to thank Judy Elson, Jeffrey Krauss, and Birgit Andersen for sharing their knowledge and providing hands-on support. Special thank you is extended to her parents and sister for their constant love and support.

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I. Introduction

1. Cellulosic Fibers

Cellulosic fibers include cotton, rayon, linen, jute, ramie, hemp, and others, but cotton has become the most important textile fiber because it has fairly good strength, softness, and moisture absorbency [1,2]. "Cotton textiles touch every aspect of our lives," the National Cotton Council of America (NCC) is proud to say. "Cotton is playing an even greater role in our every day lives. For years, cotton clothing, home furnishings and industrial goods have enhanced our quality of life by providing comfort, expression and individuality. From towels to T-shirts, from bedding to blue jeans, cotton surrounds us on a daily basis [3]."

1.1 Fiber Structures

Under the microscope, cotton fibers have a ribbon like structure that is twisted at irregular intervals along its length. Cross-sectionally, the fiber is kidney-shaped with a central hollow core known as the lumen [4,5].

Cotton fiber is based on a high molecular weight polymer. It is almost 100 percent cellulose [1,4]. Cellulose is a carbohydrate containing 44.4 percent carbon, 6.2 percent hydrogen, and 49.4 percent oxygen [4,6]. The repeating unit is shown in Figure 1 [7].

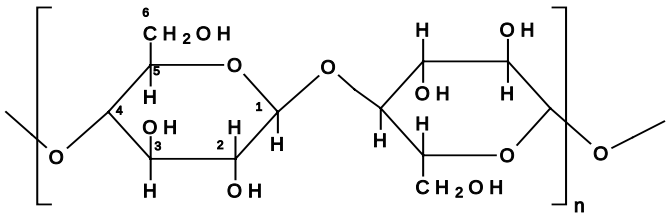


Figure 1. Structure of the polymer in cellulosic fibers.

To form cellulose, two beta-glucose monomer units combine to form cellobiose. Then many cellobiose units combine to form the polymer. Cellulose has a linear chain in which the oxygen links are in the same plane as the glucose rings [1,4,7]. This structure allows the molecular chains to pack together in parallel rows. This well-ordered structure gives cellulose its strong, rigid and water insoluble properties [4,8].

The hydroxyl group (-OH) is the chemically reactive unit in cellulose [4]. In the application of certain finishes and dyestuffs, this group undergoes substitution reactions. Substitution occurs when the hydrogen atom of the hydroxyl group is removed by chemical action. Then, the reacting compound is attached to the oxygen atom [7,9,10].

1.2 Fiber Properties

1.2.1 Physical Properties

Cotton is one of the few fibers that gains strength when wet. This is due to the good alignment of its polymer chains [4]. Cotton fibers are relatively inelastic, due to their crystalline polymer system. Therefore, cotton textile materials wrinkle and crease readily. Cotton fiber is also very absorbent, due to an abundance of polar hydroxyl groups that attract water molecules. The hydrophilic nature also prevents cotton-based textiles from developing static electricity on the surface [4,7].

1.2.2 Chemical Properties

1.2.2.1 Effects of Acid and Alkali

Cotton fibers are weaken and destroyed by acids, especially mineral acids. Acidic conditions hydrolyze the cellulose molecules at the glucosidic bonds [4,11]. Cotton fibers possess excellent resistance to alkali and are relatively unaffected by normal laundering. This is due to the stability of the glucosidic bonds between the cotton to alkaline hydrolysis. Mercerization without tension causes cotton fibers to swell greatly. This is due to hydroxide ions entering the amorphous regions of the fibers and interacting with accessible hydroxyl groups [12,13].

1.2.2.2 Effect of Sunlight and Atmospheric Components

In the presence of atmospheric oxygen, moisture and air pollutants, cotton fibers can be degraded by the ultraviolet (UV) rays of sunlight. The combination of UV light moisture (humidity) can break down the polymer chains on the surface of cotton fibers through hydrolytic reactions. Polymer degradation via hydrolysis is observed as a slight fiber discoloration. Similarly, the fading of colored cotton substrates is caused by a breakdown of dye molecules in the fiber structure [4,7].

2. Dye Classes for Cotton

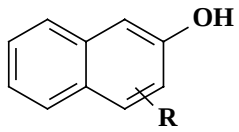
Cotton is considered to be a relatively easy fiber to dye. The reason that cotton takes up dyes easily is attributed to its hydrophilic nature [1,4]. This

hydrophilic fiber will readily attract polar dye molecules into its porous system. As long as the dye molecules can be dissolved in water, they can be taken up by cotton. Dye molecules can enter the amorphous regions of cotton fibers but cannot enter the small spaces in the crystalline regions [1,4,7].

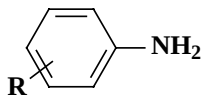
The dye classes that can be used to color cotton are azoic dyes, direct dyes, sulfur dyes, vat dyes, and fiber reactive dyes.

2.1 Azoic Dyes

Azoic dyes are water insoluble molecules containing an azo group. Unlike other dyes, azoic dyes do not exist on the shelf. They are also described as azoic combinations and are produced by combining coupling components and diazo components inside the fiber [14]. The coupling component (1) is mostly a beta-naphthol derivative. The diazo component (2) is an aromatic primary amine.



(1)



(2)

For coupling component (1), the R group attached must be large enough so that the molecule will have the required substantivity to cellulosic fibers [15].

2.1.1 General Properties of Azoic Dyes

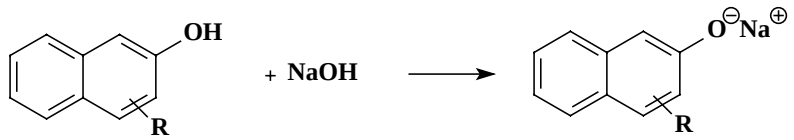
Azoic dyes are used mainly for coloring cellulosic materials. With proper modifications, they can also be applied to hydrophobic fibers such as polyester and triacetate [15].

Since azoic dyes are water insoluble, they have very good washfastness, which also can be attributed to the high degree of aggregation [4]. Even washing with hot water does not affect the color of the dyed fabric significantly. Azoic dyes also have good lightfastness, which is mainly due to aggregation and the absence of substituents that are readily attacked by UV light [4,14]. Azoic dyes are noted for their red colors along with maroons, scarlets and burgundies. The azoic dyes lack most colors in the visible spectrum. Another problem associated with azoic dyes is their tendency to have poor crocking fastness, unless efficient scouring is conducted. This is due to the dye formation on the surface rather than inside the fiber [15].

2.1.2 Formation of Azoic Dyes

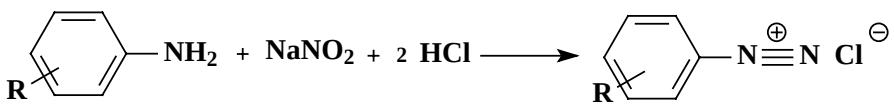
Azoic dyes are formed in three stages by the dyer on the fiber. The first stage is called naphtholation, which involves dissolving the naphthol in water using NaOH and impregnating the fiber with this solution at room temperature.

Stage 1



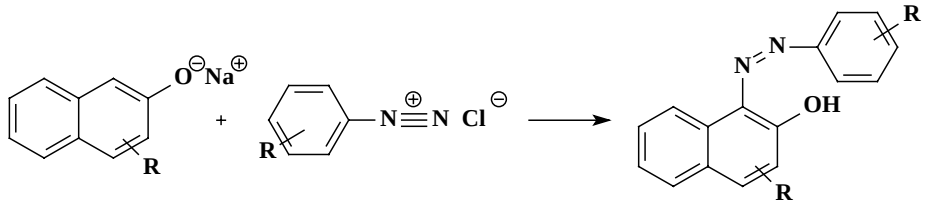
The second stage is called diazotization, which involves converting the diazo component to the soluble diazonium salt by using $NaNO_2$ and HCl.

Stage 2



In stage 3, the naphtholated fabric is then passed through the liquor containing the diazonium salt, to form the azoic dye inside the fiber [15,16].

Stage 3



A summary of the chemical reactions involved the application of azoic dyes is shown for a specific combination in Figure 2 [15].

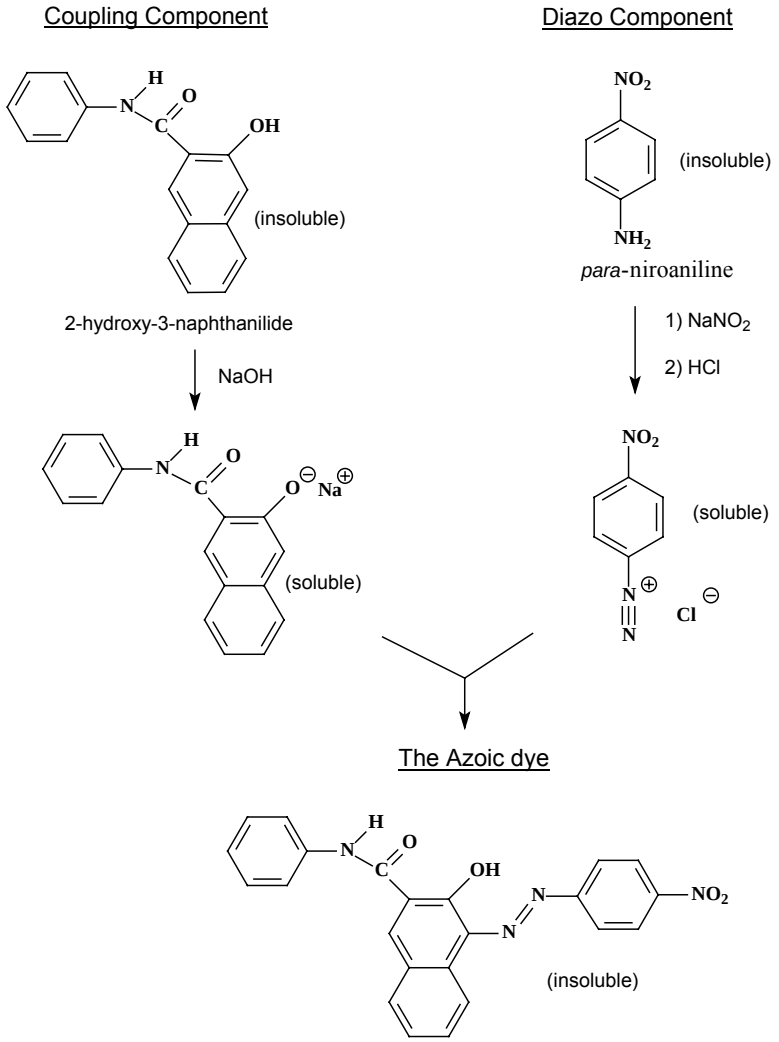
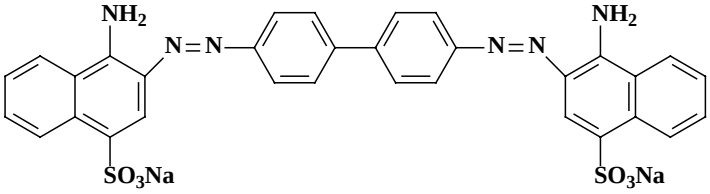


Figure 2. Steps involved in azoic dye formation.

Azoic dyes can be applied to cotton by batch and continuous methods. In batch dyeing, the naphtholate is applied at temperatures between 20 °C and 50 °C, for 30-40 min. In continuous dyeing, the padding bath is kept at temperatures as high as 80-90 °C. A hot dissolving method for naphthols is suitable for this application [15].

2.2 Direct Dyes

Direct dyes are soluble anionic dyes that consist of an aromatic structure containing a chromogen and solubilizing groups. Direct dyes are so called because they were the first dyes that had direct cotton affinity. They do not require pretreatment with a mordant to be used for cotton [15]. C.I. Direct Red 28 (3) was marketed in 1884 by AGFA as Congo Red and became the first member of this important class of dyes for cellulosic fibers [16,17].



(3)

2.2.1 General Properties of Direct Dyes

Direct dyes provide a simple and relatively inexpensive way of dyeing cellulosic fibers. The main disadvantage of direct dyes is their characteristic low washfastness. Since direct dyes are attached to cotton through weak bonds and are water soluble, they tend to come off during laundering. In order to improve their washfastness, different after-treatments have been developed.

Lightfastness of direct dyes varies from poor to good. Direct dyes that are metallized with copper gave good lightfastness [4,15].

Direct dyes are available in all shades, but there are few bright colors. The majority of the direct dyes are azo compounds with extend conjugation. These dyes often have broad absorptions in the visible region and possess relatively dull colors [15].

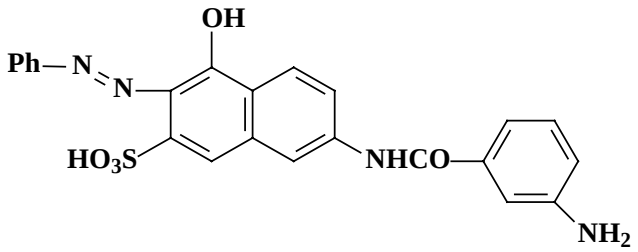
2.2.2 Classification of Direct Dyes

2.2.2.1 Azo Direct Dyes

This class of dyes is dominated by azo structures that usually containing more than one azo group and relatively few monoazo direct dyes are still in use. The majority of the direct dyes are disazo and trisazo structures [14].

Monoazo Direct Dyes

Most of the monoazo direct dyes are based on J-acid (6-amino-1-naphthol-3-sulfonic acid) as coupling component. An example is C.I. Direct Red 118 (4) [16].



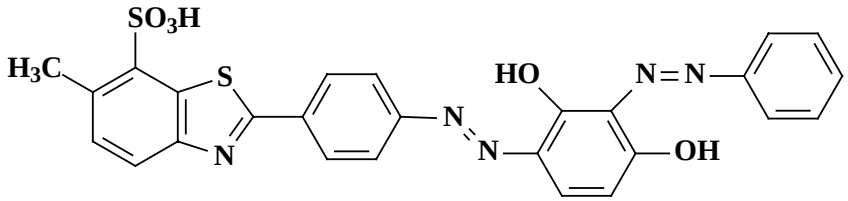
(4)

C.I. Direct Red 118 is made from a coupler prepared by condensation of J-acid with 3-nitrobenzoyl chloride followed by reduction of the nitro group. Coupling in alkaline solution with benzenediazonium chloride completes the synthesis [16].

Disazo Direct Dyes

Disazo direct dyes are usually classified according the nature of diazonium component and the coupling component used. A shorthand classification has evolved and is known as Winther symbols (**A,D,E,M** and **Z**), where **A** refers to a diazotizable amine; **D** refers to a tetrazotizable diamine; **E** refers to a coupler that couples once; **M** refers to a 1° amine that couples once and can be diazotized and coupled again; **Z** refers to a coupler that couples twice [16].

A→Z←A' molecules, known as primary disazo dyes, are formed by diazotization of compound **A** and coupling with **Z** and completed by diazotization of **A'** and coupling with **A→Z**. An example is C.I. Direct Orange 18 (5).

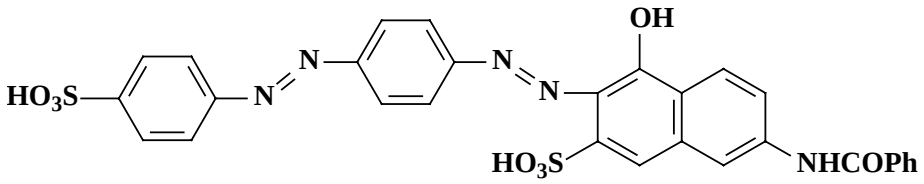


(5)

C.I. Direct Orange 18 is made from resorcinol coupled with diazotized dehydrothio-*para*-toluidinesulfonic acid and benzenediazonium chloride [14.16].

Secondary disazo direct dyes are classified as **A→M→E**. Type **A** components can be substituted aniline or α-naphthylamines, **M** components are

chosen from aniline or α-naphthylamines or aminonaphthols, and **E** components can be selected from J-acid, H-acid, Chicago acid, and γ-acid. The most useful direct dyes are those having J-acid (alone or N-substituted derivative) as the **E** component [16]. When **A** and **M** components are aniline derivatives the dyes are red, as in the case of C.I. Direct Red 81 (6) and C.I. Direct Red 110 (7). When J-acid use as middle component also gives red dyes, such as C.I Red 16 (8) [14,16].



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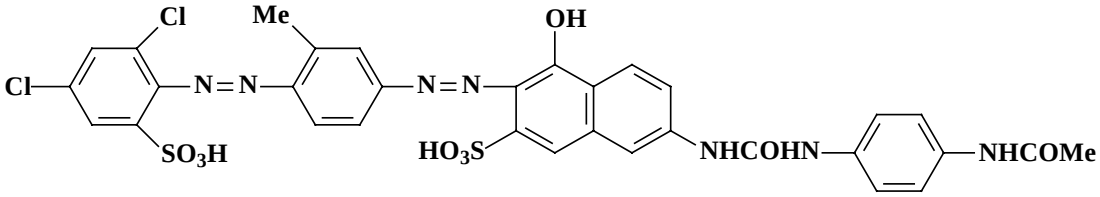

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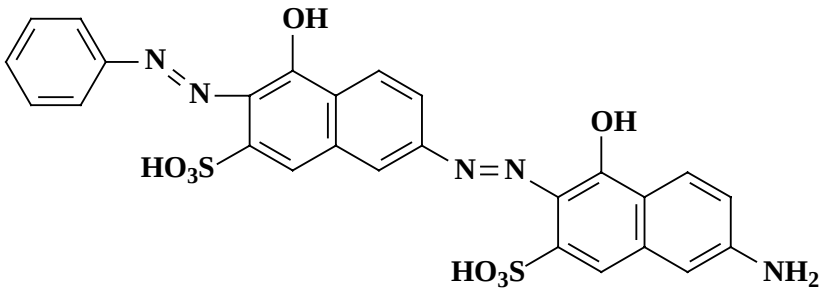
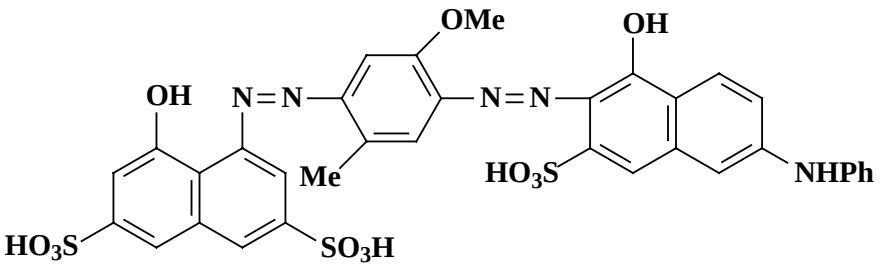


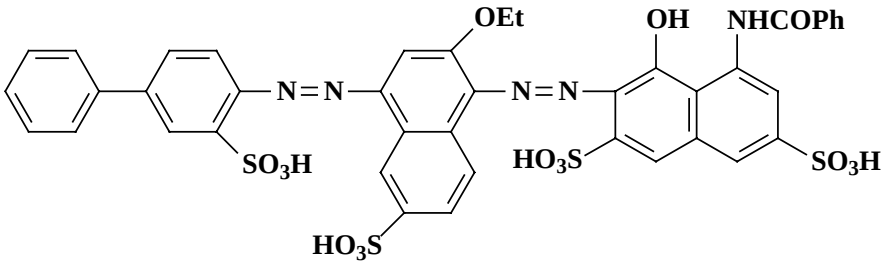
(8)

Replacing aniline derivatives with naphthylamines will give a bathochromic shift, such that violet and blue dyes are available. H-acid is used as **A** components in violet to blue dyes. An example is C.I. Direct Blue 67 (9) [16].



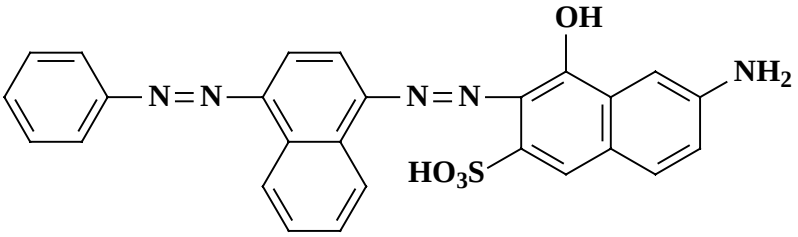
(9)

Green direct dyes can be produced by increasing the length of the conjugated chain in both **A** an **M** components. For example, using 4-aminobiphenyl-3-sulfonic acid as the **A** component, 2-ethoxy-1-naphthylamine-6-sulfonic acid as the **M** component, and N-substituted H-acid derivative as **E** component will provides C.I. Direct Green 13 (10) [16].



(10)

γ-acid is often used as an **E** component in black and gray dyes. An example is C.I Direct Black 3 (11), which is produced by coupling aniline to α-naphthylamine and the product is coupled to γ-acid in alkaline solution [16].



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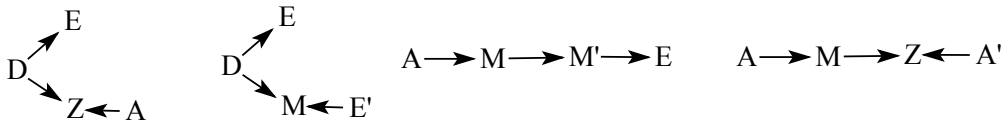
Trisazo Direct Dyes

The number of possibilities of disazo structures is very large and the choice is increased further in the trisazo and polyazo series. There are four possible structural combinations described by Winther symbols (see 12-15).

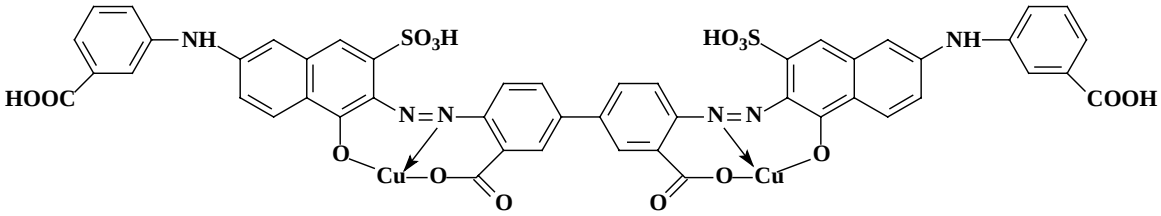


(12) (13) (14) (15)

The dyes produced with type (12) and (13) structures have dull colors such as olive green, navy blue, and black. Type (14) is the most useful, producing brighter hue and grays than other trisazo molecules, especially when J-acid or N-phenyl-J-acid is used as the **E** component [14,16].

Metal Complex Direct Dyes

In certain cases, the lightfastness of direct dyes can be improved after treatment with copper salts. An example of a copper complexed direct dye is C.I. Direct Blue 93 (16) [16].



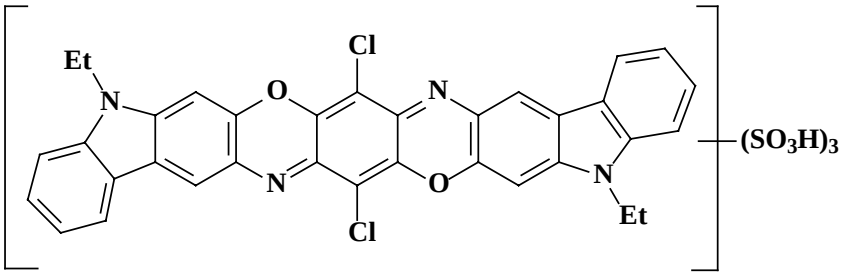
(16)

C.I. Direct Blue 93 is prepared via tetrazotization of 3,3'-benzidinedicarboxylic acid and coupling with N-[3'-carboxyphenyl]-J-acid followed by reaction with $CuSO_4$. Ammoniacal aminophenolic, 2-aminocarboxylic acid, or 2-aminoalkoxy

type and coupling components based on J-acid predominate in this direct dye family [16].

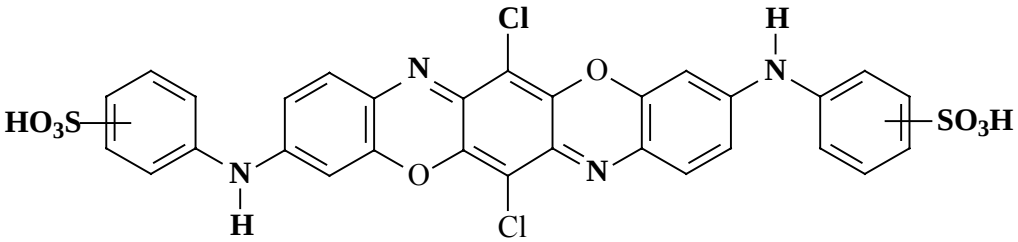
2.2.2.2 Triphenodioxazine Direct Dyes

The need for bright blue direct dyes is often satisfied by the use of triphenodioxazines. They are synthesized by condensation of two molecules of an aromatic amine with chloranil to produce a dianilide intermediate which is converted to triphenodioxazine direct dyes by oxidative cyclization in sulfuric acid to effect simultaneous sulfonation [16]. An example is C.I. Direct Blue 108 (17) [16].



(17)

C.I. Direct Blue 108 is prepared by condensation of two molecules of 3-amino-N-ethylcarbazole with one molecule of chloranil and cyclization using benzensulfonyl chloride, followed by sulfonation [16]. Another example is C.I. Direct Blue 106 (18), which is obtained from 4-aminodiphenylaminesulfonic acid.



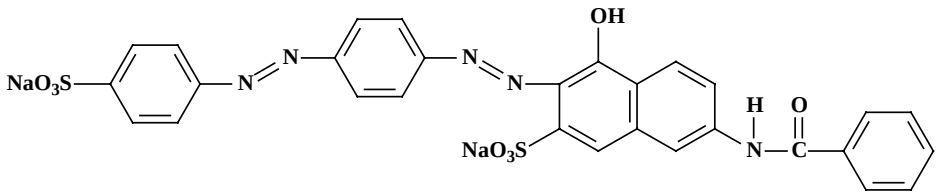
(18)

2.2.3. Application of Direct Dyes

Direct dyes can be applied to cotton by both batch and continuous methods. In batch dyeing the dyes are usually applied at temperatures near the boiling point. In continuous dyeing they are usually applied by the pad/steam method. In a typical batch dyeing process direct dyes are dissolved in the dyebath. The cellulosic substrate is placed in the dyebath at 49 °C [15,18]. The dyeing is continued at this temperature for 15-20 min. Then a total amount of 5-25% salt (NaCl) is added portion-wise, over a period of 45-60 min. In the meantime, the temperature is slowly raised to the dyeing temperature of dyeing [15]. When NaCl is added to the dye liquor, it dissociates completely into Na^+ and Cl^-. The cellulosic fiber, when immersed in water, has a negative surface charge attracting to the Na^+. This neutralizes the negative surface charge of the fiber enabling the dye anion to enter the fiber. After the dyeing period is finished, the dyed material is rinsed with cold water. An after-treatment may follow to improve the washfastness of the dyes [4,15].

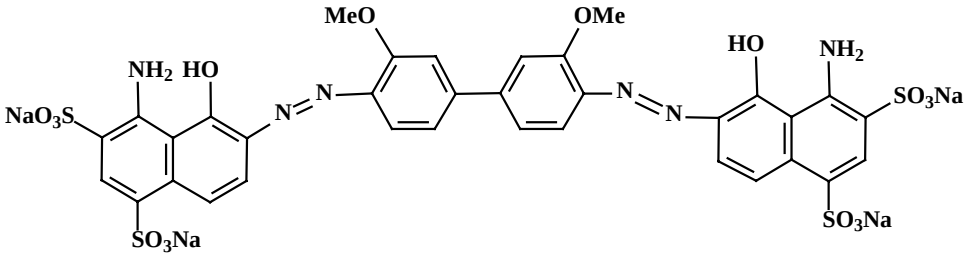
To aid the dyeing process, dyes that have similar dyeing characteristics are placed in the same group. There are three groups of direct dyes: A, B and C [18].

Class A: Self-Leveling Direct Dyes. Dyes in this group have very good leveling and migration properties. These dyes require relatively large amounts of salts for exhaustion. An example is C.I. Direct Red 81 (19) [15,18].



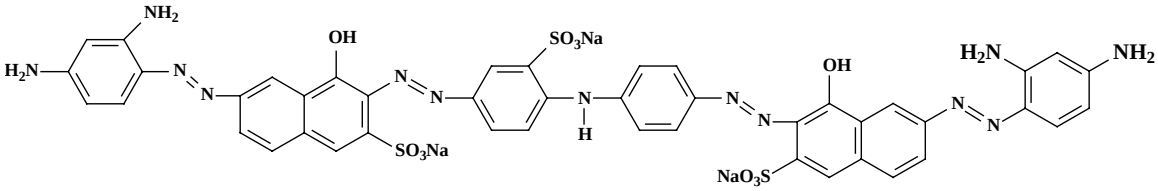
(19)

Class B: Salt-Controllable Dyes. These dyes have fair leveling or migration properties. They can be dyed uniformly by controlled addition of salt after the dyebath has reached the dyeing temperature. An example is C.I. Direct Blue 1 (20) [18].



(20)

Class C: Salt and Temperature Controllable Dyes. These dyes have poor leveling or migration properties and their substantivity increases very rapidly with increasing temperature. They have to be applied under carefully controlled condition, both the addition of salt and the raising of temperature. These dyes are applied with a minimum amount of salt or no salt at all. An example is C.I. Direct Black 22 (21) [15,18].



(21)

2.3 Vat dyes

Vat dyes are insoluble aromatic compounds containing two or more carbonyl groups connected through conjugated double bands. They can be applied to cellulosic fibers after converting them to their soluble form [15]. As shown in Figure 3, in the reduction stage carbonyl groups are reduced to phenolic type groups. In presence of a strong base, such as sodium hydroxide, the sodium salt of the reduced vat dye is formed. After the dyeing step the dye is oxidized and remains inside the fibers in its original insoluble form. Oxidation can take place by exposing the dyed fibers to air or oxidizing agents [15].

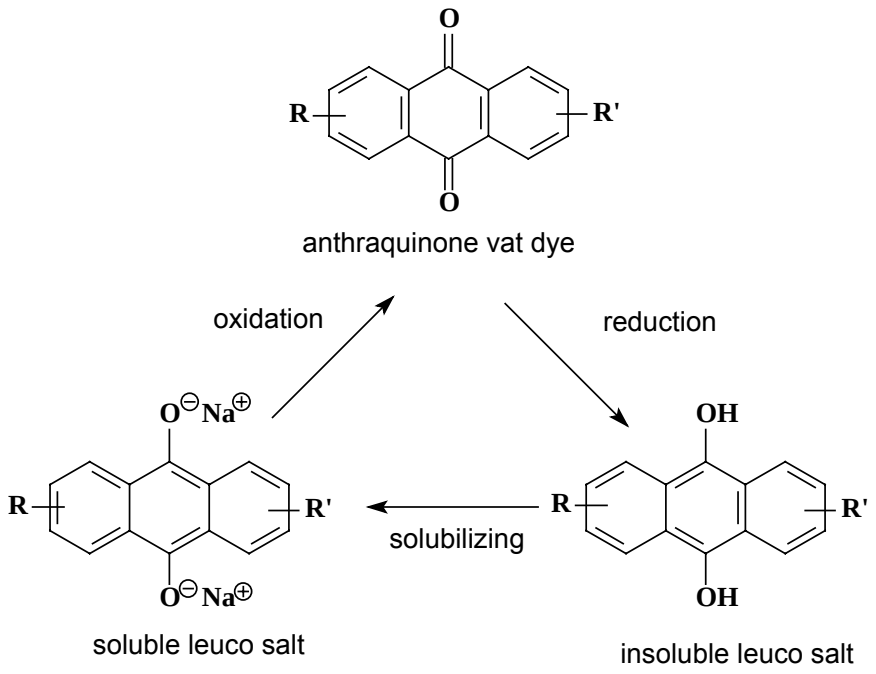
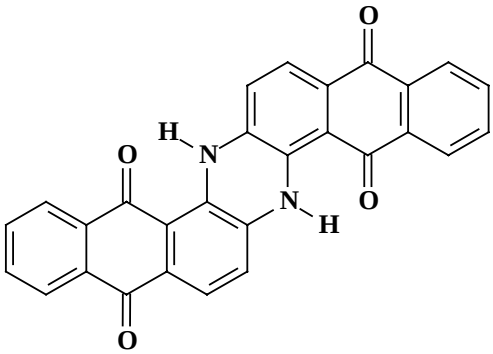


Figure 3. The changes that a vat dye undergoes during application.

2.3.1 General Properties of Vat Dyes

There are two main types of vat dyes - anthraquinone and indigoid derivatives. The majority of the vat dyes are anthraquinone derivatives. C.I. Vat

Blue 4 (22) is an example of an anthraquinone vat dye. It was the first anthraquinone vat dye of commercial value. C.I. Vat Blue 1 (23) is an example of indigoid vat dyes. This is by far the most important indigoid dye.



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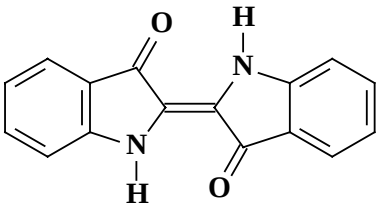


(23)

Vat dyes are always used on cellulosic materials. The indigoids have brilliant colors with high intensities. However, the fastness properties of indigoid vat dyes are not satisfactory. Anthraquinone vat dyes have much better fastness properties and many are outstanding. Most of the anthraquinone dyes have washfastness ratings of 4-5 and show very good fastness to light, bleaching, and crocking. However, their colors are of lower intensity and brightness [4,15].

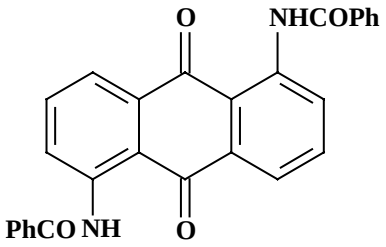
2.3.2 Classification of Vat Dyes

2.3.2.1 Anthraquinone Vat Dyes

The most important vat dyes belong to the smaller class of substituted anthraquinones or the large class of higher-anelated anthraquinones and analogous compounds [14]. The structurally simple anthraquinone vat dyes are the acylaminoanthraquinones, which are mainly used for yellow shades, although orange, red and violet dyes are available. An example is C.I. Vat Yellow 3 (24), which is produced by the benzoylation of 1,5-diaminoanthraquinone. Introducing

electron-donation groups (e.g. NH_2) in the 4,8 positions of (24) will produce bathochromic shift and give a violet color [16].

The “anthrimides” are anthraquinone structures in which two anthraquinone molecules are linked via a secondary amino group. They are used as intermediate in the synthesis of anthraquinonecarbazoles, which are dyes of outstanding fastness to wet treatment [16]. For example, C.I. Vat Black 27 (25) is prepared by condensation of 1-aminoanthraquinone with 1-chloroanthraquinone to form 1,1’-dianthrimide, followed by dinitration, reduction, benzoylation, and cyclization in sulfuric acid [14,16].



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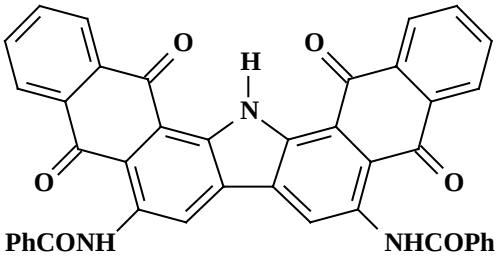
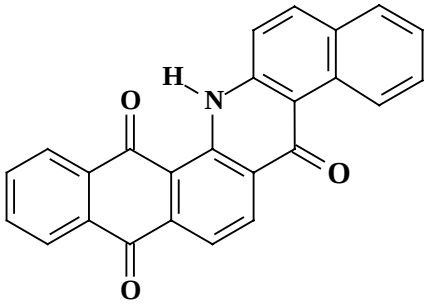


(25)

The anthraquinoneacidones can be used for producing hues from orange to blue. C.I. Vat Red 35 (26) is prepared by reaction of 2-aminonaphthalene-1-sulfonic acid with 1-chloroanthraquinone-2-carboxylic acid [16].

The best known of the anthraquinone vat dyes is indanthrone (C.I. Vat Blue 4). Indanthrone (27) is a beautiful blue anthraquinoneazine prepared by the alkali fusion of 2-aminoanthraquinone at 220 °C.



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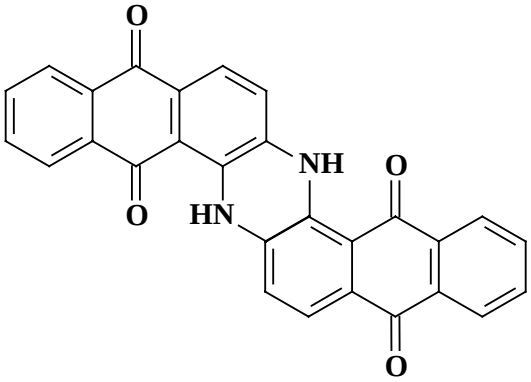
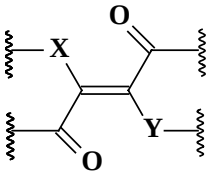


(27)

2.3.2.2 Indigoid Vat Dyes

Indigo is an important dyestuff with a distinctive blue color. Originally, indigoid came from several species of plants, but nearly all indigoid produced today are synthetic. It is used primarily for dyeing cotton warp yarns for blue denim fabric [20].

All indigoid dyes contain the structural unit (28). The majority of the indigoids have X/Y and the carbonyl groups in a ring system because the ease of synthesis and the stability. By far the most important indigoids are the indigos (29) and thioindigos (30) [21].



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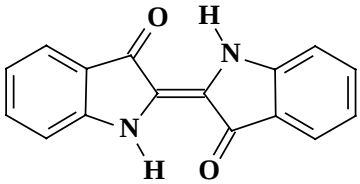
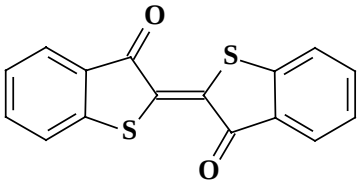


(29)



(30)

The synthesis indigo starts from aniline. First, aniline is condensed with formaldehyde-sodium bisulfate and sodium cyanide to give N-cyanomethyl-aniline. This intermediate is hydrolyzed to sodium phenylglycinate to give indoxyl. The latter is then oxidized in air to give indigo (Figure 4) [21].

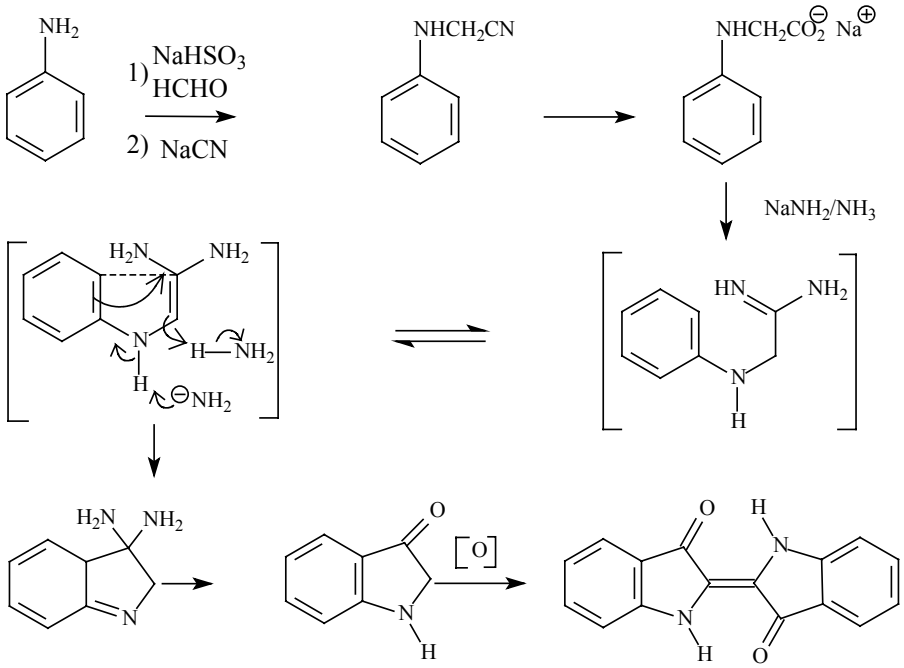


Figure 4. Synthesis of indigo from aniline.

Thioindigo dyes are produced by the condensation of a substituted benzenethiol (31), which is prepared from aniline as shown in Figure 5, with chloroacetic acid to give the corresponding thioglycollic acid (32). The final step is an oxidation using oxidizing agent [21].

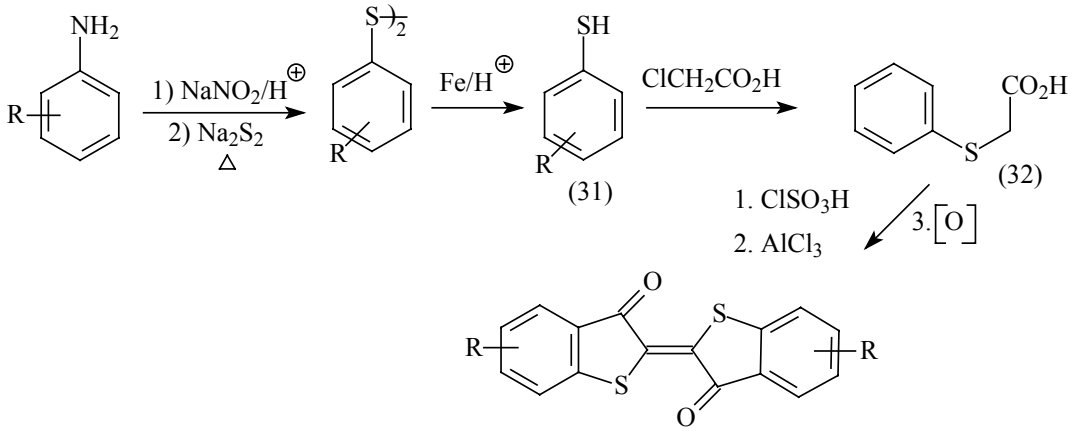


Figure 5. Synthesis of substituted thioindigoid dyes.

2.3.3 Application of Vat Dyes

The conventional exhaust method for vat dyes consist four major stages: reduction (vatting), dyeing, oxidation, and soaping [15].

At the reduction (vatting) stage vat dyes is converted into its soluble form. The dyes is first mixed with NaOH and after adding the reducing agent, the temperature is raised to speed up the reduction process [15]. At the dyeing stage, scoured fabric/yarn is added to the dyebath and the temperature is gradually raised to the dyeing temperature. Salt and additional amounts of the reducing agent may be added to assist in exhaustion [15]. Before the oxidation step, the goods are rinsed to remove residual of salt and reducing agent. Hydrogen peroxide and sodium perborate are commonly used oxidizing agents. When using hydrogen peroxide, high concentrations of alkali must be avoided in order to prevent fiber damage [15]. The last stage, the dyed goods are treated with soap or surfactant solution at the boil. Soaping at the boil increases the washfastness and crockfastness of the dyes.

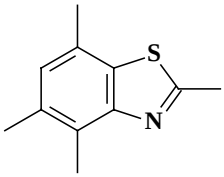
2.4 Sulfur Dyes

Sulfur dyes are the highest volume dyes manufactured for cotton because they are economical and afford high washfastness [22]. These dyes are called sulfur dyes because sulfur is used in their synthesis and they contain lots of sulfur. They are produced by reacting aromatic amines, phenols, or nitro-benzene derivatives with sulfur or sodium sulfide at high temperatures in sealed containers [14.15]. Like vat dyes, sulfur dyes are water-insoluble compounds

that must be reduced to a water-soluble form in order to have affinity for the fiber. Like direct dyes the reduced form of sulfur dyes can be exhausted onto the fabric. Therefore, they can be applied by padding in their reduced form and then fixing [4,14].

2.4.1 General Properties of Sulfur Dyes

In general sulfur dyes have a high molecular weight and a complex structure. Structures (32) and (33) are typical parts of chromogens in sulfur dyes [15].



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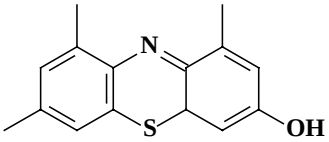
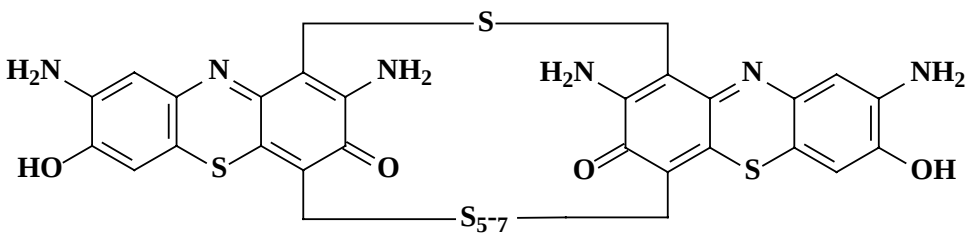


(33)

Sulfur dyes are widely used since they provide a relatively easy way to dye cellulosics at a low cost with good to excellent washfastness. The main disadvantage of sulfur dyes is their dull and limited colors and the poor lightfastness in pastel shades. Useful red and violet colors are unavailable among sulfur dyes. They are mainly used to apply wetfast black, brown, navy blue shades on cotton in medium to dark depths [15]. C.I. Sulfur Black 1 is the most widely used dye in the world, a no black for cellulose can compare with its economy. C.I. Sulfur Black 1 is prepared by heating 2,4-dinitrophenol with sodium polysulfide and the structure (34) has been assigned to the dye by Hiyama [21].



(34)

2.4.2 Classification of Sulfur Dyes

Sulfur dyes are polymeric, and can be divided into three categories. Those in the first category are polymeric and water-insoluble. To be applied, their sulfide (S-S) bonds must be broken by employing sodium sulfide in an alkaline medium (pH > 10), before they become water-soluble [14,15]. The second category consists pre-reduced leuco sulfur dyes. They are sold in their leuco form and are ready to be used. For commercial dyes, the process involves putting dye into the bath, adjusting the pH, exhausting the dye and then reoxidizing the dye inside the fiber [15]. Those in the third category contain thiosulfate groups ($R\text{-}S\text{-}SO_3^-Na^+$) and are known as Bunte salts. They are also applied in the presence of sodium sulfide in order to cleave the sulfur sulfur bond. In the final step, sulfide linkages are produced by oxidation [14,15].

2.4.3 Application of Sulfur Dyes

Sulfur dyes are applied by exhaust or continuous methods. In exhaust dyeing, the soluble sulfur dye is applied in a manner similar to that of the direct dye application [18]. Sulfur dyes tend to exhaust at lower temperatures with a higher rate. The dyebath is prepared by diluting the soluble sulfur dye with water. Small amounts of sodium polysulfide and sequestering agent are added,

and then the goods are put into the dyebath at 50 °C. Salt is added portion-wise, while the temperature is gradually raised to the dyeing temperature. After the dyeing period is finished, the goods are rinsed with mild alkali, and dried [15]. Continuous dyeing usually consists of five steps: pad, steam, rinse, oxidize, and rinse.

2.5 Fiber Reactive dyes

Fiber reactive dyes are arguably the best dyes, by far, for cotton. They are brighter, long lasting and easier to use than other dyes [23]. Unlike other dyes, fiber reactive dyes are the only class of dyes that form a covalent bond to cellulosic fibers. Once the bond is formed, the dye molecule has become an actual part of the cellulose molecule. Therefore, fiber reactive dye is the most permanent type of all dyes [16,23].

2.5.1 General Properties of Fiber Reactive dyes

Since the discovery of reactive dyes in 1956, the AATCC Buyers Guide list almost 200 different reactive dyes by Color Index name, representing more than 400 different commercial products [18]. Fiber reactive dyes are available in a complete range of colors and especially bright shades on cotton. They have very good washfastness and fair to good lightfastness. They provide high flexibility in the choice of method of application. They are readily soluble in water and it is easy to obtain level dyeings [15]. However, the cost of using reactive

dyes is high. Another disadvantage of reactive dyes is that many are sensitive to oxidation, in particular to the effects of chlorine bleach [18].

2.5.1 Chemical Nature of Fiber Reactive dyes

2.5.1.1 Procion Reactive Dyes

Procion dyes are synthesized from cyanuric chloride (trichloro-1,3,5 triazine). The chlorines in this molecule react readily with hydroxyl groups, amino groups, and water through nucleophilic substitution reaction [15]. When decreasing the number of chlorine atoms on the ring, the reactivity of the chlorines decreases. Therefore the first chlorine will react by just mixing the compounds at room temperature. For the second chlorine, the presence of a weak base, such as $NaHCO_3$ is required. When only one chlorine is left on the triazine ring, the reaction will take place at elevated temperature and in the presence of stronger base (e.g. Na_2CO_3) [15,18]. To make a Procion dye, chlorine is used as the leaving group to bond a chromogen to the reactive group, as shown in Figure 6. The reactive dye obtained contains two reactive chlorines and will react with cellulose in the presence of Na_2CO_3 at room temperature [15].

