CHAPTER 5

Synthesis of Calix[4]resorcinarene Based Dyes and Their Application in Dyeing of Fibres
Four new ‘upper rim’ calix[4]resorcinarene based dyes have been synthesized by coupling calix[4]resorcinarene with different diazotized aromatic compounds of sulphanilic acid, anthranilic acid, $o$-aminophenol, and $p$-aminobenzoic acid. These dyes have been used for the dyeing of textile fibres like cotton and wool. Their fastness properties such as fastness to sunlight, water, washings, and perspiration have also been studied. The synthesized dyes have been employed for computerized colour strength determination through colour matching with known standards. Their $L$, $a^*$, $b^*$ values as well as the colour difference values such as $\Delta L$, $\Delta a^*$, $\Delta b^*$, $\Delta C$, and $\Delta H$ have also been reported.
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5.1 INTRODUCTION

A survey of the recent literature reveals that calix[4]resorcinarenes have been mostly studied for their complexation properties with metal ions as well as for the host-guest complexes formed with neutral organic molecules. However, no work has been reported wherein derivative of calix[4]resorcinarenes have been used as the active colouring materials.

Hence, the present investigation was undertaken, with an aim of studying the dyeing potential of calix[4]resorcinarene based dyes on textile fibres like cotton and wool.

Dyes and pigments are chemical components that are responsible for much of the colour in the natural world and which are added to manufactured goods such as textiles, and foodstuffs to generate a desired colour. Unlike pigments, dyes are soluble in material in which they are applied and hence are absorbed to a certain extent by the material. Dyes may either be natural or synthetic in origin. Colourants obtained from animal or vegetable matter with little or no chemical processing are known as natural dyes. Most of the natural dyes have little or no commercial use in modern industry, but some are still employed in cottage industries and by handicraft workers.

The first synthetic dye Mauveine was discovered by William Henry Perkin in 1856 and since then, many thousands of dyes have been prepared and utilized. The colours from some dyes are more stable than others, however a dye that does not fade when the material on which it is applied is exposed to conditions associated with its intended use is called a fast dye. On the contrary, a dye that loses its colouring during proper usage is referred to as a fugitive dye. Dyes are now classified according to their applications type.
Acid dye

Acid dyes are water-soluble anionic dyes. They are applied primarily to fibres such as wool, silk, nylon and all of which contain basic groups. Attachment to the fibre is attributed, at least partly, to salt formation between anionic groups in the dyes and cationic groups in the fibre. Although some acid dyes stain cellulosic fibres considerably, none are sufficiently substantive to be of commercial value for colouring cellulosic materials.

Basic dye

Basic dyes are defined as cationic dyes characterized by their substantivity for acidic type of fibres like acrylic, tannin-mordanted cotton etc. They are also used in the colouration of papers. The earliest synthetic dyes including Perkin’s Mauveins, were basic dyes.

Direct (Substantive) dye

They are defined as anionic dyes substantive to cellulose when applied from an aqueous bath containing an electrolyte. They provide the simplest means of dyeing cellulosic materials since a single-stage process from neutral or slightly alkaline solution to which sodium chloride or sulphate is added normally applies them as necessary to promote dye uptake. Direct dyes are also used on paper, leather, wool, silk, and nylon. They are also used as pH indicators and as biological stains.

Mordant dye

As the name suggests these dyes require a mordant. This improves the fastness of the dye on the fibre for water, light, and perspiration. The choice of mordant is very important as different mordants can change the final colour significantly. A number of different compounds may be used as mordants, but
metallic hydroxides of tin, iron, chromium, or aluminum are most common. Most natural dyes are mordant dyes and therefore, there is a large literature base describing dyeing techniques.

**Vat dye**

Vat dyes are coloured, insoluble in water, and incapable of dyeing fibres directly. However, reduction in alkaline sodium hydrogen sulphite to colourless soluble form (leuco). In this leuco form these dyes have an affinity for the textile fibre. Subsequent oxidation by exposure to air or an oxidizing agent reforms the original insoluble dye.

**Reactive dye**

First appeared commercially in 1956 and were used to dye cellulosic fibres. The dyes contain a reactive group that, when applied to a fibre in a weakly alkaline dyebath, form a chemical bond with the fibre. Reactive dyes can also be used to dye wool and nylon, in the latter case they are applied under weakly acidic conditions.

**Disperse dye**

It is originally developed for the dyeing of cellulose acetate. They are substantially water insoluble. The dyes are finely ground in the presence of a dispersing agent then sold as a paste or spray dried or as a powder. They can also be used to dye nylon, triacetate, polyester, and acrylic fibres. In some cases a dyeing temperature of 130 °C is required and a pressurized dyebath is used. The very fine particle size gives a large surface area that aids dissolution to allow uptake by the fibre. The dyeing rate can be significantly influenced by the choice of dispersing agent used during the grinding.
Azoic dye

A dyeing technique in which an insoluble azo dye is produced directly onto or within the fibre. This is achieved by treating a fibre with a diazo component and a coupling component. With suitable adjustment of dyebath conditions the two components react to produce the required insoluble azo dye. This technique of dyeing is unique as the final colour is controlled by the choice of the diazo and coupling components.

The other class of dyes, is food dyes. These are special class of dyes of very high purity. They include direct, mordant and vat dyes. Their use is strictly controlled by legislation. Many azo dyes, anthraquinone and triphenylmethane compounds are used to give different colours to the food articles. Some naturally occurring dyes are also used.

In the present investigation, dyeing characteristic of azo dye derived from calix[4]resorcinarene have been studied for cotton and wool fibres. The complete understanding of dyeing involves several stages4 namely

1) Nature of the fibre.
2) General procedure for dyeing cotton.
3) Attachment of dye molecules to fibre.
4) Various fastness properties of the dyed cotton fibre.
5) Computerized colour matching.

1) Nature of the fibres

a) Nature of the Cotton Fibre

Cotton consists of the seed-hair of the cotton plant, and is obtained from the ripened husks. There are several kinds of cotton, which are distinguished according to the country of origin and the species of plant grown there. They are valued
according to the widely varying staple, diameter, tensile strength, colour, twists, and evenness of the fibres. The superior long-stapled cottons have a smaller diameter than the inferior short-stapled varieties, even as the latter show a greater affinity for dyestuffs. The cotton fibre consists of a long, flat, ribbon-like cell twisted to an irregular longitudinal spiral. Down the center of this cell runs a canal (lumen), whilst outside it is covered by a thin skin, the cuticula.

In chemical composition, cotton is the purest form of cellulose found in nature. It contains only 5% impurities, mainly pectines, also saponifiable and unsaponifiable cotton wax, cotton oil, minute amounts of colouring matter (gossypol) and albumen. The object of scouring and bleaching cotton materials is the removal of these impurities.

**b) Nature of Wool Fibres**

Wool is an extremely complex protein, evolved over millions of years for the protection of warm-blooded animals in a great variety of climates and conditions. Wool fibre is a resilient and elastic that it can be bent 30,000 times without danger of breaking or damage. Every wool fibre has a natural elasticity and crimp that allows it to stretched as much as one third and then spring back into its original place. Its complex cellular structure enables it to absorb moisture vapour but repel liquid-try and soak up water with a wool cloth. No synthetic fibre has been able to combine all these characteristics.

Wool fibre comprises an outer layer of scales and the bulk of the fibre, called the cortex. This is made up of millions of long cells held together by a strong natural binding material. This material is made up of paracortex and ortocortex, each with slightly different quantities that give wool fibre the characteristic “crimp” or small curls.
2) **General procedure for cotton dyeing**

Before dyeing, it is essential to give the fibre a wetting out or scouring treatment, so that the dye liquor may penetrate the fibrous material thoroughly and produce level dyeing. Pretreatment for dyeing depends on various factors such as the nature of the fibre and the form in which it is used, the depth of the shade, and the subsequent processing to which the dyed material is to be presented. Usually dyeing is carried out at or near the boiling point, but temperatures as low as 40°C-50°C is suitable in some cases. Building up of the shade and exhaustion of the dye are affected by the addition of common salt, sodium sulphate, Glauber’s salt or sodium phosphate. After dyeing, the material is rinsed with cold water and dried.