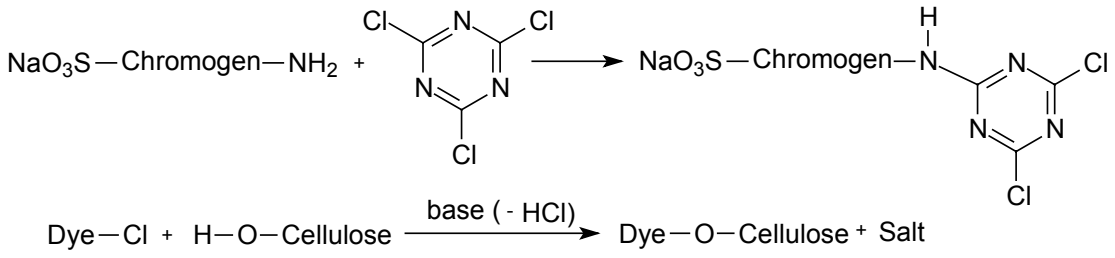


Figure 6. Formation of a Procion reactive dye and its reaction with cellulose.

2.5.1.2 Vinylsulfone Reactive Dyes

This group of reactive dyes contains the sulfatoethylsulfone group ($-SO_2-CH_2-CH_2-OSO_3H$) as their reactive group. In the presence of a base this group undergoes an elimination reaction to form a vinylsulfone group ($-SO_2-CH=CH_2$) which then combines with cellulose through an addition reaction, as show in Figure 7 [15].

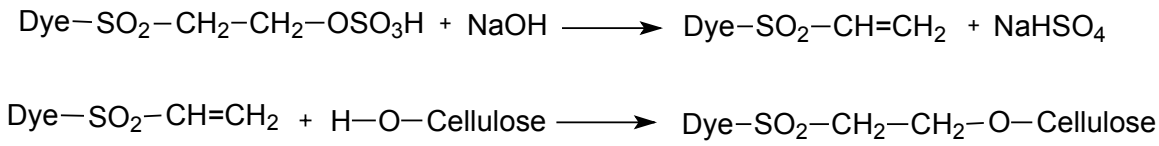


Figure 7. Reaction of a vinylsulfone reactive dye with cellulose.

2.5.2 Characteristic Structural Features of Reactive Dyes

In general, fiber reactive dyes consist of an electrophilic reactive group (RG), the chromogen (D), and one or more water- solubilizing groups (W). The reactive group is the functional group that contains a nucleofugic leaving group (X), a bridging linker (Q). It can react with nucleophilic groups, such as NH_2, -SH, and –OH, by addition or substitution reactions [14,31]. The chromogen is a conjugated double bond system, which provides the color. The bridging linker connects the reactive group to the chromogen. The bridging linker preserves the original dye color by preventing resonance interactions between the chromophore and reactive groups [14]. They also have a significant influence on reactivity, degree of fixation, stability and dyeing characteristics such as

substantivity and migration [16]. The imino (-NH-) group is a typical bridging group especially for N-heterocyclic reactive dyes. Carboxamide and sulphonamide groups can be used as bridging groups to a limited extent [14]. Water-solubilizing groups provide water solubility, substantivity, migration and wash off. For reactive dyes, the dominant solubilizing group is the sulphonic substituent. Figure 8 illustrates the components of a reactive dye using C.I. Reactive Red 1 as an example [14,28].

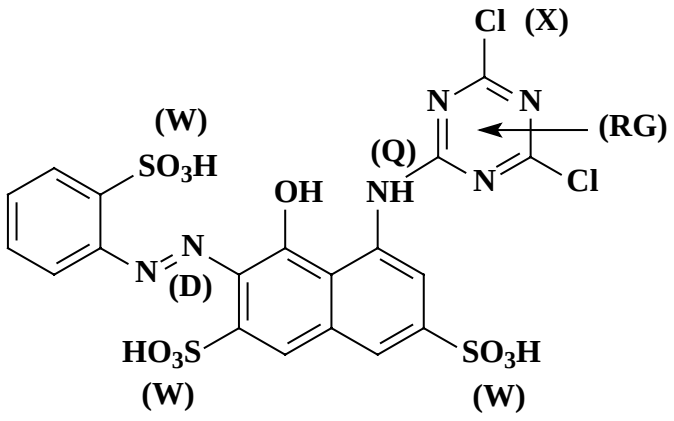


Figure 8. Components of reactive dyes.

2.5.2.1 Reactive Groups

Reactive groups provide the capability of forming a covalent bond with the fiber. A large number of functional reactive groups have been developed and commercialized. Some important monofunctional and bifunctional reactive systems are, monochlorotriazine (MCT), monofluorotriazine (MFT), dichlorotriazine (DCT), nicotinoyltriazine (NT), dichloroquinoxaline (DCQ), difluorochloropyrimidine (DFCP), trichloropyrimidine (TCP), and vinylsulfone (VS). Their structures are illustrated in Figure 9 [18,29].

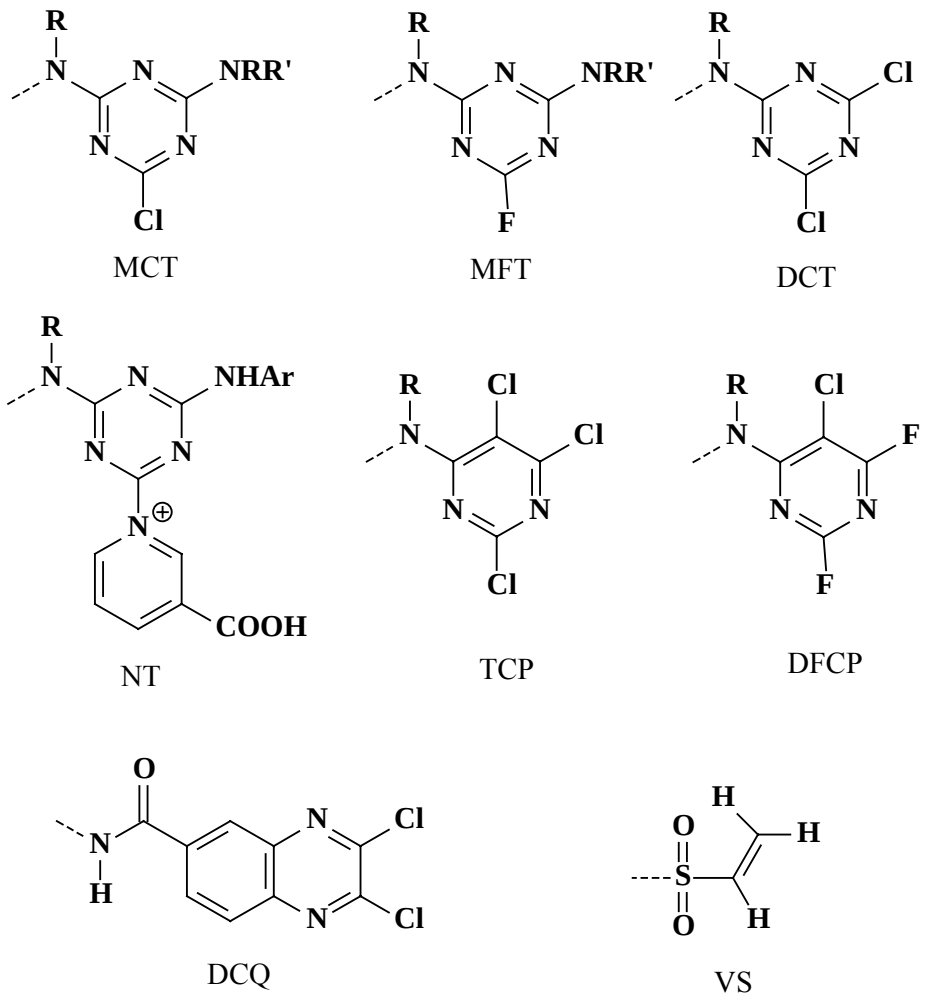
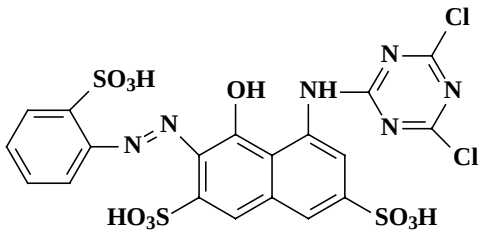


Figure 9. Structure of reactive groups used in commercial reactive dye.

Monofunctional Reactive Systems

Monofunctional reactive systems can react only once with the nucleophilic group in the fiber by nucleophilic addition or substitution reactions. Reactive Red 1 (35) and Reactive Blue 19 (36) are examples of reactive dyes that contain a monofunctional reactive system [29,31].



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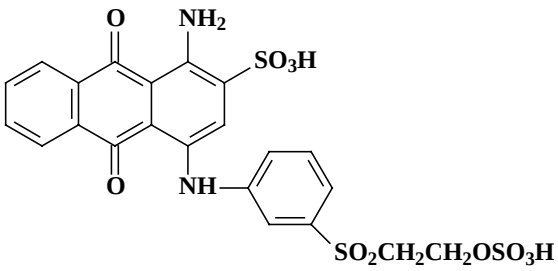
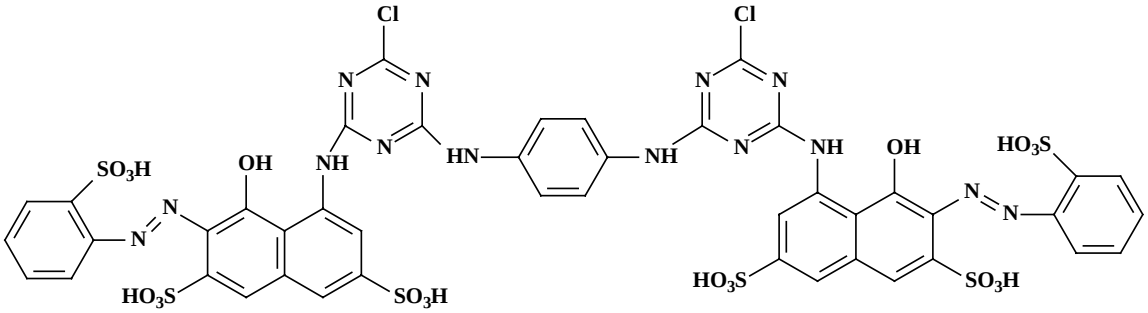


(36)

Bifunctional Reactive Systems

These systems contain two separate reactive groups. Since both of them can react with suitable groups in the fiber, covalent bond formation may occur either within the same polymer chain or between two adjacent chains (33). Reactive dyes that consist of two similar reactive groups are homobifunctional reactive dyes. Those that consist of two different types of reactive groups are heterobifunctional reactive dyes [12]. Reactive Red 120 (37), which containing a Bis-monochlorotriazine system, and Reactive Red 221 (38), containing a bis-mononicotinotriazine system, are examples of homobifunctional reactive dyes [29].



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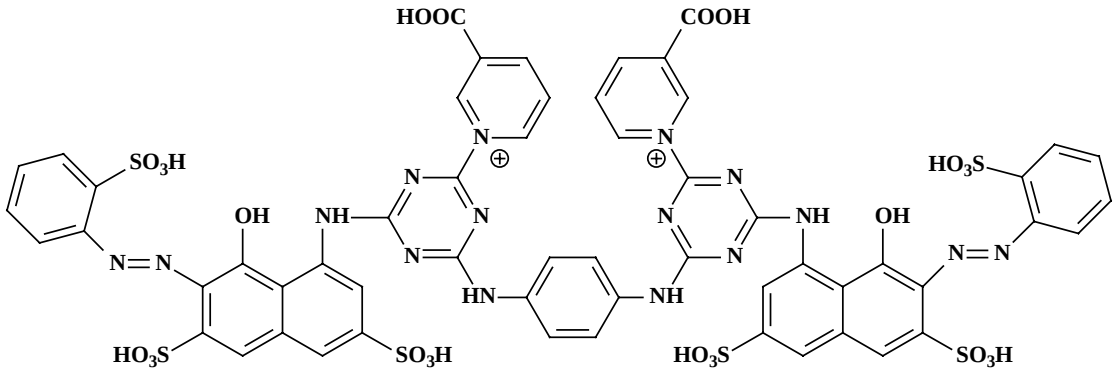
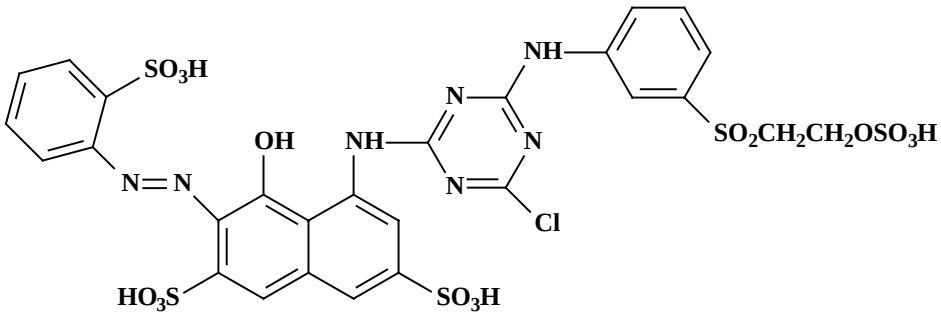


(38)

Dyes that contain a monochlorotriazine / sulphatoethylsulfone system or a monofluorotriazine / sulphatoethylsulfone system are heterobifunctional reactive dyes. Having monohalotriazine and sulphatoethylsulfone groups within the same dye molecule leads to a higher fixation value [34,35]. Reactive Red 194 (39) is an example of the heterobifunctional reactive dyes [29,33].

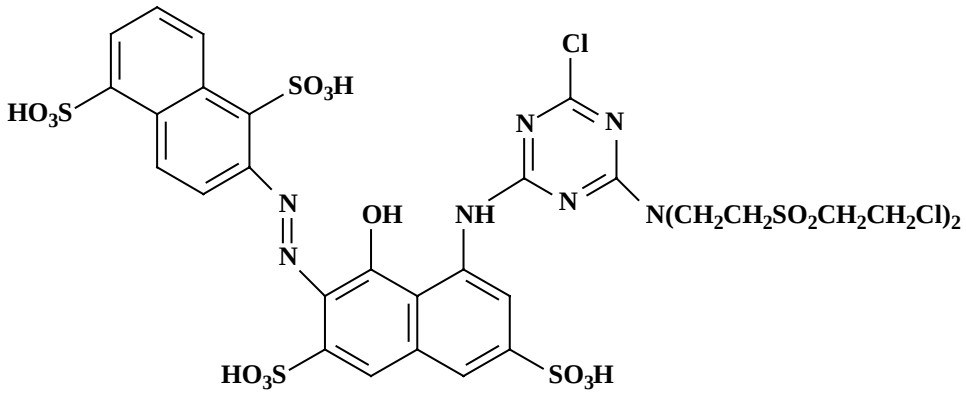


(39)

Polyfunctional Reactive Systems

Several polyfunctional reactive dyes have been patented. Trifunctional reactive systems have three halotriazine (monochlorotriazine / monofluoro-triazine), vinylsulfone, bis-vinylsulfone / difluorochloropyrimidine, or bis-monofluorotriazine / vinylsulfone groups [29]. Theoretically, incorporating

additional reactive groups into the dye molecule would lead to a higher fixation level, but this is not always true. The fixation level depends on the physical properties of the reactive groups, such as solubility, aggregation, substantivity, and migration [36]. Additional reactive groups increase molecular weight and sometimes may lead to a lower fixation. For this reason, relatively few polyfunctional reactive dyes have been marketed. Reactive Red 181 (40) is an example of a polyfunctional reactive dye [29,30,36].



(40)

2.5.2.2 Chromophoric Groups

The color of organic dyes is attributed to chromophoric groups. In order to give color, they must be part of the conjugated system [15]. Azo, formazan, anthraquinone, triphenodioxazine, and phthalocyanine chromophores have been used most often for the preparation of reactive dyes [15,37]. The chromophores used in the synthesis of reactive dyes influence fiber affinity or substantivity, and the diffusion coefficient. Figure 10 shows common chromophores used for reactive dyes [38].

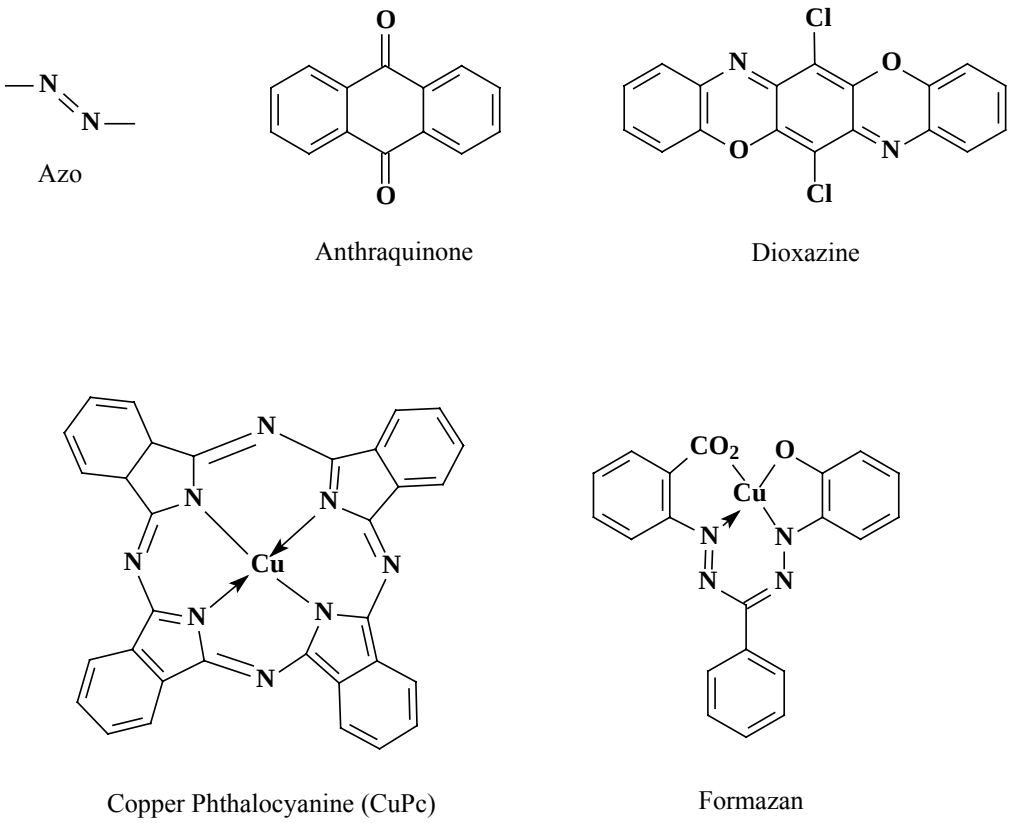
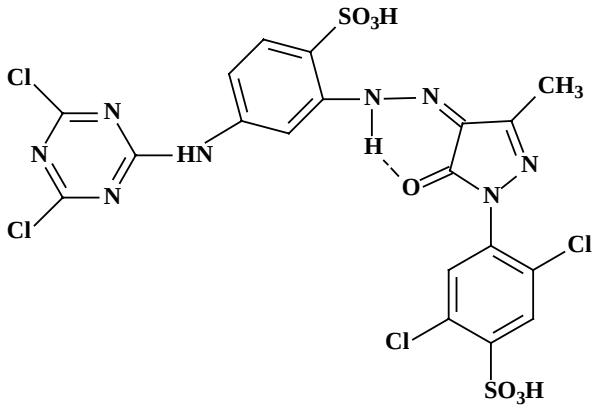


Figure 10. Chromophores used for reactive dyes.

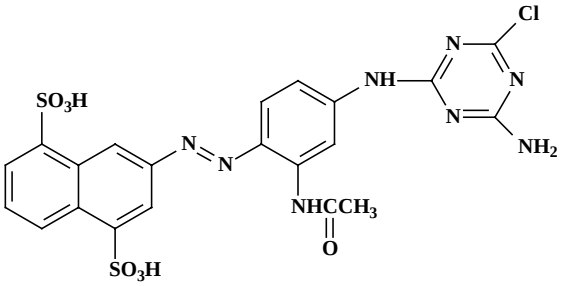
Azo Reactive Dyes

About 80% of all reactive dyes are azo compounds. Almost all hues in the color spectrum can be generated with either monoazo or disazo groups and various combinations of aromatic rings. Simple metal-free monoazo dyes based on pyrazolone couplers give a greenish yellow color, an example of which is Reactive Yellow 1 (41) [15,25].

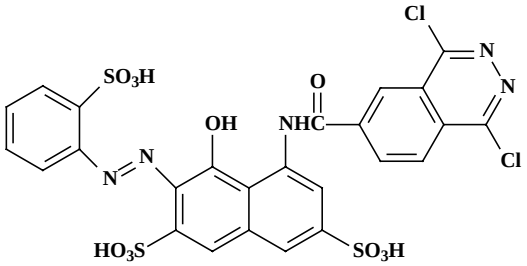


(41)

Monoazo dyes produced from aniline or naphthylamine couplers give a reddish yellow color, an example of which is Reactive Yellow 3 (42) [19]. When H-acid is used as the coupler, the dye will have a bright bluish-red color. See for example Reactive Red 96 (43) [29].

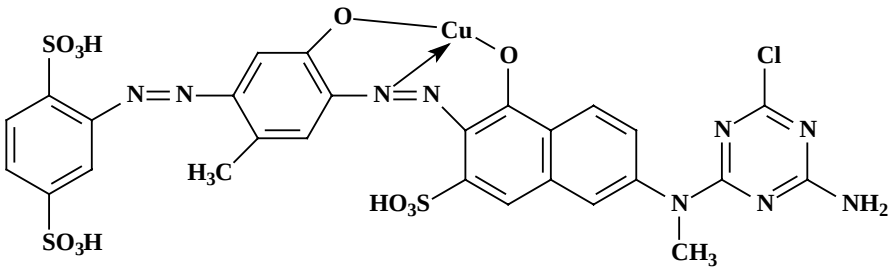


(42)

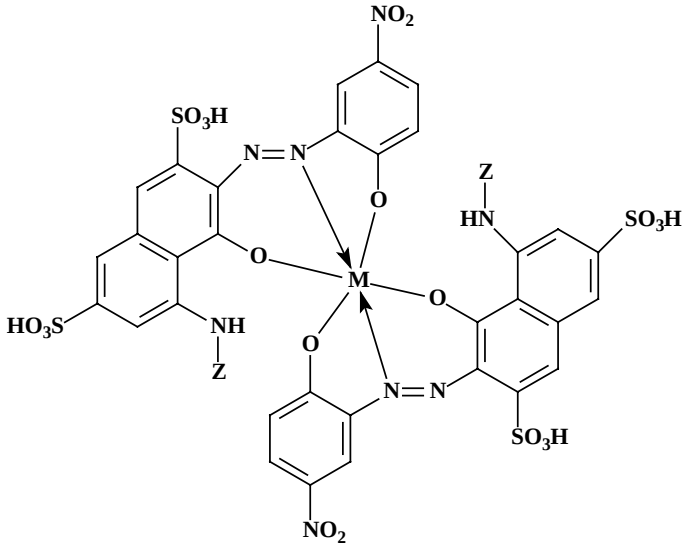


(43)

Metal-complexed mono and disazo dyes give violet, ruby, navy-blue colors. Reactive Blue 40 (44) is an example of a disazo reactive dye that gives navy-blue color [39]. Cobalt and chromium complexes are used to produce gray and black dyes of type (45) [29].



(44)



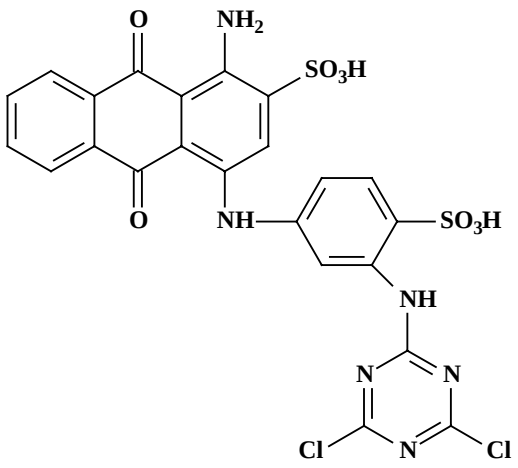
M = Cr or Co

Z = a halogeno heterocyclic reactive group

(45)

Anthraquinone Reactive Dyes

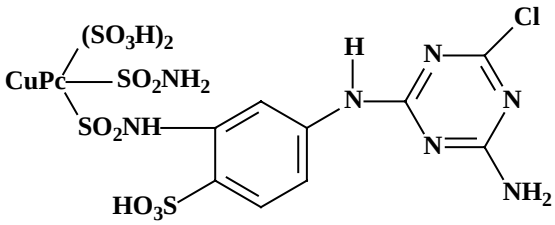
Anthraquinone reactive dyes are often derived from bromamine acid. By the variation of ring substituents, anthraquinone reactive dyes provide bluish-violet to bluish-green hues [15]. They have good light fastness and stability over a wide pH range, but have low color strength and high cost. An example is Reactive Blue 5 (46) [29].

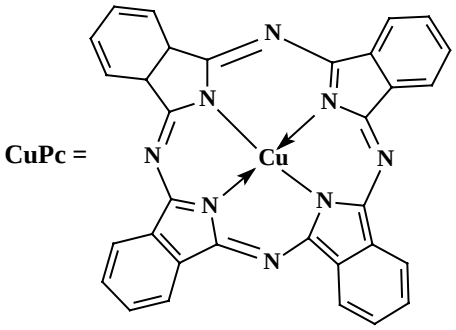


(46)

Phthalocyanine Reactive Dyes

The only practical way to get turquoise shade is through the phthalocyanine system. Copper and nickel phthalocyanine derivatives dominate the turquoise blue dyes. An example is Reactive Blue 7(47) [39].



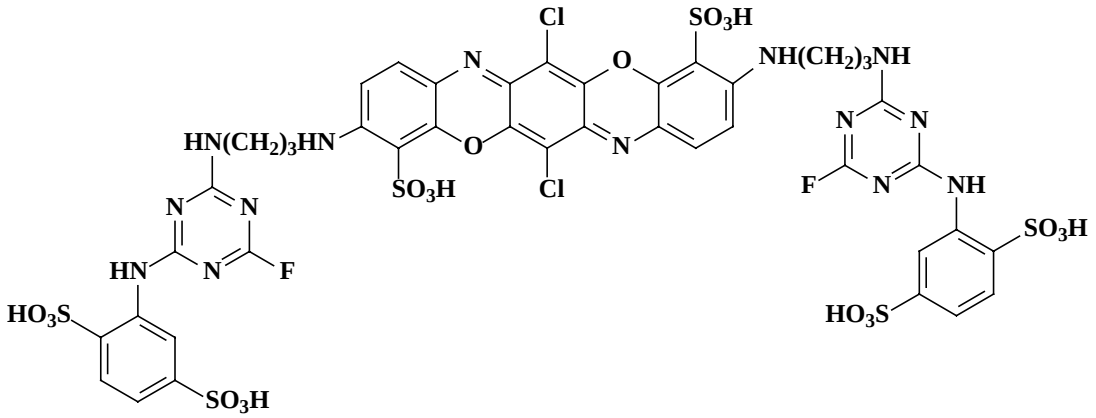


(47)

Triphenodioxazine Reactive Dyes

Dyes derived from the triphenodioxazine ring system give a bright blue shade on cotton. Due to its high color strength and low cost, the triphenodioxazine chromophore is gradually replacing the anthraquinone

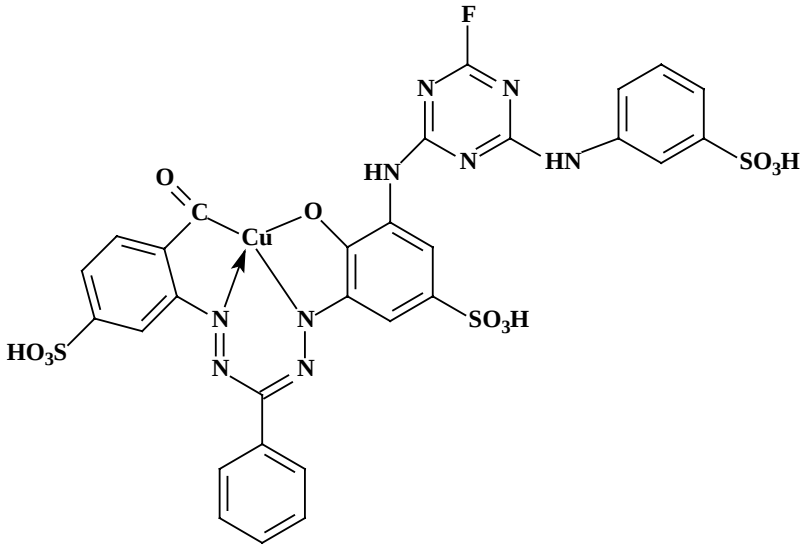
chromophore [29,40]. Reactive Blue 204 (48) is an example of the triphenodioxazine reactive dyes.



(48)

Formazan Reactive Dyes

Reactive dyes containing the formazan system are capable of producing red to greenish blue shade. These dyes also provide an alternative to the anthraquinone structure due to their higher color strength, solubility and reactivity. Structure (49) an example of a formazan reactive dye [29,40].



(49)

2.5.3 Application of Reactive dyes

Batch and continuous dyeing are the main methods used for applying reactive dyes to cellulose fibers [18].

2.5.3.1 Batch dyeing

The batch dyeing process can vary with in dye selection, dyeing equipment and controls, and sometimes the preference of the dyer [18]. The basic principle in the batch dyeing process is to exhaust as much of the dye as possible onto fiber at neutral or weakly acidic conditions. After a dye dissolved in water, a solubilizing agent such as urea, and an electrolyte such as common salt are added to the dye bath in order to facilitate good leveling on the fiber [18,29]. The dye-fiber fixation takes place once the pH of dye bath is increased by the addition of alkali. The unfixed dye, alkali and electrolyte will be removed at the wash off stage. Batch dyeing procedures are often divided into the four categories described below [18,42].

Traditional or conventional

For this method, the temperature is raised to the fixation temperature and dye is exhausted with salt prior to the addition of alkali. During this process, the rate of salt addition and temperature rise need to be controlled carefully, otherwise unlevelness may occur. Therefore, this method is viable if the dyeing equipment has efficient heating control and rapid exhaustion is not expected [18,29].

One Step or All-In

This is the simplest and quickest method available, because all bath components which include dye, salt and alkali, are circulated with the fabric before the heating of the bath to the dyeing temperature, and there are no adds during the process. Since alkali is used at the beginning, the starting temperature must be low enough to minimize hydrolysis. During this process exhaustion and irreversible fixation are occurring simultaneously from the beginning and this may cause a lower color yield. Therefore, this method is less suitable for goods that are difficult to penetrate and level [18,29].

Constant Temperature

In this method, dyeing is carried out at the fixation temperature and remains constant throughout the process. This eliminates problems due to improper control over the rate of heating. Salt can be added all in once at the start, or in portions. Alkali is added after a suitable time interval. This method is widely used because it is easy to control [18,29].

High Temperature

In this method, dyeing starts at a temperature that is higher than the fixation temperature. After adding salt, the temperature is lowered to the fixation temperature prior to the addition of alkali. This method is useful for fabrics from high twist yarns, woven goods, or viscose rayon [18,29,42].

2.5.3.2 Continuous Dyeing

In the continuous dyeing process, the fabric is passed through a dye bath of sufficient length. The dye is fixed to the fabric using chemicals or steam, and then washed to remove any excess dyes and chemicals [46]. Continuous dyeing processes offer economic advantages when long runs are required, especially in a limited range of colors, by saving in handling and labor costs. There are four application methods for continuous dyeing process: pad-steam, wet-on-wet (pad-pad-steam), pad-dry-steam and pad-dry-cure. Each has its unique aspects, and the conventional method for dyeing 100% cotton is the pad-dry-steam process [18].

Pad Batch Dyeing

Pad-batch dyeing is an important process that offers simplicity, versatility and flexibility without major capital investment in equipment. It can increase production and improve dyeing quality and reproducibility, while reducing processing costs [18]. Pad batch dyeing is an exhaust method conducted at low liquor ratios and ambient temperature. The only requirement for the process is to pad on dye and alkali and to batch the goods as uniformly as possible. During the process, the goods are wrapped with plastic in order to prevent evaporation and the reaction of alkali with the carbon dioxide in the air [18,43]. Very high reproducibility may be achieved if the goods are stored in a temperature-controlled area. Goods containing cellulosic fiber either knitted or woven can take advantage of this process [18,45].

2.5.4 Recent Developments In Reactive Dyes

New reactive dyes have been developed with the desire to give better technical properties, environmental performance and economy [29]. Teegafix dye technology is among the newest developments in this field. Teegafix dyes are alternatives to traditional dichlorotriazine dyes and were patented by Proctor and Gamble in 2002 [47]. Preliminary investigations have shown that these dyes provide higher levels of exhaustion and fixation than the corresponding commercial fiber reactive dyes [48].

A variety of haloheterocycles can be modified to give Teegafix dyes suitable for application on cotton [48]. A previous study at North Carolina State University involved four types of homobifunctional reactive Teegafix dyes. The generic formulas for these dyes are given in Figure 11, which shows them to be bis-DCT and bis-MCT systems [49].

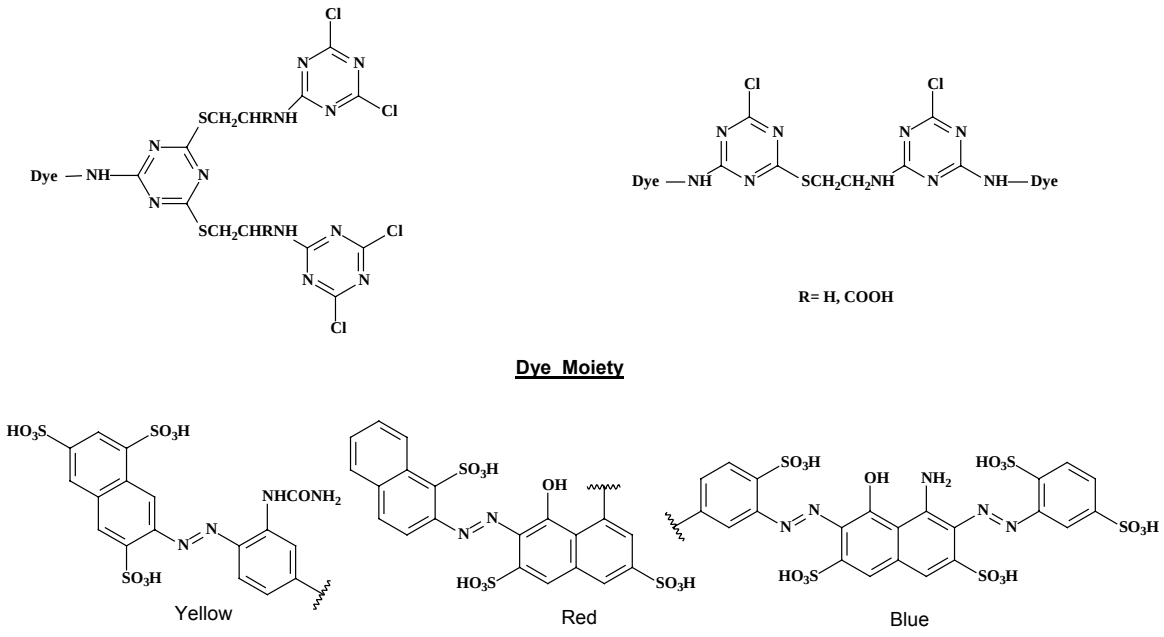


Figure 11. Examples of homobifunctional reactive Teegafix dyes.

The homobifunctional reactive Teegafix dyes are produced in two steps from dichlorotriazine (DCT) reactive dyes. Step one involves a reaction with cysteamine or cysteine. In the next step, the intermediate reacts with either cyanuric chloride or a second molecule of the starting dye. The synthesis is illustrated in Figure 12 for the yellow dyes [28].

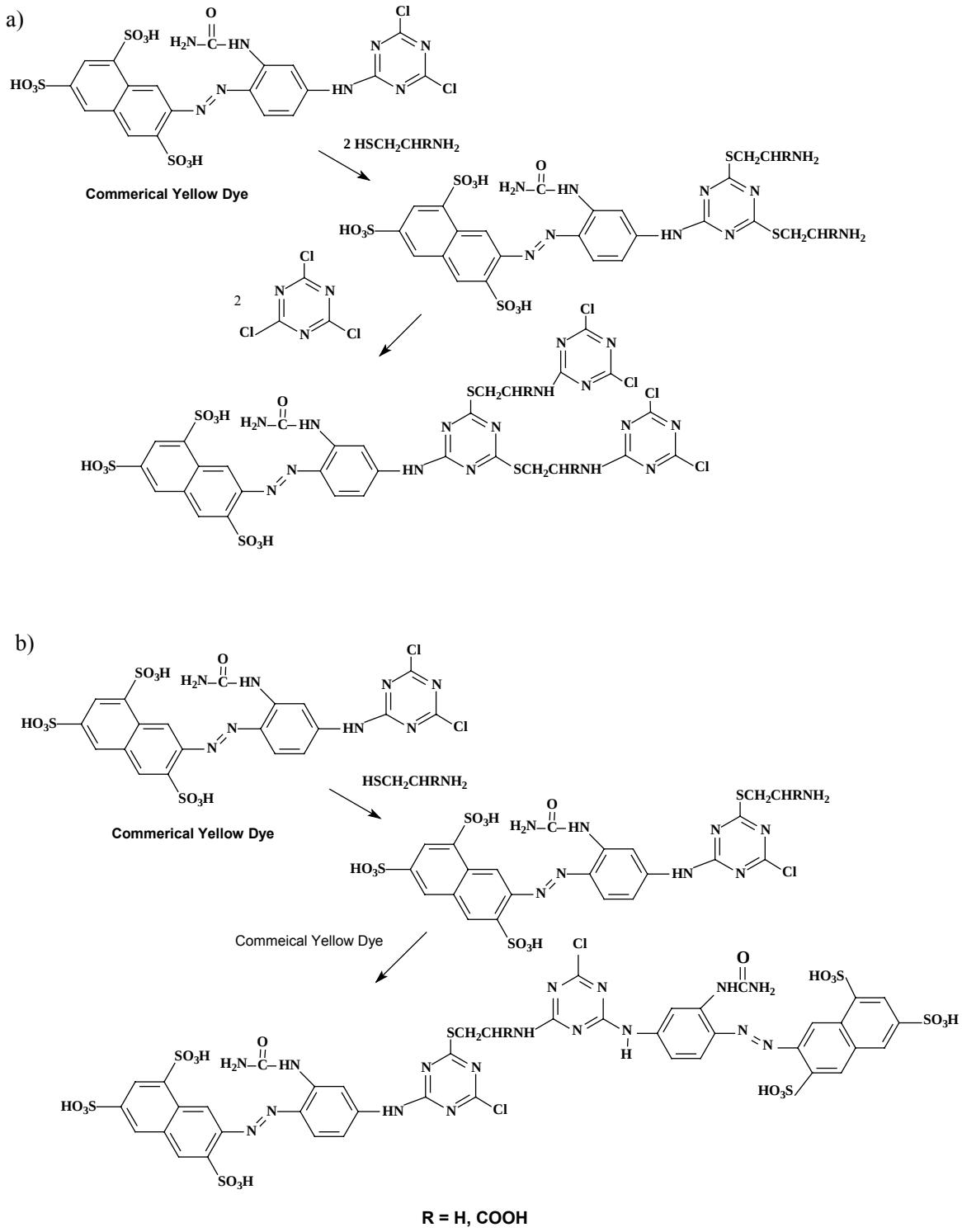
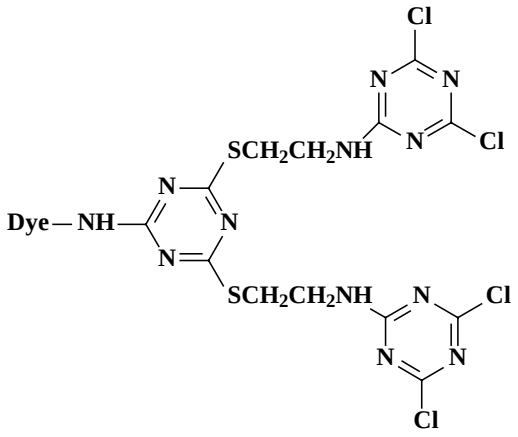


Figure 12. Synthesis of homobifunctional reactive Teegafix dyes.

The direct cotton affinity of the new teegafix dyes has been assessed using equilibrium exhaustion and laboratory dyeing experiments. The results showed that the modified (Teegafix) dyes had higher affinity and greater fixation levels than the corresponding commercial DCT dyes. Fastness testing results showed that there were no significant decreases in the performance properties of the Teegafix dyes compared to the commercial dyes. Among the four types of homobifunctional reactive teegafix dyes, modified structure (50) containing a bis-DCT system and cysteamine groups gave the best results in affinity and laboratory dyeing studies [28].



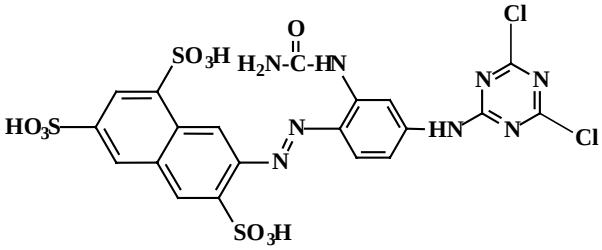
(50)

In subsequent studies, the type (50) modified dyes were applied using a commercial-scale dyeing machine to further assess the utility of these dyes. The results showed that the application of yellow, red and blue modified dyes to cotton fabric on a pilot plant scale afforded a significant increase in color strength compared to shade depths obtained using the corresponding commercial dyes. The yellow modified dye was 40% stronger than its counterpart, and the modified

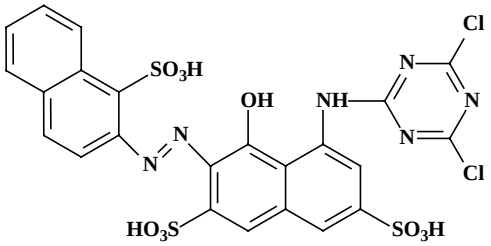
blue dye was >160% stronger than the commercial blue dye on a pound to pound basis [50].

3. Research Proposal

The objectives of this present research are to expand previous studies involving Teegafix dyes to the synthesis and evaluation of heterobifunctional reactive dyes derived from the commercial yellow (51) and red (52) dyes.



(51)



(52)

Type 1 yellow (58) and red (65) dyes will be prepared by a reaction of one equivalent of a DCT-based dye with two equivalents of cysteamine (53) followed by two equivalents of cyanuric chloride (55) and para-aminobenzene-sulfatoethylsulfone (56). To make type 2 yellow (61) and red (67) dyes, cysteine (59) will be used instead of cysteamine. The synthesis of type 3 yellow (63) and red (69) dyes employ a DCT dye and one equivalent of cysteamine, cyanuric chloride, and *para*-aminobenzenesulfatoethylsulfone. The syntheses are outlined in Figures 13-18.

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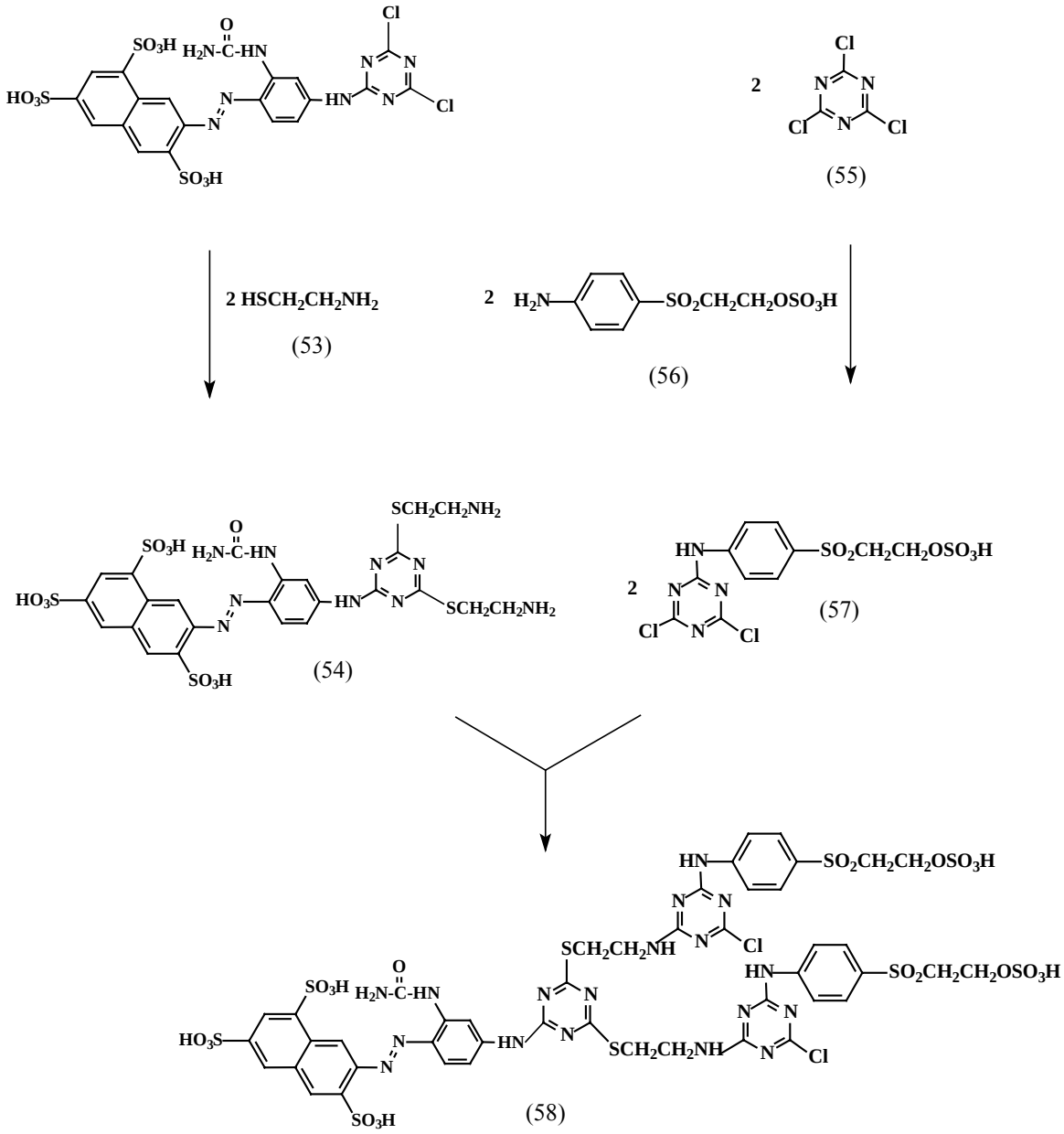


Figure 13. Synthesis of type 1 heterobifunctional reactive yellow dye (58).