To increase its fastness towards light, water, washing, perspiration, cross-dyeing is desirable. Such improvement can be effected by an after-treatment of direct dyes on the fibre by means of formaldehyde, copper sulphate, chloride of lime, and some quaternary ammonium salts.

3) **Attachment of dye molecule to fibre**

In general, dyeing is carried out in aqueous solution. The process of attachment of the dye molecules to the fibre is of absorption. There are four kinds of forces by which dye molecules are bound to fibre.

a) **The hydrogen bond (4 - 120 kJ mol⁻¹)**

A hydrogen bond may be regarded as a particular kind of dipole-dipole interaction in which a hydrogen atom attached to an electronegative atom (or electron withdrawing group) is attracted to a neighbouring dipole as an adjacent molecule or functional group. It is the hydrogen bond between cellulose molecules that keep the molecules together as fibres (and it is because they are easily broken...
and re-formed that cotton wrinkles). Hydrogen bonds play a role in dyeing with direct dyes, and may be present as “temporary” bonds with other dye types.

b) **Van der Waals forces (25 kJ mol⁻¹; variable)**

Van der Waals interaction arises from the polarization of an electron cloud by the proximity of an adjacent nucleus, resulting in a weak electrostatic attraction. Van der Waals forces are non-directional weak and can be easily broken, but they play an important role in dyeing process. They can be important in affinity, and hold dye molecules on the fibre near to where a much stronger bond may ultimately be formed.

c) **Ionic or electrostatic forces (100 – 350 kJ mol⁻¹)**

A bond, which results due to electrostatic interaction between positive and negative ions is called an ionic bond or also called salt linkage. In a typical ionic bond, there is a net transfer of one or more electrons transferred from one atom or group to another. These electrical charges produce strong attraction between differently charged ions. Ionic bonds are quite strong and are comparable in strength to covalent bonds. Such bondings are important with acid and basic (cationic) dyes.

d) **Covalent bond**

Covalent bonding results from sharing one or more electron pairs between two atoms. Covalent bonds are generally formed between the fibres and reactive dyes. These are the strongest type of chemical bonds, and are responsible for the excellent wash fastness of reactive dyes.

4) **Fastness properties**

It is a fundamental requirement that coloured fibres should withstand the conditions encountered during processing after colouration and during their
subsequent use. When a coloured fibre is subjected to particular conditions, e.g. light, washing, perspiration etc. alteration in depth, or in hue, or in brightness may take place. In certain cases there may be alteration in all the three. Further, under certain conditions, e.g. during washing, adjacent white material may become coloured due to the transfer of dye from the original dyed material. This is generally described as 'staining' or 'marking-off'.

The 'colour fastness' of a coloured fibre is therefore defined as its resistance to these changes when subjected to a particular set of conditions. It follows that colour fastness must be specified in terms of these changes and also in terms of their magnitude. Further, determination of the colour fastness of a particular material requires that the magnitude of these changes be assessed as objectively and precisely as the circumstances demand. There are various highly advanced and standardized comparative tests\(^{2,5,6}\) which quantitatively express the colour fastness of sample under observation.

5) Colour assessment

Colour is something, which makes the object more appealing, attractive and gives pleasure to the observer. Colour is associated with several aspects that create feelings and sensations or stimulus in the observer's mind. There are various theories of colour vision that were prevalent during the 19th century, the most important among them being the trichromatic theory postulated by Young and later on by Helmholtz. The theory is based on Maxwell's colour matching experiments, which demonstrated that most colours could be matched by superimposing three separate light sources known as primaries; a process known as additive mixing. If the primaries chosen are red, green, and blue, a very large numbers of colours can be matched. Based on this theory, in 1931 the CIE [Commission Internationale de
l’Eclairage (CIE) 7 developed a system for specifying colour stimuli using three imaginary primaries having tristimulus values \(X\), \(Y\), and \(Z\), defined as the amount of the three imaginary primaries that specify a colour stimulus values of \(x\), \(y\), and \(z\), can be mathematically expressed as:

\[
X = \frac{1}{k} \sum R(\lambda) S(\lambda) x(\lambda) \quad (1)
\]
\[
Y = \frac{1}{k} \sum R(\lambda) S(\lambda) y(\lambda) \quad (2)
\]
\[
Z = \frac{1}{k} \sum R(\lambda) S(\lambda) z(\lambda) \quad (3)
\]

Where \(R(\lambda)\) - spectral reflectance of the coloured surface.

\(S(\lambda)\) - spectral power distribution of a chosen illuminant.

\(x(\lambda), y(\lambda), z(\lambda)\) - colour matching functions of a standard observer.

\(K = \sum E(\lambda) y(\lambda)\) and \(\lambda =\) wavelength

The tristimulus values \(x\), \(y\), and \(z\) are often transformed and plotted in terms of a chromaticity diagram having chromaticity coordinates \(x\), \(y\), and \(z\). These can be derived by calculating the fractional components of the tristimulus values:

\[
x = \frac{X}{X+Y+Z} \quad (4)
\]
\[
y = \frac{Y}{X+Y+Z} \quad (5)
\]
\[
z = \frac{Z}{X+Y+Z} \quad (6)
\]

since, by definition \(x + y + z = 1\), only two chromaticity coordinates \(x\) and \(y\) has been recommended by CIE to specify chromaticity.

But there are various problems encountered by specification of colours in terms of tristimulus values and chromaticity. Firstly, this specification is not easily interpreted in terms of the psychophysical dimensions of colour perception namely,
brightness, hue, and colourfulness. Secondly, the X, Y, and Z system and the associated chromaticity diagrams are not perceptually uniform.

In 1976 the CIE specified a new colour space known as CIE 1976 ($L^* a^* b^*$) colour space or CIELAB. CIELAB allows the specification of colour stimuli in terms of a three-dimensional space. The $L^*$-axis is known as the lightness and extends from 0 (black) to 100 (white). The other two coordinates $a^*$ and $b^*$ represent redness-greenness and yellowness-blueness respectively. The quantities $L^*$, $a^*$, and $b^*$ are obtained from the tristimulus values according to the following transformations:

$$L^* = 116 \left( \frac{Y}{Y_n} \right)^{1/3} - 16 \quad (7)$$

$$a^* = 500 \left[ \left( \frac{X}{X_n} \right)^{1/3} - \left( \frac{Y}{Y_n} \right)^{1/3} \right] \quad (8)$$

$$b^* = 200 \left[ \left( \frac{Y}{Y_n} \right)^{1/3} - \left( \frac{Z}{Z_n} \right)^{1/3} \right] \quad (9)$$

where $X_n$, $Y_n$, and $Z_n$ are the values of $X$, $Y$, and $Z$ for the illuminant that was used for the calculation of $X$, $Y$, and $Z$ of the sample, and the quotients $X/X_n$, $Y/Y_n$, and $Z/Z_n$ are all greater than 0.008856.

6) Colour Difference

If the sample differs from the standard, the difference is to be expressed in numerical terms as well as lighter-darker, redder-greener, or yellower-blue, as compared to the standard. Various formulas based on tristimulus values have been suggested to calculate the colour difference.

$$\Delta E = [(\Delta L^*)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2} \quad (10)$$

where $\Delta E$ is the total colour difference between the standard and sample. The nature of difference can be provided in two ways:

(a) \[ \Delta L^* = L_{\text{sample}} - L_{\text{standard}} \]

\[ \Delta a = a_{\text{sample}} - a_{\text{standard}} \]
\[ \Delta b = b_{\text{sample}} - b_{\text{standard}} \]

where \( \Delta L \) indicates any difference in lightness; positive, if sample is lighter than standard; negative, if darker. \( \Delta a \) and \( \Delta b \) indicate difference in their position in CIE space.