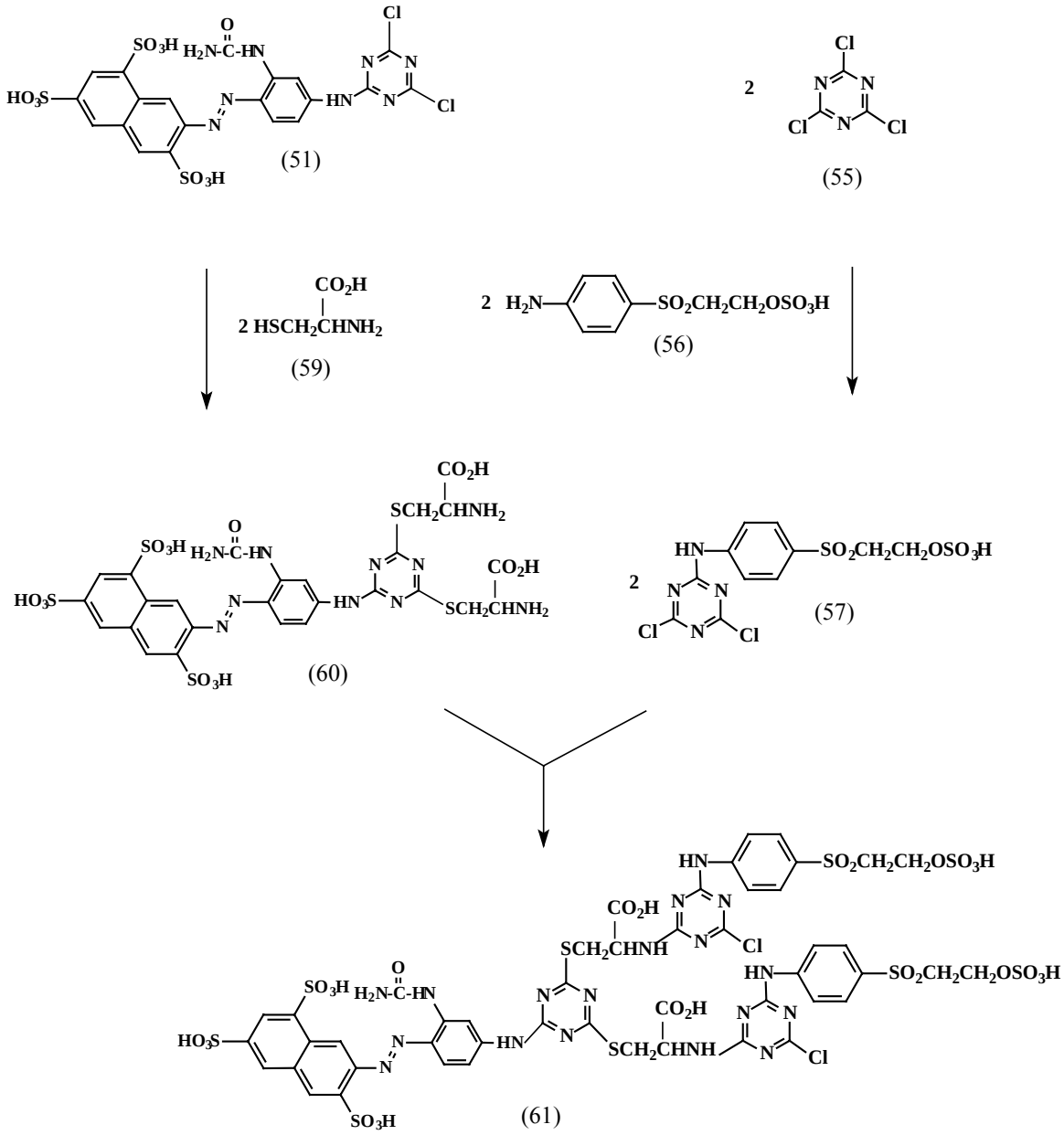


Figure 14. Synthesis of type 2 heterobifunctional reactive yellow dye (61).

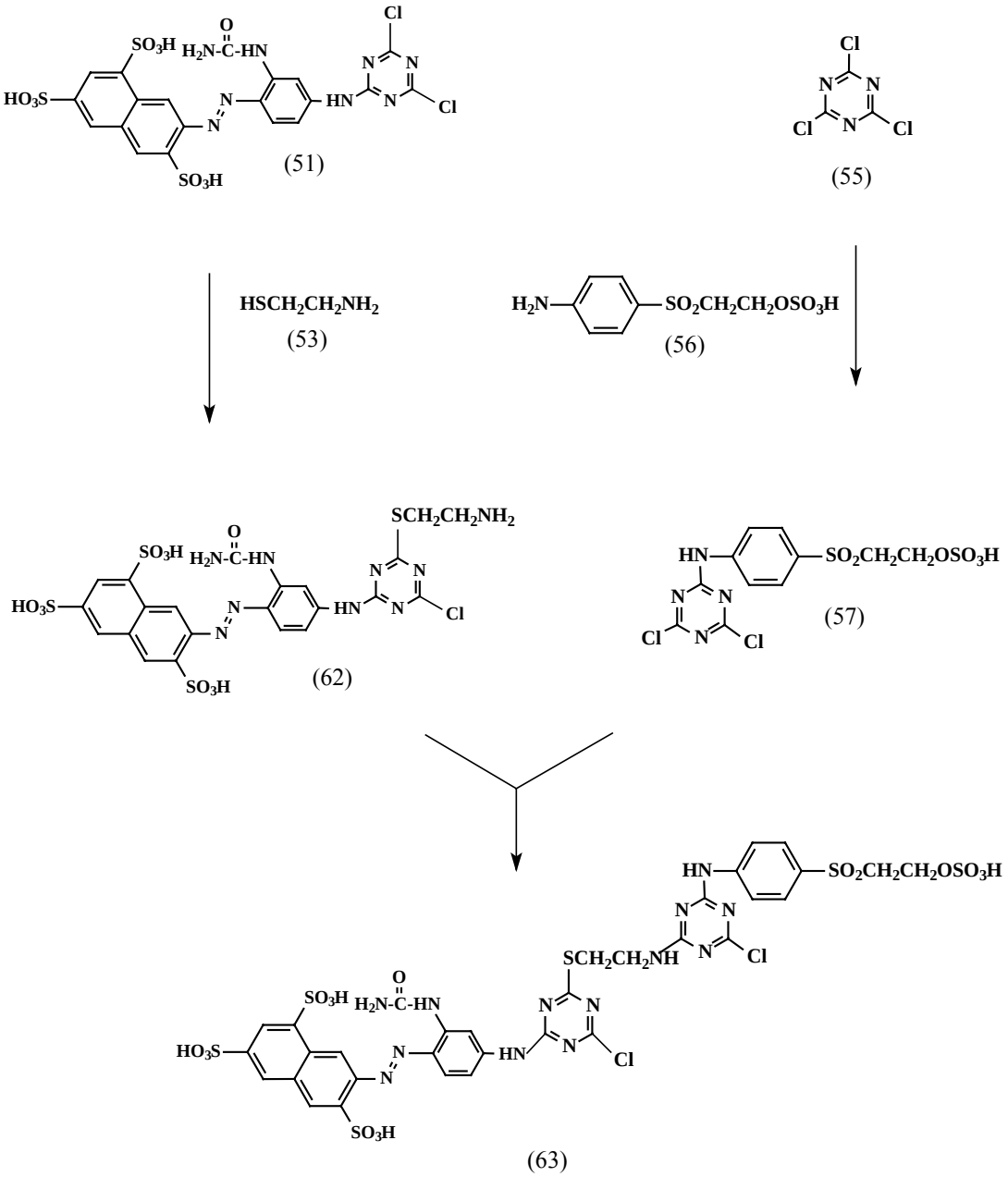


Figure 15. Synthesis of type 3 heterobifunctional reactive yellow dye (63).

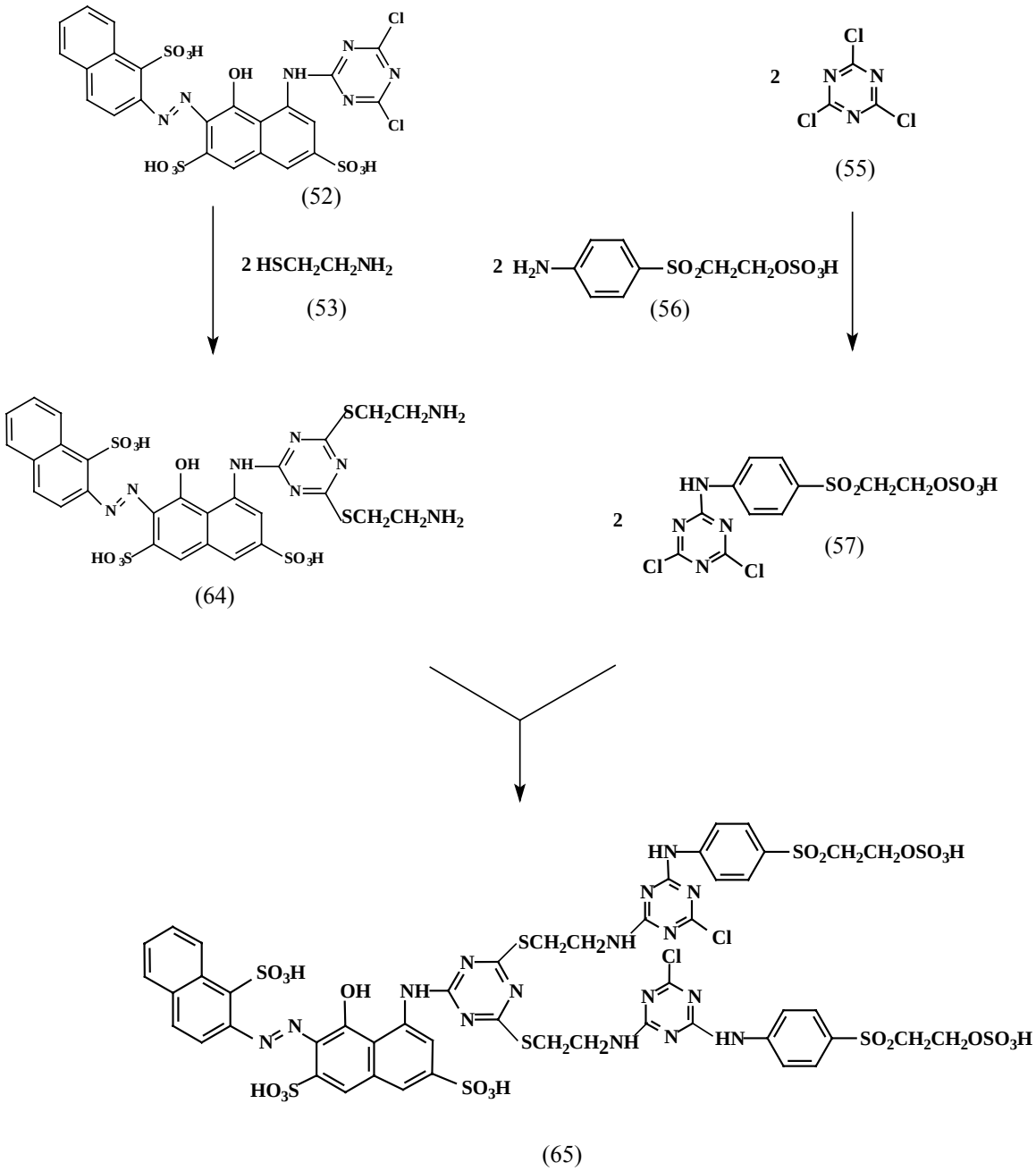


Figure 16. Synthesis of type 1 heterobifunctional reactive red dye (65).

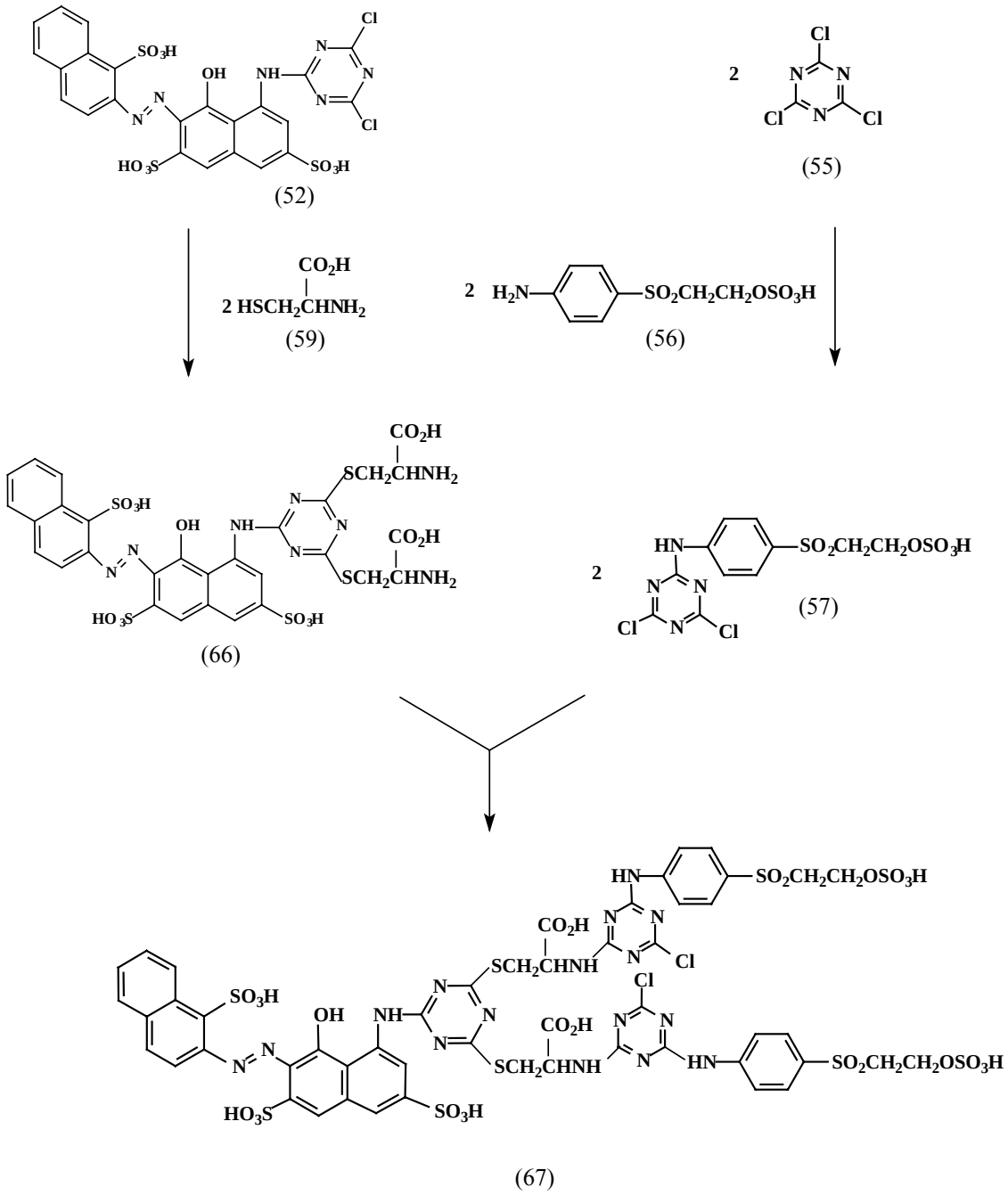


Figure 17. Synthesis of type 2 heterobifunctional reactive red dye (67).

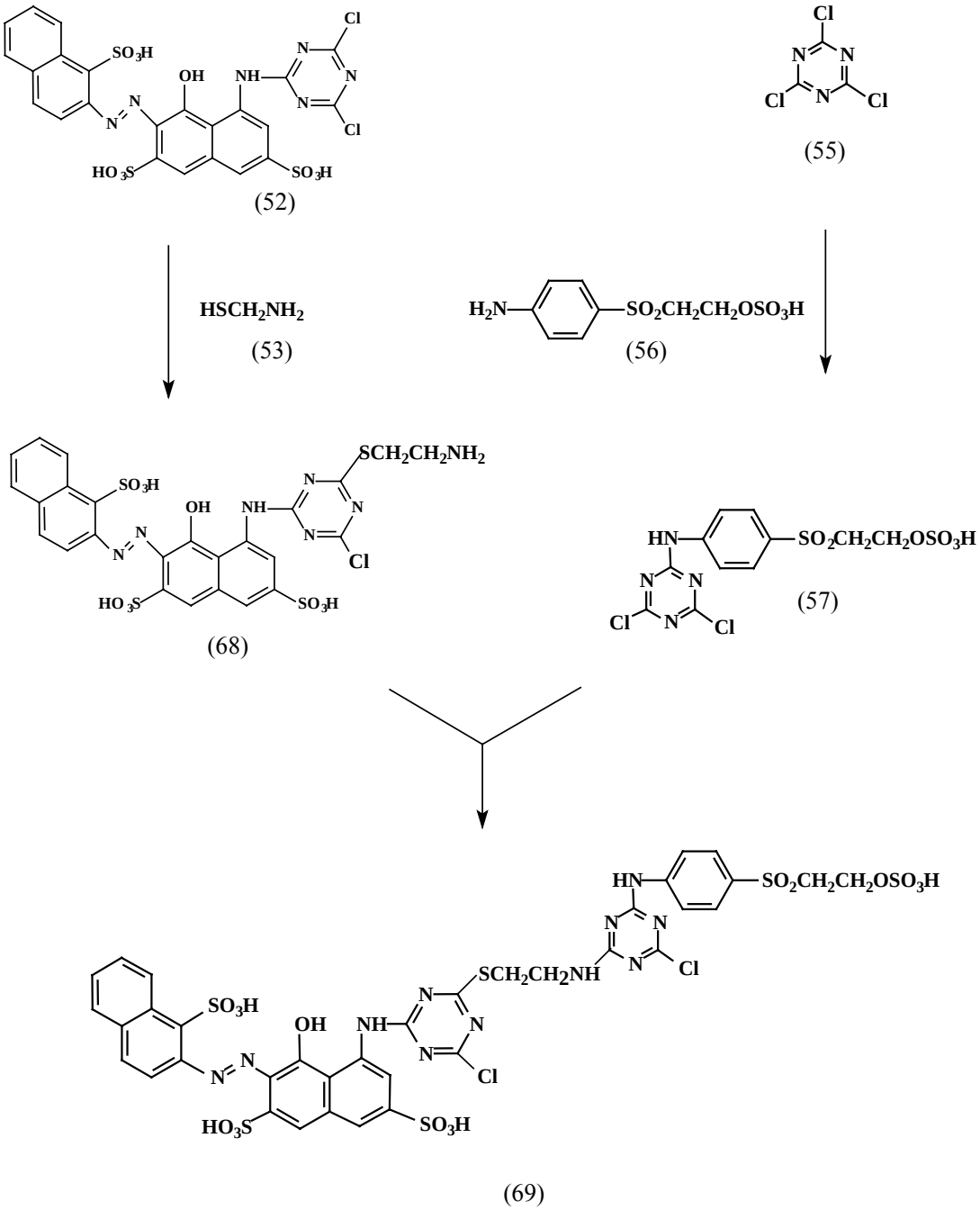


Figure 18. Synthesis of type 3 heterobifunctional reactive red dye (69).

II. Experimental

1. General Information

The commercial yellow (75.0% active) and red (61.7% active) dyes used in this study were obtained from DyStar L. P., Charlotte, NC. All other chemicals were purchased from Aldrich Chemical Co., Milwaukee, WI. Thin layer chromatography (TLC) was conducted using Whatman PE silica gel plates with UV254 indicator. The structures of target reactive dyes were confirmed by negative ion ESI mass spectrometry, using a MALDI- TOF Tandem mass spectrometer. The purity of the final products was evaluated by HPLC analysis, using a Waters Breeze system equipped with a dual λ absorbance detector set at 415 nm, a C_{18} column, and a mobile phase consisting of solvent A: acetonitrile + 0.025M $Bu_4^+Br^-$ (TBAB) and solvent B: 30/70 mixture of acetonitrile + 0.025M TBAB and deionized water + 0.05M $NH_4H_2PO_4$. Visible absorption spectra were recorded on a Varian Cary 3 UV-Visible spectrophotometer. Fabrics used for equilibrium exhaustion experiments were 100% bleached cotton woven crocking squares weighing 1.0± 0.01g, and a Boekel Grant ORS200 shaker bath was used. Plain weave cotton fabric weighing 10.0± 0.01g was used for laboratory dyeing studies on an Ahiba Texomat dyeing machine. Washfastness and lightfastness were assessed using an Atlas Lauder-ometer and Atlas 3Sun Hi35 high irradiance xenon weatherometer, respectively. AATCC test methods 61 and 16E were used for fastness assessments. Colorimetric data (L*, a*, b* and K/S) were measured using a Datacolor International Spectroflash SFX instrument equipped with SLI-form N/G software. The spectrophotometer setup was as

follows: specular included, illuminant D65, 10˚ standard observer. Measurements were made 4-ply fabric and each sample was measured four times and data averaged (DE_{CMC} less than 0.25 from average).

2. Synthesis

2.1 Yellow Dye (58)

Commercial yellow dye (4.9 g, 0.005 mol) was dissolved in water (20 mL) and stirred at room temperature. Cysteamine hydrochloride (1.2 g, 0.01 mol) was dissolved in water (20 mL) and stirred at room temperature as the dye solution was added dropwise over 2 h. During the addition, the pH of the reaction was maintained at 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Activated charcoal was added and the mixture was stirred for 10 min. Following collection by filtration, the filtrate was diluted by adding 20% (w/v) KCl (70 mL), and the precipitated dye was collected, washed with 20% (w/v) KCl and with acetone, and dried to give intermediate (54) (3.9 g). TLC: R_f = 0.72 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

4-β-Sulfatoethylsulfonylaniline (3.1 g, 0.01 mol) was dissolved in 50 mL cold water (0 -10°C) and stirred as the pH was adjusted to 6.0 - 7.0 by adding 20% (w/v) Na_2CO_3. The solution was stirred with activated charcoal, filtered, and stirred as a solution of cyanuric chloride (1.9 g, 0.01 mol) in 30 mL acetone was added at 0 - 5 °C. The reaction pH was maintained at 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3. After 1 h, the mixture was filtered and washed by acetone to give intermediate (57). TLC: R_f = 0.68 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

Intermediate (54) was dissolved in water (20 mL) and stirred at 45 - 50 °C as the pH was adjusted to 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Solid intermediate (57) was added to the solution of (54). The reaction was maintained at pH 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3 and stirred at 45 - 50 °C. After 4 h, the product (58) was precipitated by adding 10% (w/v) KCl (50mL) and pH was lowered to 5 by adding 20% (w/v) HCl. The mixture was stirred 2 h to complete precipitation, filtered and the solid was washed with acetone. Drying gave 4.8 g dye (58). TLC: R_f = 0.71 (n-PrOH: n-BuOH: EtOAc: H_2O / 2:4:1:3).

Dye (58) was dissolved in 100 mL *N,N*-dimethylformamide, stirred for 1 h, and the mixture was filtered to remove the insoluble solid. Ethyl acetate (150 mL) was added to the filtrate, and the mixture was stirred at room temperature for 1 h. After the precipitation was completed, the mixture was filtered and dried to give the salt-free final product (58) (2.2 g, 28.7%).

2.2 Yellow Dye (61)

Commercial yellow dye (4.9 g, 0.005 mol) was dissolved in water (15 mL) and stirred at room temperature. L-Cysteine (1.2 g, 0.01 mol) was dissolved in water (50 mL) and stirred at room temperature as the dye solution was added dropwise over 2 h. During the addition, the pH of the reaction was maintained at 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Activated charcoal was added and the mixture was stirred for 10 min. Following collection by filtration, the filtrate was diluted by adding 20% (w/v) KCl (50 mL), and the precipitated dye was collected,

washed with 20% (w/v) KCl and with acetone, and dried to give intermediate (60) (3.6 g). TLC: R_f = 0.68 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

4-β-Sulfatoethylsulfonylaniline (3.1 g, 0.01 mol) was dissolved in 50 mL cold water (0 -10°C) and stirred as the pH was adjusted to 6.0 - 7.0 by adding 20% (w/v) Na_2CO_3. The solution was stirred with activated charcoal, filtered, and stirred as a solution of cyanuric chloride (1.9 g, 0.01 mol) in 30 mL acetone was added at 0 - 5 °C. The reaction pH was maintained at 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3. After 1 h, the mixture was filtered and washed by acetone to give intermediate (57). TLC: R_f = 0.63 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

Intermediate (60) was dissolved in water (15 mL) and stirred at 45 - 50 °C as the pH was adjusted to 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Solid intermediate (57) was added to the solution of (60). The reaction was maintained at pH 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3 and stirred at 45 - 50 °C. After 4 h, the product (61) was precipitated by adding 10% (w/v) KCl (50mL), and pH was lowered to 5 by adding 20% (w/v) HCl. The mixture was stirred 2h to complete precipitation, filtered, and solid was washed with acetone. Drying gave dye (61) (5.6g). TLC: R_f = 0.65 (n-PrOH: n-BuOH: EtOAc: H_2O / 2:4:1:3).

Dye (61) was dissolved in 80 mL *N,N*-dimethylformamide, stirred for 1 h, and the mixture was filtered to remove the insoluble solid. Ethyl acetate (120 mL) was added to the filtrate, and the mixture was stirred at room temperature for 1 h. After the precipitation was completed, the mixture was filtered and dried to give the salt-free final product (61) (2.0 g, 24.0%).

2.3 Yellow Dye (63)

Commercial yellow dye (4.9 g, 0.005 mol) was dissolved in water (20 mL) and stirred at room temperature. Cysteamine hydrochloride (0.6 g, 0.005 mol) was dissolved in water (10 mL) and stirred at 0-10 °C as the dye solution was added dropwise over 2 h. During the addition, the pH of the reaction was maintained at 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Activated charcoal was added and the mixture was stirred for 10 min. Following collection by filtration, the filtrate was diluted by adding 20% (w/v) KCl (50 mL), and the precipitated dye was collected, washed with 20% (w/v) KCl and with acetone, and dried to give intermediate (62) (3.2 g). TLC: R_f = 0.65 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

4-β-Sulfatoethylsulfonylaniline (1.5 g, 0.005 mol) was dissolved in 25 mL cold water (0 -10°C) and stirred as the pH was adjusted to 6.0 - 7.0 by adding 20% (w/v) Na_2CO_3. The solution was stirred with activated charcoal, filtered, and stirred as a solution of cyanuric chloride (0.9 g, 0.005 mol) in 15 mL acetone was added at 0 - 5 °C. The reaction pH was maintained at 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3. After 1 h, the mixture was filtered and washed by acetone to give intermediate (57). TLC: R_f = 0.66 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

Intermediate (62) was dissolved in water (20 mL) and stirred at 45 - 50 °C as the pH was adjusted to 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Solid intermediate (57) was added to the solution of (62). The reaction was maintained at pH 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3 and stirred at 45 - 50 °C. After 4 h, the product (63) was precipitated by adding 10% (w/v) KCl (40mL), and pH was lowered to 5 by adding 20% (w/v) HCl. The mixture was stirred 2 h to complete

precipitation, filtered and the solid was washed with acetone. Drying gave 5.5 g dye (63). TLC: R_f = 0.73 (n-PrOH: n-BuOH: EtOAc: H_2O / 2:4:1:3).

Dye (63) was dissolved in 80 mL *N,N*-dimethylformamide, stirred for 1 h, and the mixture was filtered to remove the insoluble solid. Ethyl acetate (120 mL) was added to the filtrate, and the mixture was stirred at room temperature for 1 h. After the precipitation was completed, the mixture was filtered and dried to give the salt-free final product (63) (2.1 g, 36.5%).

2.4 Red Dye (65)

Commercial red dye (5.7 g, 0.005 mol) was dissolved in water (50 mL) and stirred at room temperature. Cysteamine hydrochloride (1.2 g, 0.01 mol) was dissolved in water (20 mL) and stirred at room temperature as the dye solution was added dropwise over 2 h. During the addition, the pH of the reaction was maintained at 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Activated charcoal was added and the mixture was stirred for 10 min. Following collection by filtration, the filtrate was diluted by adding 20% (w/v) KCl (100 mL), and the precipitated dye was collected, washed with 20% (w/v) KCl and with acetone, and dried to give intermediate (64) (5.2 g). TLC: R_f = 0. 60 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

4-β-Sulfatoethylsulfonylaniline (3.1 g, 0.01 mol) was dissolved in 50 mL cold water (0 -10°C) and stirred as the pH was adjusted to 6.0 - 7.0 by adding 20% (w/v) Na_2CO_3. The solution was stirred with activated charcoal, filtered, and stirred as a solution of cyanuric chloride (1.9 g, 0.01 mol) in 30 mL acetone was

added at 0 - 5 °C. The reaction pH was maintained at 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3. After 1 h, the mixture was filtered and washed by acetone to give intermediate (57). TLC: R_f = 0.65 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

Intermediate (64) was dissolved in water (50 mL) and stirred at 45 - 50 °C as the pH was adjusted to 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Solid intermediate (57) was added to the solution of (64). The reaction was maintained at pH 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3 and stirred at 45 - 50 °C. After 4 h the product (65) was precipitated by adding 10% (w/v) KCl (70mL) and pH was lowered to 5 by adding 20% (w/v) HCl. The mixture wash stirred 2h to complete precipitation, filtered and the solid was washed with acetone. Drying gave 6.4 g dye (65). TLC: R_f = 0.65 (n-PrOH: n-BuOH: EtOAc: H_2O / 2:4:1:3).

Dye (65) was dissolved in 100 mL *N,N*-dimethylformamide, stirred for 1 h and the mixture was filtered to remove the insoluble solid. Ethyl acetate (150 mL) was added to the filtrate, and the mixture was stirred at room temperature for 1 h. After the precipitation was completed, the mixture was filtered and dried to give the salt-free final product (65) (3.5 g, 44.3%).

2.5 Red Dye (67)

Commercial red dye (5.7g, 0.005 mol) was dissolved in water (50 mL) and stirred at room temperature. L-Cysteine (1.2 g, 0.01 mol) was dissolved in water (50 mL) and stirred at room temperature as the dye solution was added dropwise over 2 h. During the addition the pH of the reaction was maintained at 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Activated charcoal was added and the mixture

was stirred for 10 min. Following collection by filtration, the filtrate was diluted by adding 20% (w/v) KCl (100 mL), and the precipitated dye was collected, washed with 20% (w/v) KCl and with acetone, and dried to give intermediate (66) (5.0 g). TLC: R_f = 0. 58 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

4-β-Sulfatoethylsulfonylaniline (3.1 g, 0.01 mol) was dissolved in 50 mL cold water (0 -10°C) and stirred as the pH was adjusted to 6.0 - 7.0 by adding 20% (w/v) Na_2CO_3. The solution was stirred with activated charcoal, filtered, and stirred as a solution of cyanuric chloride (1.9 g, 0.01 mol) in 30 mL acetone was added at 0 - 5 °C. The reaction pH was maintained at 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3. After 1 h, the mixture was filtered and washed by acetone to give intermediate (57). TLC: R_f = 0.64 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

Intermediate (66) was dissolved in water (50 mL) and stirred at 45 - 50 °C as the pH was adjusted to 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Solid intermediate (57) was added to the solution of (64). The reaction was maintained at pH 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3, and stirred at 45 - 50 °C. After 4h, the product (67) was precipitated by adding 10% (w/v) KCl (70mL) and pH was lowered to 5 lowered by adding 20% (w/v) HCl, The mixture was stirred 2h to complete precipitation, filtered, and the solid was washed with acetone. Dyeing gave 4.8 g dye (67). TLC: R_f = 0.51 (n-PrOH: n-BuOH: EtOAc: H_2O / 2:4:1:3).

Dye (67) was dissolved in 80 mL *N,N*-dimethylformamide, stirred for 1 h, and the mixture was filtered to remove the insoluble solid. Ethyl acetate (120 mL) was added to the filtrate, and the mixture was stirred at room temperature for

1 h. After the precipitation was completed, the mixture was filtered and dried to give the salt-free final product (67) (3.4 g, 41.2%).

2.6 Red Dye (69)

Commercial red dye (5.7g, 0.005 mol) was dissolved in water (50 mL) and stirred at room temperature. Cysteamine hydrochloride (0.6 g, 0.005 mol) was dissolved in water (10 mL) and stirred at room temperature as the dye solution was added dropwise over 2 h. During the addition, the pH of the reaction was maintained at 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Activated charcoal was added and the mixture was stirred for 10 min. Following collection by filtration, the filtrate was diluted by adding 20% (w/v) KCl (80 mL), and the precipitated dye was collected, washed with 20% (w/v) KCl and with acetone, and dried to give intermediate (68) (4.8 g). TLC: R_f = 0. 55 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

4-β-Sulfatoethylsulfonylaniline (1.5 g, 0.005 mol) was dissolved in 20 mL cold water (0 -10°C) and stirred as the pH was adjusted to 6.0 - 7.0 by adding 20% (w/v) Na_2CO_3. The solution was stirred with activated charcoal, filtered, and stirred as a solution of cyanuric chloride (0.9 g, 0.005 mol) in 15 mL acetone was added at 0 - 5 °C. The reaction pH was maintained at 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3. After 1 h, the mixture was filtered and washed by acetone to give intermediate (57). TLC: R_f = 0.66 (n-PrOH:n-BuOH:EtOAc:H_2O/2:4:1:3).

Intermediate (68) was dissolved in water (45 mL) and stirred at 45 - 50 °C as the pH was adjusted to 7.0 - 7.5 by adding 20% (w/v) Na_2CO_3. Solid intermediate (57) was added to the solution of (68). The reaction was maintained

at pH 6.5 - 7.0 by adding 20% (w/v) Na_2CO_3, and stirred at 45 - 50 °C. After 4h, the product (69) was precipitated by adding 10% (w/v) KCl (50mL), and pH was lowered to 5 by adding 20% (w/v) HCl. The mixture was stirred 2h to complete precipitation, filtered and the solid was washed with acetone. Drying gave 6.0 g dye (65). TLC: R_f = 0.54 (n-PrOH: n-BuOH: EtOAc: H_2O / 2:4:1:3).

Dye (69) was dissolved in 80 mL *N,N*-dimethylformamide, stirred for 1 h, and the mixture was filtered to remove the insoluble solid. Ethyl acetate (120 mL) was added to the filtrate, and the mixture was stirred at room temperature for 1 h. After the precipitation was completed, the mixture was filtered and dried to give the salt-free final product (69) (3.6 g, 64.2%).

3. Dyeing Experiments

3.1 Equilibrium Exhaustion

The equilibrium exhaustion experiments for the two commercial dyes and six new heterobifunctional reactive dyes synthesized in this study were conducted in 50 mL Erlenmeyer flasks by using a pair of Boekel Grant ORS200 shaker baths at 100 orbital revolutions per minute. Woven cotton squares (4) weighing a total of 1.0± 0.01g were added to each flask along with salt and 40mL dyebath ([C] = 0.25g/L) to give a bath ratio of 40:1 and 1% dye (owg). Four salt levels (0 g/L, 10 g/L, 40 g/L and 70g/L), three dyeing temperatures (30 °C, 60 °C, and 90 °C), and four dyeing times (24h, 48h, 72h and 96h) were used. After the dyeing cycle ended, the flasks were removed from the shaker bath and the baths were allowed to cool to room temperature. The fabric samples were removed,

washed with running tap water until there was no color coming off (about 1 min), and then placed on paper towels to dry. The remaining dyebaths were covered and stored for subsequent analysis.

3.1.1 Determination of Dye in Solution (C^s)

The stock dye solutions ([c] = 0.25g/L) used for the equilibrium exhaustion experiments were diluted to concentrations of 2.50 $X10^{-3}$ g/L, 1.25 $X10^{-2}$ g/L, 2.50 $X10^{-2}$ g/L, 0.50$X10^{-2}$ g/L, and 1.00 $X10^{-1}$ g/L. The absorbance value for each of these solutions was recorded and a linear regression was employed to generate a standard calibration curve ($r^2 > 0.9997$). The absorbance of each bath remaining from dyeing experiments was recorded using the absorption spectrophotometer and the corresponding dye concentration was determined by using the standard calibration curve.

3.1.2 Determination of Dye in the Fiber (C^f)

Based on the law of conservation of mass, the total amount of dye used for dyeing must equal to the amount of dye in the dyebath after dyeing plus the amount of dye in the fiber.

$$c_{initial}\, m_{initial} = c^f\, m^f + c^s\, m^s$$

Where $m_{initial}$ is the mass of the initial solution, $c_{initial}$ is the concentration of the initial solution; m^s is the mass of the solution after dyeing; c^s is the concentration of dye in the solution after dyeing; c^f is the concentration of dye in the fiber; and m^f is the mass of the fiber [28].

3.1.3 Determination of the Substantivity Ratio (K)

The substantivity ratio of the dye for the fiber in the exhaustion equilibrium experiments was calculated by dividing the concentration of dye in the solution by the concentration of the dye in the fiber after dyeing, as shown in the following equation [51].

$$K = c^f / c^s$$

3.1.4 Determination of Percent Exhaustion (%E)

The percent exhaustion (%E) for each equilibrium exhaustion experiments was calculated using the equation below [51].

$$\% E = [(c^s_{initial} - c^s)/ c^s_{initial}] \times 100\%$$

3.1.5 Determination of Apparent Standard Affinity (-Δμ°)

The apparent standard affinity was calculated from substantivity ratio (K) for the exhaustion experiments by using the following equation:

$$-\Delta\mu° = RT\ln K$$

where R is a rate constant (8.31433 J/mol K), T is the temperature (K) and K is the affinity of the dye for the fiber [51].

3.2 Laboratory Dyeing

Laboratory dyeings were conducted using an Ahiba Texomat machine with a 40:1 bath ratio. Plain weave 100% cotton fabric (10 g) and 0.1 g dye were

used for each experiment. Dyeings were carried out at two salt levels (40 g/L and 70 g/L) and two temperatures (30 °C and 60 °C).

3.2.1 Dyeing Process

1. Pre-wet fabric
2. Load the Texomat with fabric and dyebath
3. Agitate fabric in bath for 5 min
4. Raise fabric out of bath
5. Add 16 g solid NaCl (for 40 g/L) or 28 g solid NaCl (for 70 g/L)
6. Lower fabric into dyebath
7. Heat bath to 30 °C or 60 °C
8. Rotate fabric in bath for 10 min
9. Raise fabric from bath
10. Add 20 mL Na_2CO_3 ([c= 200 g/L]) to give bath concentration of 10g/L
11. Lower fabric into dyebath
12. Rotate fabric in bath for 10 min
13. Add 20 mL NaOH ([c = 20 g/L]) to give bath concentration of 1g/L
14. Lower fabric into dyebath
15. Rotate fabric for 60 min
16. Cool dyebath to room temperature
17. Remove the fabric from dyebath

3.2.2 Washing Process

After removal from the dyebath, the dyed fabrics were rinsed under running tap water until there was no color coming off (about 2 min), placed in a steam-heated kettle and washed 20 min at 80 °C in 10 L water containing Apolloscour SDRS (2 g/L). Excess detergent was removed by rinsing the fabric with cold water.

3.3 Colorimetric Data

L*, a*, b* and K/S data were recorded on cotton fabric from equilibrium exhaustion and laboratory dyeing experiments using a Datacolor International Spectraflash SF600X instrument equipped with SLI-Form® software. The samples were pressed with an iron set on medium high (162 °C) before making measurements.

4. Washfastness Testing

The washfastness of cotton fabrics from laboratory dyeing experiments was evaluated using AATCC test method 61-1999, test No. 2A. The test was conducted in an Atlas Launder-ometer using conditions shown in Table 1 [52].

Table 1. Washfastness testing conditions.

Temperature	49 °C
Total Bath Volume	150 mL
% Detergent	0.15%
Number of Steel Balls	50
Time	45 min

Each piece of dyed cotton fabric (2.0 x 6.0 inch) was attached to a multifiber test fabric (2.0 x 2.0 inch) to assess staining. The color change of each washed sample was evaluated using a DataColor international spectro-photometer. AATCC Gray Scale for staining was used for evaluating color staining of attached multifiber fabric using AATCC evaluation procedure 2. A rating of 1 (poor) to 5 (excellent) was assigned to each washed sample and attached multifiber fabric.

5. Lightfastness Testing

The lightfastness of all dyed cotton fabrics from laboratory dyeing experiments was evaluated using AATCC test method 16-1998 E. An Atas 3SUN Hi 35 high irradiance xenon weather-ometer was used under the conditions shown in Table 2 [53].

Table 2. Lightfastness testing conditions.

Light Source	Xenon arc
Lamp Cooling	Water
Black Panel Temperature	63 ± 1 °C
Dry Bulb Temperature	43 ± 2 °C
% Relative Humidity	30 ± 5 %
Duration of Test	20 h
Irradiance Level	1.10 ± 0.03 w/m^2

The dyed cotton fabrics were cut into a size of 2.0 x 6.0 cm. Color change was evaluated using a DataColor International Spectrophotometer and a rating of 1 (poor) to 5 (excellent) was assigned.

III. Results and Discussion

1. Visible Absorption Spectra

The visible absorption spectra of DCT-based commercial yellow dye (51), DCT-based commercial red dye (52), type 1 yellow dye (58), type 2 yellow dye (61), type 3 yellow dye (63), type 1 red dye (65), type 2 red dye (67), and type 3 red dye (69) are shown in Figures 20-27. The spectra of yellow dyes contained one peak and those of red dyes contained two peaks. Unlike the yellow dyes, the red dyes have hydroxyl groups ortho to the azo naphthyl group. Due to this structural feature the red dyes exhibit azo-hydrazone tautomerism, as illustrated in Figure 19. The hydrazone form is bathochromic compared to the azo form [14].

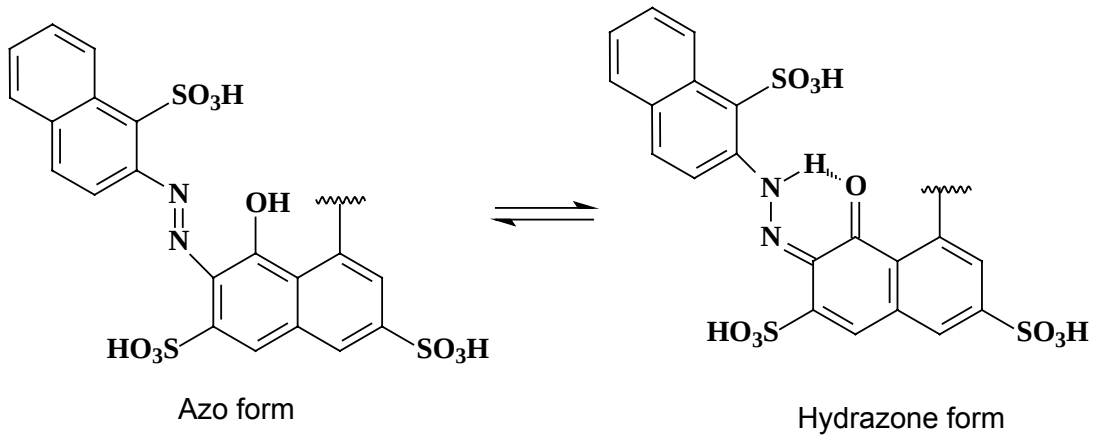
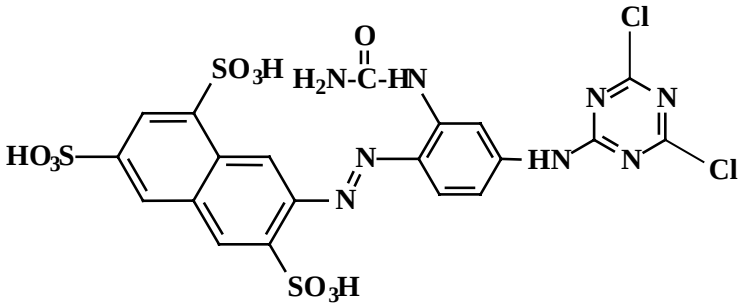


Figure 19. Azo-hydrazone tautomerism in arylazonaphthol red dyes.

Commercial Yellow Dye (51)



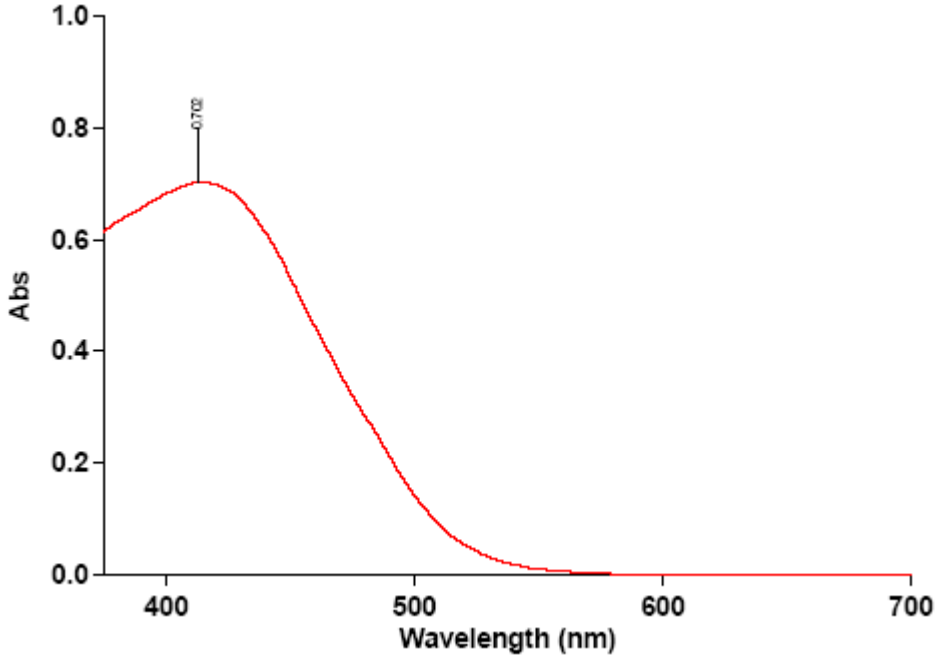
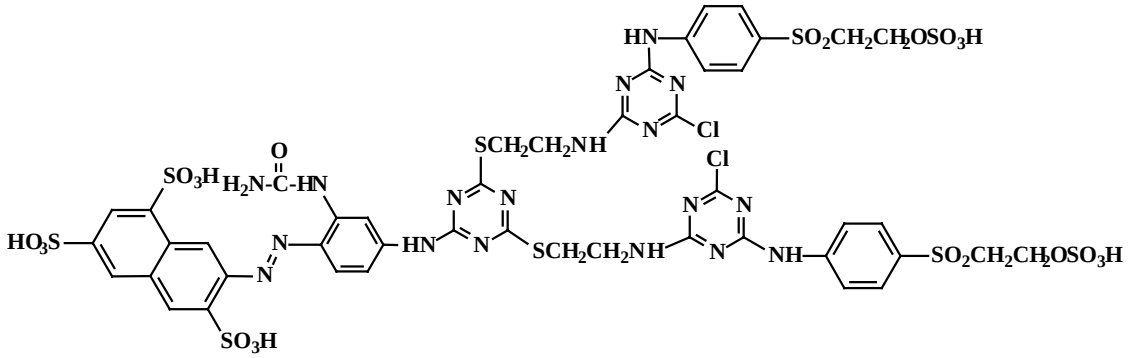


Figure 20. Visible absorption spectrum of the commercial yellow dye (51).

Yellow Dye (58)



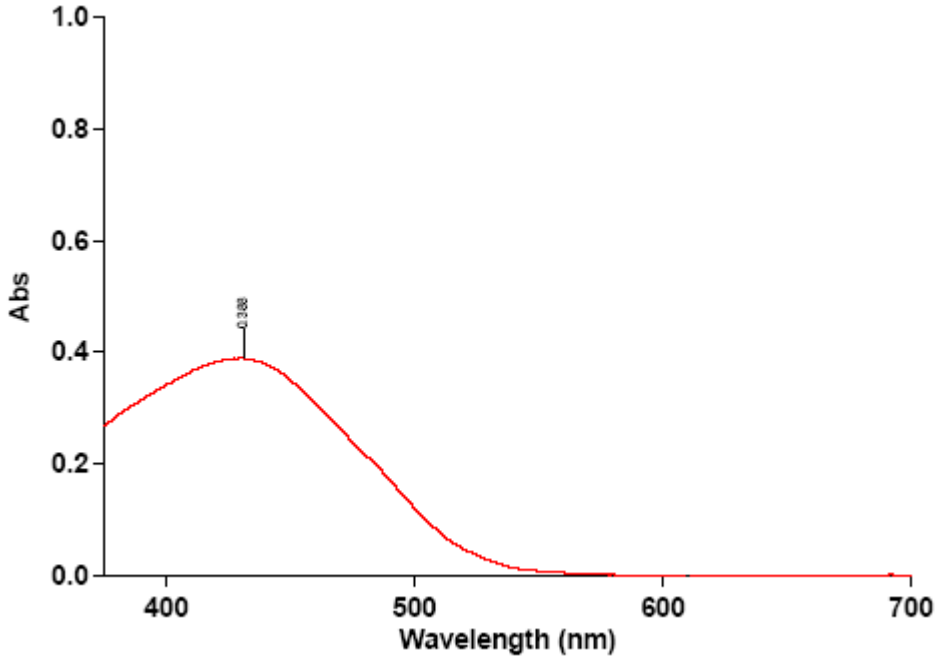
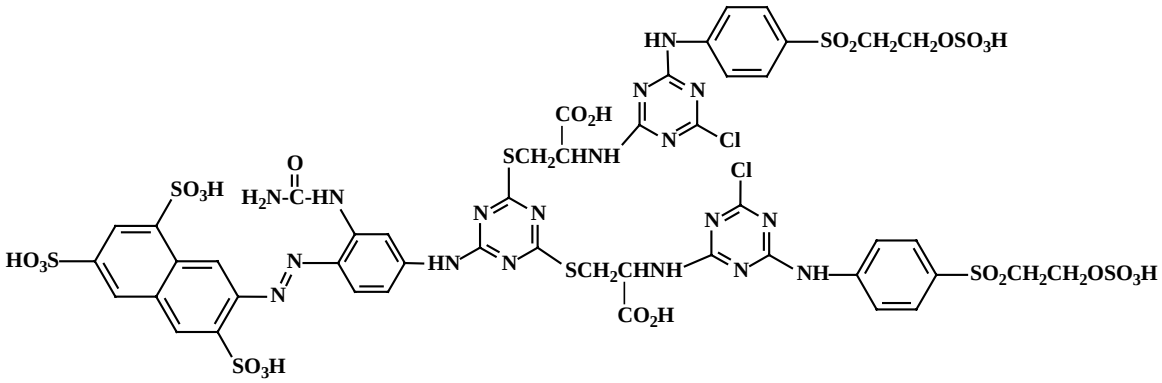


Figure 21. Visible absorption spectrum of yellow dye (58).