\[(b) \quad \Delta L^* = L_{\text{sample}} - L_{\text{standard}}
\]
\[\Delta C^* = C_{\text{sample}} - C_{\text{standard}}\]
\[\Delta H = [(\Delta E)^2 + (\Delta L)^2 + (\Delta C^*)^2]^{1/2}\]

If \( \Delta L^* \) is positive the sample is lighter than the standard, but if \( \Delta L^* \) is negative the sample is darker than the standard. If \( \Delta C^* \) is positive the sample is stronger than the standard, but if \( \Delta C^* \) is negative the sample is weaker than the standard. \( \Delta H \) indicates difference in hue.

<table>
<thead>
<tr>
<th>Hue of standard</th>
<th>Sign of ( \Delta H )</th>
<th>Nature of hue difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red</td>
<td>+</td>
<td>Sample is yellower than standard</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Sample is bluer than standard</td>
</tr>
<tr>
<td>Yellow</td>
<td>+</td>
<td>Sample is greener than standard</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Sample is redder than standard</td>
</tr>
<tr>
<td>Green</td>
<td>+</td>
<td>Sample is bluer than standard</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Sample is yellower than standard</td>
</tr>
<tr>
<td>Blue</td>
<td>+</td>
<td>Sample is redder than standard</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>Sample is greener than standard</td>
</tr>
</tbody>
</table>

The choice of the formula is based on the accuracy of the result, which resembles visual assessment.

In the present investigation, the applications of azo dyes derived from calix[4]resorcinarene are described for dyeing of cotton and wool fibres. The computerized colour matching of the dyed fabrics with a known standard has also
been studied. Their L, a*, b* values as well as the colour difference values such as 
\(\Delta L^*, \Delta a^*, \Delta b^*, \Delta C^*, \text{ and } \Delta H\) have also been reported.

5.2 EXPERIMENTAL

5.2.1 Chemicals and Reagents

All the chemicals used were of analytical reagent grade of BDH, E-Merck or Qualigens unless otherwise specified.

5.2.2 Instrumentation

Elemental analysis was done on Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were recorded on an FTIR-410 ratio recording Jasco infrared spectrophotometer as KBr pellets. The \(^1\)H-NMR spectra were recorded on DRX300 operating at 300MHz for proton in DMSO-\(\text{d}_6\) with tetramethyl silane as the internal standard. The absorption spectra were recorded on Hitachi U - 3210 UV-Visible spectrophotometer using 10-mm quartz cell. The colour matching spectra were recorded on “Mac beth Colour Eye” spectrophotometer, with attached computer system.

5.2.3 Synthesis of calix[4]resorcinarene-based dyes

The synthesis of calix[4]resorcinarene-dyes involves the following steps

I. Preparation of calix[4]resorcinarene


5.2.3.1 Synthesis of calix[4]resorcinarene

Synthesis of calix[4]resorcinarene was carried out as per procedure given in chapter II, page-60.

Into a 250 ml beaker, 0.04 mol of various amino compounds such as sulphanilic acid, anthranilic acid, o-aminophenol, and p-aminobenzoic acid were dissolved in 10 ml 5-6 M hydrochloric acid and the solution was cooled to 0 to 5° C. A cold solution of 0.04 mol sodium nitrite in 5 ml water was added dropwise and the reaction mixture was stirred for 30-min. to obtain the diazonium salts of the different amino compounds.

An aqueous solution of 0.01 mol calix[4]resorcinarene in sodium hydroxide was cooled to -5 to 0° C, and the diazonium salt solution was added dropwise in 25-30 min. maintaining the temperature below 5° C. The solution was stirred for 2 h and the product was obtained by salting out with sodium chloride, yield 60-70% (Figure 1).