Yellow Dye (61)



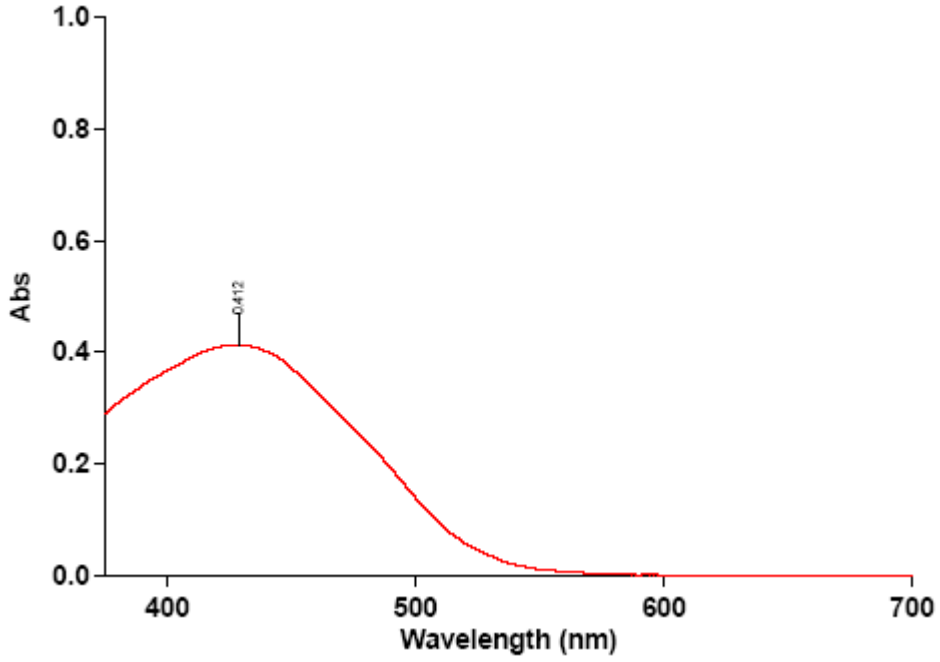
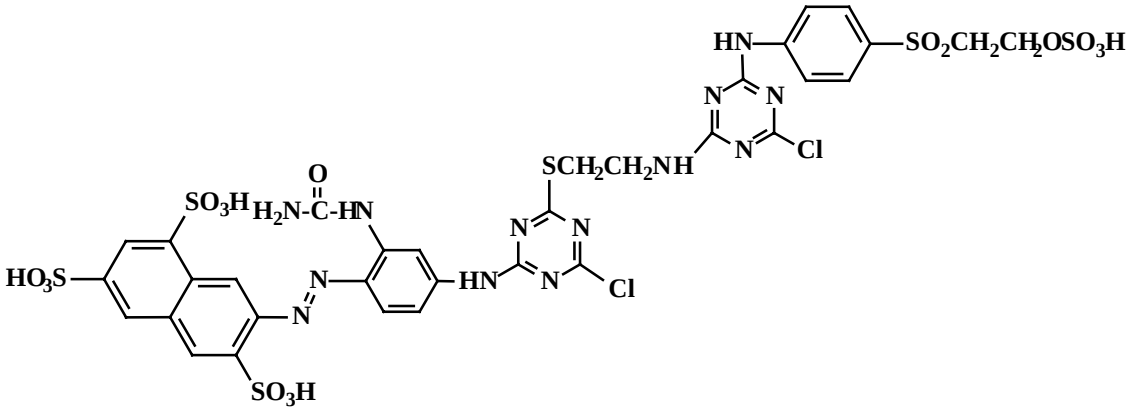


Figure 22. Visible absorption spectrum of yellow dye (61).

Yellow Dye (63)



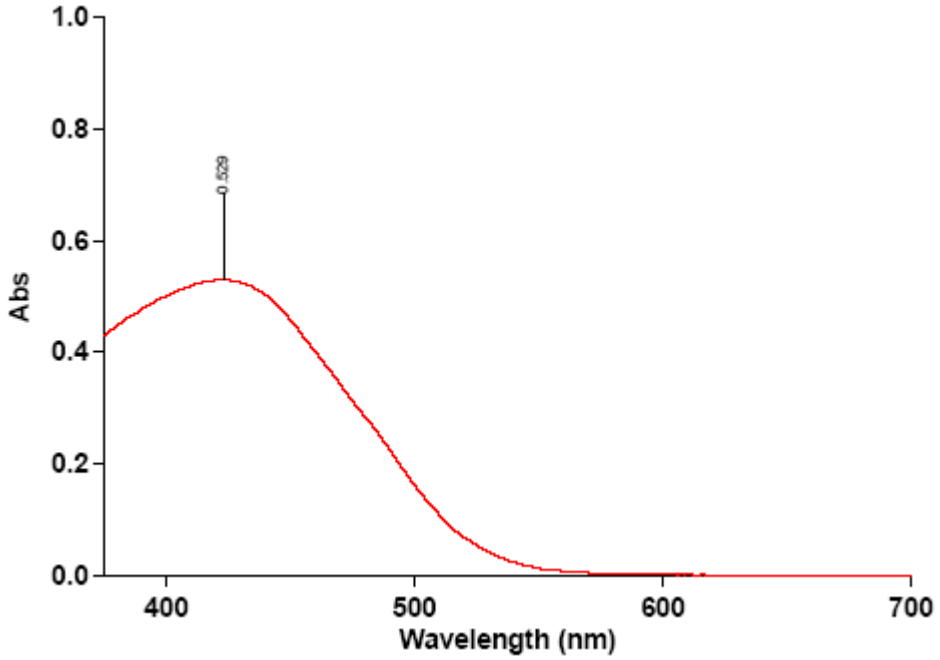
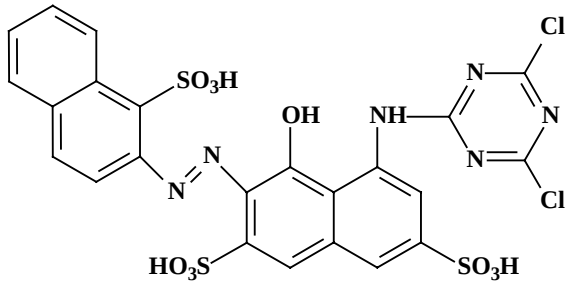


Figure 23. Visible absorption spectrum of yellow dye (63).

Commercial Red Dye (52)



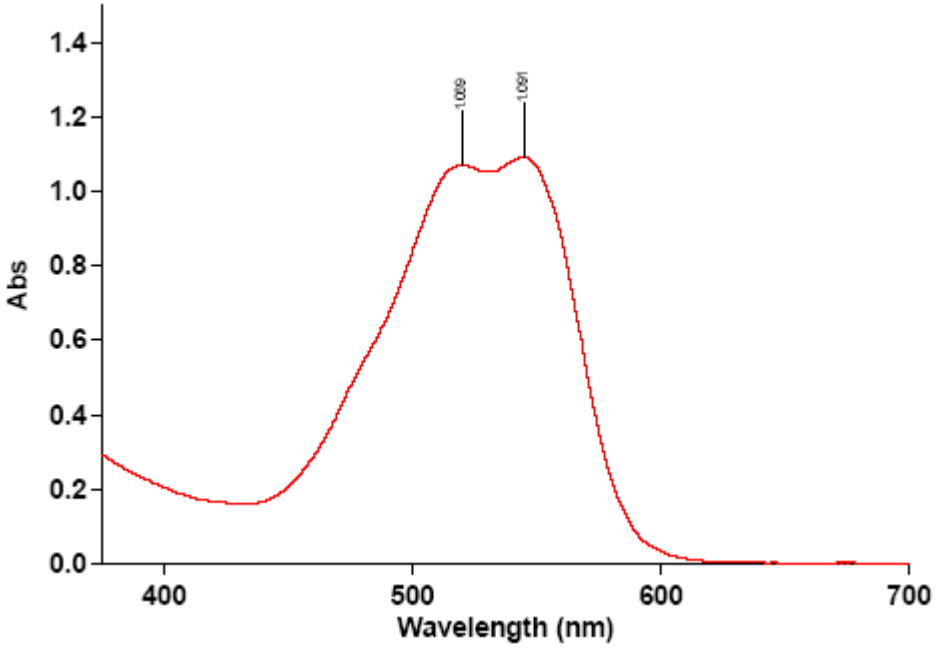
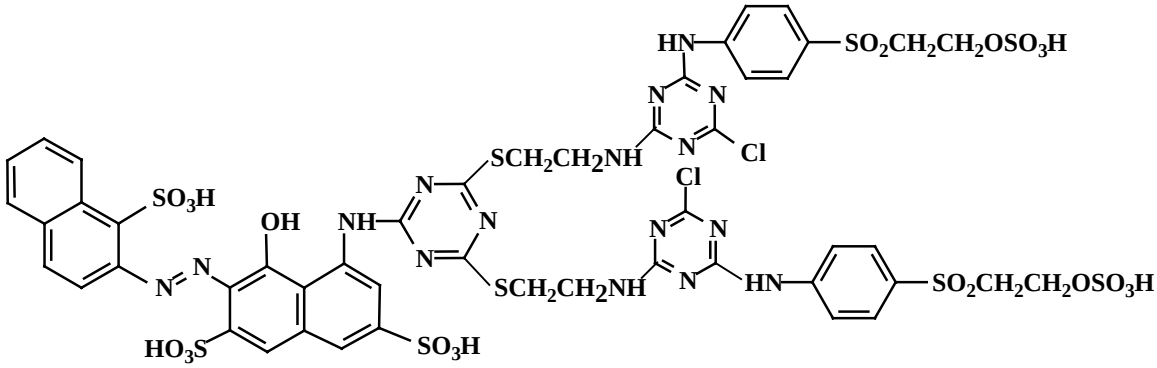


Figure 24. Visible absorption spectrum of the commercial red dye (52).

Red Dye (65)



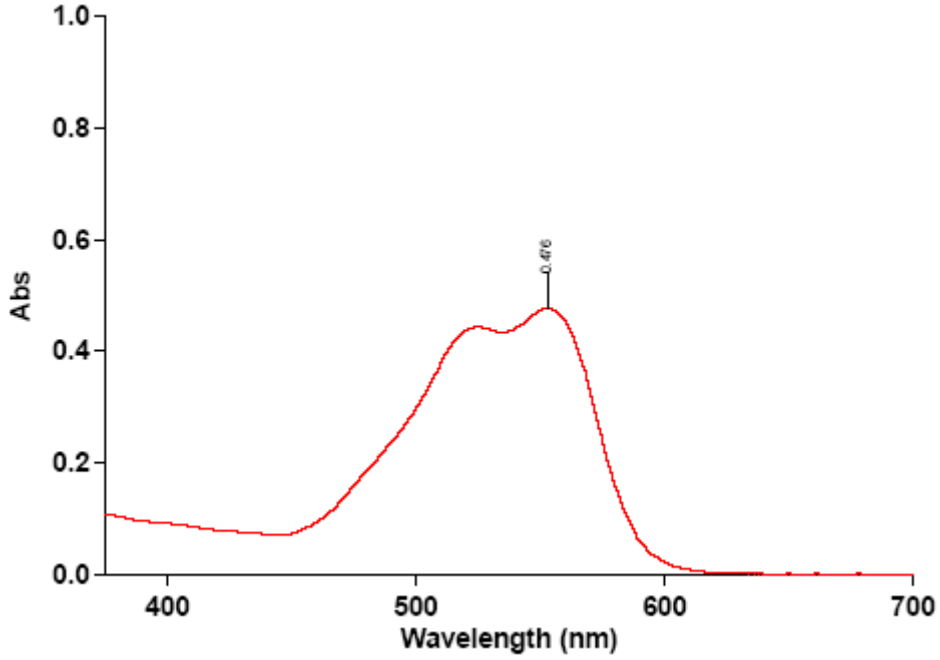
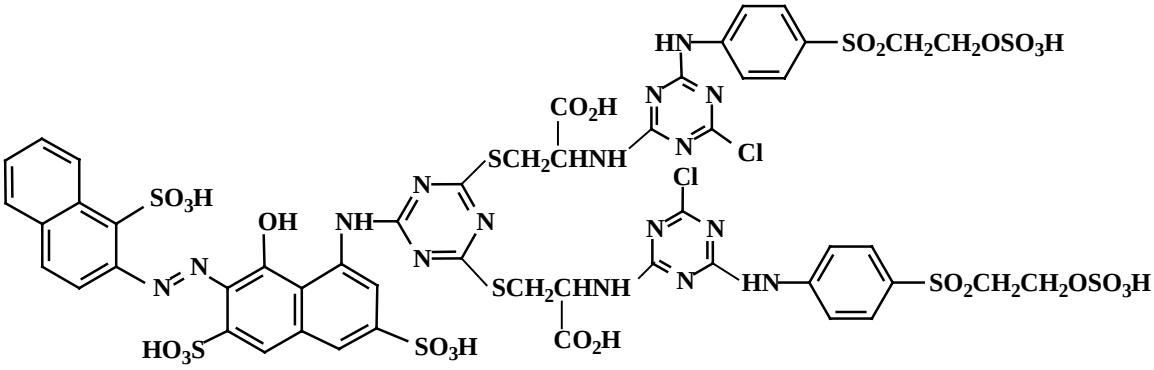


Figure 25. Visible absorption spectrum of red dye (65).

Red Dye (67)



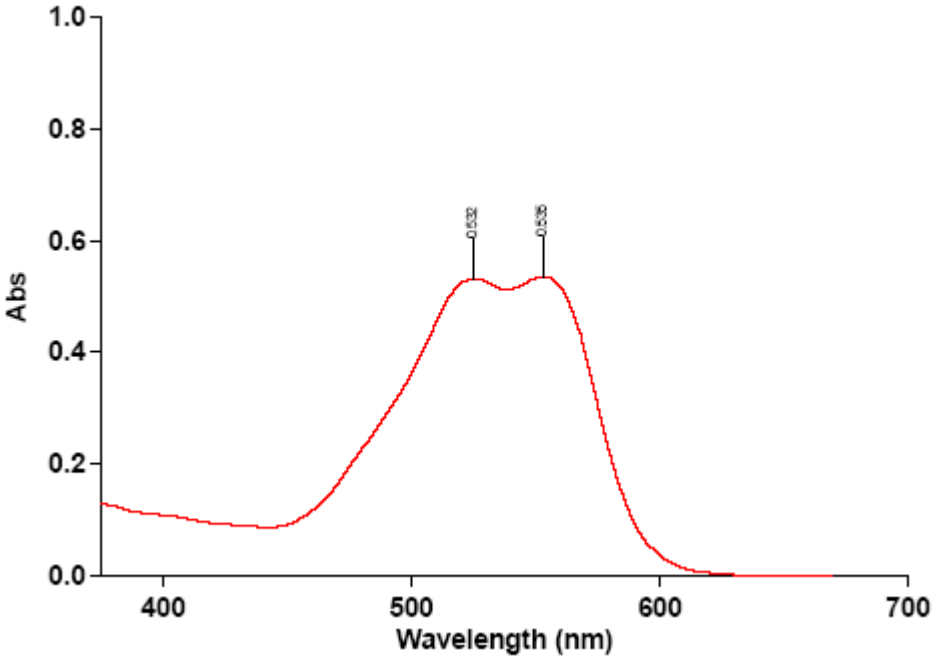
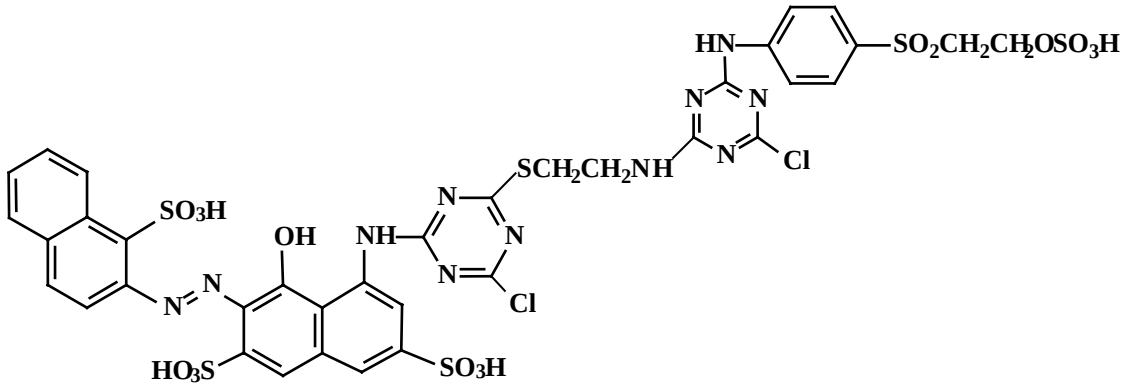


Figure 26. Visible absorption spectrum of red dye (67).

Red Dye (69)



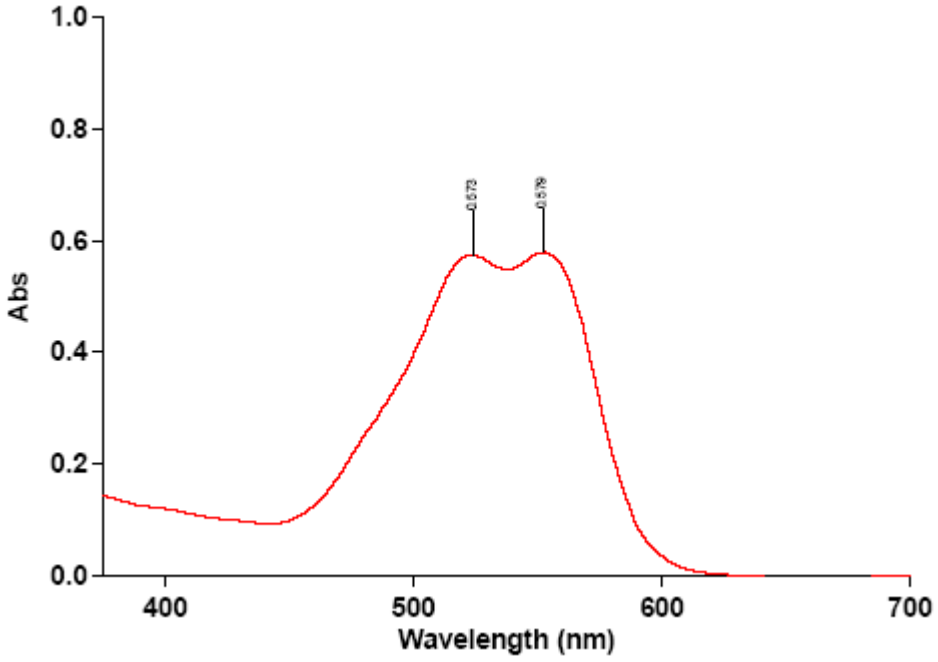


Figure 27. Visible absorption spectrum of red dye (69).

The absorption maximum (λ_{max}) and molecular absorptivity (ε_{max}) for each dye are shown in Table 3. The ε_{max} values were calculated based on the Beer-Lambert Law: $A = \varepsilon b c$, where A is the absorbance at λ_{max}; b is the path length of the cuvette in which the sample is contained, and c is the dye concentration.

Table 3. λ_{max} and ε_{max} data for commercial dyes and heterobifunctional reactive dyes.

Dye	λ_{max} (nm)	ε_{max} (L moL^{-1}cm^{-1})
Commercial Yellow (51)	413	19,000
Type 1 yellow (58)	431	24,000
Type 2 yellow (61)	429	27,000
Type 3 yellow (63)	423	24,000
Commercial (52)	545	30,000
Type 1 red (65)	553	30,000
Type 2 red (67)	553	35,000
Type 3 red (69)	552	26,000

The results in Table 3 show that the new heterobifunctional reactive dyes have higher λ_{max} values than the commercial counterparts. These results indicate that the incorporation of the linking group causes a bathochromic shift despite its attachment through an insulating group (triazine group). Similarly, an increase in ε_{max} was observed following each yellow dye modification, while only the type 2 red dyes had a higher ε_{max} value. The ε_{max} values are higher than the

absorbance values would suggest, since a significant decrease in absorbance was observed for the heterobifunctional dyes. One might expect the increase in molecular weight but no changes in the sized of the chromogen to afford lower ε_{max} values. However, this was observed only in the case of the type 3 red dye.

2. Mass Spectrometry

The six new heterobifunctional reactive dyes were assessed using negative-ion electrospray ionization mass spectrometry (ESI-MS), which has proved to be the most suitable method for sulfonated dyes [29]. Copies of the resulting spectra are shown in Figures 28-33.

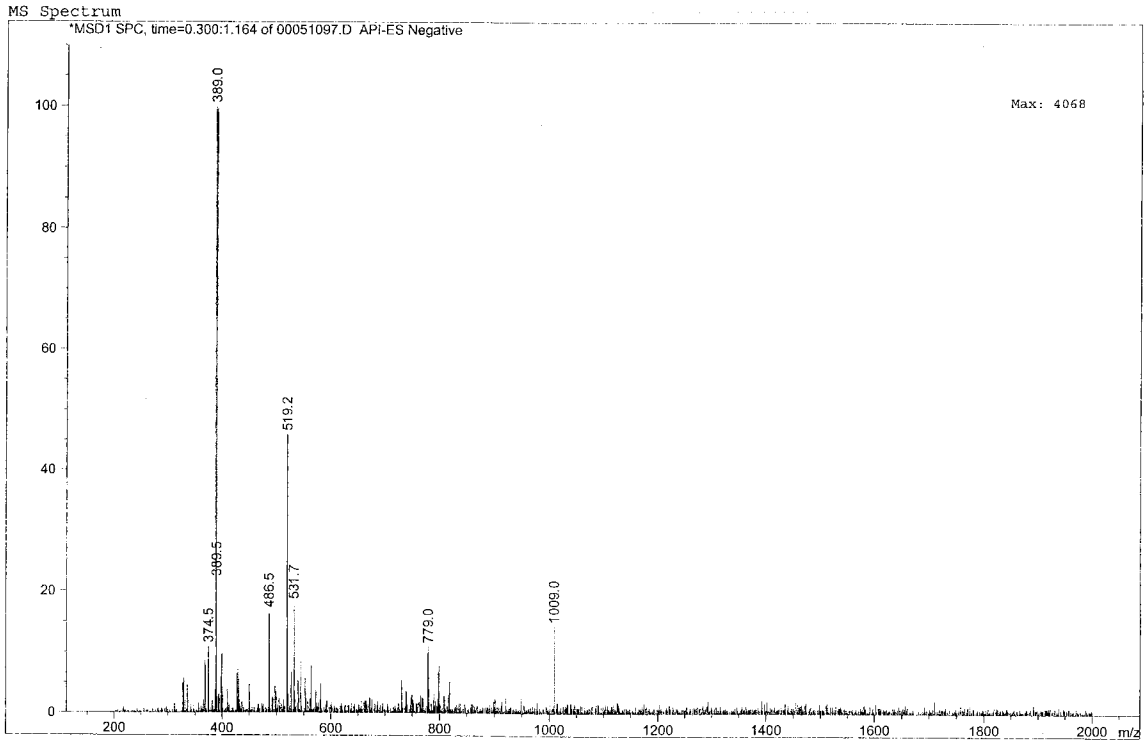


Figure 28. ESI mass spectrum for yellow dye (58).

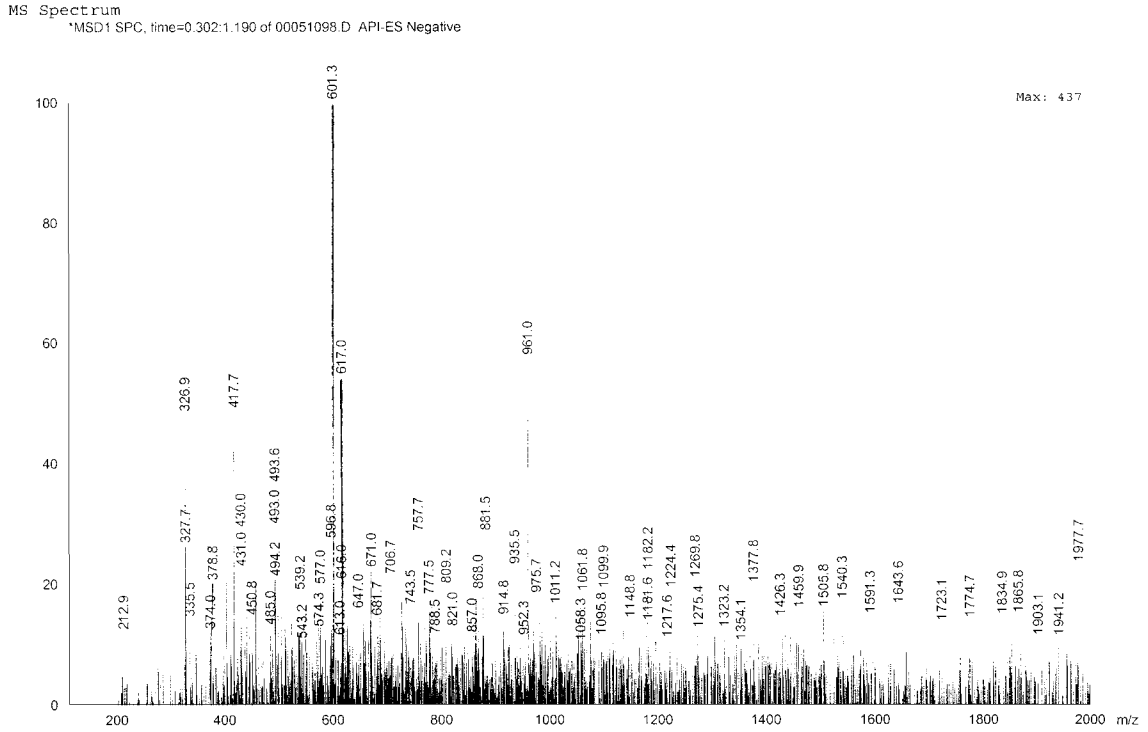


Figure 29. ESI mass spectrum for yellow dye (61).

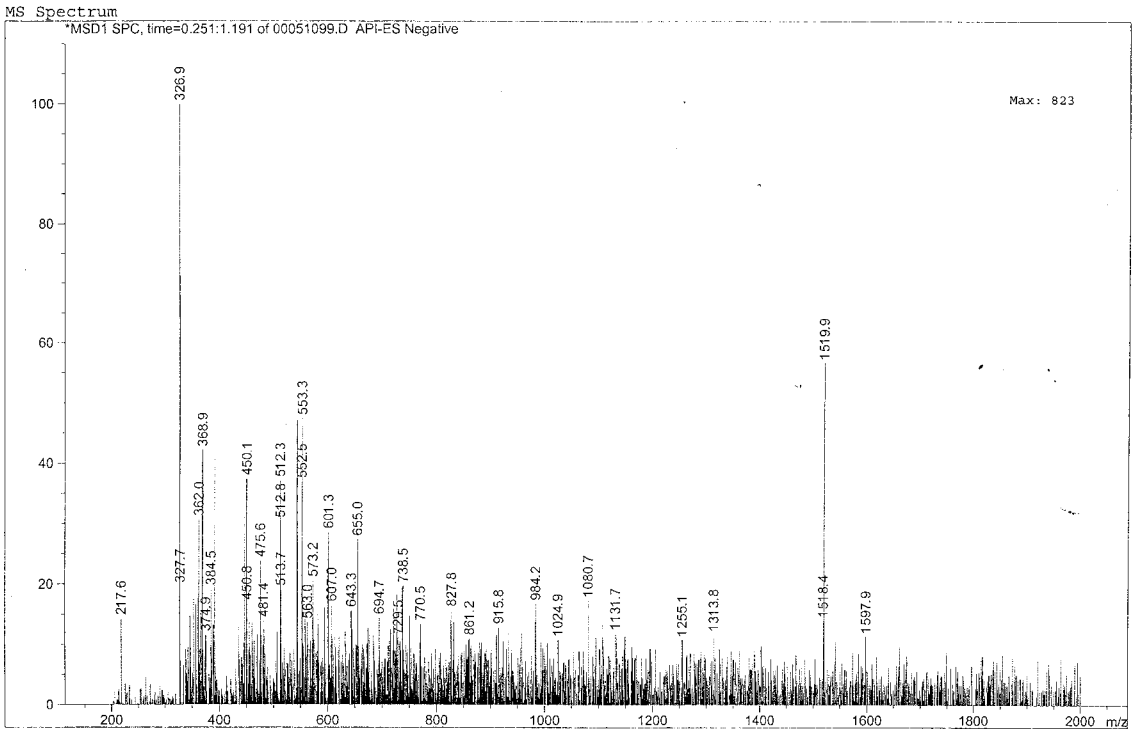


Figure 30. ESI mass spectrum for yellow dye (63).

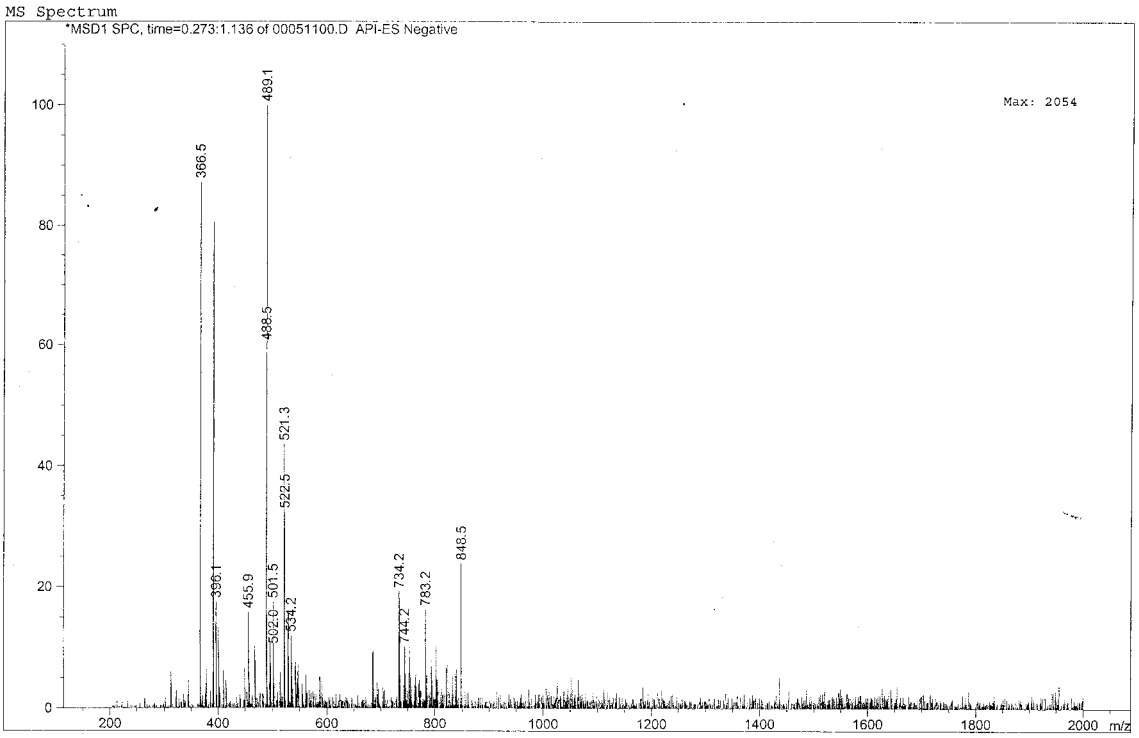


Figure 31. ESI mass spectrum for red dye (65).

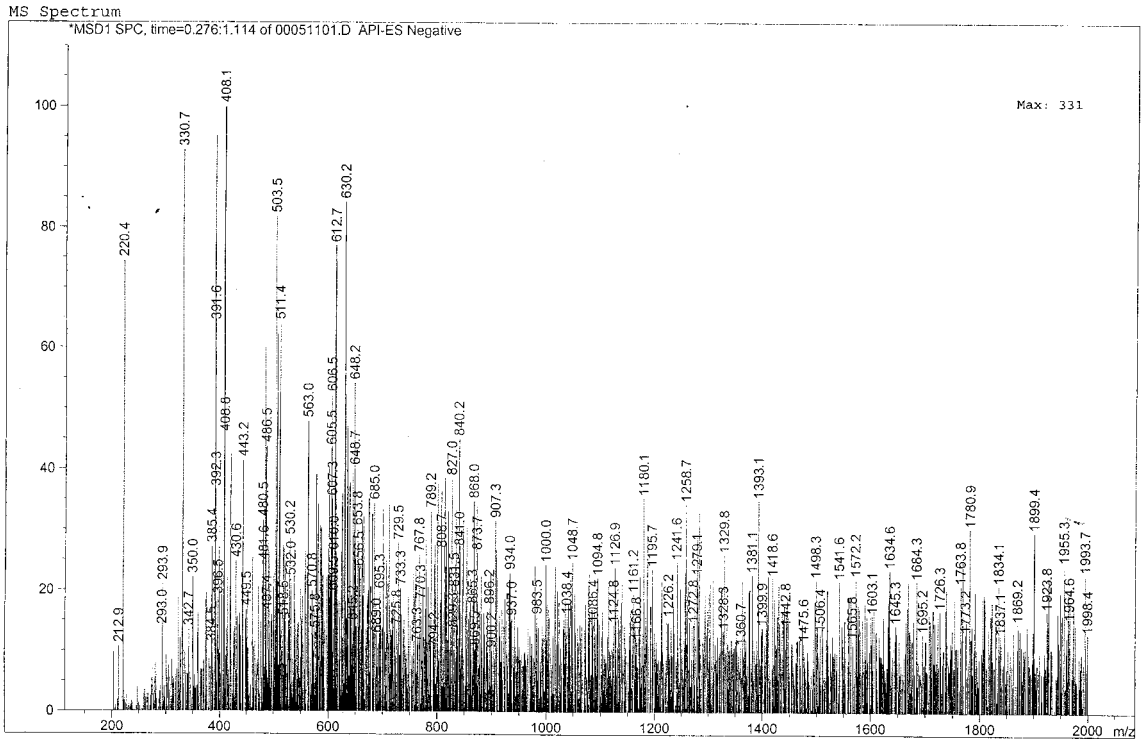


Figure 32. ESI mass spectrum for red dye (67).

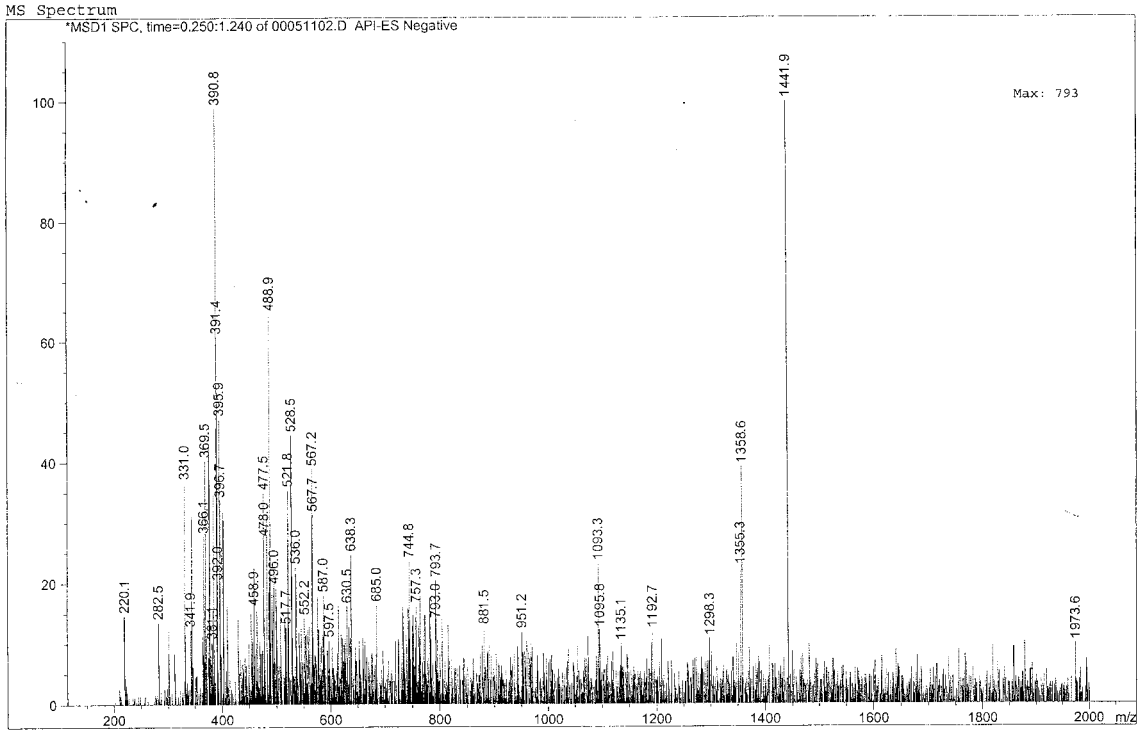
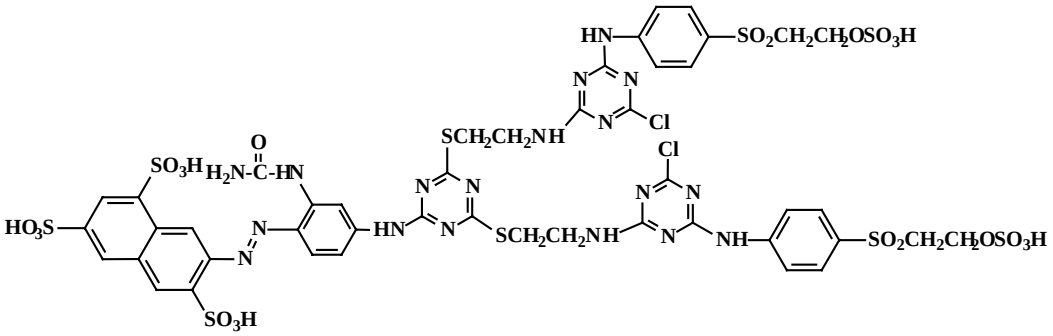


Figure 33. ESI mass spectrum for red dye (69).

Yellow Dye (58)



Yellow dye (58) has MW = 1560, based on the formula $C_{46}H_{44}C_{l2}N_{18}O_{22}S_9$. With the loss of 2 H^+ ions, a peak corresponding to an $[M-2H]^{2-}$ ion was observed at m/z = 779 (Figure 34). With the loss of 3 H^+ ions, a peak corresponding to an $[M-3H]^{3-}$ ion was observed at m/z= 519 (Figure 35). With the loss of 4 H^+ ions, a peak corresponding to an $[M-4H]^{4-}$ ion was observed at m/z =389 (Figure 36), and was the base peak of the spectrum. Table 4 provides a list of the structures corresponding to signals from ESI-MS analysis of yellow dye (58).

Table 4. Yellow dye (58) ions corresponding to signals from ESI-MS analysis.

Dye ion	Structure	m/z	Relative Intensity
$[M-2H]^{2-}$	Figure 34	779	12
$[M-3H]^{3-}$	Figure 35	519	46
$[M-4H]^{4-}$	Figure 36	389	100

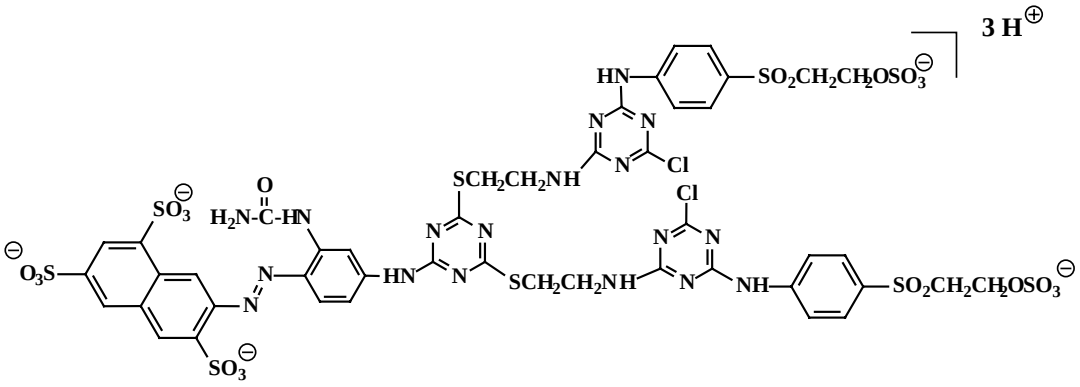


Figure 34. Structure of [M-2H] $^{2-}$ ion of yellow dye (58).

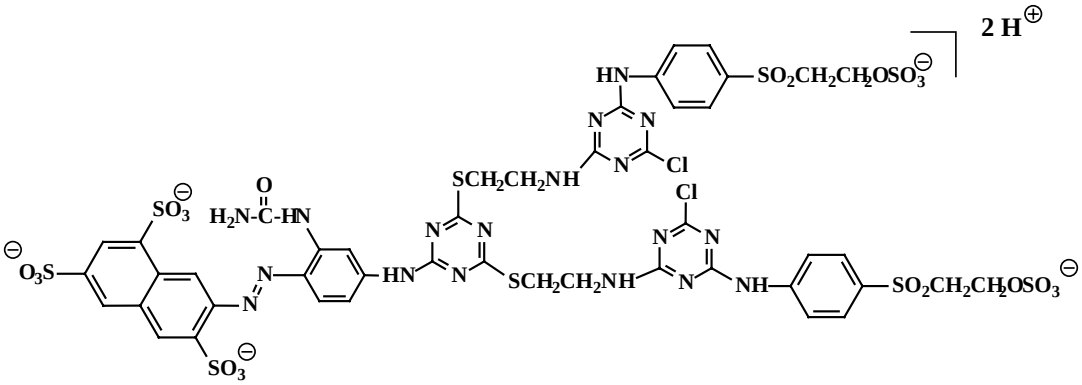


Figure 35. Structure of [M-3H] $^{3-}$ ion of yellow dye (58).

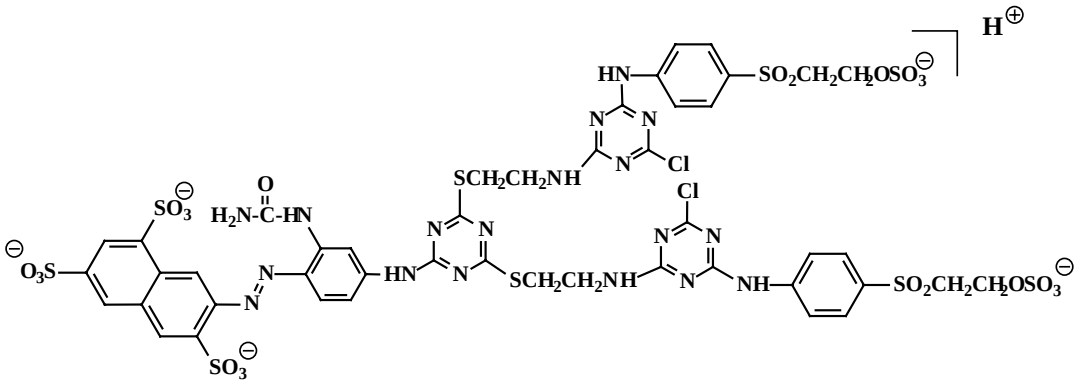
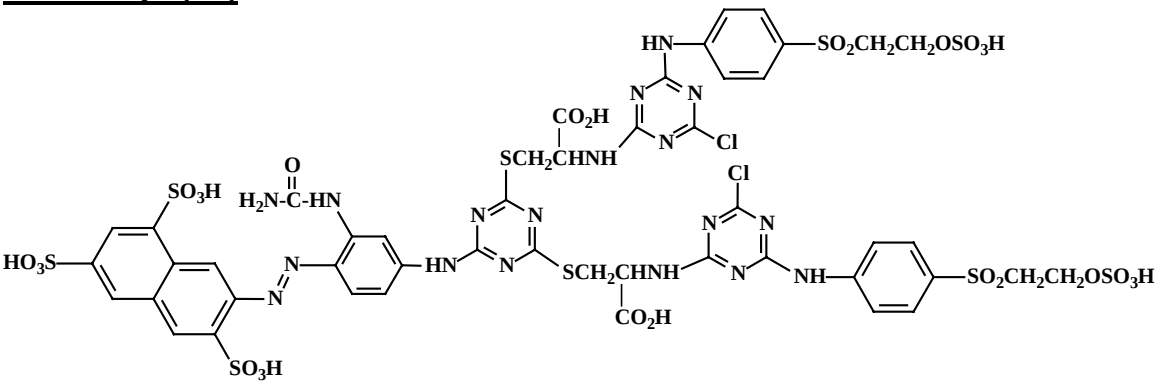


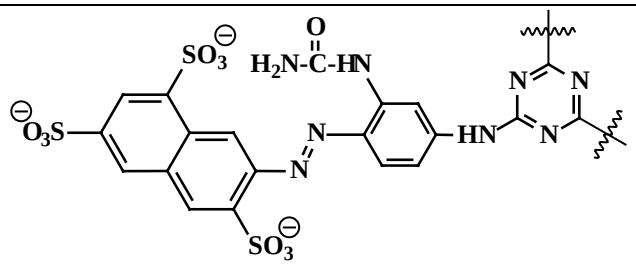
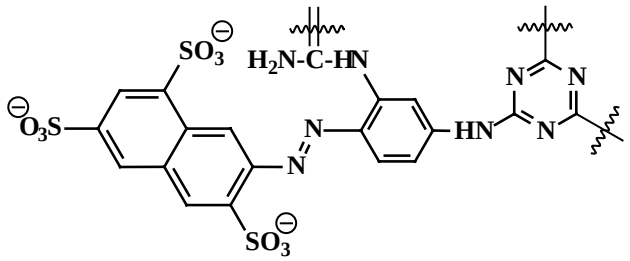
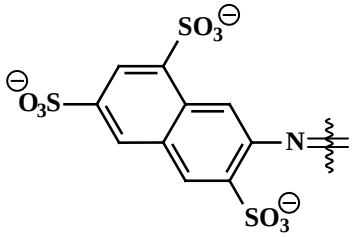
Figure 36. Structure of [M-4H] $^{4-}$ ion of yellow dye (58).

Yellow Dye (61)

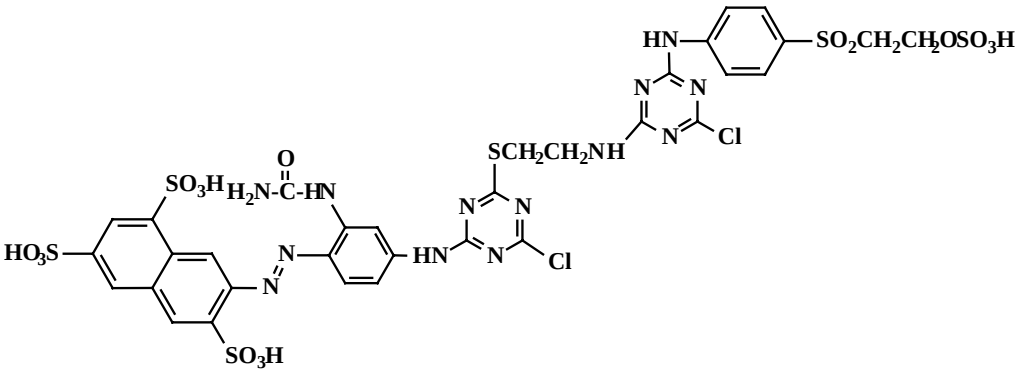


Yellow dye (61) has MW = 1648, based on the formula $C_{48}H_{44}Cl_2N_{18}O_{26}S_9$. The peak observed at m/z = 617 probably arose from cleavage of the triazine-cysteine linkage (F1). Peaks were also observed at m/z = 601 (F2) and m/z = 378 (F3), which would correspond to the structures shown in Table 5.

Table 5. Fragment ions corresponding to signals from ESI-MS analysis of yellow dye (61).