Dark brown powder; mp > 300° C; λ_max 425 nm in DMF; IR (KBr) 3431.73 (-OH), 1598 (-N=N-), 834 (Ar-S) cm⁻¹; ¹H NMR (DMSO-d₆) δ 1.63 ppm (d, 12H, CHCH₃), δ 5.01 ppm (q, 4H, CHCH₃), δ 7.48-8.03 ppm (m, ArH), 8.34 (s, 12H, OH).

b. Calix[4]resorcinarene-anthranilic acid dye II (2-{(11,17,23-trisf(2-carboxyphenyl)diazenyl}4,6,10,12,16,18,22,24-octahydroxy-2,8,14,20-

Brown powder; mp > 300° C ; $\lambda_{\text{max}}$ 431 nm in DMF; IR (KBr) 3467.38 (OH), 1534.06 (-N=N-), 1631.48 (C=O) cm^{-1}; $^1$H NMR (DMSO-d_6) δ 1.65 ppm (d, 12H, CHCH_3), δ 4.98 ppm (q, 4H, CHCH_3), δ 7.48-8.43 ppm (m, ArH), 8.92 ppm (s, 12 H, OH).


Reddish brown powder; mp > 300° C ; $\lambda_{\text{max}}$ 440 nm in DMF; IR (KBr) 3429.78 (Ar-OH), 1607.38 (-N=N-) cm^{-1}; $^1$H NMR (DMSO-d_6) δ 1.65 ppm (d, 12H, CHCH_3), δ 4.88 ppm (q, CHCH_3), δ 7.1-8.0 ppm (m, ArH), δ 10.12 ppm (s, 12H OH).


Brown powder; mp > 300° C ; $\lambda_{\text{max}}$ 435 nm in DMF; IR (KBr) 3410.49 (Ar-OH), 1517.02 (-N=N-), 1637.27 cm^{-1}; $^1$H NMR (DMSO-d_6) δ 1.65 ppm (d, 12H, CHCH_3), δ 4.96 ppm (q, 4H, CHCH_3), δ 7.8-8.5 ppm (m, ArH), 9.02 ppm (s, 12H, OH).
Amino Derivative

I) $R_1 = H$, $R_2 = SO_3H$
II) $R_1 = COOH$, $R_2 = H$
III) $R_1 = OH$, $R_2 = H$
IV) $R_1 = H$, $R_2 = COOH$


calix[4]resorcinarene-dyes

Figure 1: Synthetic Route for Calix[4]resorcinarene-Dyes
5.2.4 Fastness Studies and Colour Matching of Dye Samples

5.2.4.1 Scouring of fibres

2.0 g caustic soda and 2.0 g common detergent in 200 ml water were mixed and 3.5 g fibres hanks were added. The mixture was boiled for 3 h, and then cooled and the hank was washed thoroughly with water to remove the adhered caustic soda and detergent completely.

5.2.4.2 Dyeing of fibres

0.25 g of calix[4]resorcinarene-dyes was added in 35 ml water and the solution was heated to 50° C. The scoured 3.5 g fibres hanks were then added and the dyeing bath was maintained at 90°C for 30 min. It was then cooled to room temperature and 1.0 g of common salt was added. The dyed hanks were then removed and rinsed with cold water and dried.

5.2.4.3 Fastness to water

Dyed and undyed specimens were immersed in water for 30 min, drained, and placed in a perspirometer. The change in colour of the dyed cloth and the staining of the undyed cloths are assessed be means of the standard grey scale.

5.2.4.4 Fastness of washing

The test specimen was cut into two parts. One part along with undyed cotton or wool was then added to 0.5 % common detergent solution in water at 40° C – 45° C. The solution was agitated for 30 min. The specimen was removed, rinsed with water, and then dried by pressing with iron. Change in colour of the dyed specimen and degree of staining of the undyed specimen was assessed by standard gray scale.
5.2.4.5 Fastness to perspiration

Since human perspiration can be acidic or alkaline, both acid and alkaline solutions have to be used for the test. The acidic condition is simulated by preparing a solution containing 10 g sodium chloride, 1.0 g disodium hydrogen phosphate, and 1.0 g lactic acid per liter. The alkaline condition is provided by a solution containing 10 g sodium chloride, 1.0 g disodium hydrogen phosphate, and 4.0 g ammonium carbonate per liter. The tests were carried out in dry atmosphere at 38 – 40°C in glass test tubes. The test specimen was made up by taking a piece of the dyed knitted yarn and rolled with the undyed knitted yarn in such a way that the roll just fits the bore of the test tube. The test specimen were thoroughly wetted with the acid solution and then inserted in different glass test tube, so that one-third of the roll projects outside. The four tests correspond to grades 1 to 4 and differ only in the time of treatment i.e. 40 min, 2, 6 and 16 h. The change in colour of the dyed yarn and the degree of staining of the undyed yarn is assessed visually. A similar test is performed with the alkaline solution also.

5.2.4.6 Fastness to light

The dyed specimen along with standard was exposed to xenotest in which half of the dyed material was kept unexposed to light. The system was allowed to stand in the light for 10 hr. The specimen was then taken away and the exposed site was compared with unexposed site along with standards.

5.2.4.7 Colour matching of dye samples

The colour and percentage strength of the dye samples were evaluated by matching reflectance measurements (colour matching system)\textsuperscript{11}. 100 mg of the dye sample was accurately weighed and dissolved in 100 ml DMF. A chromaticity curve was obtained, and with the help of the computer, their L, a, b values and
colour difference values such as $\Delta L$, $\Delta a$, $\Delta b$, $\Delta C$, $\Delta H$, the total colour and the percentage strength were evaluated.

5.3 RESULTS AND DISCUSSIONS

5.3.1 Dyeing of fibres

The structural and physical properties of the calix[4]resorcinarene-dyes I to IV, reveals that they may be classified as “Direct dyes” for the dyeing of cotton and wool fibres. Direct dyes are often known as “Salt dyes” since common salt or glauber’s salt is generally added to the dye for exhaustion. It is generally seen that direct dyes on cotton, have poor fastness to washing and light, however the washing and light fastness can be somewhat improved by various after-treatments on the fibres$^{4,12-17}$. The after-treatment process includes:

- Diazotization and development.
- Treatment with formaldehyde.
- Treatment with cation-active organic compounds.
- Treatment with copper salts.
- Treatment with chromium salts.

All the above after-treatment processes increases the expenditure, time, labour, material, and makes the process disadvantageous over other dyeing process, i.e., vat dye, mordant dye, azoic dye etc. It has been seen that the synthesized calix[4]resorcinarene-dyes I to IV, have good fastness towards washing and light for dyeing cotton and wool fibres without the use of any after-treatment method. Figure 2,3 shows the dyed cotton and wool fibres with dye I to IV.

5.3.2 Effect of dyestuff concentrations

The behaviour of varying dye concentration was studied on the dyeing of the fibre. The results (Figure 4) showed that with the increase in dye concentration
from 0.2 to 0.4 % there was an increase in reflectance on the fibres, which suggest the greater availability of dyestuff in solution and its penetration into the fibre material.

5.3.3 Effect of salt concentration

The effect of varying the concentration of salt (1.0 to 5.0 %) was assessed for the dyed fabrics. The results showed that 3.0 to 5.0 % concentration of salt did not have much effect on the reflectance intensity of the fibre (Figure 5).

5.3.4 Effect of pH

The cotton fibres were dyed at various pH between 3-10.5 and its effect was studied by the reflectance measurements. The data showed (Figure 6) that at a lower pH the dyeing was incomplete, however, the maximum reflectance value was achieved between pH 6.5 and 8 but beyond pH 8, the dyeing capacity decreased gradually.