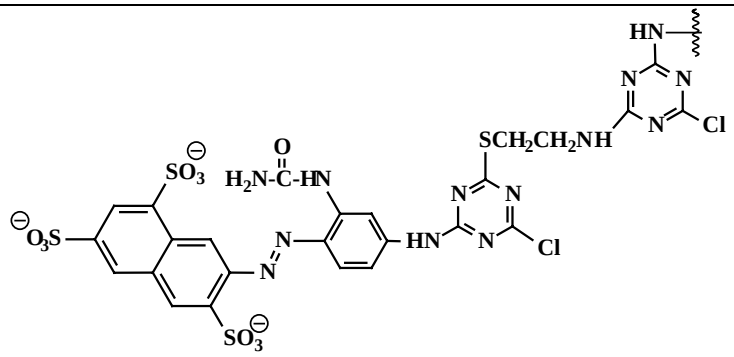
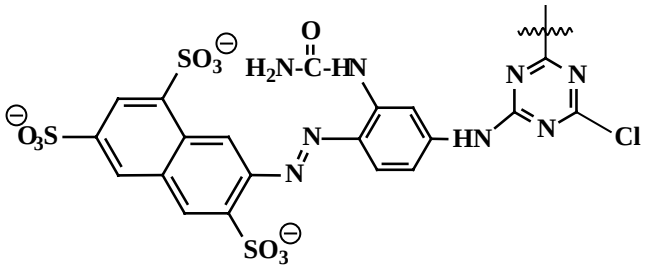
Fragment ions	Structure	m/z	Relative Intensity
F1		617	54
F2		601	100
F3		378	20

Yellow Dye (63)



Yellow dye (63) has MW = 1127, based on the formula $C_{33}H_{29}Cl_2N_{23}O_{16}S_6$. With the loss of 2 H^+ ions, a peak corresponding to an $[M-2H]^{2-}$ ion at m/z = 563 (Figure 37). Similarly, the loss of 3 H^+ ions gave a peak corresponding to an $[M-3H]^{3-}$ ion at m/z= 375 (Figure 38). The peak observed at m/z = 861 (F4) would correspond to the structure shown in Table 6. The peak observed at m/z = 655 may arise from cleavage at the triazine-cysteamine linkage (F5).

Table 6. Fragment ions corresponding to signals from ESI-MS analysis of yellow dye (63).

Fragment ion	Structure	m/z	Relative Intensity
$[M-2H]^{2-}$	Figure 37	563	15
$[M-3H]^{3-}$	Figure 38	375	14
F4		861	10
F5		655	28

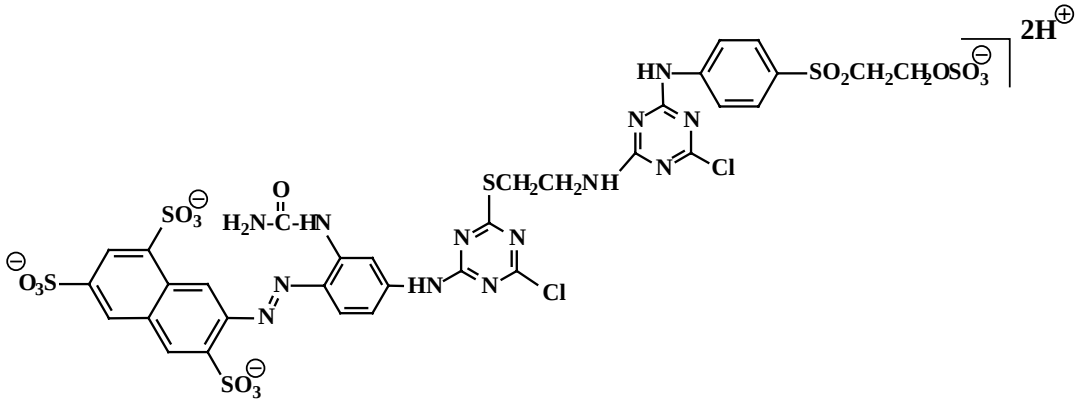


Figure 37. Structure of [M-2H] $^{2-}$ ion of yellow dye (63).

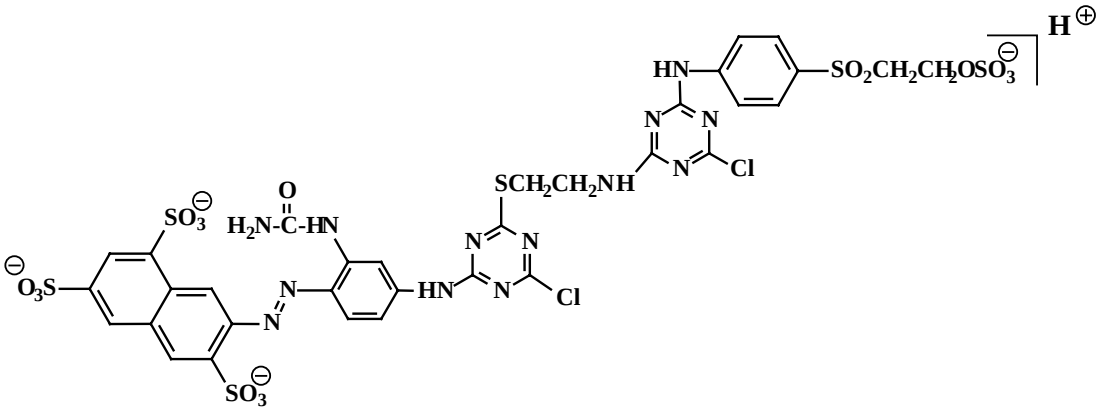
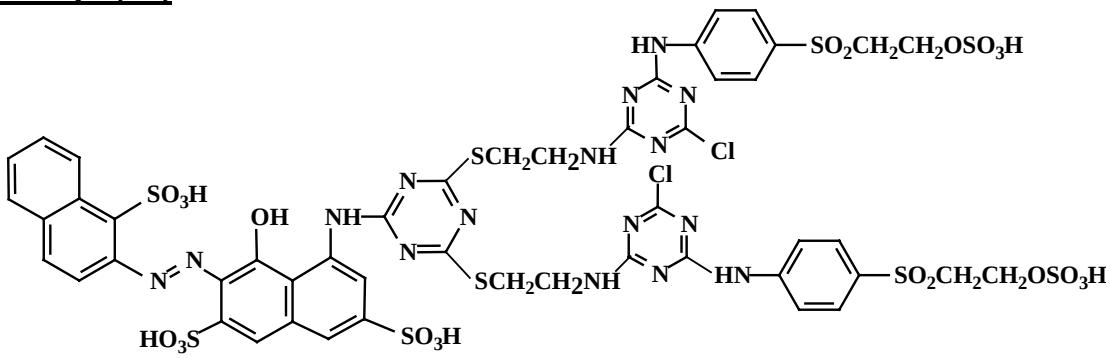


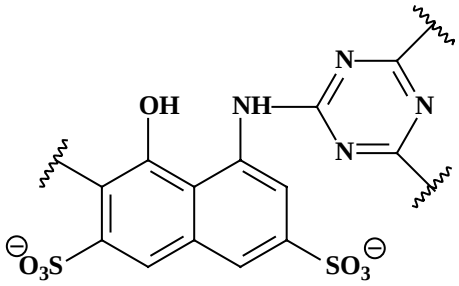
Figure 38. Structure of [M-3H] $^{3-}$ ion of yellow dye (63).

<u>Red Dye (65)</u>



Red dye (65) has MW = 1568, based on the formula $C_{49}H_{44}Cl_2N_{16}O_{22}S_9$. The loss of 2 H^+ ions gave a peak corresponding to an $[M-2H]^{2-}$ ion at m/z = 783 (Figure 39). Similarly, the loss of 3 H^+ ions gave a peak corresponding to an $[M-3H]^{3-}$ ion at m/z = 521 (Figure 40). The peak observed at m/z = 396 may be due to cleavage at triazine-cysteamine linkage (F6), as shown in Table 7.

Table 7. Fragment ions corresponding to signals from ESI-MS analysis of red dye (65).

Fragment ion	Structure	m/z	Relative Intensity
$[M-2H]^{2-}$	Figure 39	783	16
$[M-3H]^{3-}$	Figure 40	521	44
F6		396	18

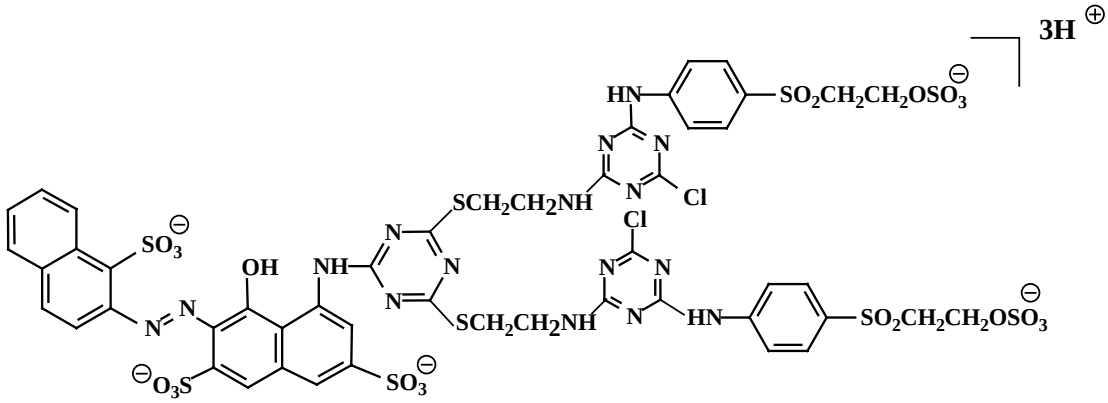


Figure 39. Structure of $[M-2H]^{2-}$ ion of type 1 red dye (65).

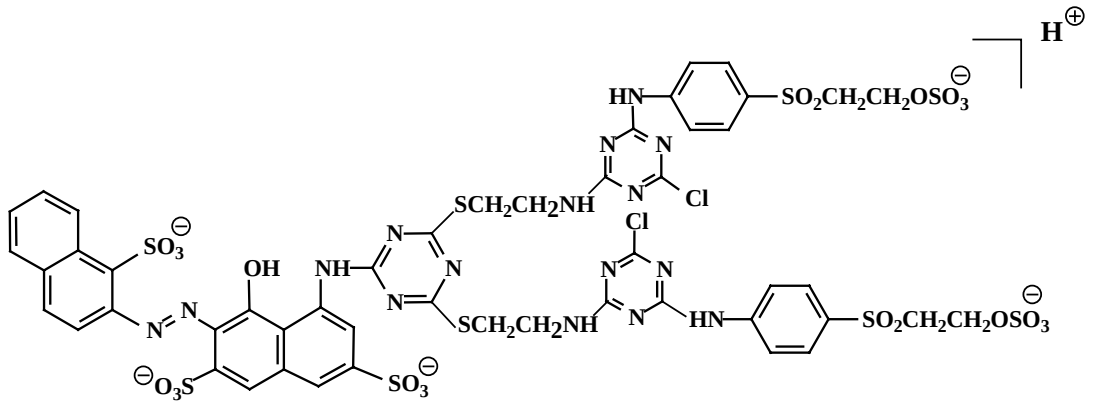
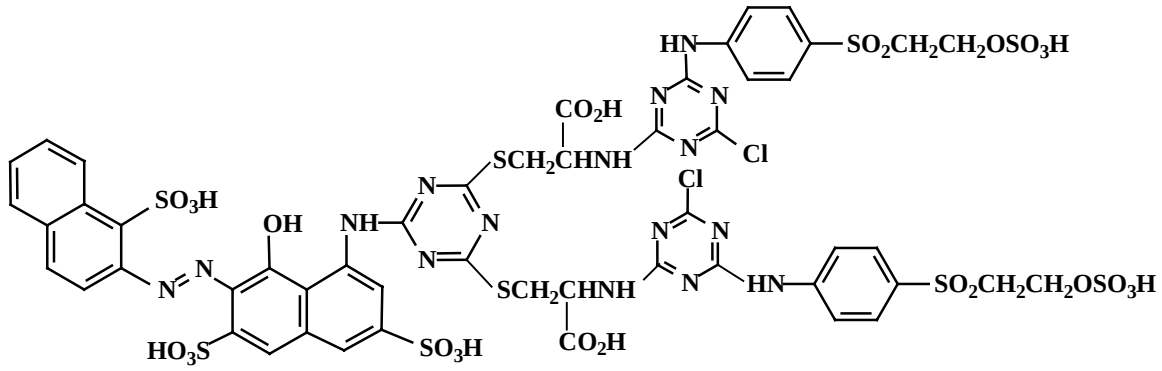


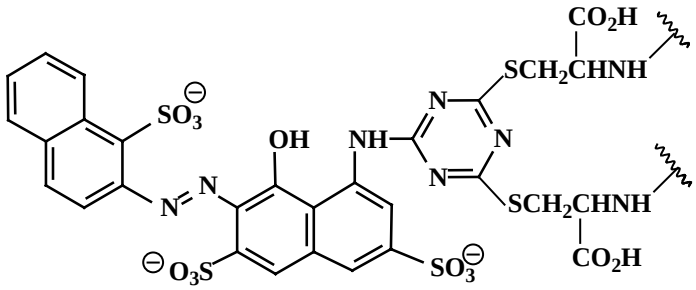
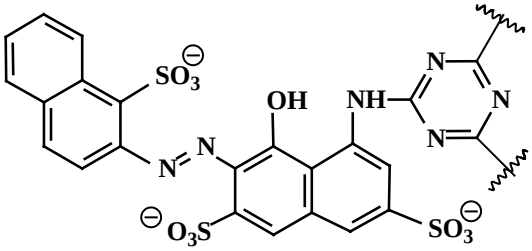
Figure 40. Structure of [M-3H] $^{3-}$ ion of red dye (65).

<u>Red Dye (67)</u>



Red dye (67) has MW = 1656, based on the formula $C_{51}H_{44}Cl_2N_{16}O_{26}S_9$. The loss of 2 H^+ ions gave a peak corresponding to an [M-2H] $^{2-}$ ion at m/z = 827 (Figure 41). The peak observed at m/z =896 (F7) and m/z = 630 (F8) would correspond to the structures shown in Table 8.

Table 8. Fragment ions corresponding to signals from ESI-MS analysis of red dye (67).

Fragment ion	Structure	m/z	Relative Intensity
$[M-2H]^{2-}$	Figure 41	827	40
F7		896	24
F8		601	85

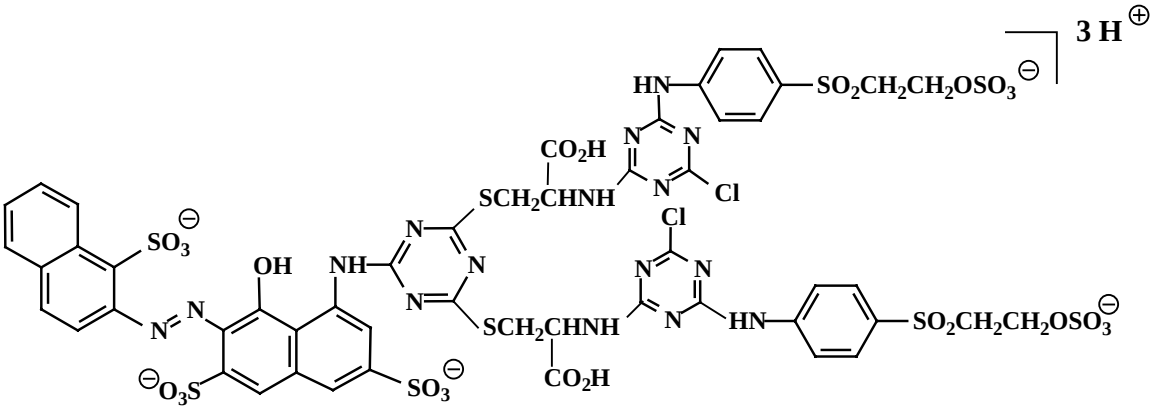
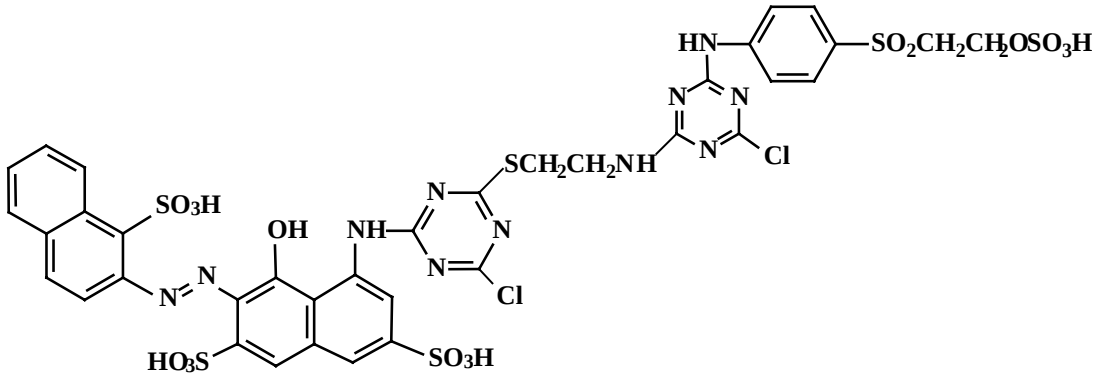


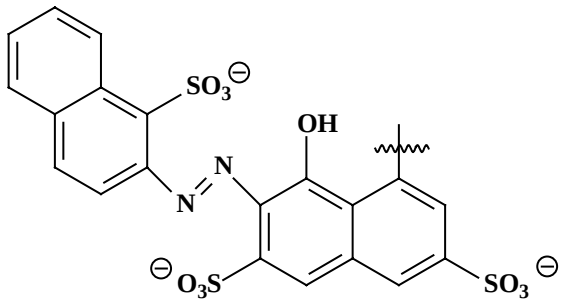
Figure 41. Structure of $[M-2H]^{2-}$ ion of red dye (67).

Red Dye (69)



Red dye (69) has MW = 1135, based on the formula $C_{33}H_{29}Cl_2N_{13}O_{16}S_6$. The loss of 2 H^+ ions gave a peak corresponding to $[M-2H]^{2-}$ ion at m/z = 567 (Figure 42) and the loss of 4 H^+ ions gave a peak corresponding to $[M-4H]^{4-}$ ion at m/z =282 (Figure 43). The peak observed at m/z = 536 could correspond to (F9) in Table 9.

Table 9. Fragment ions corresponding to signals from ESI-MS analysis of red dye (69).

Fragment ion	Structure	m/z	Relative Intensity
$[M-2H]^{2-}$	Figure 42	567	40
$[M-3H]^{4-}$	Figure 43	282	14
F9		536	24

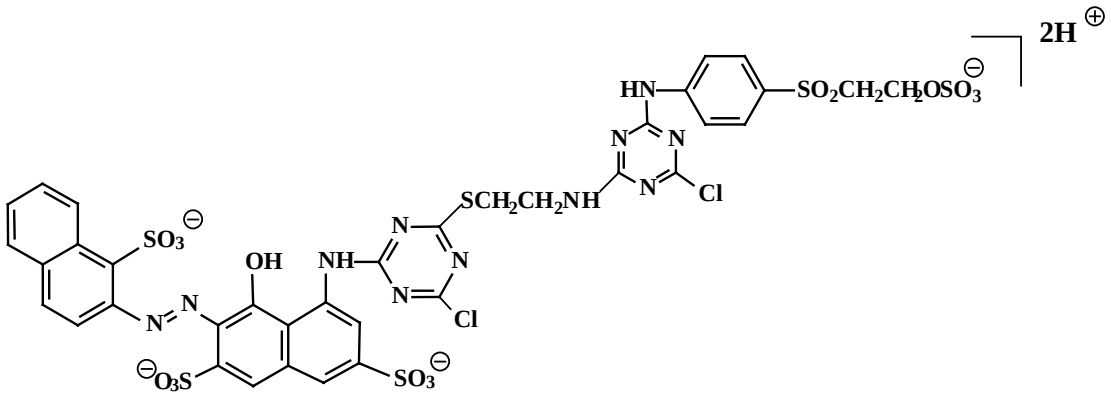


Figure 42. Structure of [M-2H] $^{2-}$ ion of red dye (69).

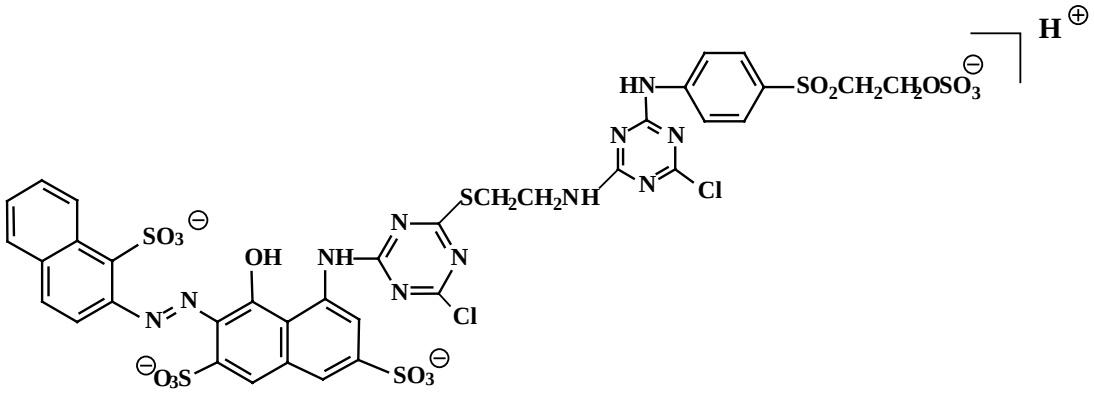
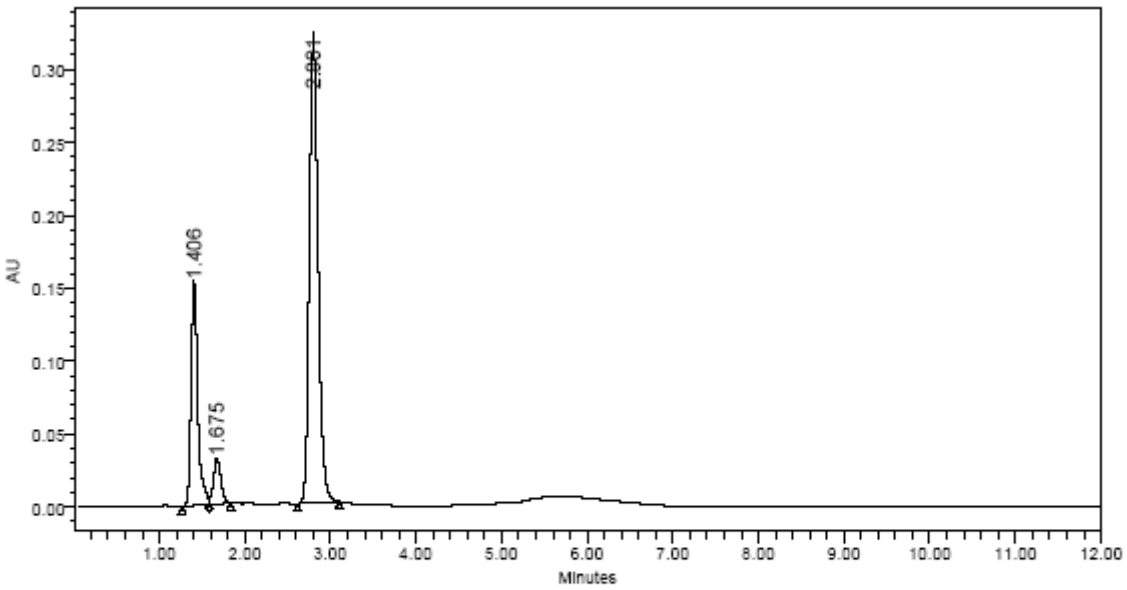


Figure 43. Structure of [M-2H] $^{4-}$ ion of red dye (69).

3. HPLC Analysis

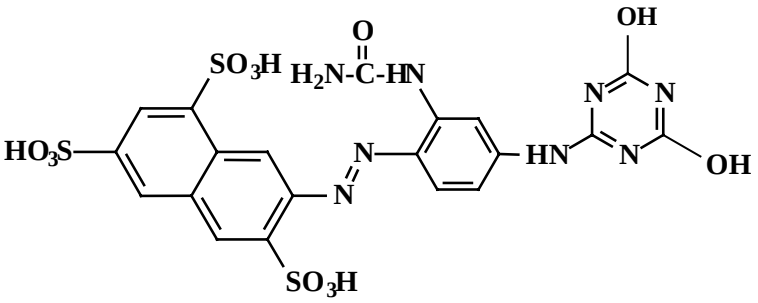
The six new heterobifunctional reactive dyes and corresponding commercial dyes were analyzed using HPLC on a reverse phase column. The results are shown in Figure 44-57. The chromatograms of starting commercial dyes indicate that each was at least 70% active dye, with ~20% hydrolyzed form also present. Comparing the chromatograms of the heterobifunctional reactive dyes with the starting commercial dyes indicated that the starting commercial dyes were fully utilized in farming heterobifunctional dyes. The chromatograms of the new dyes also indicated that they have a dominant component, along with a number of small impurities.



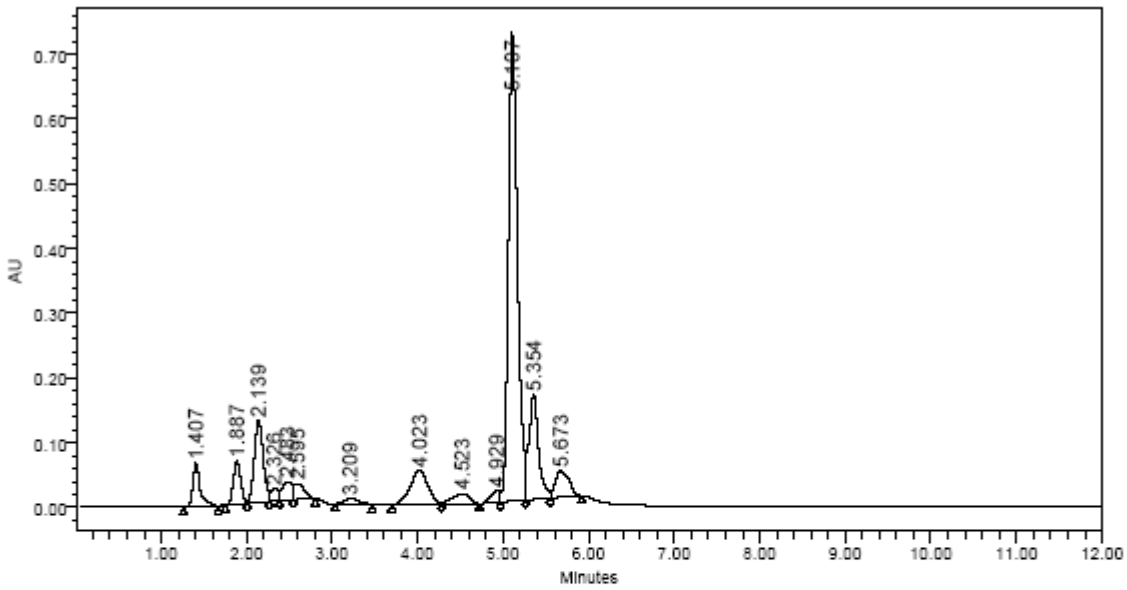
	RT	Area	% Area	Height
1	1.406	813810	24.71	153825
2	1.675	190658	5.79	31761
3	2.801	2288762	69.50	321325

Figure 44. HPLC chromatogram for commercial yellow dye (51).

The reactive form of commercial yellow dye (51) is 70% of the sample and has a retention time of 2.8 min the peak eluting at 1.4 min is probably a hydrolyzed structure, such as structure (70).



(70)



	RT	Area	% Area	Height
1	1.407	381120	3.61	66789
2	1.887	404491	3.83	67990
3	2.139	931788	8.82	127469
4	2.326	120539	1.14	19507
5	2.483	231355	2.19	28353
6	2.595	196475	1.86	23836
7	3.209	106439	1.01	8290
8	4.023	747480	7.08	52205
9	4.523	216012	2.04	15972

	RT	Area	% Area	Height
10	4.929	129058	1.22	17824
11	5.107	5385649	50.98	728288
12	5.354	1259304	11.92	161404
13	5.673	454847	4.31	41943

Figure 45. HPLC chromatogram for yellow dye (58).

This chromatogram has principle peaks at 5.1 and 5.4 min with smaller but significant peaks at 4.0 and 2.1 min. The major peak (51%) corresponds to one of several possible reactive forms (Figure 46), with the method of synthesis suggesting structure (58) as most likely. The peak with 12% peak area could be structure (72).

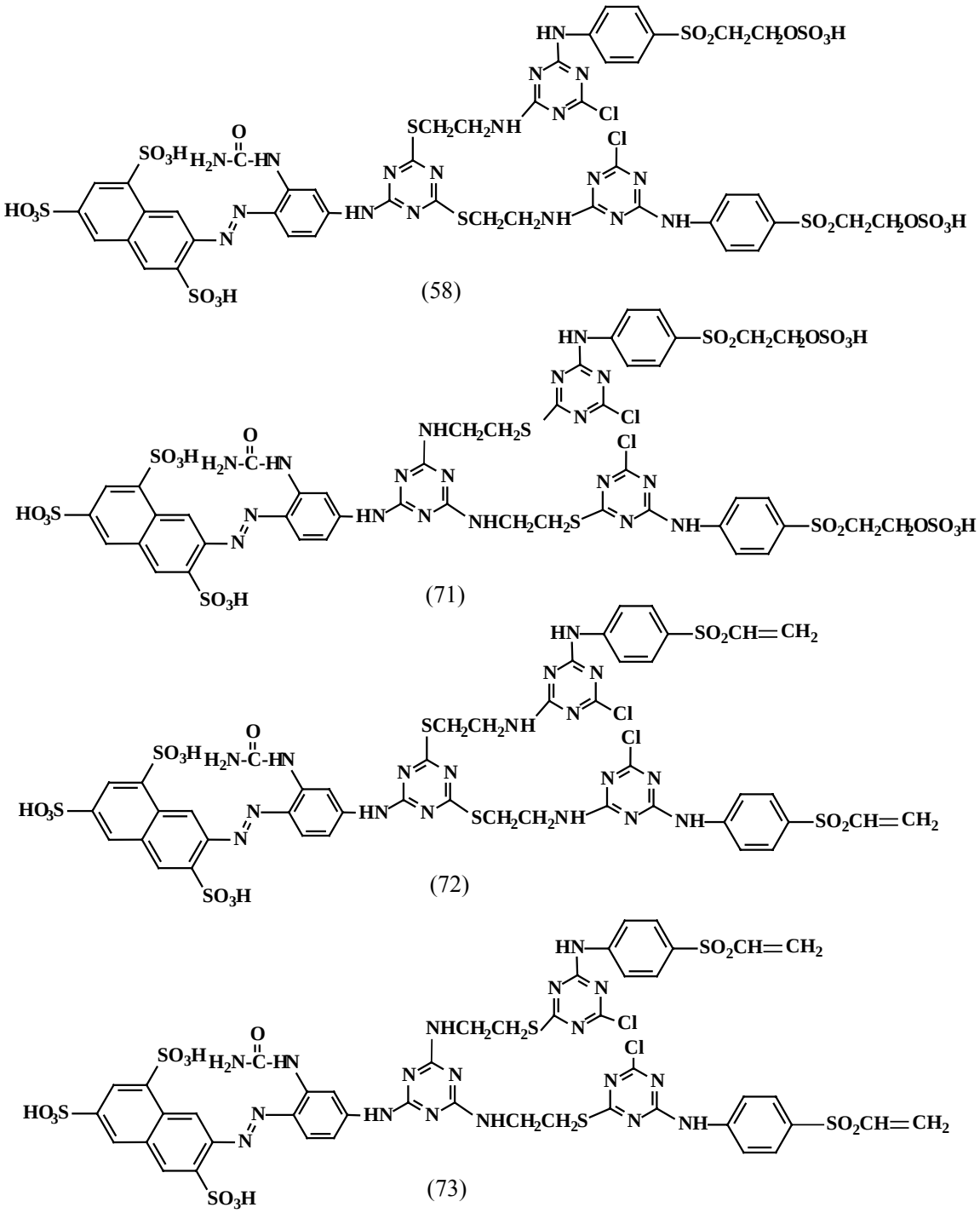
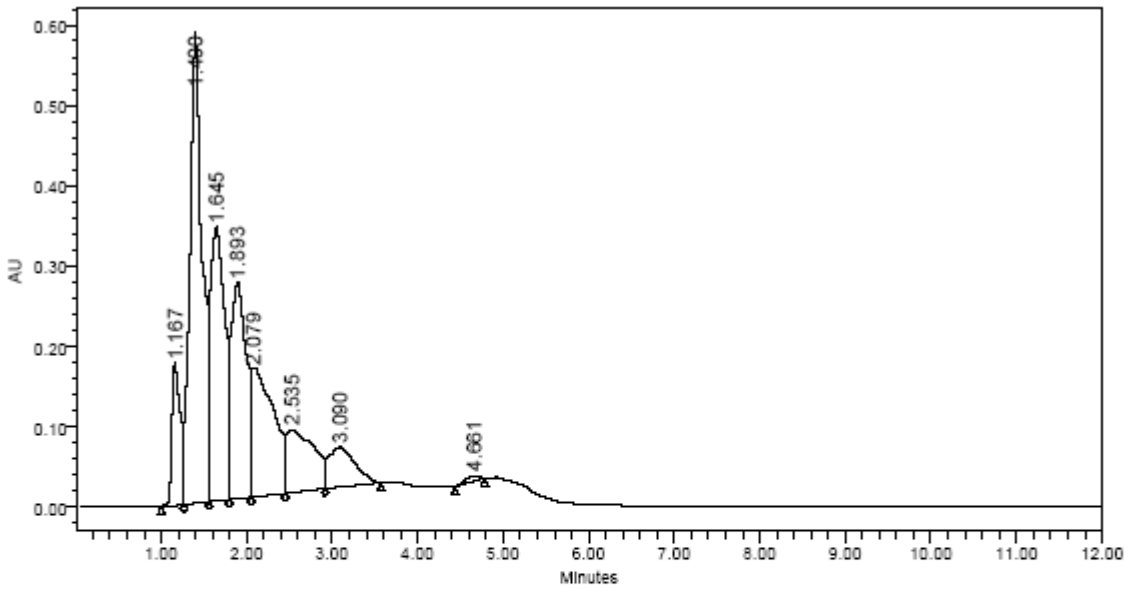


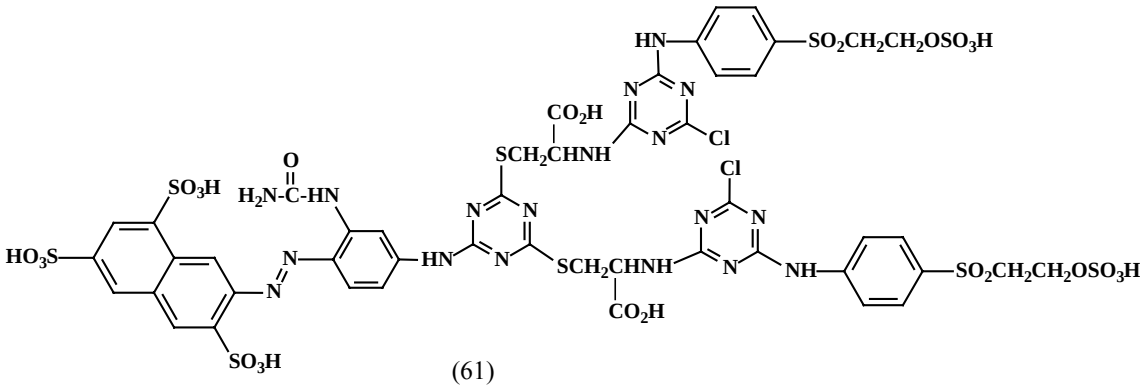
Figure 46. Possible structures for reactive forms of type 1 yellow dye.



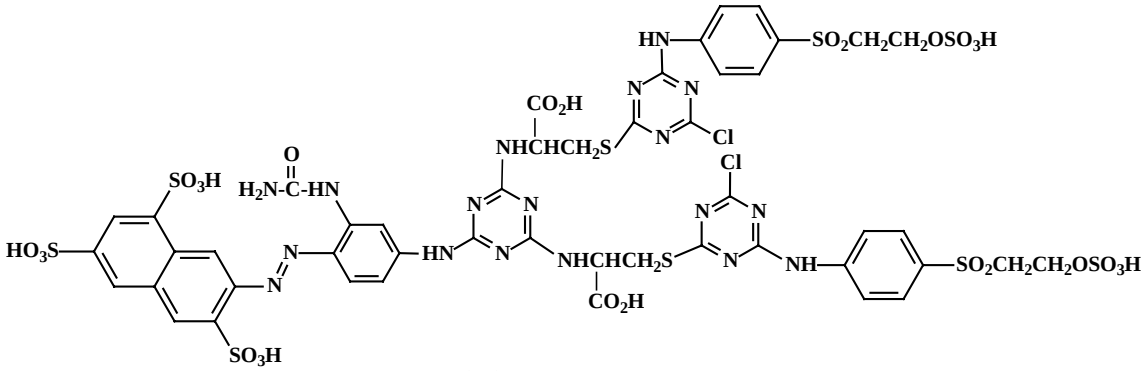
	RT	Area	% Area	Height
1	1.167	1229559	6.11	176621
2	1.400	5708313	28.38	582897
3	1.645	4131681	20.54	342024
4	1.893	3261437	16.22	270948
5	2.079	2890065	14.37	160002
6	2.535	1740562	8.65	78196
7	3.090	1074278	5.34	49350
8	4.661	75768	0.38	6719

Figure 47. HPLC chromatogram for yellow dye (61).

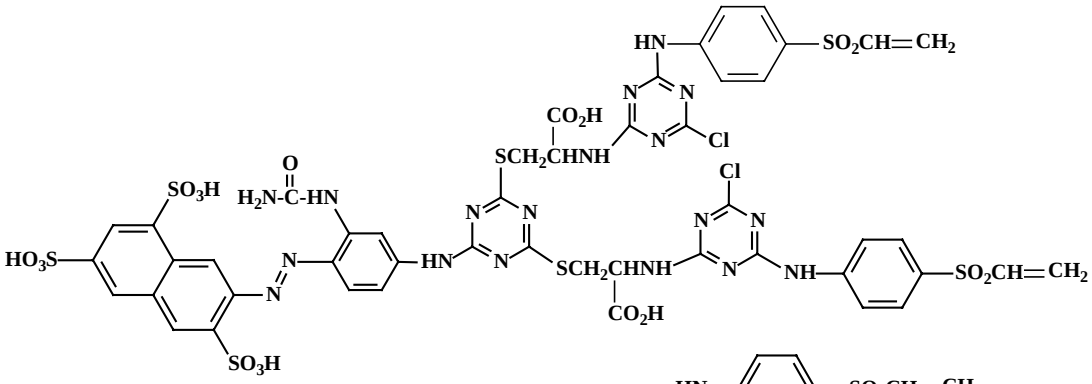
The presence of a $–CO_2H$ moiety in the linking group led to a more complicate product mixture, with 4 components in the 14-28% peak area range. Two other peaks were observed in the 6-8% peak area range. Structures consistent with these observations are shown in Figure 48.



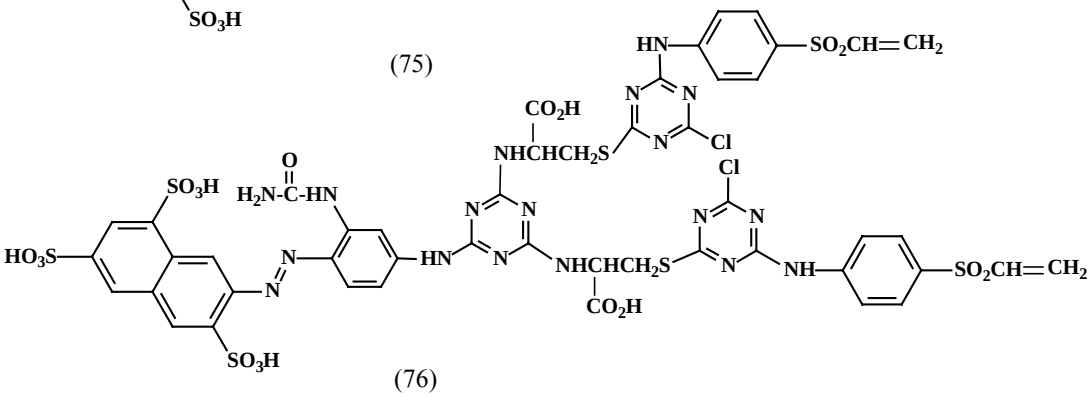
(61)



(74)

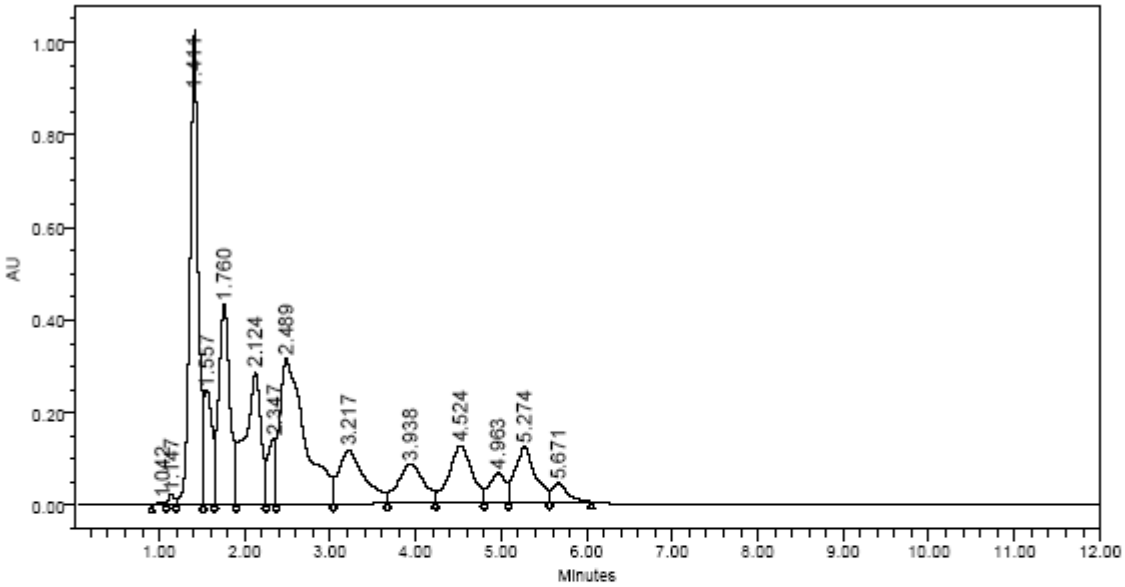


(75)



(76)

Figure 48. Possible structures for reactive forms of type 2 yellow dye.

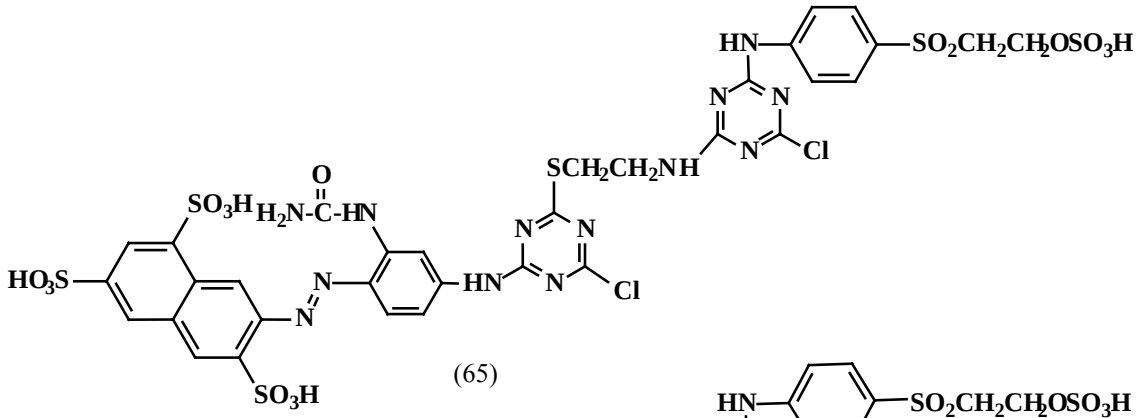


	RT	Area	% Area	Height
1	1.042	40492	0.12	7462
2	1.147	112487	0.34	23220
3	1.411	6799831	20.35	1019453
4	1.557	1686965	5.05	249727
5	1.760	3992240	11.95	436111
6	2.124	3688619	11.04	287624
7	2.347	874867	2.62	141013
8	2.489	6433554	19.25	314671
9	3.217	2463154	7.37	115790

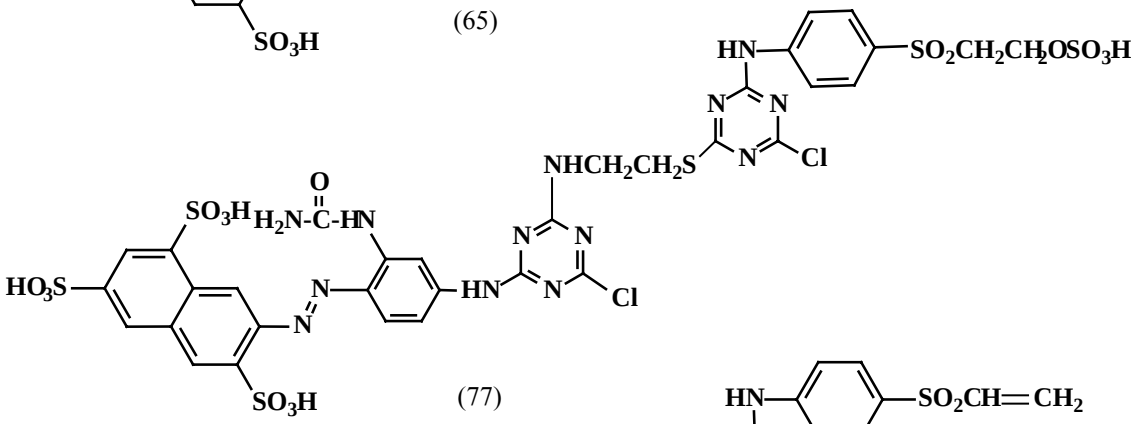
	RT	Area	% Area	Height
10	3.938	1741361	5.21	83852
11	4.524	2298014	6.88	122980
12	4.963	829562	2.48	63678
13	5.274	1960566	5.87	119922
14	5.671	497059	1.49	39887

Figure 49. HPLC chromatogram for yellow dye (63).

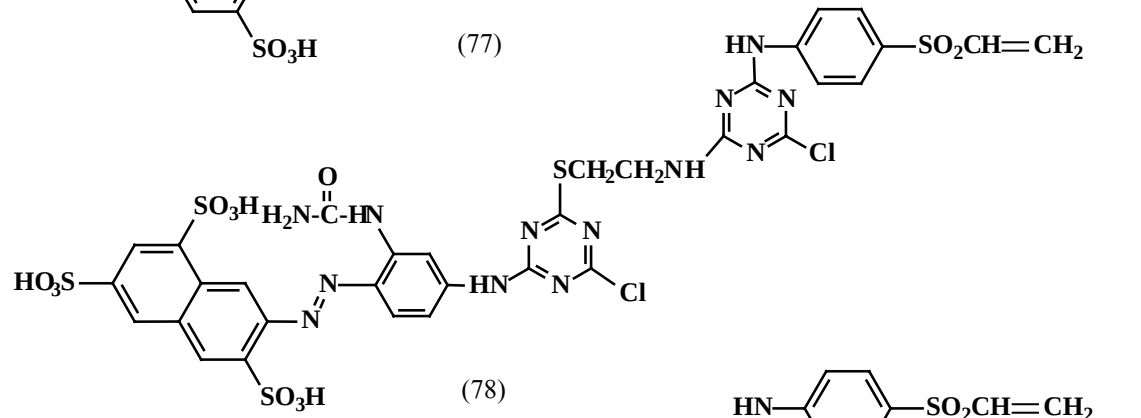
Like the previous chromatogram, this one has 4 significant peaks, two with ~20% peak area and two that are half this size. In addition, this chromatogram shows that the most intense peak eluted at 1.4 min. A peak of comparable peak area eluted at 2.5 min. Figure 50 shows the possible reactive forms for type 3 yellow dye.



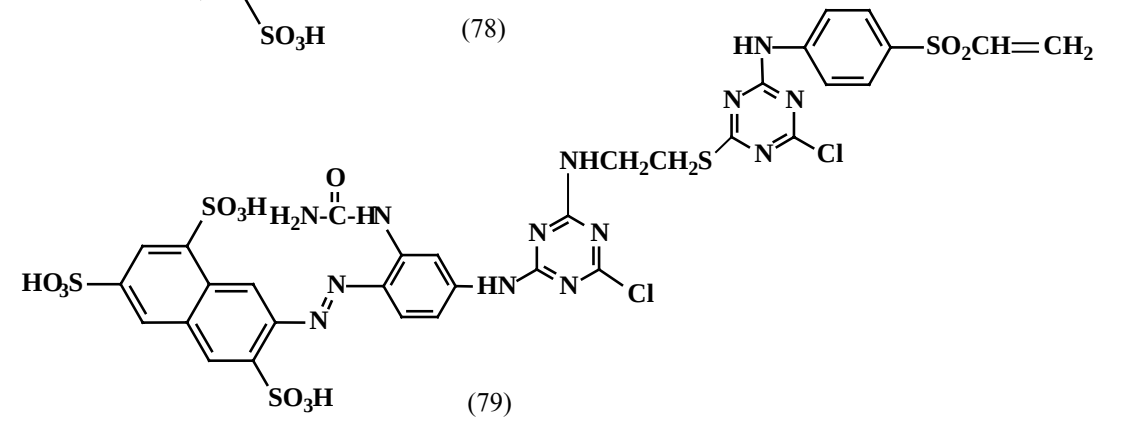
(65)



(77)

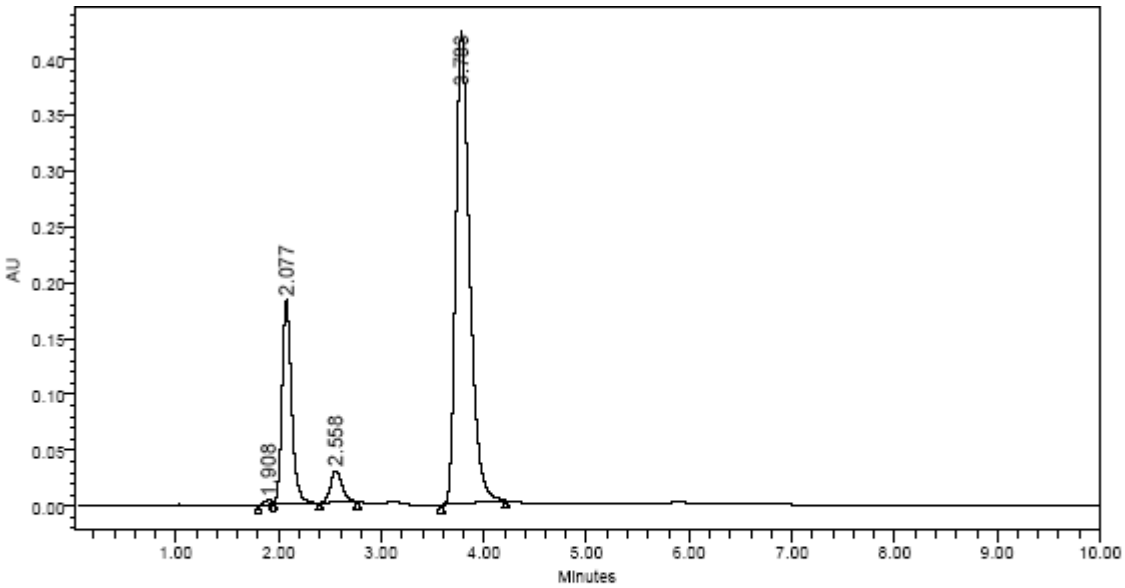


(78)



(79)

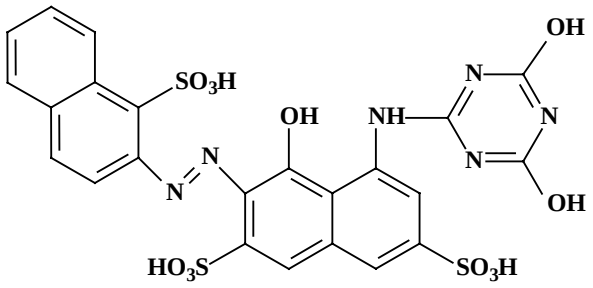
Figure 50. Possible structures for reactive forms of type 3 yellow dye.



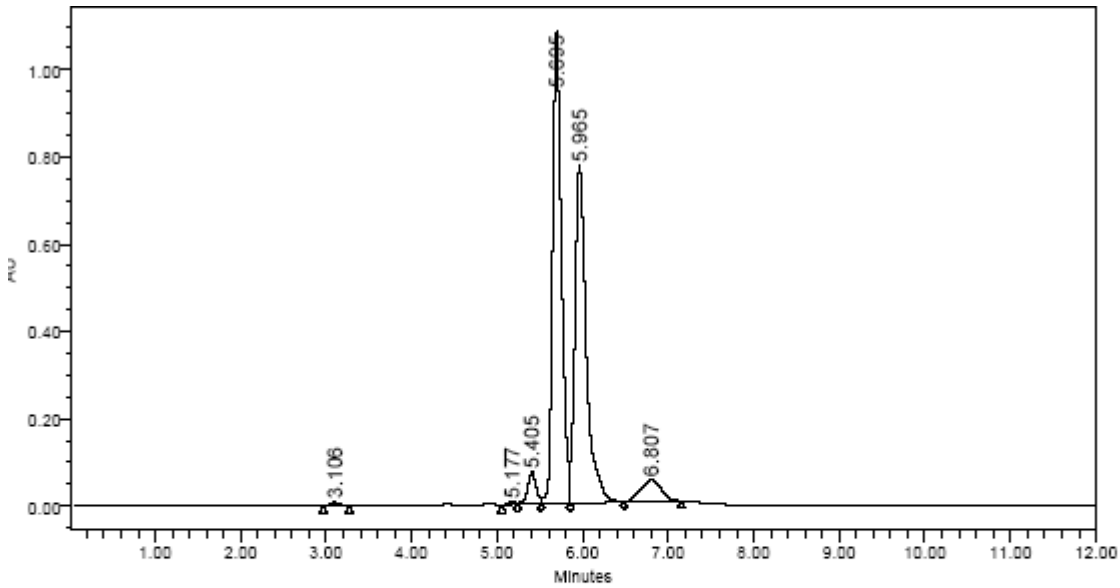
	RT	Area	% Area	Height
1	1.908	21576	0.40	4627
2	2.077	1185407	21.85	183402
3	2.558	222490	4.10	28571
4	3.783	3996232	73.65	422387

Figure 51. HPLC chromatogram for commercial red dye (52).

This chromatogram has major peaks at 3.8 and 2.1 min, with the one at 3.8 min being three-fourths of the sample and corresponding to the active dye form. The peak at 2.1 min is probably due to hydrolyzed dye, such as structure (80).



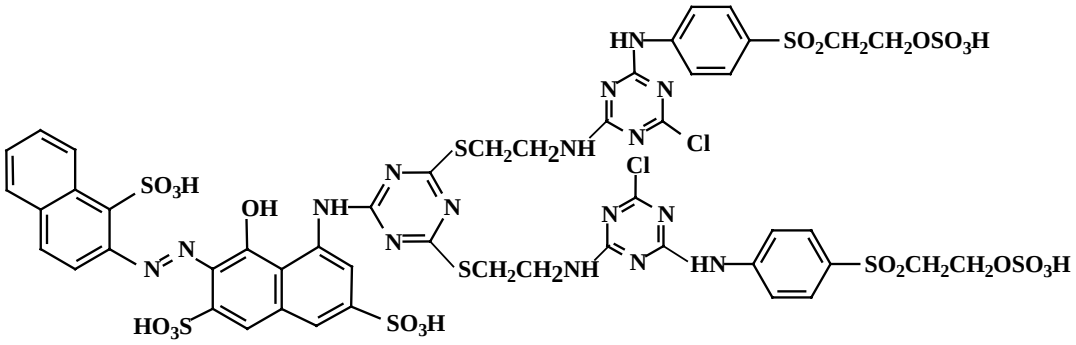
(80)



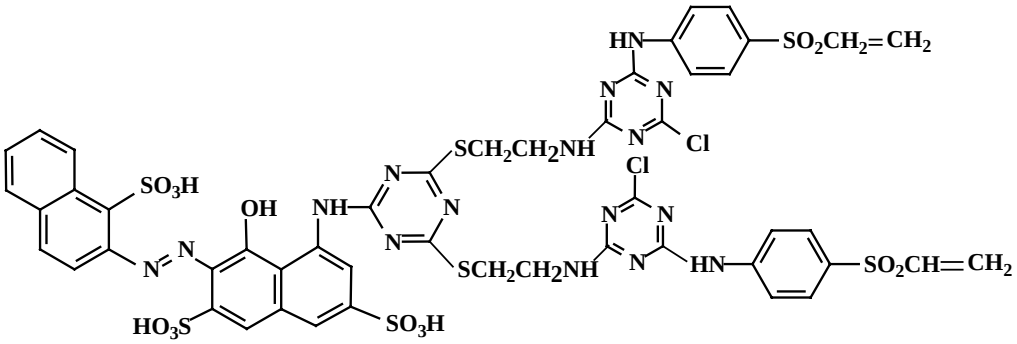
	RT	Area	% Area	Height
1	3.106	59489	0.36	7547
2	5.177	33767	0.21	5430
3	5.405	525093	3.21	73948
4	5.695	7788511	47.62	1084162
5	5.965	7094098	43.38	774066
6	6.807	853296	5.22	51161

Figure 52. HPLC chromatogram for red dye (65).

This chromatogram shows twin peaks in the 5.7-6.0 min region, both of which would correspond to reactive forms of the target dyes (see Figure 53). Very little, if any hydrolyzed dye is present.

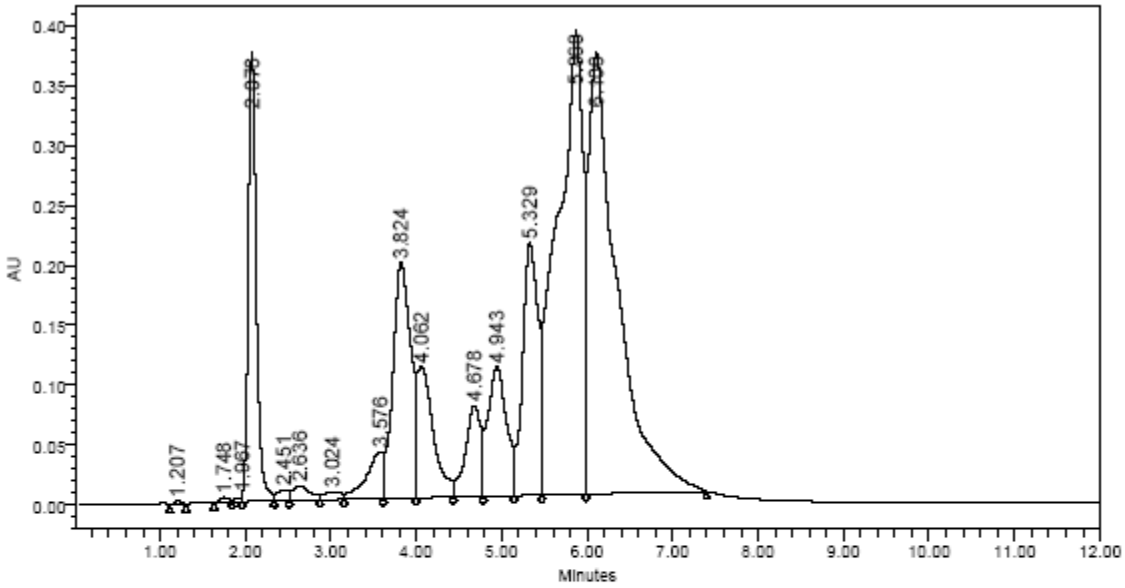


(65)



(81)

Figure 53. Possible structures for reactive forms of the twin peaks in the 5.7-6.0 min region.

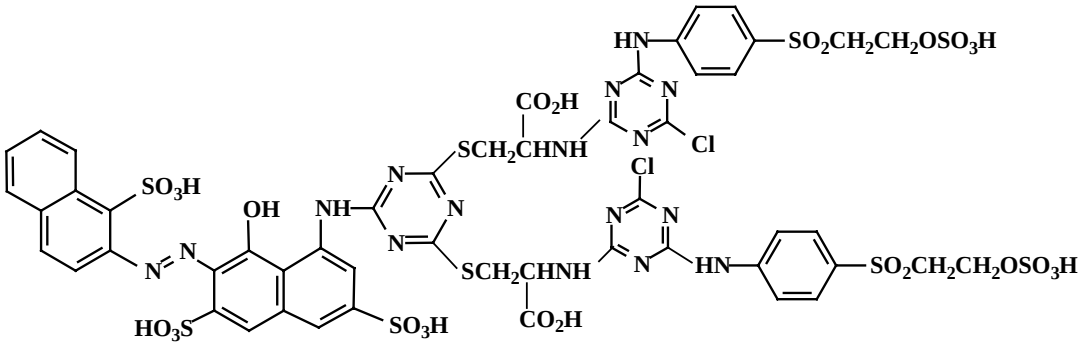


	RT	Area	% Area	Height
1	1.207	18270	0.06	3307
2	1.748	24977	0.08	3989
3	1.967	20878	0.07	5264
4	2.078	2431454	8.16	375802
5	2.451	85660	0.29	8826
6	2.636	178062	0.60	12077
7	3.024	96620	0.32	6815
8	3.576	532934	1.79	39231
9	3.824	2876206	9.65	196764

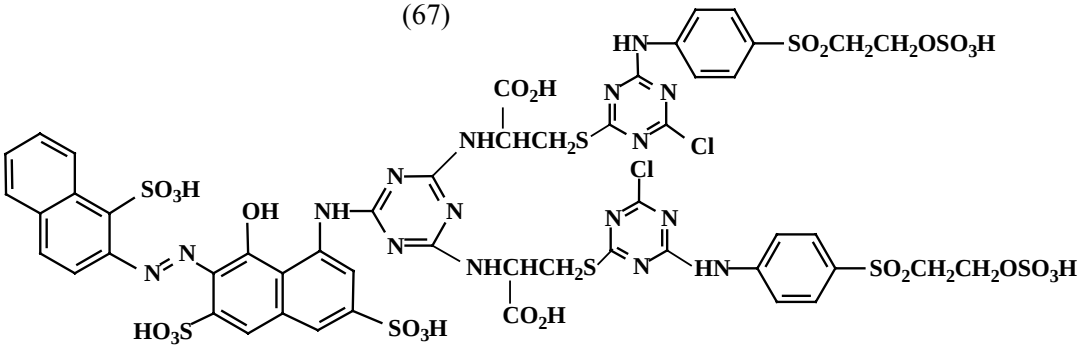
	RT	Area	% Area	Height
10	4.062	1455506	4.88	109422
11	4.678	957668	3.21	76360
12	4.943	1637776	5.49	108716
13	5.329	2641236	8.86	211378
14	5.868	8062974	27.04	387320
15	6.106	8793338	29.49	369544

Figure 54. HPLC chromatogram for red dye (67).

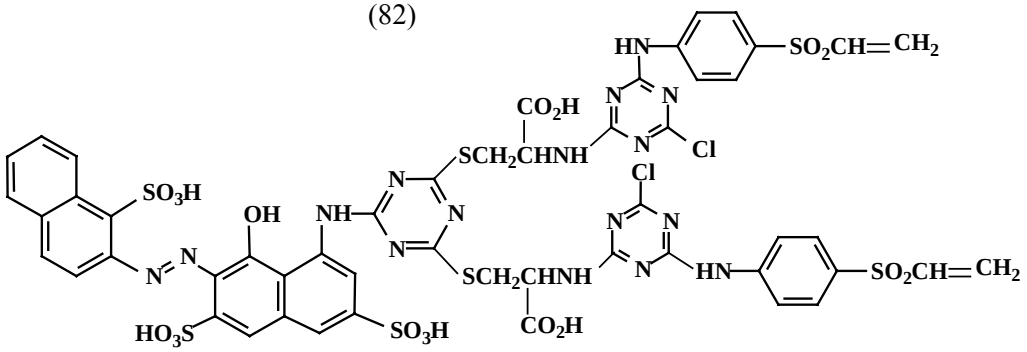
This chromatogram also has twin peaks near the retention time of 6 min. In this case, however, the combined peaks encompass 55% rather than 91% of the total peak area. As observed with the yellow dye, the use of cysteine gave a more complex chromatogram than the previous one involving cysteamine. Figure 55 shows the possible reactive forms for the type 2 red dye.



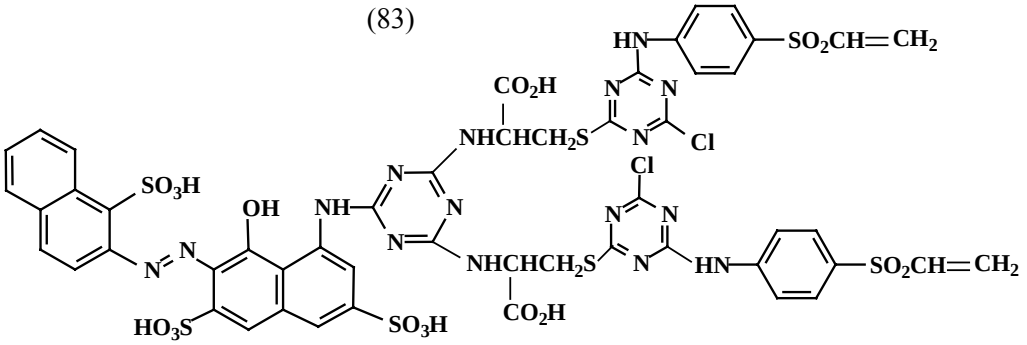
(67)



(82)

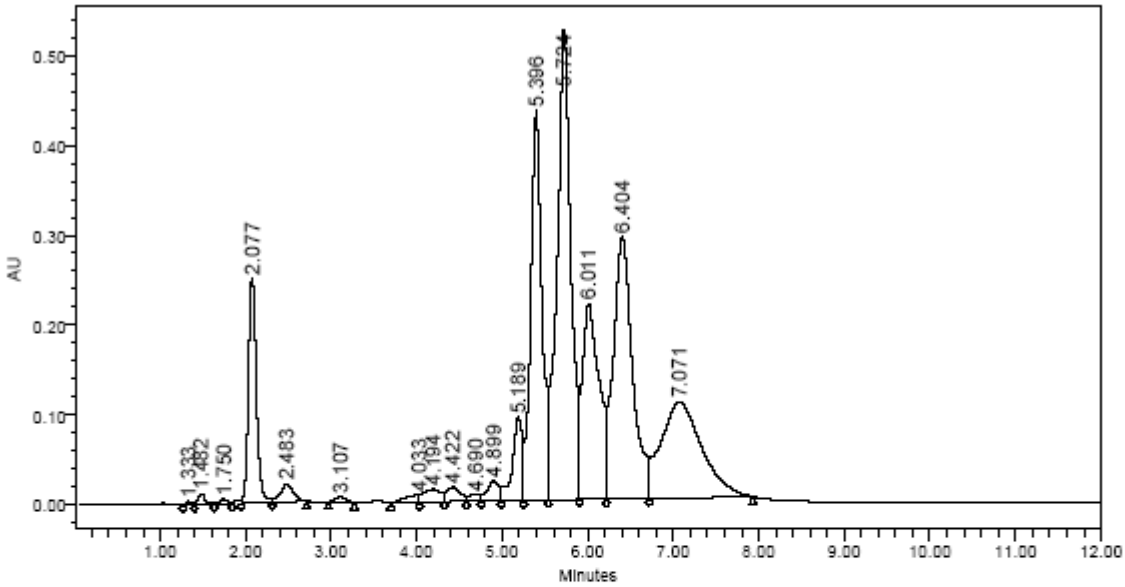


(83)



(84)

Figure 55. Possible structures for reactive forms of type 2 red dye.

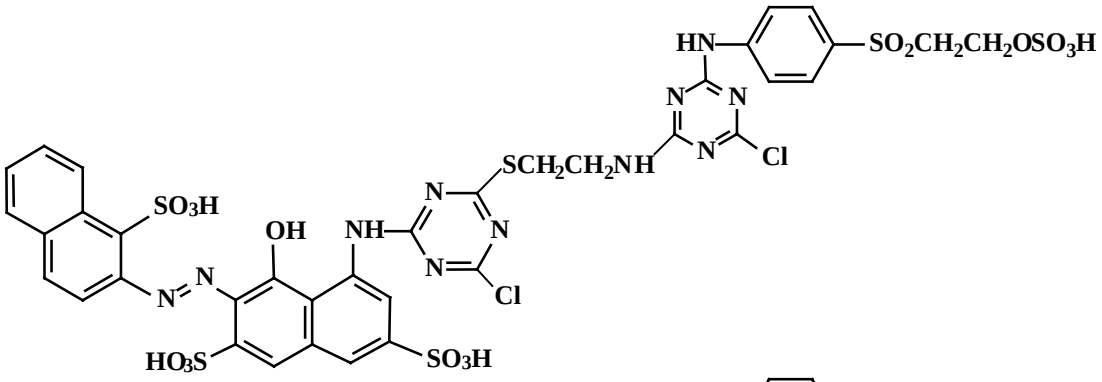


	RT	Area	% Area	Height
1	1.333	17948	0.07	3898
2	1.482	66101	0.27	11887
3	1.750	34693	0.14	5071
4	2.077	1601885	6.55	251301
5	2.483	207086	0.85	20140
6	3.107	45376	0.19	5632
7	4.033	90191	0.37	8371
8	4.194	193868	0.79	13847
9	4.422	178264	0.73	16059

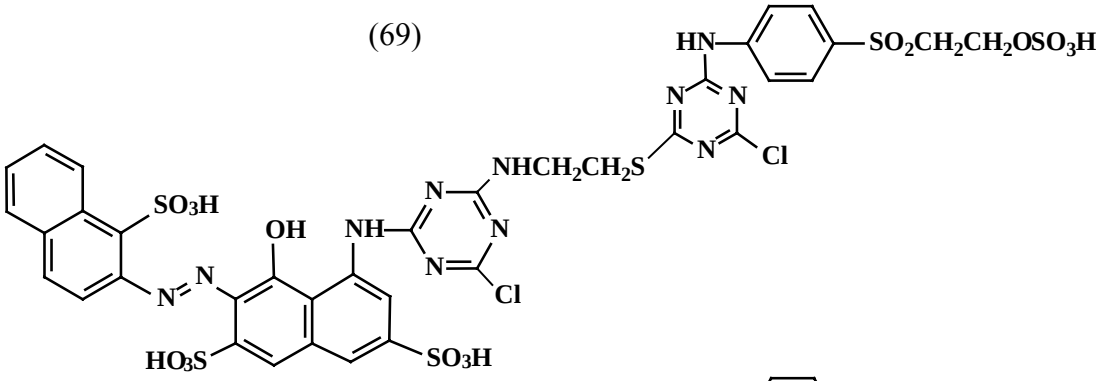
	RT	Area	% Area	Height
10	4.690	71392	0.29	7775
11	4.899	208338	0.85	22278
12	5.189	747730	3.06	92820
13	5.396	3888842	15.91	435444
14	5.724	5972797	24.44	525423
15	6.011	2968768	12.15	218744
16	6.404	4578417	18.73	293342
17	7.071	3567711	14.60	107365

Figure 56. HPLC chromatogram for red dye (69).

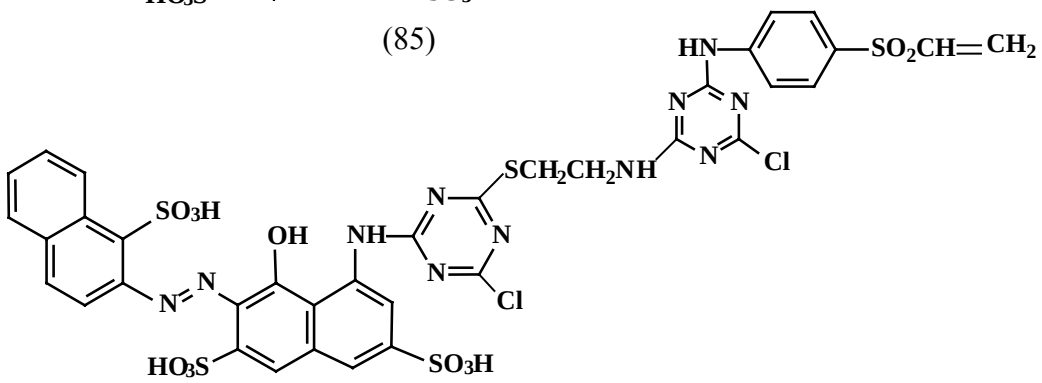
The chromatogram for red dye (69) contains 5 significant peaks in the region of 5.4 – 7.1 min, with peak areas of 12-24%. These peaks could arise from structures shown in Figure 57.



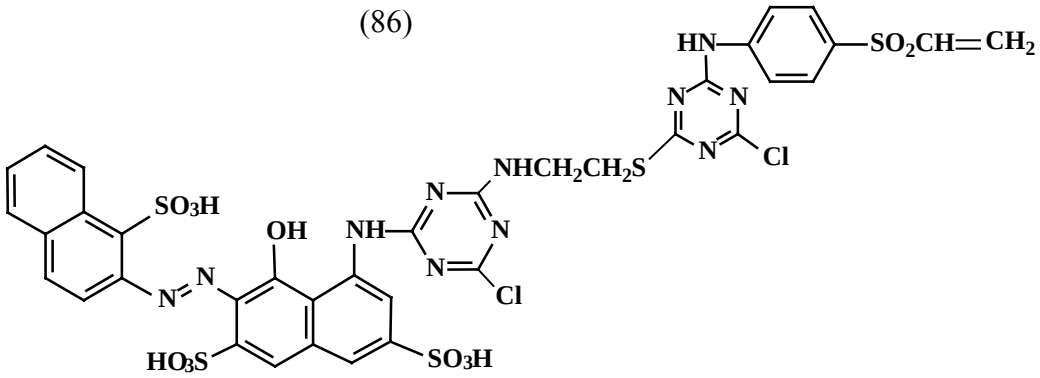
(69)



(85)



(86)



(87)

Figure 57. Possible structures for reactive forms of type 3 red dye.

4. Equilibrium Exhaustion

Equilibrium exhaustion experiments were conducted on the two commercial dyes and six new heterobifunctional reactive dyes. The goal was to determine whether the modified structures had better affinity for cotton and to determine the optimum temperature and salt level for laboratory dyeing studies. The raw data collected from these experiments are given in the Appendix.

Figure 58 show equilibrium exhaustion data for the yellow dyes on cotton using a bath ratio of 40:1 and 1% (owg) dye. The graph obtained from the commercial yellow dye shows that dye affinity increases with salt levels but decreases with increasing temperature and that the optimum temperature is 30 °C. The commercial yellow dye had low affinity at high temperature because increasing temperature caused this small dye to prefer to remain in solution. In other studies involving dyeing at different temperatures it has been shown that the % exhaustion at elevated temperatures can be lower at equilibrium [51].

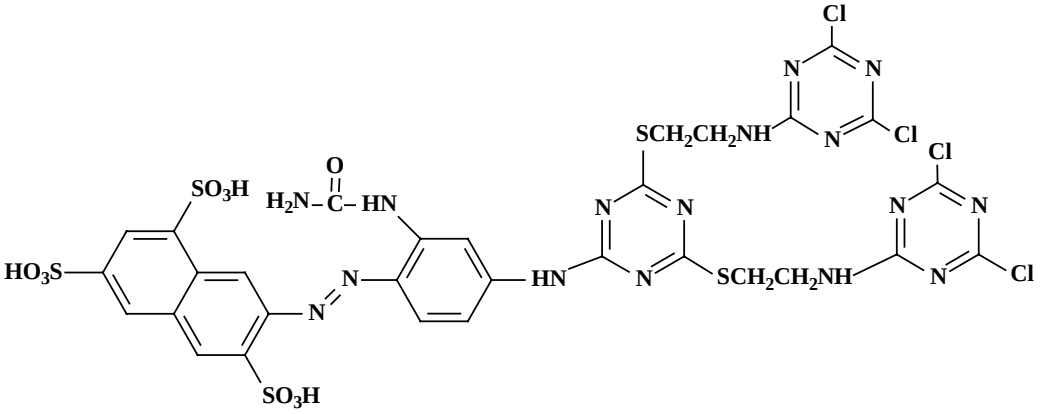
For type 1 yellow dye (58), affinity increases with salt levels but is not affected much by temperature. The optimum temperature is 60 °C. This dye has higher affinity than commercial yellow dye and the highest overall. This is due to the increased molecular size arising from introducing cysteamine and two MCT-VS systems.

Type 2 yellow dye (61) has lower affinity than the commercial dye and lowest overall. This result indicated that using cysteine as the linking group compromises affinity for cotton. It is believed that the presence of a carboxyl group on the linking moiety distorts the geometry of the dye structure, giving a

non-linear shape [28]. The optimum dyeing temperature for the type 2 yellow dye is 30 °C.

Type 3 yellow dye (63) has higher affinity than the commercial dye but lower than the type 1 yellow dye (61). These results indicated that two MCT-VS systems are preferred. The optimum temperature for the type 3 yellow dye (63) is 60 °C.

Comparing results for these heterobifunctional reactive yellow dyes with those obtained from homobifunctional reactive yellow dye (88) [28], which gave the best dyeing performance of the four types of homobifunctional reactive yellow dyes, the outcomes can be summarized as follows:



(88)

1) At 30 °C, type 1 yellow dye (58) has similar % E values to the homobifunctional reactive yellow dye (88) at 0 g/L, 10g/L and 40g/L salt levels, but a slight lower % E value than yellow dye (88) at 70g/L.

2) At 60 °C and 90 °C, the % E values of yellow dye (58) are much higher than those of yellow dye (88) at 40 g/L and 70 g/L salt levels.

3) Type 3 yellow dye (63) has lower %E values than yellow dye (88) at 30 °C and 90 °C. However, the % E values of yellow dye (61) at 60 °C are much higher than those of yellow dye (88) at 90 °C, at 40g/L and 70g/L salt levels.

4) Type 2 yellow dye (61) has lower % E values than yellow dye (88) at all corresponding dyeing conditions.

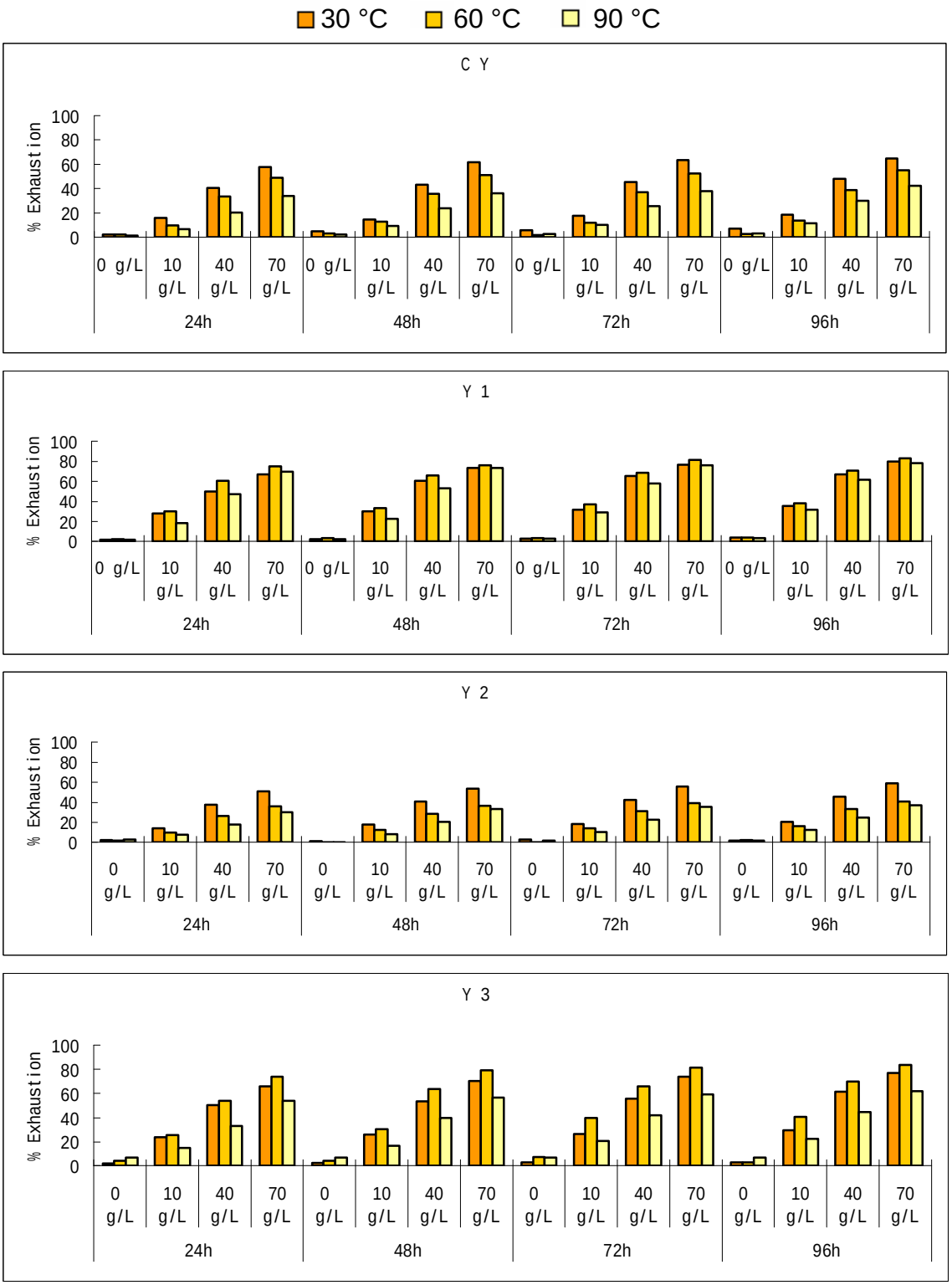


Figure 58. Equilibrium exhaustion data for the yellow dyes (CY = commercial yellow dye, Y1 = type 1 yellow dye, Y2 = type 2 yellow dye, Y3 = type 3 yellow dye) on cotton using a 40:1 LR and 1% (owg) dye concentration.

Figure 59 contains equilibrium exhaustion data for the red dyes on cotton using a bath ratio of 40:1 and 1% dye (owg). For the commercial red dye, affinity increases with salt level but decreases with temperature, and the optimal dyeing temperature is 30 °C.

For type 1 red dye (65), affinity increases with salt levels and temperature. This type heterobifunctional reactive dye has very high molecular weigh (MW = 1568). Dyes with such high molecular weight generally diffuse slowly. As temperature increases the fibers open up, allowing a faster absorption of dye [51]. The optimum dyeing temperature for the type 1 red dye is 90 °C. It has higher affinity than commercial red dye.

Type 2 red dye (67) has lower affinity than commercial red and the lowest overall. This result indicated that using cysteine as the linking group did not provide good affinity for cotton, for the reason indicated for the type 2 yellow dye (67). The optimum dyeing temperature for the type 2 red dye is 30 °C.

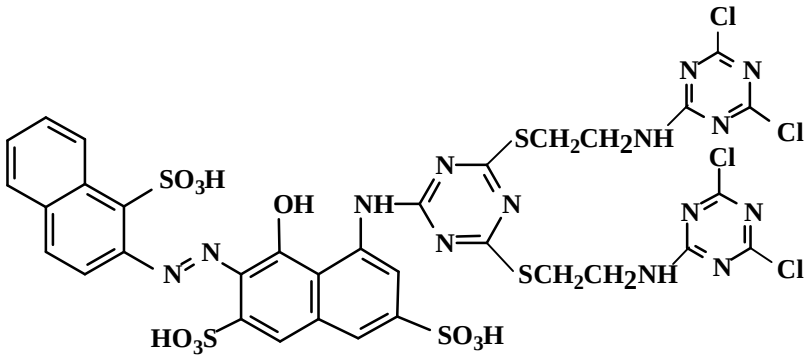
Type 3 red dye (69) has higher affinity than the commercial red dye and is very similar to type 1 red dye (67). These results indicated that bis- MCT/ mono VS systems is preferred. The optimum dyeing temperature for the type 3 red dye (69) is 30 °C.

Comparing the results from these heterobifunctional reactive red dyes with those obtained from homobifunctional reactive red dye (89) [28], which had the best dyeing performance of the four types of homobifunctional reactive red dyes, the outcomes can be summarized as follows:

1) Type1 red dye (65) has lower % E values than red dye (89) at 30 °C, but has higher %E values at 90 °C for all salt levels.

2) Type 3 red dye (69) has lower %E values than red dye (89) at 30 °C and 90 °C. However, the % E values of red dye (69) at 60 °C are similar to those of red dye (89) at 90 °C at all salt levels.

3) Type 2 yellow dye (65) has lower % E value than red dye (89) at all corresponding dyeing conditions.



(89)

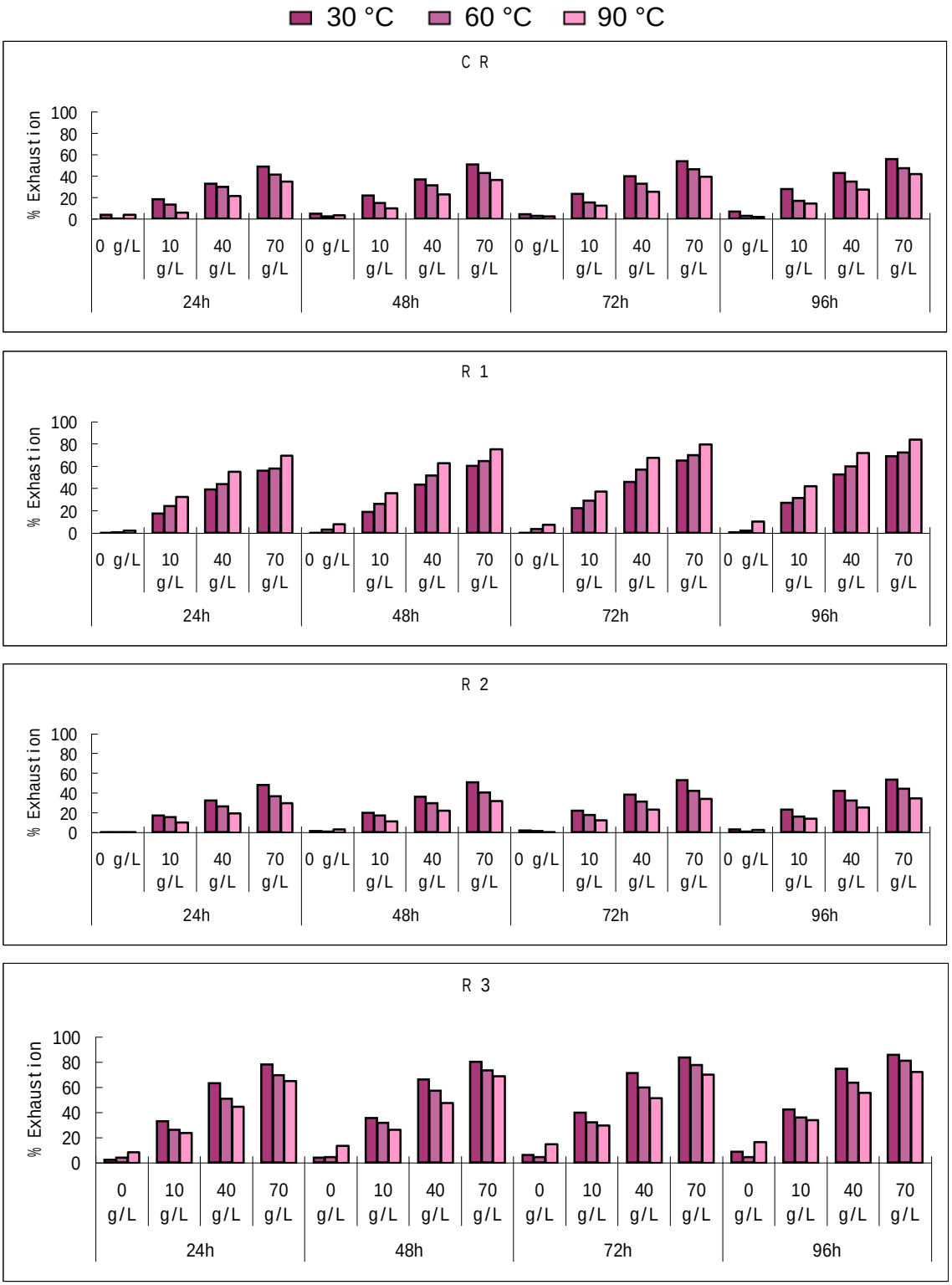


Figure 59. Equilibrium exhaustion data for the red dyes (CR = commercial red dye, R1= type 1 red dye, R2 = type 2 red dye, R3= type 3 red dye) on Cotton Square, using a 40:1 LR and 1% (owg) dye concentration.

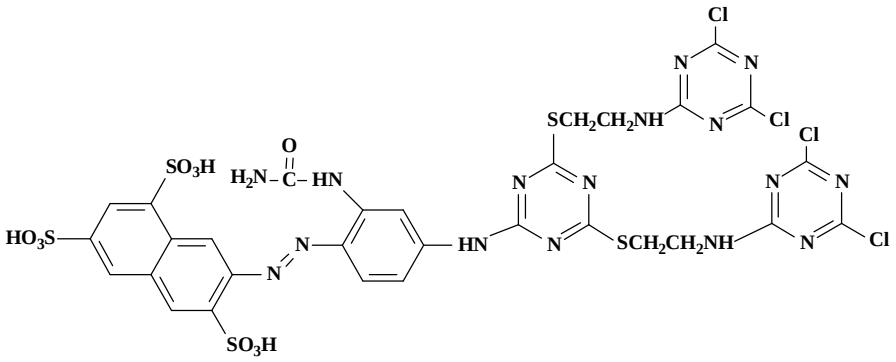
Figures 60 - 62 show the K/S data for cotton fabric dyed with the yellow dyes. For commercial yellow dye, K/S (shade depth) decreases after 48 h. At equilibrium (96h), the K/S at 40g/L is comparable to K/S value at 70g/L. Increasing temperature decreases K/S value.

For type 1 yellow dye (58), increasing temperature does not reduce shade depth. The K/S value decreases after 24 h but begins to increase after 48h. At 60 °C and 90 °C, type 1 yellow dye (58) gives better shade depth than commercial yellow dye but not as good as type 3 yellow dye (63).

Type 2 yellow dye (61) has an extremely low K/S, especially at equilibrium, and not increase after 24 h. It has the lowest K/S value comparing to other yellow dyes.

For type 3 yellow dye (63), K/S value reduces after 24 h. Comparing to type 1 yellow dye, its K/S value is lower at equilibrium but higher at 24, 48 and 72 h stages. Type 3 yellow dye (63) has a higher K/S value than the commercial yellow dye at the corresponding dyeing conditions.

Comparing the K/S data from previous equilibrium exhaustion studies using the homobifunctional reactive yellow dye (88) [28] with those using hetero-bifunctional reactive yellow dyes, the results can be summarized as follows:



(88)

1) K/S values for cotton fabrics dyed using type 1 yellow dye (58) are slightly lower than those obtained using homobifunctional reactive yellow dye (88) at 30 °C and 90 °C. However the K/S value for cotton fabrics dyed using yellow dye (58) at 60 °C are greater than those using yellow dye (88) at 90 °C.

2) K/S values from cotton fabrics dyed using type 3 yellow dye (61) are slightly smaller than those using yellow dye (88) at 30 °C, but greater at 90 °C. K/S data on the cotton fabrics dyed using yellow dye (61) at 60 °C are greater than those using yellow dye (88) at 90 °C.

3) K/S values from cotton fabrics dyed using type 3 yellow dye (63) are lower than those using yellow dye (88) at all comparable dyeing conditions.

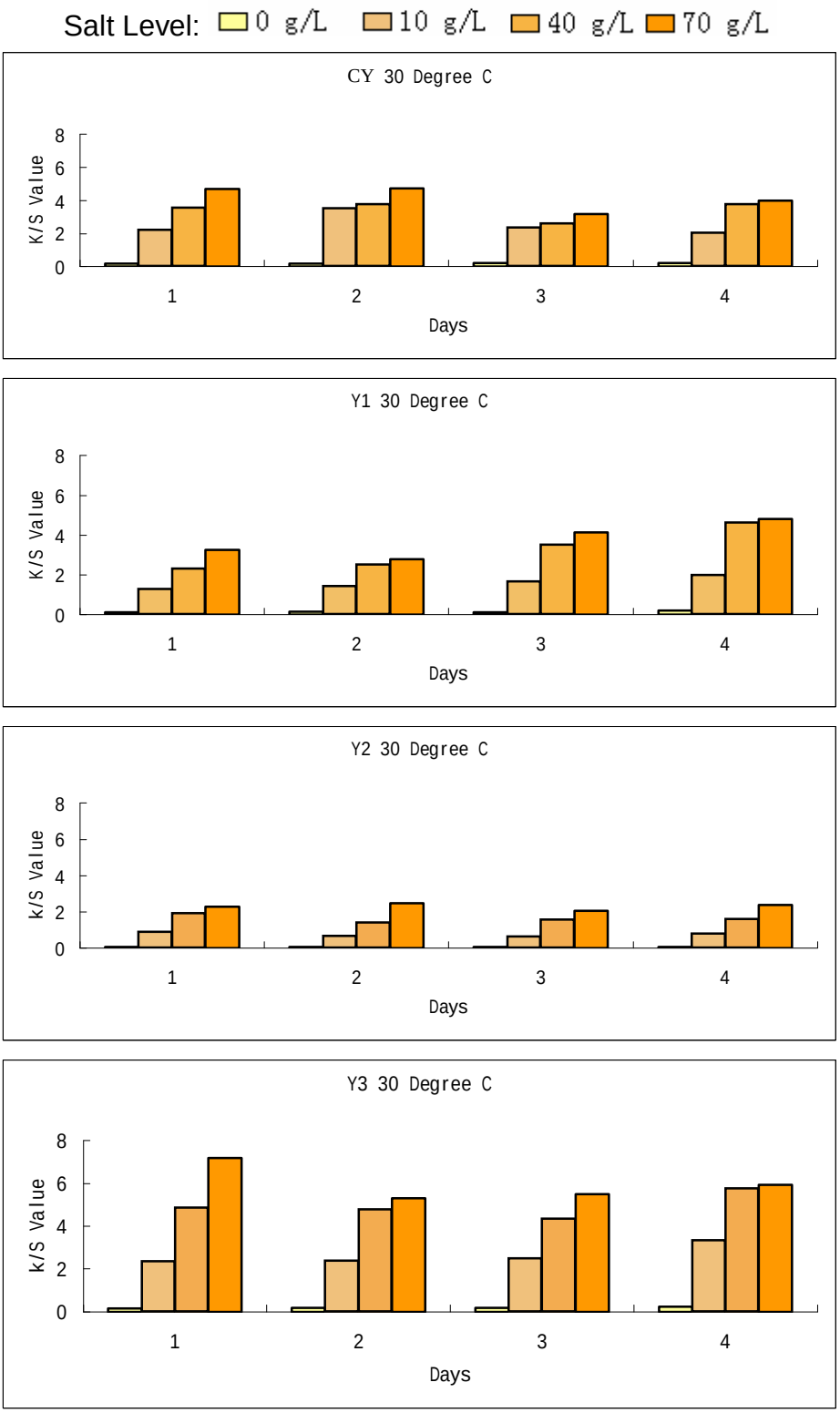


Figure 60. Changes in K/S data from equilibrium exhaustion for the yellow dyes at 30 °C, 40:1 LR and 24 intervals (CY= Commercial yellow, Y1 = type 1 yellow dye, Y2= type 2 yellow dye, Y3= type 3 yellow dye).

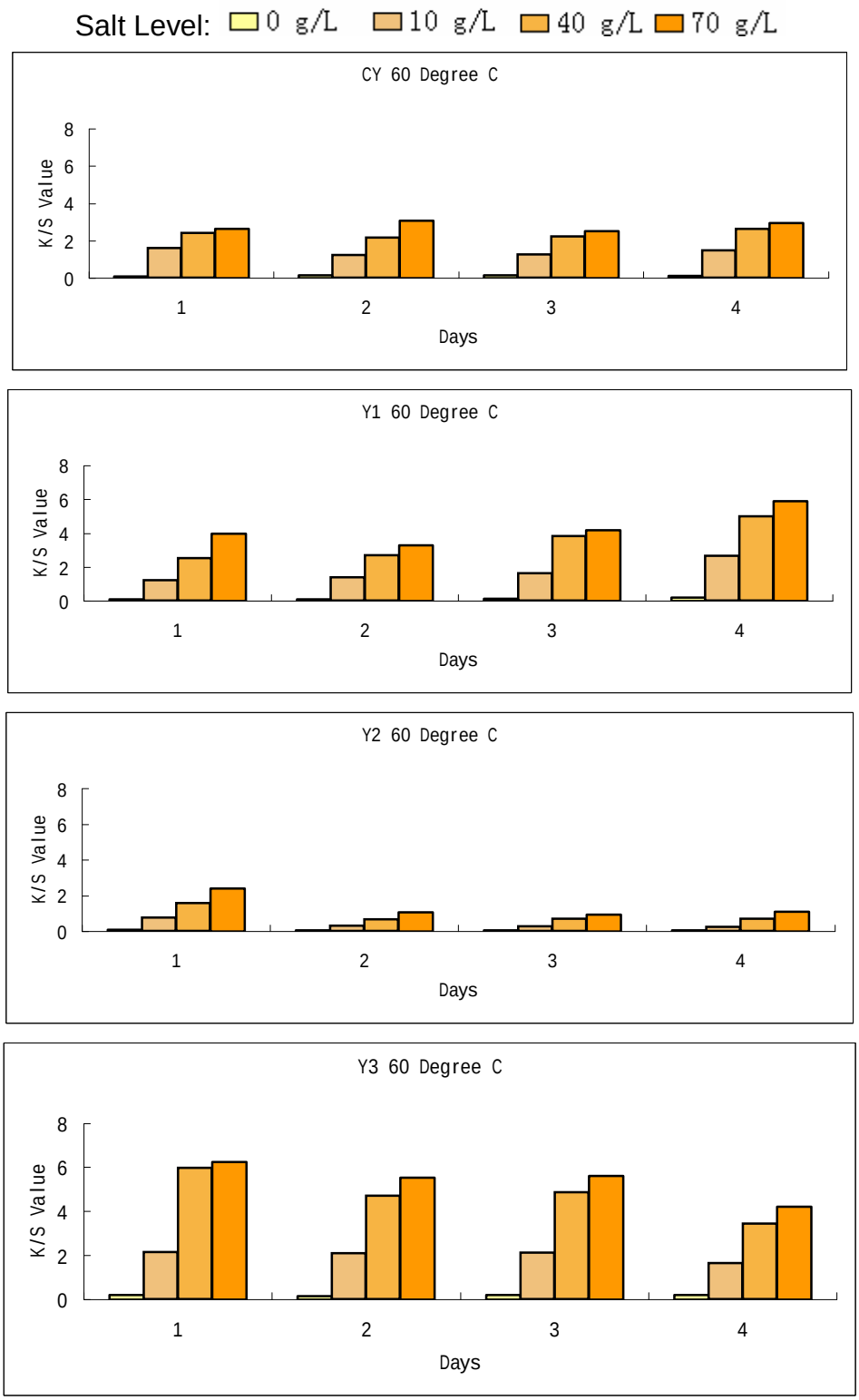


Figure 61. Changes in K/S data from equilibrium exhaustion for the yellow dyes at 60 °C, 40:1 LR and 24 intervals (CY= Commercial yellow, Y1 = type 1 yellow dye, Y2= type 2 yellow dye, Y3= type 3 yellow dye).

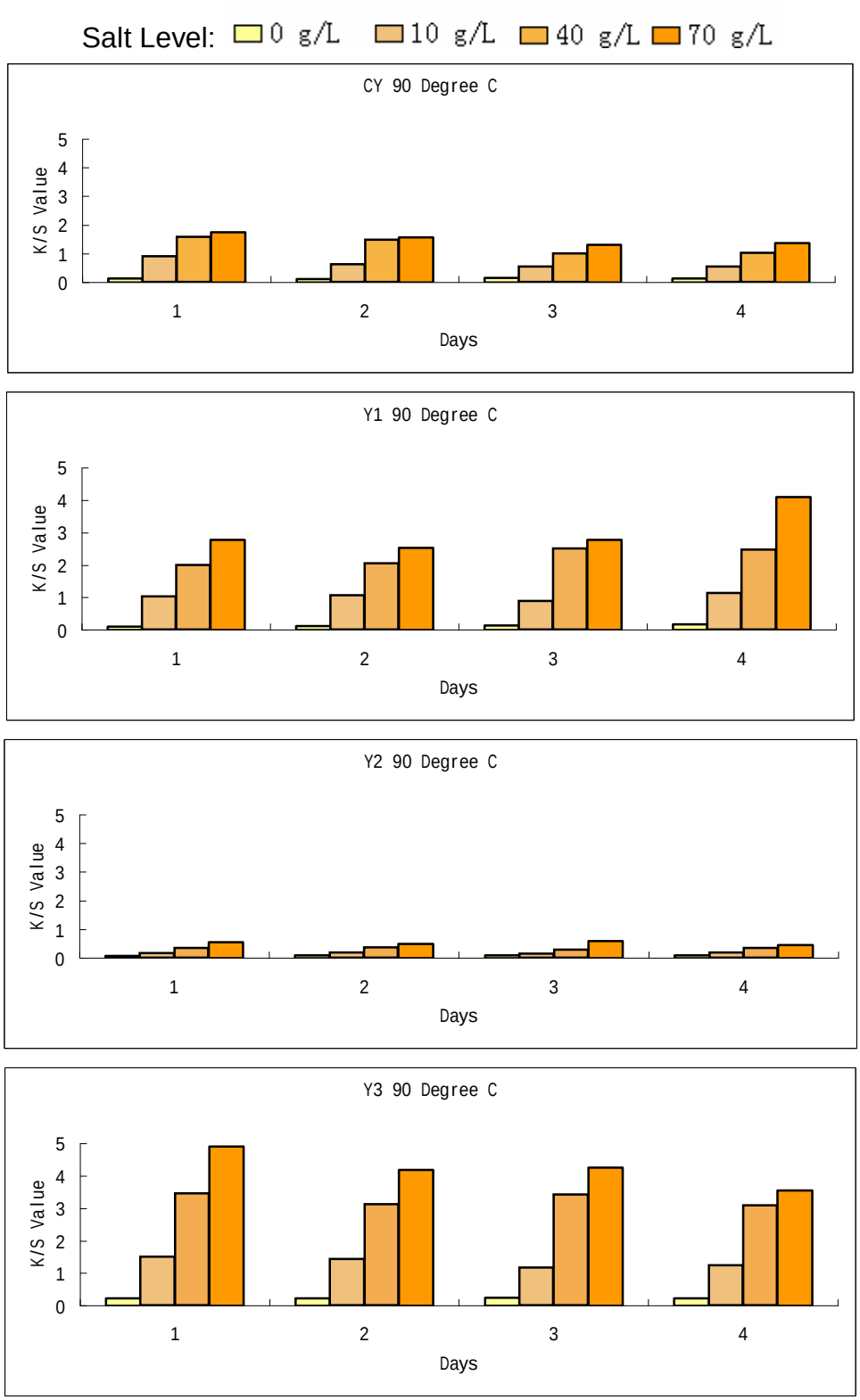


Figure 62. Changes in K/S data from equilibrium exhaustion for the yellow dyes at 90 °C, 40:1 LR and 24 intervals (CY= Commercial yellow, Y1 = type 1 yellow dye, Y2= type 2 yellow dye, Y3= type 3 yellow dye).

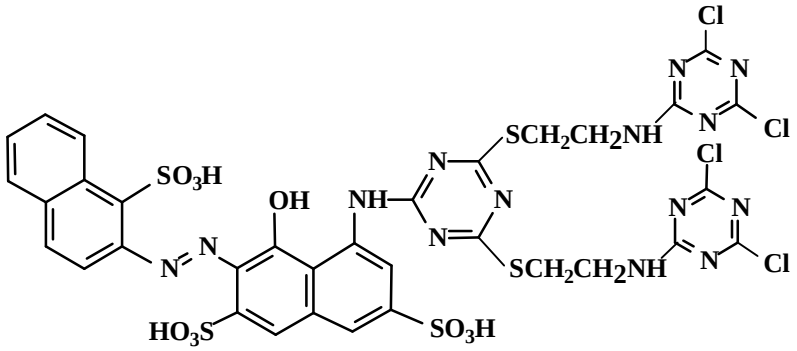
Figures 63-65 show the K/S values from cotton fabric following the application of red dyes. For commercial red dye, increasing temperature decreases K/S. At 30 °C the color depth does not increase much with increasing dyeing time. At 60 °C, K/S increases after 24 h and decreases after 96 h.

For type 1 red dye (65), increasing temperature increases the shade depth. At 30 °C, the K/S value slightly increases after 24h and begins to decrease after 48 h. At 60 °C, the K/S value increases after 24 h, decreases after 48h, but increases again after 72 h. Dye (65) gives a higher K/S value than the commercial dye at 90 °C.

Type 2 red dye (67) has the lowest K/S value of the red dyes. K/S decreases with increasing temperature but does not change much with the increasing of dyeing time.

Type 3 red dye (69) has the highest K/S value overall. The K/S values are similar at 60 °C and 90 °C, but lower than at 30 °C.

Comparing the K/S data from previous equilibrium exhaustion studies using the homobifunctional reactive red dye (89) [28] with those using hetero-bifunctional reactive red dyes, the results can be summarized as follows:



(89)

1) K/S values for the cotton fabrics dyed using type 1 red dye (63) are smaller than those using homobifunctional reactive red dye (89) at 30 °C and 90 °C.

2) K/S values for cotton fabrics dyed using type 3 red dye (61) are slightly lower than those using red dye (89) at 30 °C, and 90 °C. However K/S values for the cotton fabrics dyed using red dye (61) at 60 °C are greater than those using red dye (89) at 90 °C.

3) K/S values for cotton fabrics dyed using type 3 red dye (63) are lower than those using red dye (89) under all comparable dyeing conditions.

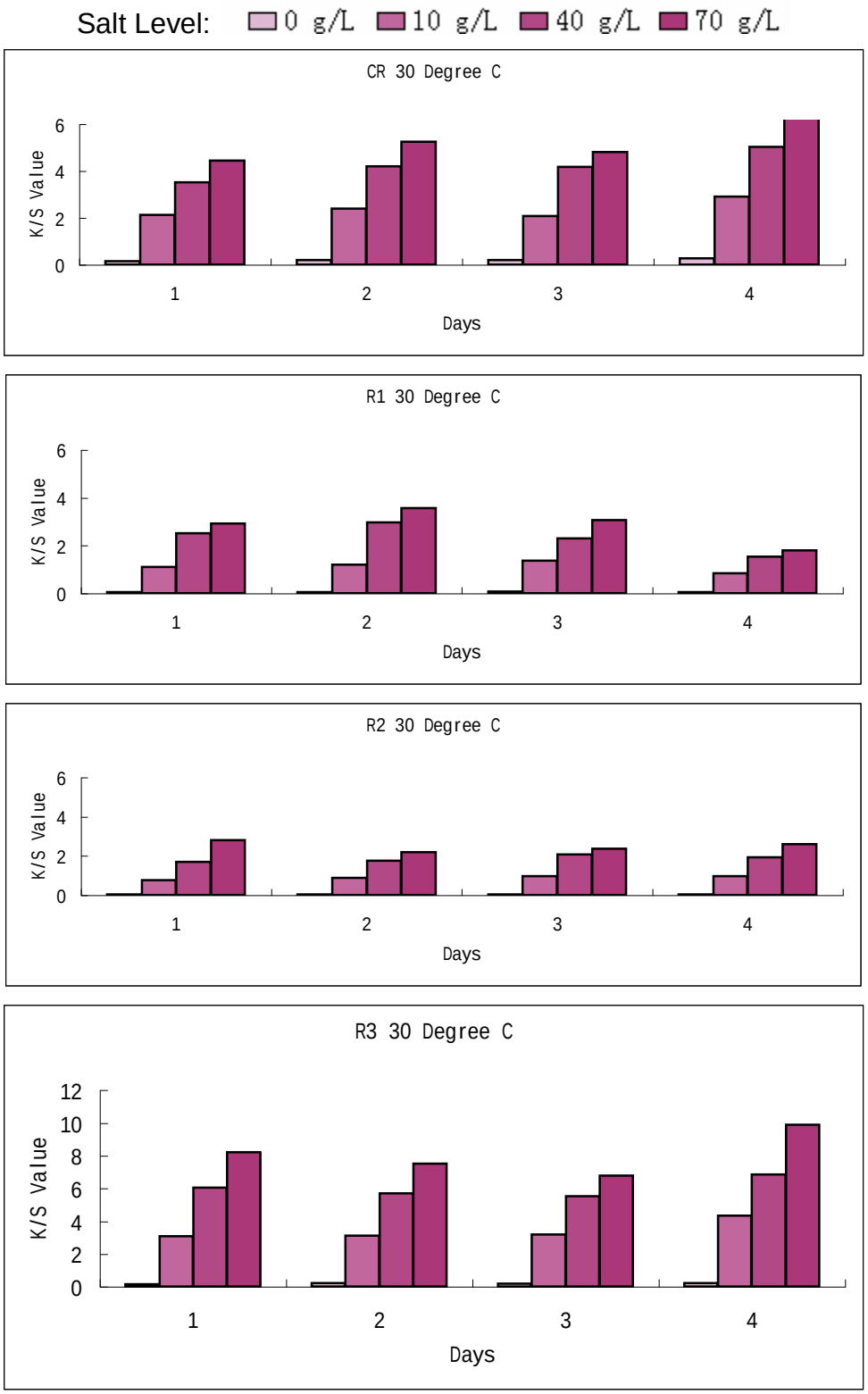


Figure 63. Changes in K/S from equilibrium exhaustion for the red dyes at 30 °C, 40:1 LR and 24 intervals (CR= commercial red dye, R1= type 1 red dye, R2= type 2 red dye, R3= type 3 red dye).

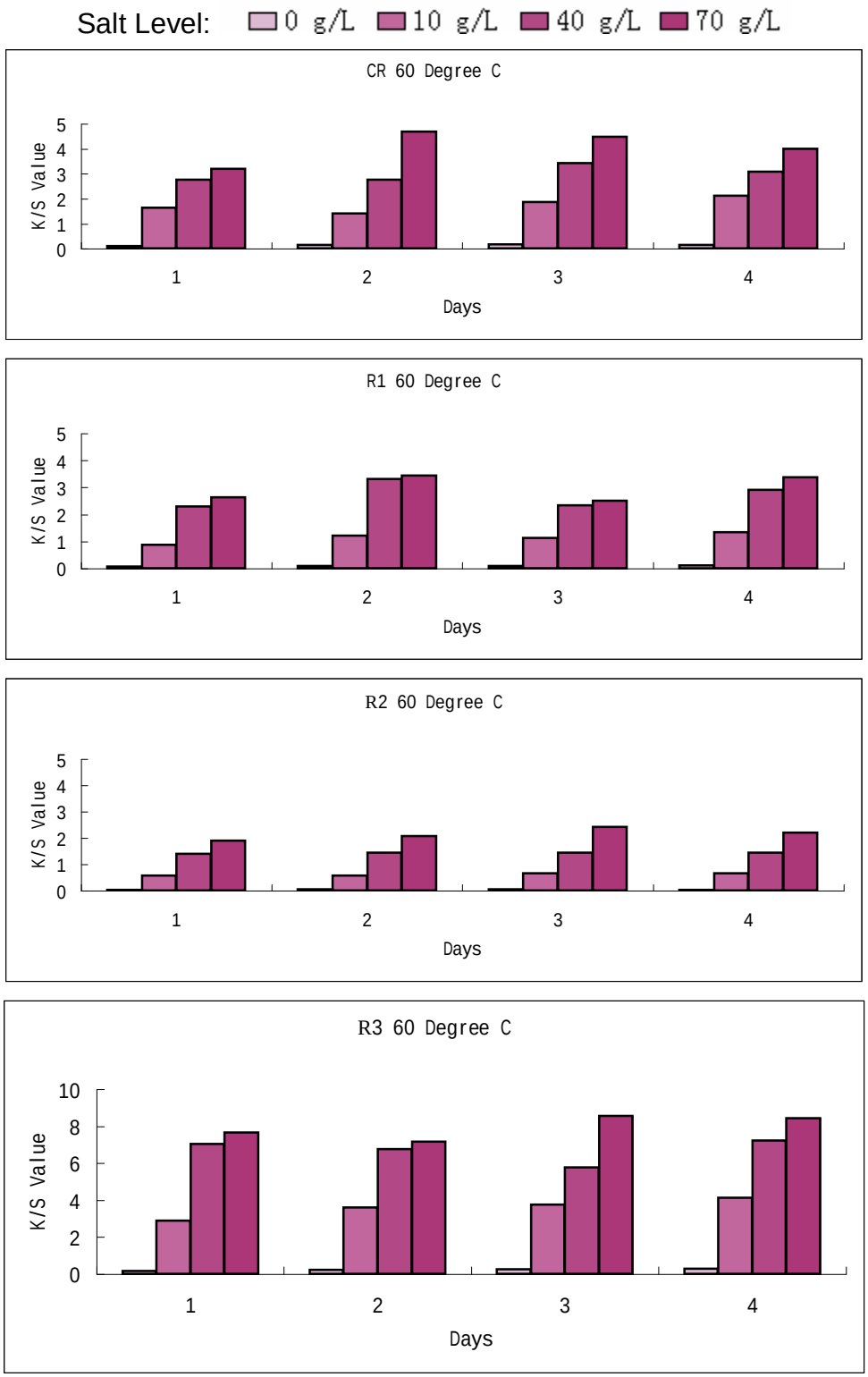


Figure 64. Changes in K/S from equilibrium exhaustion for the red dyes at 60 °C, 40:1 LR and 24 intervals (CR= commercial red dye, R1= type 1 red dye, R2= type 2 red dye, R3= type 3 red dye).

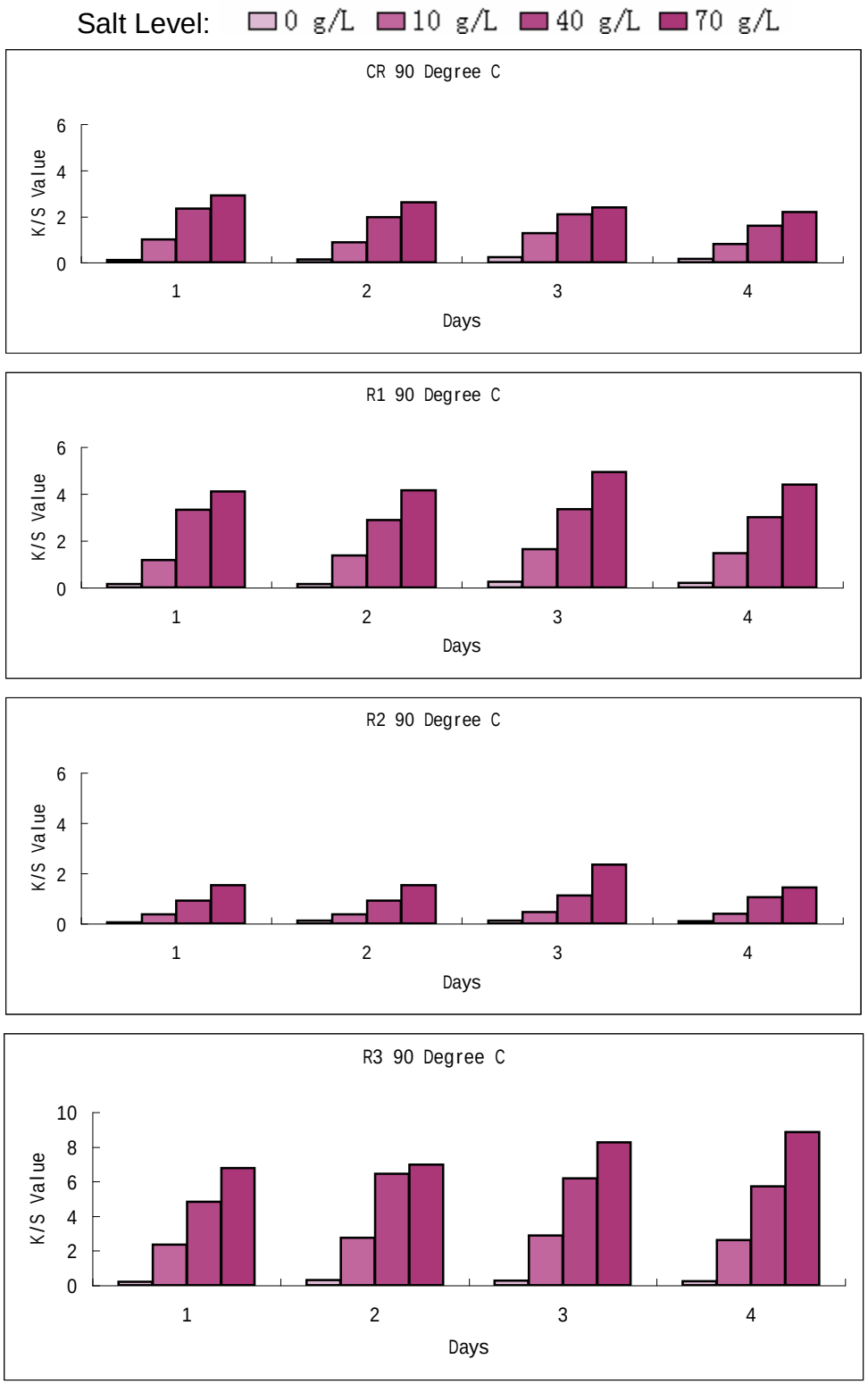


Figure 65. Changes in K/S from equilibrium exhaustion for the red dyes at 90 °C, 40:1 LR and 24 intervals (CR= commercial red dye, R1= type 1 red dye, R2= type 2 red dye, R3= type 3 red dye).

5. Laboratory Dyeing

Using the results from equilibrium exhaustion experiments, the two commercial dyes and new heterobifunctional reactive dyes were evaluated in laboratory dyeing studies. In these experiments, alkali was used for dye fixation. The addition of alkali to the dyebath causes dye to become covalently bond to the fiber.

The photographs in Figures 66-67 illustrate dye bath changes after dyeing from 1% dyebaths. It can be seen that color depths for the initial dyebaths have the order: type 3 dyes > type 1 dyes > commercial dye. Comparing the dyebath after dyeing, the color depths have the order: commercial dyes > type 3 dyes> type 1 dyes. For the yellow dyes, the dyebath after dyeing at 60 °C has a deeper color than at 30 °C, at 40g/L and 70g/L salt levels. For the red dyes, the dyebath remaining after dyeing at 30 °C has more color than at 60 °C, at 40g/L and 70g/L salt levels.

Commercial Yellow Dye

(1) (2) (3) (4) (5)

Type 1 yellow dye (58)

(1) (2) (3) (4) (5)

Type 3 yellow dye (63)

(1) (2) (3) (4) (5)

Figure 66. Aliquots of yellow dye dyebaths taken before dyeing (1) and after dyeing at 30 °C and 40g/L (2), at 30°C and 70g/L (3), at 60 °C and 40 g/L (4) and at 60 °C and 70g/L (5).

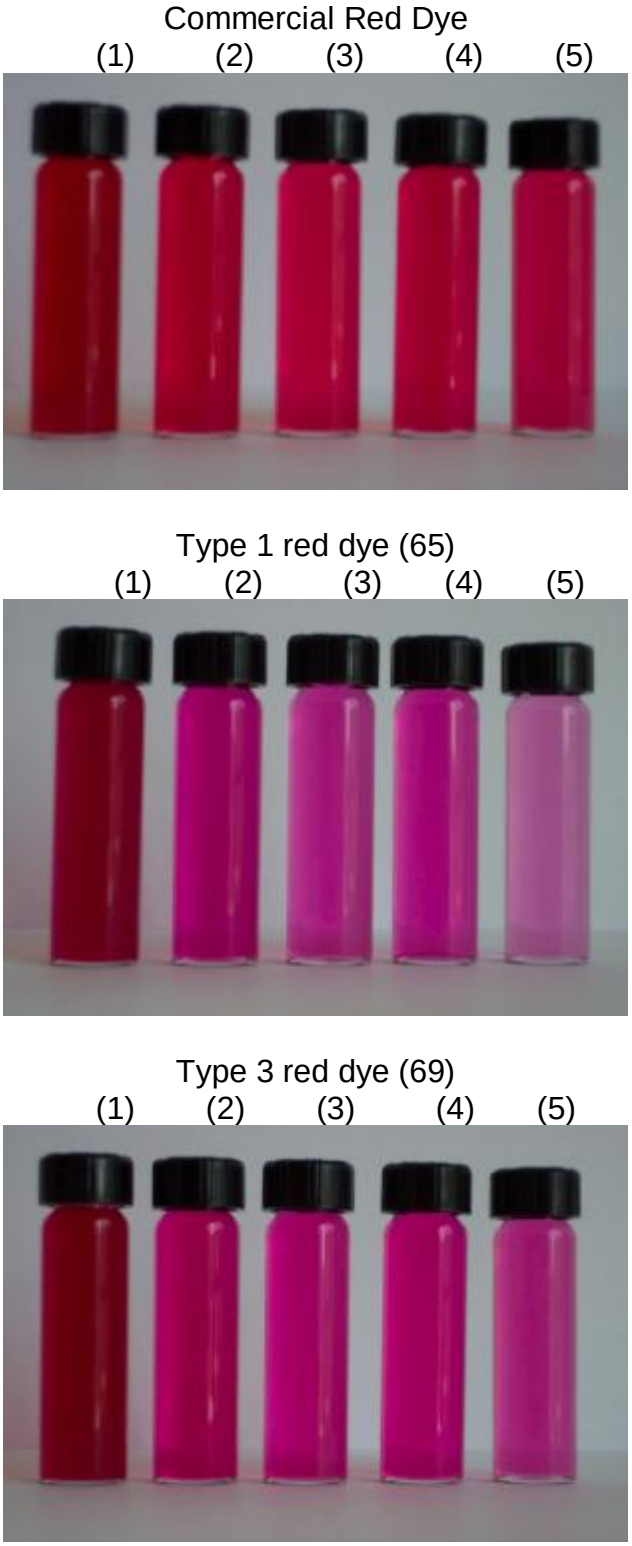


Figure 67. Aliquots of red dye dyebaths taken before dyeing (1) and after dyeing at 30 °C and 40g/L (2), at 30°C and 70g/L (3), at 60 °C and 40 g/L (4) and at 60 °C and 70g/L (5).

L*, a*, b* and K/S values were recorded on each fabric sample, the results of which are provided in Table 10.

Table 10. K/S, L*, a*, b* and % fixation data of laboratory dyeing studies.

Sample	Salt Level (g/L)	Temp. (°C)	K/S	L*	a*	b*	% Fixation
Commercial Yellow (51)	40	30	3.02	82.70	12.56	61.94	76.6
	70	30	3.34	81.28	15.20	62.36	84.5
	40	60	2.55	82.56	13.20	58.02	64.1
	70	60	3.88	80.89	16.21	65.73	74.6
Yellow Dye (58)	40	30	3.09	80.73	16.79	60.90	83.6
	70	30	3.80	79.68	19.33	64.70	90.2
	40	60	4.02	78.89	19.27	64.38	78.9
	70	60	5.12	78.17	21.37	69.24	87.5
Yellow Dye (63)	40	30	2.80	80.59	17.48	59.11	81.4
	70	30	3.76	78.78	20.37	63.71	88.7
	40	60	3.22	79.14	19.08	60.37	75.4
	70	60	4.81	77.04	22.62	67.32	86.1
Commercial Red (52)	40	30	3.39	55.97	50.02	-11.13	63.0
	70	30	5.98	50.2	55.34	-8.89	74.5
	40	60	3.67	55.07	50.48	-11.67	55.2
	70	60	5.13	51.58	53.63	-10.87	68.1
Red Dye (65)	40	30	5.73	49.48	52.53	-14.01	73.2
	70	30	6.11	48.68	52.58	-13.55	83.2
	40	60	7.96	46.01	54.65	-12.64	81
	70	60	9.35	43.94	54.75	-11.53	90.6
Red Dye (69)	40	30	6.46	47.85	52.65	-12.64	75.5
	70	30	6.91	47.2	53.17	-12.41	82.2
	40	60	7.85	45.81	53.81	-11.63	78.4
	70	60	10.36	42.76	55.03	-10.17	87.2

The % fixation values for yellow and red dyes employed in laboratory dyeings are also summarized in Figure 68. The results indicate that laboratory dyeings conducted at the higher salt level produce higher % fixation. For the commercial dyes, higher % fixation level occurs at 30 °C than at 60 °C. The two new heterobifunctional reactive yellow dyes gave slightly higher % fixation level at 30 °C than 60 °C. However, the two new red dyes give higher % fixation level at 60 °C than 30 °C, probably due to their higher molecular size. The new dyes also give higher % fixation levels than their commercial counterparts. These results are consistent from equilibrium exhaustion studies, which indicated that the modified structures have better affinity on cotton than the commercial dyes. The % fixation levels for the new dyes at the lower salt level (40 g/L) were comparable or higher than those obtained using commercial dyes at the higher level (70 g/L). Comparing the heterobifunctional reactive dyes with the homobifunctional reactive dyes, they do not give a higher % fixation level at 30 ˚C, 60˚C, and 40g/L salt level [28].

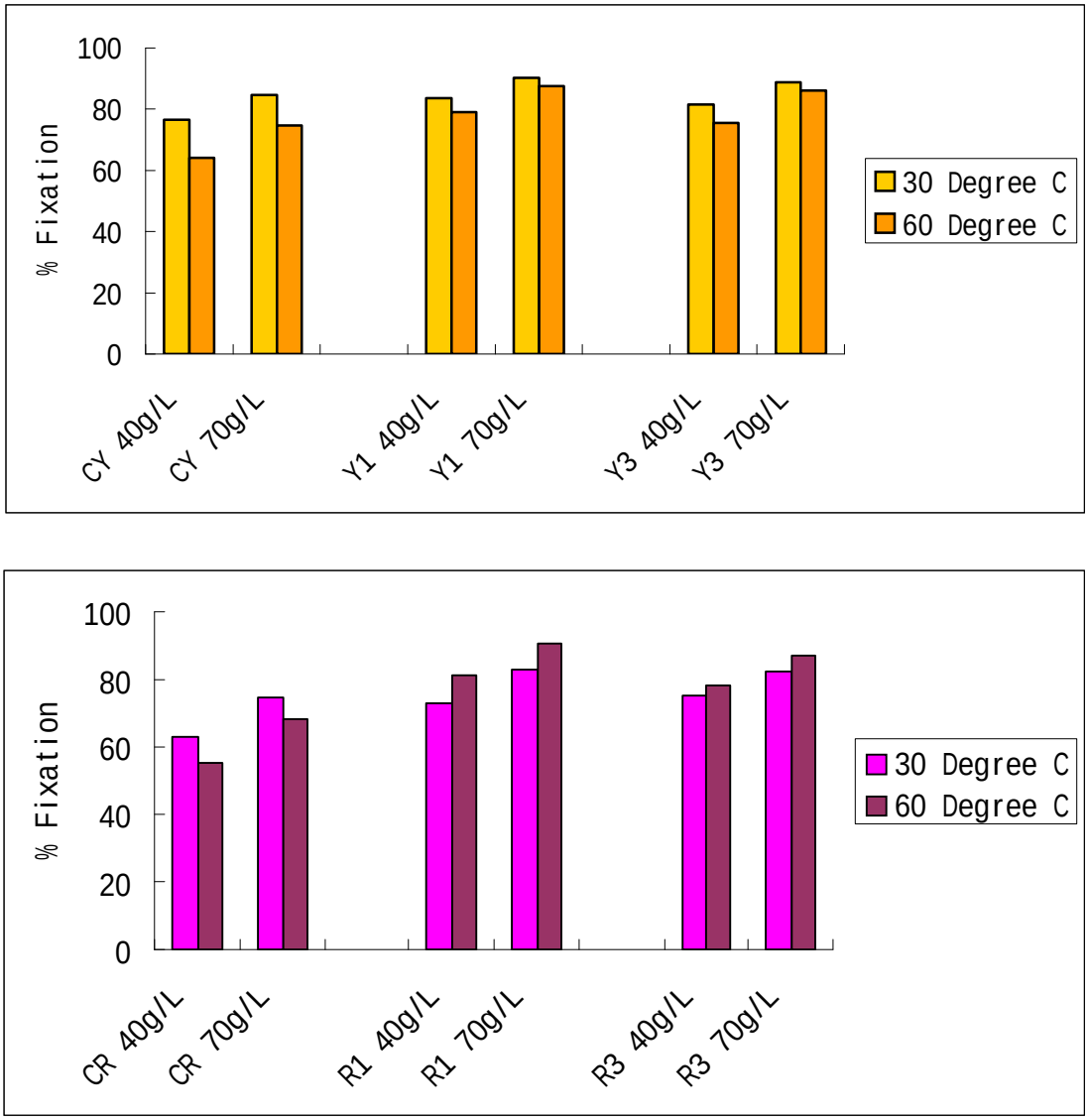
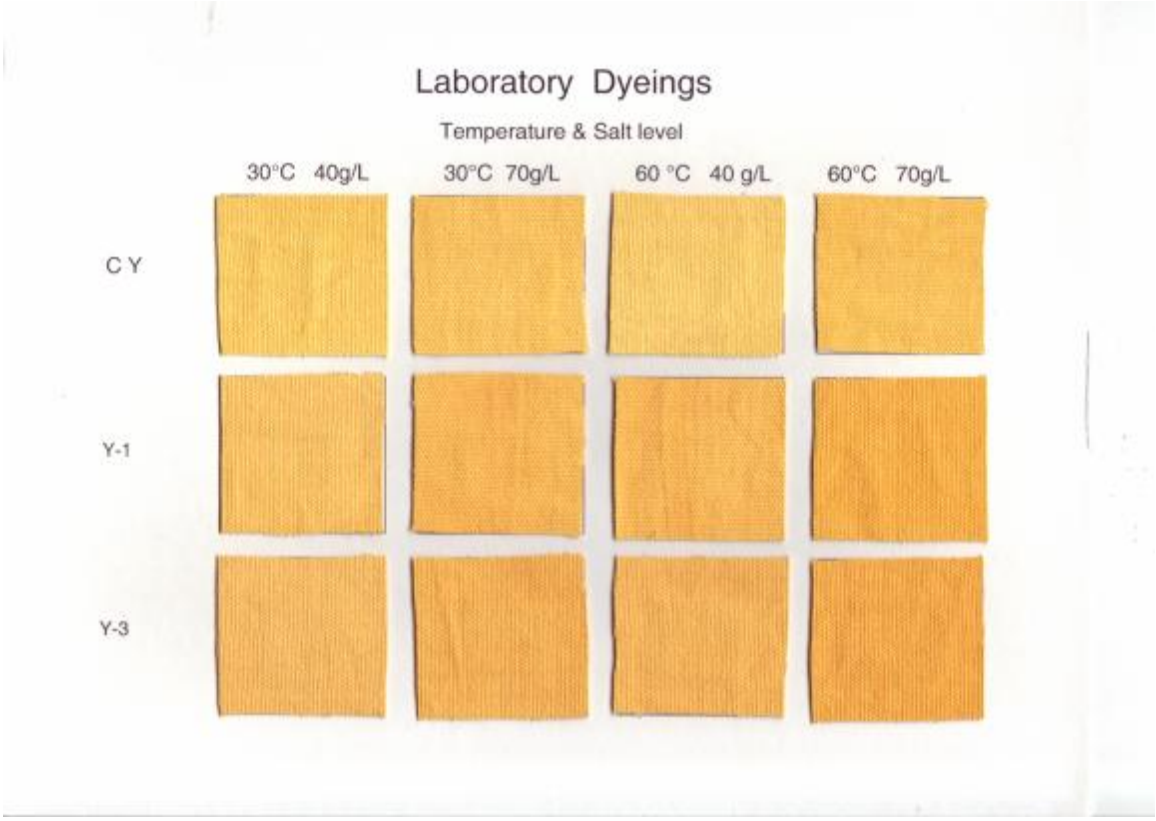


Figure 68. % Fixation values for yellow and red dyes employed in laboratory dyeings at 40:1 LR, 1% (owg) dyebath concentration. CY= commercial yellow dye, Y1= type 1 yellow dye, Y3= type 3 yellow dye, CR= commercial red dye, R1 = type 1 red dye, R3= type 3 red dye.

Photographs in Figures 69-70 are representative of fabrics from laboratory dyeing conducted at 30 °C and 60 °C and 40 g/L and 70g/L salt levels. Each figure also contains a plot of K/S values obtained under the same conditions. The results indicate that the new heterobifunctional reactive dyes give higher K/S values than the commercial DCT dyes, especially when the dyeings were conducted at 60 °C. The results also show that these new dyes give comparable or even deeper shades on cotton at the 40 g/L salt level than the commercial DCT dyes at the 70 g/L salt level. The new heterobifunctional reactive yellow dye (58) and (61) give lower K/S values on cotton than the homobifunctional reactive yellow dye (88) at the 40g/L salt level, 30 °C and 60 °C. The new hetero-bifunctional reactive red dye (69) gives a higher K/S value than homo-bifunctional reactive red dye (89) at the 40g/L salt level and 30 °C [28].



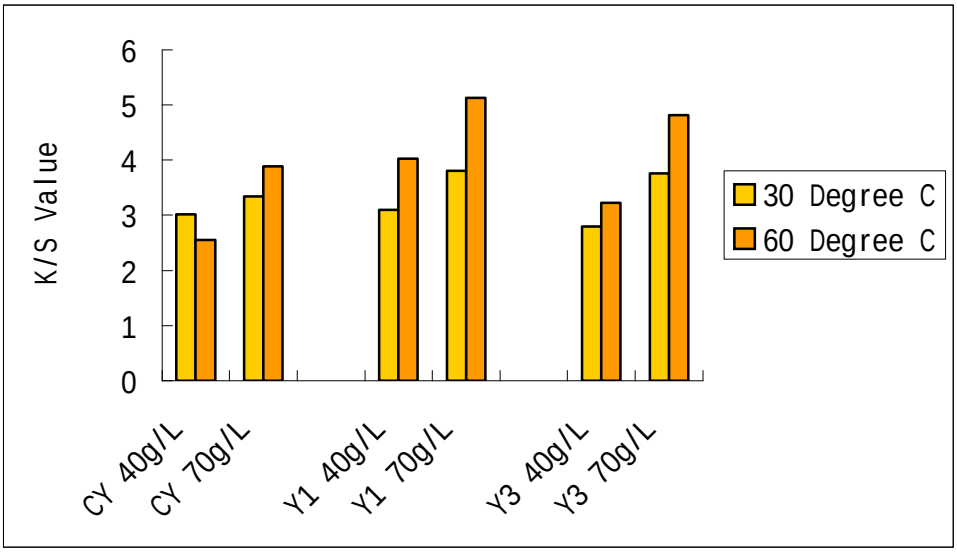
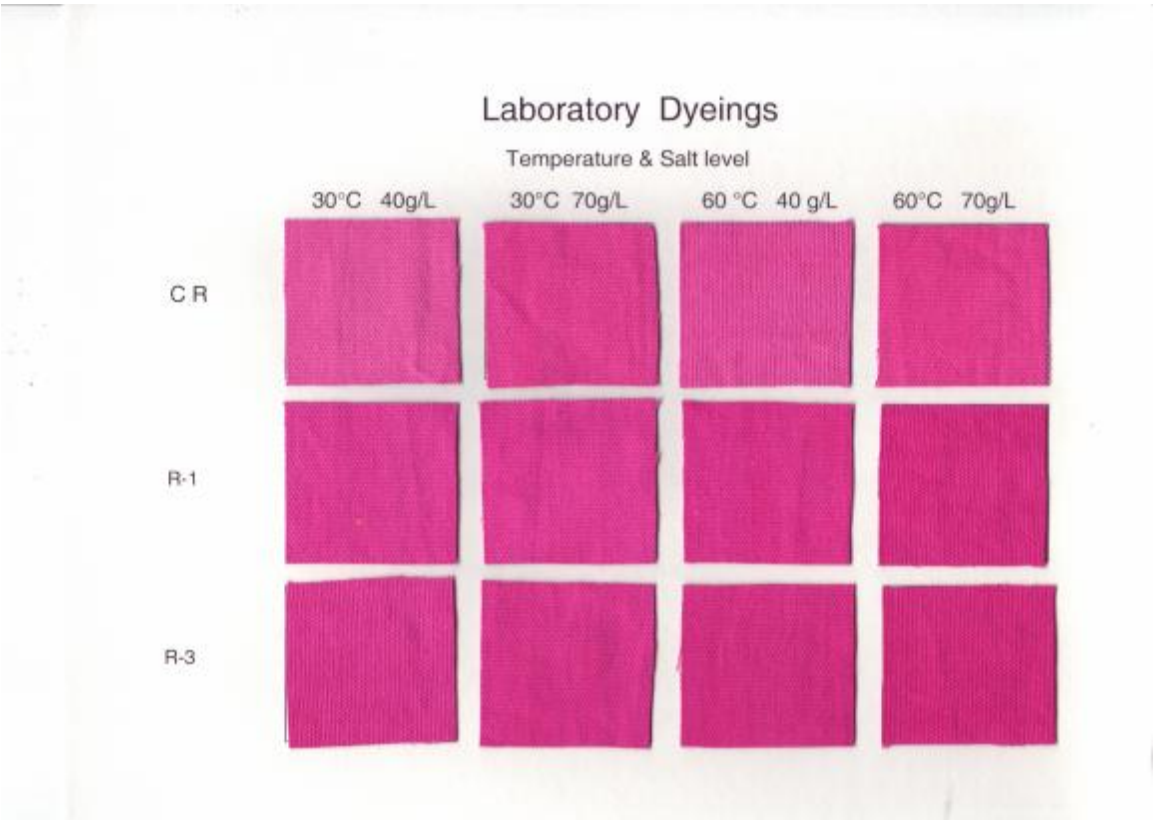


Figure 69. Yellow fabric samples obtained in laboratory dyeing conducted from 1% (owg) dyebaths (top) and the associated K/S data (bottom). CY= commercial yellow dye, Y1= type 1 yellow dye, and Y3= type 3 yellow dye.



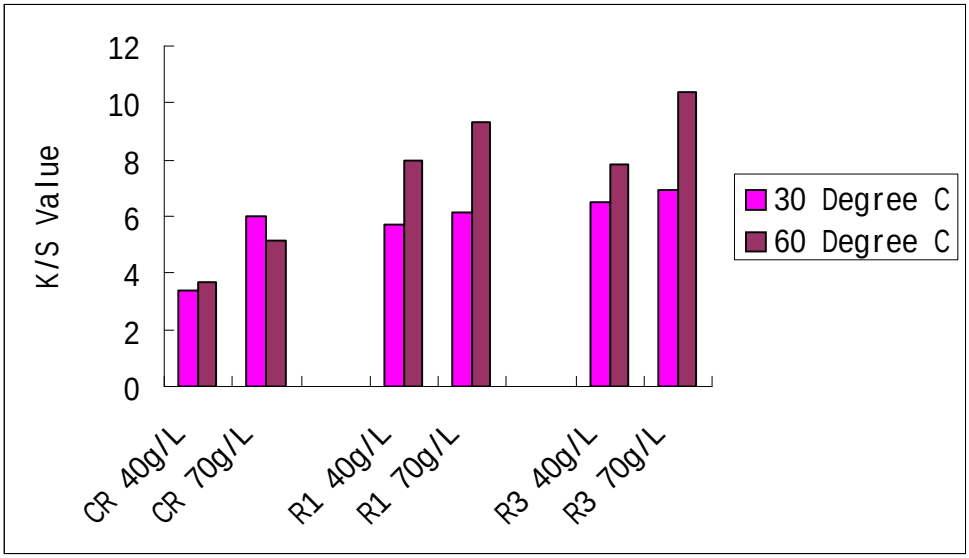


Figure 70. Red fabric samples obtained in laboratory dyeing conducted fro1% (owg) dyebaths (top) and the associated K/S data (bottom). CR= commercial red dye, R1 = type 1 red dye, and R3= type 3 red dye.

6. Fastness Testing

6.1 Washfastness

Washfastness studies were conducted on fabrics from laboratory dyeings, the results of which are recorded in Table 11. The results can be summarized as follows:

1) Very good fastness ratings are obtained for each dye on cotton
2) Salt level and, except for commercial yellow dye, temperature has no effect on washfastness.
3) For the commercial yellow dye, a slight reduction in washfastness (color change) is observed from dyeing at 60 °C and 70g/L salt.
4) Modification of commercial DCT dyes to produce the new dyes does not adversely affect washfastness.
5) Minimum staining of cotton, wool and nylon occurs when these dye were used.
6) The new heterobifunctional reactive dyes give better washfastness results, when compared with the homobifunctional reactive dyes [28]. The gray scale values associated with the color staining of attached multifiber fabrics for heterobifunctional reactive dyes range from 4.5 - 5.0, while those for homobifunctional reactive dyes range from 2.5 - 4.5.

Table 11. Data from washfastness testing. *

Sample	Salt Level (g/L)	Temp. (°C)	Color Change	Color Staining		
				Cotton	Wool	Nylon
Commercial Yellow dye (51)	40	30	4.0	4.5	4.5	4.5
	70	30	4.5	4.5	4.5	4.5
	40	60	4.0	4.5	4.5	4.5
	70	60	3.5	4.5	4.5	4.5
Type 1 yellow dye (58)	40	30	4.5	4.5	4.5	4.5
	70	30	4.5	4.5	4.5	4.5
	40	60	4.5	4.5	4.5	4.5
	70	60	4.5	4.5	4.5	4.5
Type 3 yellow dye (61)	40	30	4.0	4.5	4.5	4.5
	70	30	4.5	4.5	4.5	4.5
	40	60	4.5	4.5	4.5	4.5
	70	60	4.5	4.5	4.5	4.5
Commercial red dye (52)	40	30	4.5	4.5	4.5	4.5
	70	30	4.0	4.5	4.5	4.5
	40	60	4.5	4.5	4.5	4.5
	70	60	4.5	4.5	4.5	4.5
Type 1 red dye (67)	40	30	4.5	4.5	4.5	4.5
	70	30	4.5	4.5	4.5	4.5
	40	60	4.5	4.5	4.5	4.5
	70	60	4.5	4.5	4.5	4.5
Type 3 red dye (69)	40	30	4.5	4.5	4.5	4.5
	70	30	4.5	4.5	4.5	4.5
	40	60	5.0	4.5	4.5	4.5
	70	60	4.5	4.5	4.5	4.5

* Rating scale = 1 (poor) to 5 (excellent).

6.2 Lightfastness

The lightfastness of dyed cotton fabrics as assessed after a 20-hour xenon arc light exposure, the results of which are recorded in Table 12 and summarized as follows:

1) Each yellow dye gives lightfastness rating of 4 or better under certain dyeing conditions, while the highest rating for the red dyes is 3.5.
2) Generally, the commercial yellow dye has good lightfastness. There is a slight reduction on lightfastness of fabric dyed at 60 °C when salt level is increased from 40 -70 g/L.
3) In the case of type 1 yellow dye (58), a more pronounced reduction in lightfastness for fabric dyed is observed at 30 °C when the salt level is increased.
4) Type 3 yellow dye (63) has good lightfastness, with no influence by temperature or salt level.
5) For the commercial red dye, lightfastness is average (3.5), with better results from dyeing at 60 °C.
6) Type 1 red dye (67) has average lightfastness, with slightly better results following dyeing at 30 °C.
7) For the type 3 red dye (69), lightfastness is minimally acceptable (3.0) and constant over both temperature and salt levels.
8) When compared with the homobifunctional reactive dyes, the new heterobifunctional dyes give better lightfastness results following dyeing at the 40g/L salt level, 30 °C and 60 °C [28].

Generally, lightfastness correlates with K/S values, with the lighter shades having better lightfastness. In this case, lightfastness of 4.0 or better is normally observed when K/S ≤ 5 and a lightfastness rating of 3.0 - 3.5 is observed when K/S >5.0. The lightfastness of the yellow dyes is higher because of greater protection of the azo bond caused by intramolecular H-bonding (Figure 71). This feature characterizes azo disperse dyes having an *ortho*-acetamido group [16].

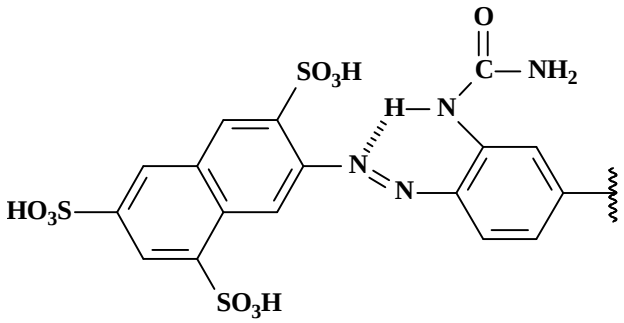


Figure 71. Light stabilizing feature of yellow dyes.

Table 12. Data from Lightfastness testing. *

Sample	Salt Level (g/L)	Temp. (°C)	Color Change	K/S
Commercial Yellow dye (51)	40	30	4.0	3.02
	70	30	4.5	3.34
	40	60	4.0	2.55
	70	60	3.5	3.88
Type 1 yellow dye (58)	40	30	4.5	3.09
	70	30	3.5	3.80
	40	60	3.5	4.02
	70	60	4.0	5.12
Type 3 yellow dye (63)	40	30	4.0	2.80
	70	30	4.0	3.76
	40	60	4.0	3.22
	70	60	4.0	4.81
Commercial red dye (52)	40	30	3.0	3.39
	70	30	3.5	5.98
	40	60	3.5	3.67
	70	60	3.5	5.13
Type 1 red dye (65)	40	30	3.5	5.73
	70	30	3.5	6.11
	40	60	3.0	7.96
	70	60	3.0	9.35
Type 3 red dye (67)	40	30	3.0	6.46
	70	30	3.0	6.91
	40	60	3.0	7.85
	70	60	3.0	10.36

* Rating scale = 1 (poor) to 5 (excellent).

IV. Conclusions

It has been shown that commercial dichlorotriazine reactive dyes can be converted to heterobifunctional reactive dyes containing MCT/VS systems by a sequence of reactions involving cysteamine or cysteine, cyanuric chloride, and *para*-aminophenyl-β-sulfatoethylsulfone. The resultant novel dyes are amenable to ESI mass spectrometric and HPLC analyses for assessment of molecular and physical composition. Using negative-ion ESI mass spectrometry molecular ions corresponding to m/2, m/3, m/4 species were observed, and using reverse-phase HPLC and a solvent gradient, it was shown that products arising from reactions at the –SH and $–NH_2$ groups of cysteamine and cysteine were obtained.

Application of the heterobifunctional reactive dyes to cotton in the presence of salt but absence of alkali revealed that these dyes have higher affinity than the commercial DCT counterparts, even when less salt is used with the new dyes than used with the commercial dyes. This is consistent with the increase in molecular size following dye modification. Similarly, the addition of alkali to the dyebaths led to higher dye-fiber fixation levels that obtained with the DCT dyes.

The technical properties of the DCT commercial dyes were improved, rather than adversely affected, by converting them to heterobifunctional reactive forms. In this regard, the color strength (ε_{max} values) of the new dyes were better than the starting dyes, despite significant increases in molecular mass. Generally, type 3 dyes (bis- MCT/ mono VS) gave the deepest shades on cotton.

It was also found that converting DCT reactive dyes to heterobifunctional reactive dyes did not adversely affect lightfastness and washfastness. The washfastness of the new dyes on cotton was very good, while lightfastness was acceptable to good.

The preferred modification is the formation of the MCT/MCT/VS trireactive system, which had the best over all application properties and reaction yields.

V. Recommendations for Future Work

The results from equilibrium exhaustion and laboratory dyeing experiments indicate that the present heterobifunctional reactive dyes derived from commercial DCT dyes have higher affinity for cotton and give better shade depths than their commercial counterparts. Since only yellow and red dyes were studied in this work, it would be instructive to make and assess heterobifunctional reactive dyes having other colors to determine the possible color gamut. Further, all dyes should be evaluated on a pilot plant scale. With results from large-scale dyeings it would be possible to assess the commercial viability of these dyes. It is also suggested to evaluate the potential cost savings from reduced wastewater treatment to judge the benefit these dyes bring dyers.

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Appendix

Appendix

Data from Equilibrium Exhaustion Experiments

1. C^s, C^f, K, %E, and -Δμ° data (Tables 13- 36)

2. L*, a* b*, and K/S data (Tables 37-40)

Table 13. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using commercial yellow dye (51) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.2446	0.2144	0.87639	2.144	-0.33256
	10	0.2102	1.593	7.5794	15.93	5.105084
	40	0.1486	4.0541	27.273	40.541	8.33248
	70	0.1062	5.7518	54.1575	57.518	10.06153
48h	0	0.2378	0.4877	2.05078	4.8769	1.810268
	10	0.2131	1.4746	6.91851	14.746	4.875131
	40	0.1425	4.2988	30.1612	42.988	8.586185
	70	0.0955	6.1813	64.7482	61.813	10.51171
72h	0	0.2349	0.6044	2.57305	6.0439	2.382098
	10	0.206	1.7594	8.54015	17.594	5.405893
	40	0.1364	4.5448	33.3245	45.448	8.837576
	70	0.0911	6.3574	69.8111	63.574	10.70147
96h	0	0.2325	0.6994	3.00798	6.994	2.775734
	10	0.2037	1.8506	9.08337	18.506	5.561321
	40	0.1302	4.7929	36.8182	47.929	9.088864
	70	0.0886	6.456	72.8662	64.56	10.80943

Table 14. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using commercial yellow dye (51) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.2438	0.249	1.021434	2.49	0.059
	10	0.2254	0.9848	4.369509	9.848	4.085
	40	0.1658	3.3692	20.32455	33.692	8.343
	70	0.1277	4.8902	38.28095	48.902	10.1
48h	0	0.2415	0.3418	1.415585	3.418	0.963
	10	0.2177	1.2926	5.937938	12.926	4.934
	40	0.161	3.5582	22.09445	35.582	8.574
	70	0.1219	5.1248	42.04792	51.248	10.36
72h	0	0.2449	0.2046	0.835494	2.046	-0.5
	10	0.2198	1.2074	5.492801	12.074	4.718
	40	0.157	3.7188	23.6821	37.188	8.766
	70	0.1194	5.2238	43.74859	52.238	10.47
96h	0	0.2428	0.2866	1.180225	2.866	0.459
	10	0.2152	1.3932	6.47488	13.932	5.174
	40	0.1533	3.8696	25.2486	38.696	8.943
	70	0.1129	5.484	48.57396	54.84	10.76

Table 15. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using commercial yellow dye (51) at 90 °C, woven cotton (1g), 40:1 LR, % and 1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.2458	0.169	0.6876	1.689864	-1.131
	10	0.2327	0.6912	2.9701	6.912	3.2868
	40	0.199	2.0399	10.251	20.39896	7.027
	70	0.1651	3.3976	20.584	33.976	9.1321
48h	0	0.2444	0.2256	0.9232	2.255902	-0.241
	10	0.227	0.9199	4.0523	9.1988	4.2249
	40	0.1904	2.3828	12.513	23.82813	7.6292
	70	0.1598	3.6066	22.565	36.066	9.4094
72h	0	0.2434	0.2625	1.0781	2.624582	0.2271
	10	0.2242	1.0302	4.5941	10.302	4.6038
	40	0.1856	2.5746	13.869	25.746	7.9399
	70	0.1549	3.8058	24.577	38.058	9.6673
96h	0	0.2424	0.3024	1.2474	3.024196	0.6675
	10	0.2206	1.1752	5.3268	11.752	5.0506
	40	0.1754	2.9848	17.019	29.848	8.5578
	70	0.1446	4.2164	29.161	42.164	10.184

Table16. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 1 yellow dye (58) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24536	0.1856	0.7565	1.8562	-0.70322
	10	0.18055	2.778	15.386	27.78	6.8896563
	40	0.12584	4.9662	39.463	49.662	9.2637168
	70	0.08318	6.6729	80.224	66.729	11.051899
48h	0	0.24396	0.2415	0.9899	2.415	-0.025575
	10	0.17407	3.0372	17.448	30.372	7.2066098
	40	0.09903	6.0389	60.982	60.389	10.360649
	70	0.06617	7.3534	111.14	73.534	11.873429
72h	0	0.24217	0.3132	1.2932	3.1318	0.6480972
	10	0.17028	3.1889	18.728	31.889	7.3850507
	40	0.0861	6.556	76.143	65.56	10.920297
	70	0.05832	7.6672	131.47	76.672	12.29683
96h	0	0.24045	0.3818	1.5879	3.8183	1.1655703
	10	0.16103	3.559	22.102	35.59	7.8025744
	40	0.083	6.6798	80.476	66.798	11.059813
	70	0.05116	7.9535	155.46	79.535	12.71932

Table17. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 1 yellow dye (58) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24395	0.242	0.992	2.42	-0.022
	10	0.175	3	17.143	30	7.871
	40	0.0985	6.06	61.523	60.6	11.41
	70	0.063	7.48	118.73	74.8	13.231
48h	0	0.242	0.32	1.3223	3.2	0.7739
	10	0.166	3.36	20.241	33.6	8.3311
	40	0.0855	6.58	76.959	65.8	12.031
	70	0.0605	7.58	125.29	75.8	13.38
72h	0	0.24139	0.3446	1.4276	3.446	0.9861
	10	0.15751	3.6996	23.488	36.996	8.7432
	40	0.07935	6.826	86.024	68.26	12.339
	70	0.0465	8.14	175.05	81.4	14.307
96h	0	0.24038	0.3847	1.6005	3.8474	1.3028
	10	0.1545	3.82	24.725	38.2	8.8854
	40	0.07329	7.0686	96.454	70.686	12.656
	70	0.043	8.28	192.56	82.8	14.571

Table 18. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 1 yellow dye (58) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24575	0.17	0.69176	1.7	-1.1127
	10	0.204	1.84	9.01961	18.4	6.64076
	40	0.13245	4.702	35.5002	47.02	10.7777
	70	0.0766	6.936	90.5483	69.36	13.6048
48h	0	0.24452	0.2193	0.89686	2.193	-0.3287
	10	0.1936	2.256	11.6529	22.56	7.41418
	40	0.118	5.28	44.7458	52.8	11.4765
	70	0.06695	7.322	109.365	73.22	14.1749
72h	0	0.24261	0.2956	1.21842	2.956	0.59648
	10	0.17775	2.89	16.2588	28.9	8.41986
	40	0.1055	5.78	54.7867	57.8	12.0878
	70	0.06005	7.598	126.528	75.98	14.615
96h	0	0.24185	0.32581	1.34713	3.2581	0.8997
	10	0.17005	3.198	18.8062	31.98	8.85934
	40	0.0955	6.18	64.712	61.8	12.5905
	70	0.0552	7.792	141.159	77.92	14.9454

Table 19. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 2 yellow dye (61) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.2439	0.2442	1.001251	2.442	0.00315
	10	0.21469	1.4126	6.579873	14.126	4.74864
	40	0.15538	3.785	24.36042	37.85	8.04782
	70	0.12291	5.0838	41.36365	50.838	9.38228
48h	0	0.24704	0.1186	0.480094	1.186	-1.8495
	10	0.20489	1.8046	8.807868	18.046	5.48369
	40	0.14793	4.083	27.60183	40.83	8.36269
	70	0.11642	5.3434	45.89958	53.434	9.64454
72h	0	0.24227	0.3092	1.276262	3.092	0.61484
	10	0.20361	1.8556	9.113501	18.556	5.56967
	40	0.14429	4.2286	29.30727	42.286	8.5138
	70	0.11015	5.5942	50.78941	55.942	9.89969
96h	0	0.24597	0.1612	0.655364	1.612	-1.0651
	10	0.19905	2.038	10.23863	20.38	5.86308
	40	0.13605	4.558	33.50239	45.58	8.85099
	70	0.10341	5.8638	56.70712	58.638	10.1775

Table 20. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 2 yellow dye (61) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.245575	0.177	0.720757	1.77	-0.907
	10	0.224775	1.009	4.488933	10.09	4.15935
	40	0.18358	2.6568	14.47216	26.568	7.40185
	70	0.16015	3.594	22.44146	35.94	8.61697
48h	0	0.249196	0.03217	0.12909	0.321686	-5.6707
	10	0.218563	1.2575	5.753503	12.575	4.84683
	40	0.17811	2.8756	16.14508	28.756	7.70485
	70	0.158577	3.65694	23.06105	36.5694	8.69241
72h	0	0.2492	0.032	0.128411	0.32	-5.6853
	10	0.21482	1.4072	6.550601	14.072	5.20622
	40	0.171845	3.1262	18.19198	31.262	8.03548
	70	0.152245	3.9102	25.6836	39.102	8.99075
96h	0	0.2447	0.21201	0.866419	2.120124	-0.3972
	10	0.209818	1.6073	7.660467	16.073	5.63976
	40	0.166845	3.3262	19.93587	33.262	8.28904
	70	0.147245	4.1102	27.91402	41.102	9.22142

Table 21. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 2 yellow dye (61) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24348	0.261	1.071979	2.61	0.20986
	10	0.23032	0.7874	3.418796	7.874	3.71165
	40	0.20481	1.80762	8.82586	18.0762	6.57519
	70	0.17417	3.0334	17.41682	30.334	8.6276
48h	0	0.24906	0.0376	0.150968	0.376	-5.7087
	10	0.22878	0.8488	3.710115	8.488	3.95856
	40	0.19875	2.0502	10.31573	20.502	7.04616
	70	0.16617	3.3534	20.18115	33.534	9.07238
72h	0	0.24549	0.1804	0.734857	1.804	-0.9302
	10	0.22422	1.03122	4.599154	10.3122	4.60714
	40	0.19398	2.241	11.55304	22.41	7.38819
	70	0.16117	3.5532	22.04629	35.532	9.33928
96h	0	0.24538	0.1848	0.753118	1.848	-0.8561
	10	0.21835	1.2662	5.799079	12.662	5.30711
	40	0.1881	2.4762	13.16462	24.762	7.78247
	70	0.15773	3.6908	23.39948	36.908	9.51914

Table 22. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 3 yellow dye (63) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24499	0.2006	0.81883	2.006	-0.5038
	10	0.19039	2.3844	12.5238	23.844	6.37086
	40	0.12389	5.0446	40.72	50.446	9.34275
	70	0.08485	6.6062	77.862	66.062	10.9766
48h	0	0.2443	0.2282	0.93412	2.282	-0.1718
	10	0.18521	2.59164	13.9931	25.9164	6.65046
	40	0.11626	5.3498	46.0178	53.498	9.65102
	70	0.07419	7.0326	94.7981	70.326	11.4726
72h	0	0.24282	0.2872	1.18277	2.872	0.42309
	10	0.18404	2.6384	14.336	26.384	6.7115
	40	0.11043	5.583	50.5592	55.83	9.88824
	70	0.06557	7.3772	112.509	73.772	11.9043
96h	0	0.24291	0.2838	1.16836	2.838	0.39219
	10	0.17642	2.9432	16.6829	29.432	7.09363
	40	0.09668	6.1328	63.434	61.328	10.46
	70	0.05745	7.7022	134.08	77.022	12.3464

Table 23. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 3 yellow dye (63) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.23929	0.4286	1.79117	4.286	1.6145
	10	0.18616	2.5536	13.7172	25.536	7.2535
	40	0.11519	5.3926	46.8169	53.926	10.654
	70	0.06454	7.4186	114.955	74.186	13.142
48h	0	0.23978	0.409	1.70577	4.09	1.4792
	10	0.17373	3.051	17.5622	30.51	7.9379
	40	0.09031	6.3876	70.7297	63.876	11.797
	70	0.05197	7.9212	152.419	79.212	13.923
72h	0	0.23131	0.7476	3.23203	7.476	3.2494
	10	0.15108	3.95678	26.1899	39.568	9.0448
	40	0.08455	6.6182	78.2802	66.182	12.078
	70	0.04655	8.1382	174.846	81.382	14.304
96h	0	0.24306	0.2776	1.1421	2.776	0.368
	10	0.14856	4.0576	27.3129	40.576	9.1611
	40	0.07486	7.0058	93.5916	70.058	12.572
	70	0.04049	8.3804	206.975	83.804	14.771

Table 24. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 3 yellow dye (63) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.23289	0.68441	2.93877	6.8441	3.254835
	10	0.21267	1.49327	7.02161	14.9327	5.884689
	40	0.16707	3.31739	19.8569	33.1739	9.023476
	70	0.11477	5.40916	47.1301	54.0916	11.63329
48h	0	0.23255	0.698	3.00151	6.98	3.318608
	10	0.20781	1.6878	8.12204	16.878	6.324271
	40	0.15103	3.9588	26.212	39.588	9.861851
	70	0.10782	5.6874	52.7515	56.874	11.97351
72h	0	0.23272	0.6912	2.97009	6.912	3.286843
	10	0.19858	2.057	10.3588	20.57	7.058746
	40	0.14479	4.2086	29.0679	42.086	10.17411
	70	0.10167	5.9334	58.3623	59.334	12.27869
96h	0	0.23263	0.695	2.98764	6.95	3.304629
	10	0.19346	2.2618	11.6916	22.618	7.42419
	40	0.13873	4.451	32.0851	44.51	10.47228
	70	0.09498	6.201	65.2909	62.01	12.61741

Table 25. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using commercial red dye (52) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24008	0.39696	1.65346	3.969564	1.26748
	10	0.2028	1.88787	9.30885	18.87865	5.623123
	40	0.1667	3.33196	19.9877	33.31963	7.549156
	70	0.12688	4.925	38.8177	49.25	9.22216
48h	0	0.23706	0.5178	2.1843	5.178	1.96925
	10	0.19404	2.2384	11.5358	22.384	6.163736
	40	0.15676	3.7296	23.7918	37.296	7.988288
	70	0.12262	5.0952	41.5528	50.952	9.393772
72h	0	0.23781	0.4876	2.05038	4.876	1.80977
	10	0.19042	2.3834	12.5169	23.834	6.369471
	40	0.14973	4.011	26.7891	40.11	8.287357
	70	0.11436	5.4258	47.447	54.258	9.728113
96h	0	0.2314	0.74418	3.21604	7.441782	2.944314
	10	0.17887	2.8454	15.9081	28.45398	6.973757
	40	0.14233	4.30689	30.2604	43.06891	8.594463
	70	0.10945	5.62209	51.3679	56.22094	9.92824

Table 26. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using commercial red dye (52) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24775	1.23876	6.19379	30.969	154.84
	10	0.21553	0.9699	4.36454	19.64	88.382
	40	0.17386	0.78238	3.5207	15.843	71.294
	70	0.14595	0.65677	2.95546	13.3	59.848
48h	0	0.24291	1.21455	6.07275	30.364	151.82
	10	0.21222	0.95497	4.29736	19.338	87.022
	40	0.17123	0.77053	3.4674	15.603	70.215
	70	0.14236	0.64061	2.88274	12.972	58.375
72h	0	0.24241	1.21203	6.06017	30.301	151.5
	10	0.21064	0.94787	4.26542	19.194	86.375
	40	0.16713	0.75211	3.38447	15.23	68.536
	70	0.1331	0.59895	2.69526	12.129	54.579
96h	0	0.24171	1.20855	6.04275	30.214	151.07
	10	0.20707	0.9318	4.19312	18.869	84.911
	40	0.16227	0.73022	3.28597	14.787	66.541
	70	0.13063	0.58784	2.64527	11.904	53.567

Table 27. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using commercial red dye (52) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.23903	0.43864	1.835053	4.3864	1.83297
	10	0.23399	0.64052	2.737417	6.4052	3.04053
	40	0.19548	2.18094	11.15704	21.8094	7.28288
	70	0.16228	3.50892	21.62303	35.0892	9.28075
48h	0	0.24021	0.39172	1.63076	3.9172	1.4766
	10	0.22414	1.03424	4.614177	10.3424	4.61699
	40	0.19175	2.33016	12.15233	23.3016	7.54089
	70	0.15839	3.66426	23.1339	36.6426	9.48468
72h	0	0.24263	0.29484	1.215189	2.9484	0.58847
	10	0.218	1.2801	5.872086	12.801	5.34488
	40	0.18598	2.56076	13.76893	25.6076	7.91799
	70	0.15119	3.95234	26.14128	39.5234	9.85369
96h	0	0.24403	0.23876	0.9784	2.3876	-0.0659
	10	0.2138	1.44806	6.773013	14.4806	5.77585
	40	0.18023	2.79066	15.48358	27.9066	8.27235
	70	0.14524	4.19052	28.85298	41.9052	10.1517

Table 28. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 1 red dye (65) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level (g/L)	C^S (g/L)	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24907	0.0372	0.14938	0.37205	-4.79216
	10	0.20644	1.7424	8.44011	17.4238	5.37619
	40	0.15241	3.9036	25.6127	39.0362	8.174172
	70	0.11038	5.5847	50.5943	55.8471	9.889991
48h	0	0.24872	0.0512	0.20585	0.512	-3.98386
	10	0.20235	1.9062	9.42054	19.062	5.653187
	40	0.14081	4.3676	31.0177	43.676	8.656765
	70	0.09877	6.0494	61.2504	60.494	10.37174
72h	0	0.24886	0.0456	0.18324	0.456	-4.27723
	10	0.19384	2.2466	11.5903	22.466	6.175617
	40	0.13534	4.5866	33.8907	45.866	8.880039
	70	0.08752	6.4994	74.2661	64.994	10.8574
96h	0	0.24779	0.0884	0.35675	0.884	-2.59789
	10	0.18253	2.699	14.787	26.99	6.789566
	40	0.11839	5.2646	44.4702	52.646	9.564799
	70	0.07753	6.899	88.9906	68.99	11.31329

Table 29. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 1 red dye (65) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24847	0.06128	0.246642	0.6128	-3.877
	10	0.18965	2.41385	12.72768	24.139	7.0461
	40	0.14037	4.38514	31.23953	43.851	9.5332
	70	0.10443	5.82297	55.76173	58.23	11.138
48h	0	0.24212	0.3154	1.302687	3.154	0.7324
	10	0.18442	2.6232	14.22405	26.232	7.354
	40	0.12025	5.1902	43.16354	51.902	10.429
	70	0.08873	6.4508	72.70145	64.508	11.873
72h	0	0.24114	0.3544	1.469686	3.544	1.0666
	10	0.17663	2.935	16.61713	29.35	7.7847
	40	0.10692	5.7232	53.52787	57.232	11.025
	70	0.07534	6.9866	92.74043	69.866	12.547
96h	0	0.24397	0.2412	0.988646	2.412	-0.032
	10	0.17073	3.1708	18.57201	31.708	8.0928
	40	0.09969	6.0126	60.316	60.126	11.356
	70	0.06903	7.2388	104.8646	72.388	12.888

Table 30. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 1 red dye (65) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24484	0.20641	0.84306	2.06414	-0.51546
	10	0.16863	3.25461	19.2997	32.5461	8.93755
	40	0.11206	5.51744	49.2347	55.1744	11.76519
	70	0.07584	6.96645	91.8589	69.6645	13.64822
48h	0	0.22958	0.817	3.55875	8.17	3.83279
	10	0.16033	3.5868	22.3714	35.868	9.383477
	40	0.09242	6.3032	68.2017	63.032	12.74911
	70	0.06146	7.5418	122.721	75.418	14.5228
72h	0	0.23121	0.7516	3.25072	7.516	3.559444
	10	0.15723	3.7108	23.6011	37.108	9.545047
	40	0.08146	6.7418	82.7672	67.418	13.33354
	70	0.05042	7.9832	158.334	79.832	15.29212
96h	0	0.22402	1.0392	4.63887	10.392	4.633104
	10	0.14512	4.19504	28.9066	41.9504	10.1573
	40	0.07067	7.1732	101.503	71.732	13.94965
	70	0.03994	8.4026	210.407	84.026	16.15063

Table 31. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 2 red dye (67) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24906	0.0376	0.15097	0.376	-4.76546
	10	0.20695	1.722	8.32085	17.22	5.340323
	40	0.1694	3.224	19.0319	32.24	7.425652
	70	0.12912	4.8352	37.4473	48.352	9.13157
48h	0	0.24689	0.12424	0.50321	1.2424	-1.73093
	10	0.20004	1.9984	9.99	19.984	5.801119
	40	0.1599	3.604	22.5391	36.04	7.851956
	70	0.12251	5.09954	41.625	50.9954	9.39815
72h	0	0.24452	0.219351	0.89708	2.19351	-0.27375
	10	0.19531	2.1876	11.2007	21.876	6.089432
	40	0.15359	3.8564	25.1084	38.564	8.124047
	70	0.11799	5.2804	44.7529	52.804	9.580776
96h	0	0.24251	0.2996	1.23541	2.996	0.532845
	10	0.19191	2.32362	12.1079	23.2362	6.285741
	40	0.14474	4.210268	29.0878	42.1027	8.494854
	70	0.11538	5.38466	46.6675	53.8466	9.686361

Table 32. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 2 red dye (67) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24921	0.03154	0.126559	0.3154	-5.726
	10	0.21177	1.5294	7.222157	15.294	5.4766
	40	0.18455	2.618	14.18586	26.18	7.3465
	70	0.15835	3.666	23.15125	36.66	8.7032
48h	0	0.24793	0.0829	0.334372	0.829	-3.034
	10	0.20766	1.6938	8.156799	16.938	5.8136
	40	0.17612	2.9554	16.78108	29.554	7.8119
	70	0.149	4.0402	27.11635	40.402	9.1411
72h	0	0.24635	0.1461	0.593065	1.461	-1.447
	10	0.20534	1.78642	8.699836	17.8642	5.9922
	40	0.17152	3.13928	18.30292	31.3928	8.0523
	70	0.14449	4.2206	29.21134	42.206	9.3472
96h	0	0.24842	0.06326	0.254651	0.6326	-3.789
	10	0.20986	1.6058	7.65195	16.058	5.6367
	40	0.16924	3.2306	19.08943	32.306	8.1689
	70	0.13879	4.4486	32.0539	44.486	9.6045

Table 33. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 2 red dye (67) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24875	0.04996	0.20086	0.49964	-4.84651
	10	0.22516	0.9936	4.412862	9.936	4.482294
	40	0.20138	1.945	9.658597	19.45	6.847426
	70	0.17614	2.9544	16.77302	29.544	8.513875
48h	0	0.24245	0.3022	1.246468	3.022	0.665205
	10	0.22191	1.12378	5.064228	11.2378	4.897993
	40	0.19467	2.2134	11.3703	22.134	7.340052
	70	0.17012	3.1952	18.78204	31.952	8.855451
72h	0	0.24853	0.0588	0.236591	0.588	-4.35216
	10	0.21968	1.2128	5.520757	12.128	5.158603
	40	0.19253	2.2988	11.93996	22.988	7.487655
	70	0.16503	3.3988	20.59504	33.988	9.133683
96h	0	0.2431	0.2762	1.136181	2.762	0.385489
	10	0.21501	1.3996	6.509465	13.996	5.656017
	40	0.18733	2.507	13.38316	25.07	7.832182
	70	0.16325	3.47	21.25574	34.7	9.229024

Table 34. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 3 red dye (69) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.24376	0.2496	1.02396	2.496	0.059674
	10	0.16752	3.2994	19.6961	32.994	7.512124
	40	0.09191	6.3236	68.8021	63.236	10.66478
	70	0.05465	7.814	142.983	78.14	12.50849
48h	0	0.23903	0.43877	1.83561	4.38766	1.53088
	10	0.16044	3.58237	22.3283	35.8237	7.828269
	40	0.08451	6.6197	78.3326	66.197	10.99176
	70	0.04905	8.03811	163.885	80.3811	12.85239
72h	0	0.23388	0.64472	2.7566	6.4472	2.555774
	10	0.15062	3.9754	26.3944	39.754	8.249948
	40	0.07176	7.1296	99.3534	71.296	11.59093
	70	0.04046	8.3818	207.188	83.818	13.44335
96h	0	0.22825	0.86981	3.81069	8.69808	3.371936
	10	0.14403	4.23877	29.4297	42.3877	8.524303
	40	0.06249	7.50055	120.035	75.0055	12.06756
	70	0.03522	8.59127	243.944	85.9127	13.85497

Table 35. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 3 red dye (69) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.23983	0.4068	1.696201	4.068	1.4636
	10	0.18447	2.62136	14.21053	26.2136	7.35132
	40	0.12276	5.08962	41.46009	50.8962	10.3172
	70	0.07601	6.959608	91.56198	69.59608	12.5118
48h	0	0.23826	0.4698	1.971837	4.698	1.88068
	10	0.17017	3.1932	18.76476	31.932	8.12135
	40	0.10645	5.74182	53.93685	57.4182	11.0459
	70	0.06661	7.3357	110.1332	73.357	13.0233
72h	0	0.23816	0.4736	1.988579	4.736	1.9041
	10	0.16976	3.2098	18.90843	32.098	8.14248
	40	0.10041	5.98368	59.59366	59.8368	11.3222
	70	0.05595	7.762	138.731	77.62	13.6627
96h	0	0.23867	0.4532	1.898856	4.532	1.77622
	10	0.15957	3.61726	22.66901	36.1726	8.64491
	40	0.09049	6.38044	70.51067	63.8044	11.7881
	70	0.04739	8.1046	171.0372	81.046	14.2426

Table 36. C^s, C^f, K, %E, and -Δμ° data from equilibrium exhaustion experiments using type 3 red dye (69) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

	Salt Level g/L	C^S g/L	C^f g/L	K	% E	-Δμ° (kJ/mol)
24h	0	0.22881	0.847533	3.704063	8.475328	3.953627
	10	0.19103	2.358634	12.34666	23.58634	7.588788
	40	0.13809	4.476313	32.4154	44.76313	10.50321
	70	0.08732	6.507193	74.52109	65.07193	13.01666
48h	0	0.21582	1.367328	6.335594	13.67328	5.574272
	10	0.18445	2.62183	14.21399	26.2183	8.014036
	40	0.13046	4.781638	36.65241	47.81638	10.87412
	70	0.07818	6.872608	87.90208	68.72608	13.51528
72h	0	0.21327	1.469139	6.888585	14.69139	5.826938
	10	0.17539	2.984306	17.01503	29.84306	8.557128
	40	0.12131	5.147578	42.43306	51.47578	11.3163
	70	0.07433	7.026869	94.53828	70.26869	13.73503
96h	0	0.20815	1.674161	8.043205	16.74161	6.294822
	10	0.16537	3.385193	20.4704	33.85193	9.115353
	40	0.11034	5.586213	50.62512	55.86213	11.84928
	70	0.06976	7.209712	103.3544	72.09712	14.00423

Table 37. L*, a* b*, and K/S data from equilibrium exhaustion experiments using commercial yellow dye (51) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	90.15	-0.74	16.48	0.18
	10	80.52	11.2	52.23	2.22
	40	78.83	16.25	61.11	3.59
	70	77.62	18.22	65.72	4.7
48 h	0	90.04	-0.52	16.85	0.19
	10	79.73	14.53	62.01	3.54
	40	78.8	15.82	62.3	3.79
	70	77.95	17.9	66.36	4.75
72 h	0	89.21	-0.13	19.09	0.24
	10	80.82	12.35	54.32	2.37
	40	80.35	13.43	56.16	2.63
	70	79.05	15.95	58.74	3.18
96 h	0	89.99	-0.25	18.72	0.21
	10	81.71	11.56	11.56	2.04
	40	78.63	16.28	61.96	3.79
	70	78.23	17.34	62.63	4

Table 38. L*, a* b*, and K/S data from equilibrium exhaustion experiments using commercial yellow dye (51) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	90.69	-0.75	11.88	0.12
	10	82.9	8.6	48.44	1.64
	40	80.86	12.43	54.92	2.43
	70	79.94	13.36	55.72	2.66
48 h	0	91.09	-0.69	13.02	0.16
	10	83.89	7.77	43.91	1.26
	40	81.08	11.31	52.54	2.17
	70	79.24	14.96	57.91	3.07
72 h	0	90.67	-0.58	13.82	0.16
	10	83.82	7.37	43.82	1.27
	40	80.92	12.15	53.02	2.26
	70	79.92	13.53	54.3	2.54
96 h	0	90.78	-0.6	10.82	0.13
	10	83.2	8.39	46.89	1.5
	40	80.05	12.85	55.57	2.65
	70	79.77	14.3	58.06	2.97

Table 39. L*, a* b*, and K/S data from equilibrium exhaustion experiments using commercial yellow dye (51) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	90.51	-0.86	13.08	0.14
	10	84.32	5.57	37.49	0.92
	40	82.11	9.17	46.42	1.59
	70	82.31	10.72	49.36	1.76
48 h	0	90.67	-0.69	10.35	0.13
	10	86.45	4	33.08	0.65
	40	82.28	8.62	45.42	1.5
	70	82.49	9.85	46.96	1.57
72 h	0	90.67	-0.62	10.14	0.17
	10	86.63	3.73	30.66	0.57
	40	83.83	7.2	39.23	1.03
	70	82.73	9.43	43.29	1.32
96 h	0	90.62	-0.31	10.54	0.14
	10	86.36	3.86	30.07	0.56
	40	83.49	8.17	39.03	1.04
	70	82.34	9.71	43.46	1.37

Table 40. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 1 yellow dye (58) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	89.91	-0.65	9.57	0.12
	10	82.9	9.28	44.42	1.3
	40	79.6	15.39	53.59	2.33
	70	77.9	18.3	59.3	3.27
48 h	0	90.28	-0.45	12.59	0.15
	10	82.66	10.26	46.52	1.45
	40	79.01	16.48	54.63	2.53
	70	78.37	17.72	56.1	2.79
72 h	0	90.46	-0.47	12.27	0.13
	10	81.6	11.89	48.48	1.68
	40	77.77	18.77	60.61	3.51
	70	77.2	18.96	63.4	4.13
96 h	0	88.25	-0.28	15.83	0.22
	10	80.2	12.75	50.58	2.01
	40	75.21	20.36	63.21	4.64
	70	75.54	20.42	64.35	4.8

Table 41. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 1 yellow dye (58) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	90.78	-0.39	11.44	0.11
	10	83.08	9.6	43.43	1.23
	40	79.45	16.34	55.27	2.53
	70	77.63	18.99	63.25	4
48 h	0	90.73	-0.35	12.38	0.13
	10	82.77	10.13	45.8	1.4
	40	78.82	16.9	55.89	2.71
	70	77.92	18.87	59.41	3.31
72 h	0	90.01	-0.3	14.18	0.15
	10	80.75	11.54	46.97	1.67
	40	76.22	19.06	60.1	3.83
	70	75.63	21.11	61.53	4.19
96 h	0	88.09	-0.07	17.32	0.23
	10	77.95	13.43	54.1	2.68
	40	73.79	20.53	62.73	5.02
	70	73.88	22.88	66.61	5.91

Table 42. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 1 yellow dye (58) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	90.64	-0.54	11.34	0.12
	10	83.65	8.29	40.32	1.05
	40	79.87	14.01	49.99	2.01
	70	78.04	17.37	55.25	2.78
48 h	0	90.73	-0.38	11.99	0.13
	10	83.73	8.52	40.95	1.08
	40	79.73	14.99	51.89	2.07
	70	78.28	17.3	53.17	2.53
72 h	0	90.61	-0.25	13.71	0.14
	10	84.24	7.99	38.07	0.91
	40	78.53	16.79	53.33	2.52
	70	77.58	17.99	54.24	2.78
96 h	0	89.87	0.07	14.08	0.18
	10	81.82	8.29	38.98	1.14
	40	77.17	16.84	50.81	2.49
	70	74.6	21.07	58.82	4.09

Table 43. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 2 yellow dye (61) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	91.74	-0.61	5.36	0.08
	10	84.78	6.22	39.05	0.92
	40	81.45	11.65	51.53	1.93
	70	80.63	13.9	54.68	2.3
48 h	0	91.7	-0.63	6.13	0.08
	10	86.17	4.45	34.72	0.69
	40	82.89	10.46	46.31	1.41
	70	80.21	14.08	55.99	2.49
72 h	0	91.44	-0.62	7.87	0.09
	10	86.01	5.16	33.48	0.65
	40	82	11.01	47.7	1.58
	70	80.44	13.95	52.07	2.08
96 h	0	91.18	-0.56	8.07	0.09
	10	85.32	5.33	36.79	0.8
	40	81.85	11.28	48.05	1.61
	70	80.04	14.54	54.93	2.4

Table 44. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 2 yellow dye (61) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	91.89	-0.52	5.58	0.08
	10	88.44	1.54	23.5	0.33
	40	85.23	5.9	33.3	0.68
	70	82.95	9.17	40.31	1.09
48 h	0	91.72	-0.49	5.32	0.08
	10	88.56	1.86	22.77	0.31
	40	85.12	6.32	34.81	0.73
	70	83.44	8.96	37.78	0.94
72 h	0	91.74	-0.32	5.15	0.08
	10	88.93	1.45	21.84	0.28
	40	85.16	5.89	34.67	0.73
	70	82.96	9.25	41.09	1.12
96 h	0	91.82	-0.53	5.95	0.08
	10	87.78	2.04	25.51	0.38
	40	85.02	6.55	34.57	0.73
	70	82.75	9.89	41.22	1.14

Table 45. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 2 yellow dye (61) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	91.38	-0.41	6.67	0.09
	10	89.57	0.79	15.87	0.18
	40	87.41	2.89	24.24	0.37
	70	85.79	5.37	30.12	0.56
48 h	0	91.39	-0.26	6.56	0.1
	10	89.34	1.56	17.94	0.21
	40	87.25	3.45	24.92	0.38
	70	86.23	5.33	28.94	0.51
72 h	0	91.35	-0.13	6.4	0.1
	10	89.32	1.12	14.38	0.17
	40	87.97	2.91	21.45	0.3
	70	85.29	5.85	30.79	0.6
96 h	0	91.19	-0.04	7.53	0.11
	10	88.96	1.86	16.91	0.2
	40	87.11	4.33	23.58	0.36
	70	86.07	5.63	27.22	0.47

Table 46. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 3 yellow dye (63) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	89.87	-0.54	11.58	0.15
	10	78.88	13.62	52.69	2.37
	40	75.48	20.4	65	4.88
	70	74.14	23.13	71.9	7.19
48 h	0	89.68	-0.21	16.44	0.19
	10	79.55	14.7	53.83	2.38
	40	75.53	21.21	64.51	4.8
	70	75.25	22.61	66.38	5.31
72 h	0	89.39	-0.03	16.17	0.19
	10	79.3	14.77	54.73	2.51
	40	74.88	21.79	60.92	4.35
	70	74.23	22.83	65.63	5.5
96 h	0	88.68	0.09	18.48	0.24
	10	77.33	16.22	58.56	3.35
	40	74.71	23.03	67.75	5.77
	70	74.49	23.87	67.81	5.94

Table 47. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 3 yellow dye (63) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	88.15	-0.41	12.88	0.2
	10	80.15	12.94	52.53	2.16
	40	73.51	24.33	66.54	5.98
	70	74.18	22.62	68.74	6.25
48 h	0	89.83	0.09	14.9	0.16
	10	79.7	13.8	51.11	2.1
	40	75.18	21.94	63.8	4.72
	70	73.8	24.07	65.38	5.54
72 h	0	89.07	0.5	18.22	0.22
	10	79.72	14.47	51.73	2.14
	40	74.82	21.64	63.77	4.87
	70	73.62	23.49	65.22	5.61
96 h	0	89.02	0.61	17.71	0.21
	10	80.15	12.5	46.37	1.67
	40	75.35	18.81	56.38	3.45
	70	73.92	21.08	59.15	4.23

Table 48. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 3 yellow dye (63) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	88.15	0.47	17.89	0.24
	10	80.51	11.1	44.68	1.52
	40	76.52	18.75	58.65	3.47
	70	74.66	22.13	63.74	4.9
48 h	0	88.48	0.79	18.5	0.24
	10	81.17	11.43	44.49	1.44
	40	76.39	18.59	55.85	3.14
	70	74.82	21.92	60.23	4.18
72 h	0	88.45	1.03	20.09	0.26
	10	82.19	8.87	41.26	1.19
	40	75.69	19.67	56.63	3.43
	70	74.42	22.07	59.98	4.26
96 h	0	88.56	0.99	17.8	0.23
	10	80.99	11.14	41.13	1.26
	40	76.66	18.4	55.75	3.09
	70	75.59	20.79	57.58	3.56

Table 49. L*, a* b*, and K/S data from equilibrium exhaustion experiments using commercial red dye (52) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	83.43	13.83	-6.09	0.18
	10	60.33	43.05	-11.33	2.16
	40	54.55	48.05	-10.47	3.55
	70	52.2	50.5	-9.49	4.47
48 h	0	81.56	16.52	-7.78	0.23
	10	58.75	44.14	-10.81	2.43
	40	52.7	49.74	-10.16	4.23
	70	50.9	52.8	-8.87	5.27
72 h	0	81.69	16.39	-7.91	0.23
	10	60.14	41.78	-10.84	2.1
	40	52.61	49.29	-9.51	4.2
	70	51.48	51.41	-9.22	4.83
96 h	0	79.75	19.66	-9.09	0.3
	10	56.36	45.66	-10.55	2.94
	40	50.57	50.62	-10.05	5.05
	70	48.55	53.43	-8.22	6.34

Table 50. L*, a* b*, and K/S data from equilibrium exhaustion experiments using commercial red dye (52) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	85.23	11.16	-5.46	0.13
	10	62.87	40.07	-10.91	1.67
	40	57.54	46.35	-10.72	2.78
	70	56.45	48.51	-11.96	3.21
48 h	0	84.18	12.77	-6.22	0.16
	10	64.72	38.6	-11.19	1.44
	40	57.42	46.04	-10.47	2.77
	70	51.86	51.25	-9.74	4.69
72 h	0	82.75	14.79	-7.28	0.2
	10	61.67	41.55	-11.09	1.89
	40	55.07	48.31	-10.67	3.45
	70	52.21	50.66	-9.39	4.49
96 h	0	83.65	13.91	-6.88	0.18
	10	60.01	42.56	-10.35	2.14
	40	55.98	46.84	-9.8	3.11
	70	53.12	49.11	-9.32	4.02

Table 51. L*, a* b*, and K/S data from equilibrium exhaustion experiments using commercial red dye (52) at90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	85.19	10.61	-4.64	0.13
	10	67.85	34.01	-10.13	1.02
	40	59.13	43.92	-10.23	2.36
	70	56.79	46.31	-10.04	2.92
48 h	0	84.17	12.46	-4.93	0.16
	10	69.38	32.57	-10.33	0.91
	40	61.06	42.43	-10.55	1.99
	70	57.94	45.37	-10.52	2.63
72 h	0	80.92	17.31	-7.63	0.26
	10	65.91	36.96	-11.37	1.29
	40	60.43	43.11	-11.06	2.12
	70	58.92	44.5	-11.05	2.42
96 h	0	83.8	13.25	-6.33	0.17
	10	70.26	31.21	-10.61	0.83
	40	63.17	39.47	-11.48	1.62
	70	59.48	42.58	-10.39	2.22

Table 52. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 1 red dye (65) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	88.19	7.05	-3.61	0.08
	10	67.17	44.01	-12.97	1.12
	40	57.74	44.01	-14.27	2.54
	70	56.69	44.88	-14.3	2.93
48 h	0	87.37	8.26	-4.39	0.09
	10	65.7	35.28	-13.27	1.23
	40	56.14	44.45	-14	3
	70	54.37	46.74	-13.69	3.58
72 h	0	87.07	8.53	-4.52	0.1
	10	64.98	36.19	-13.66	1.38
	40	58.47	42.41	-14.34	2.33
	70	55.97	45.15	-14.28	3.09
96 h	0	88.23	6.84	-3.53	0.08
	10	69.93	30.34	-12.12	0.86
	40	63.15	37	-12.65	1.57
	70	61.53	38.77	-13	1.82

Table 53. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 1 red dye (65) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	87.42	8.3	-4.24	0.09
	10	69.16	31.31	-12.44	0.89
	40	59.4	42.32	-14.33	2.3
	70	57.37	42.98	-13.55	2.65
48 h	0	86.42	9.84	-5.38	0.11
	10	65.86	34.42	-12.51	1.24
	40	54.78	45.22	-13.74	3.33
	70	54.45	46.38	-13.64	3.46
72 h	0	86.5	9.66	-5.05	0.11
	10	66.73	33.58	-12.64	1.14
	40	58.34	40.82	-13.01	2.35
	70	57.69	41.9	-13.08	2.52
96 h	0	85.2	10.94	-5.77	0.14
	10	64.26	35.76	-12.93	1.36
	40	55.75	42.81	-13.29	2.93
	70	54.58	45.24	-13.4	3.38

Table 54. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 1 red dye (65) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	83.9	13.49	-6.93	0.17
	10	66.27	34.5	-12.94	1.21
	40	54.34	44.72	-12.77	3.35
	70	52.04	46.48	-13.19	4.14
48 h	0	83.54	13.79	-7.05	0.18
	10	64.52	35.85	-12.76	1.39
	40	55.93	43.21	-12.83	2.92
	70	51.45	47.04	-12.93	4.18
72 h	0	80.94	17.53	-8.65	0.26
	10	62.33	37.27	-12.63	1.67
	40	54.17	44.43	-12.92	3.37
	70	49.67	48.11	-12.56	4.96
96 h	0	82.29	15.46	-7.77	0.22
	10	63.65	36.5	-12.72	1.5
	40	55.37	43.3	-13.35	3.04
	70	51	47.19	-12.69	4.41

Table 55. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 2 red dye (67) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	88.63	5.41	-2.19	0.07
	10	70.73	29.91	-11.44	0.8
	40	62.77	39.27	-13.73	1.71
	70	57.17	44.89	-13.9	2.83
48 h	0	89.38	4.69	-2.71	0.06
	10	69.67	31.43	-12.27	0.9
	40	62.2	39.26	-13.38	1.77
	70	59.7	41.66	-13.6	2.21
72 h	0	87.66	5.55	-2.16	0.08
	10	68.48	32.37	-12.36	1
	40	60.13	40.38	-13.21	2.1
	70	58.51	41.71	-13.28	2.39
96 h	0	88.27	6.3	-3.63	0.07
	10	68.79	32.89	-12.87	0.99
	40	61.13	40.52	-13.64	1.96
	70	57.59	43.26	-13.63	2.63

Table 56. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 2 red dye (67) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	90.19	3.58	-1.99	0.05
	10	74.17	26.83	-11.87	0.58
	40	64.64	36.7	-13.71	1.42
	70	61.05	39.71	-13.35	1.92
48 h	0	89.4	4.88	-2.86	0.06
	10	73.64	26.21	-11.07	0.59
	40	64.29	37.06	-13.48	1.47
	70	60.16	40.62	-13.46	2.08
72 h	0	88.94	6.01	-3.43	0.07
	10	72.77	27.95	-12.02	0.67
	40	64.16	36.31	-13.3	1.45
	70	58.32	42.17	-13.69	2.44
96 h	0	89.66	4.56	-2.69	0.05
	10	72.73	28.12	-11.9	0.67
	40	64.15	36.86	-13.17	1.47
	70	59.11	40.2	-13.15	2.21

Table 57. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 2 red dye (67) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	88.45	6.34	-3.45	0.07
	10	77.66	21.2	-10.17	0.39
	40	68.85	31.35	-12.44	0.94
	70	63.1	36.24	-12.62	1.54
48 h	0	84.59	11.98	-6.3	0.15
	10	77.61	20.71	-9.91	0.38
	40	68.88	30.67	-12.3	0.93
	70	63.24	36.44	-13.01	1.54
72 h	0	85.51	10.28	-5.41	0.13
	10	75.58	23.54	-10.65	0.48
	40	66.72	33.27	-12.86	1.14
	70	58.54	41.61	-13.73	2.37
96 h	0	86.39	8.28	-4.44	0.11
	10	76.89	21.67	-10.52	0.42
	40	67.27	32.32	-12.6	1.08
	70	63.45	34.63	-12.21	1.45

Table 58. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 3 red dye (69) at 30 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	82.91	12.5	-4.94	0.19
	10	55.14	45.68	-13.16	3.13
	40	47.85	50.64	-12.15	6.09
	70	44.9	53.73	-11.1	8.24
48 h	0	81.62	16.04	-7.75	0.24
	10	55.33	44.46	-12.75	3.15
	40	48.13	49.21	-11.93	5.75
	70	45.41	51.75	-11.36	7.56
72 h	0	81.76	15.95	-7.86	0.23
	10	55.32	45.22	-13.29	3.21
	40	48.48	48.86	-12.3	5.55
	70	46.74	51.54	-11.89	6.83
96 h	0	80.64	16.82	-8.18	0.27
	10	51.91	48.17	-12.66	4.37
	40	45.98	50.39	-11.16	6.89
	70	42.34	52.77	-9.81	9.92

Table 59. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 3 red dye (69) at 60 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	83.13	13.24	-5.89	0.19
	10	56.13	43.57	-12.92	2.91
	40	46.37	51.69	-11.92	7.06
	70	44.7	50.8	-10.99	7.68
48 h	0	81.25	16.55	-8.34	0.25
	10	53.75	45.78	-12.89	3.63
	40	46.61	51.04	-11.88	6.78
	70	45.77	50.98	-11.98	7.2
72 h	0	80.7	16.87	-8.21	0.27
	10	53.3	46.01	-13.08	3.77
	40	47.81	48.86	-12.07	5.8
	70	43.94	52.3	-10.94	8.6
96 h	0	79.66	18.21	-8.42	0.3
	10	52.05	46.72	-12.35	4.15
	40	45.29	50.14	-11.3	7.24
	70	44.15	52.5	-10.69	8.46

Table 60. L*, a* b*, and K/S data from equilibrium exhaustion experiments using type 3 red dye (69) at 90 °C, woven cotton (1g), 40:1 LR, and %1 (owg) dye.

Time	Salt Level (g/L)	L*	a*	b*	K/S
24 h	0	81.86	15.57	-7.65	0.23
	10	58.39	40.95	-13.41	2.36
	40	49.72	47.35	-12.76	4.86
	70	45.93	49.76	-11.75	6.81
48 h	0	79.01	19.13	-9.01	0.33
	10	56.96	43.47	-13.32	2.77
	40	46.7	49.9	-11.45	6.47
	70	46.35	51.46	-11.42	7.02
72 h	0	79.75	18.47	-8.72	0.3
	10	56.27	43.74	-13.37	2.9
	40	47.07	49.33	-11.55	6.2
	70	44	51.31	-10.92	8.3
96 h	0	80.78	16.69	-7.73	0.26
	10	56.97	42.06	-12.47	2.65
	40	47.96	48.89	-11.81	5.74
	70	43.38	52.22	-10.16	8.89