5.3.5 Fastness studies

The method adopted for the present investigation is visual examination of the tested materials alongside a series of quantitatively specified contrasts as reference standards. The reference standards chosen for light fastness is a series of eight blue dyes on wool. Light fastness is assessed on a scale of eight with 1 representing the least fastness and 8 the best. A specimen of the dyed or printed textile is exposed to daylight under standard conditions, including protection from rain, along with eight-dyed wool standard. Thus if the test specimen is assigned a rating of 1 to 3 it correspond to a very low light fastness, 4 corresponds to medium fastness. The rating 5 is assigned if the fastness is similar to that of the standard. A rating of 6 to 8 indicates the outstanding fastness of the test specimen (Table I).
### Table I

**Standard Wool Dyes**

<table>
<thead>
<tr>
<th>Light Fastness Rating</th>
<th>Standard Wool Dyes</th>
<th>C.I. Designation</th>
<th>C.I. Number</th>
<th>Chemical Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acilan Brilliant Blue FFR</td>
<td>C.I. Acid Blue 104</td>
<td>42735</td>
<td>Triarylmethane</td>
</tr>
<tr>
<td>2</td>
<td>Acilan Brilliant Blue FFB</td>
<td>C.I. Acid Blue 109</td>
<td>42740</td>
<td>Triarylmethane</td>
</tr>
<tr>
<td>3</td>
<td>Comassie Brilliant Blue R</td>
<td>C.I. Acid Blue 109</td>
<td>42660</td>
<td>Triarylmethane</td>
</tr>
<tr>
<td>4</td>
<td>Supramine Blue EG</td>
<td>C.I. Acid Blue 109</td>
<td>50310</td>
<td>Azine</td>
</tr>
<tr>
<td>5</td>
<td>Solway Blue RN</td>
<td>C.I. Acid Blue 109</td>
<td>62085</td>
<td>Anthraquinonide</td>
</tr>
<tr>
<td>6</td>
<td>Alizarine Light Blue 4GL</td>
<td>C.I. Acid Blue 109</td>
<td>61125</td>
<td>Anthraquinonide</td>
</tr>
<tr>
<td>7</td>
<td>Soledon Blue 4 BC Pdr</td>
<td>C.I. Solubilized Vat Blue 5</td>
<td>73066</td>
<td>Indigoid</td>
</tr>
<tr>
<td>8</td>
<td>Indigosol Blue AGG</td>
<td>C.I. Solubilized Vat Blue 8</td>
<td>73801</td>
<td>Indigoid</td>
</tr>
</tbody>
</table>

Fastness to all other agencies e.g. washing, perspiration etc. is assessed on scale of 5. The change in colour is assessed by visual examination, with reference to five pairs of grey dyed cloths, each pair representing a visual difference and contrast.

**Alteration in Shade**

- Corresponding to fastness 5 = shade unaltered.
- Corresponding to fastness 4 = Very slight alteration or lose in depth.
- Corresponding to fastness 3 = Appreciable alteration or lose in depth.
- Corresponding to fastness 2 = Distinct alteration or lose in depth.
- Corresponding to fastness 1 = Shade much altered or great lose in depth.
Degree of Staining

Degree of Staining 5 = No staining of adjacent white.
Degree of Staining 4 = Very slight staining of adjacent white.
Degree of Staining 3 = Appreciable staining of adjacent white.
Degree of Staining 2 = Deep staining of adjacent white.
Degree of Staining 1 = Adjacent white dyed deeply.

The light fastness of dyeing on the cotton was of the level 5-6. For other fastness tests, a specimen of dyed fabric was kept in intimate contact with an undyed specimen of the same or a different fabric and was subjected on the laboratory test. In all cases the change in colour of the dyed specimen and the staining of the undyed textile was assessed visually using the standard grey scale. The results show that fastness to water, washing, acidic, and alkaline perspiration were at the level 3-5, indicating very slight alteration in the shade or lose in depth of the dye. Same, in the case of staining this was of level 3 to 5 as shown in Table II. Therefore, the calix[4]resorcinarene-dyes could be considered as good candidate for dyeing cotton and wool fibres, due to their easy process of dyeing and normal to high value of fastness.

5.3.6 Computerized Colour Matching

The samples were evaluated with the ‘Mac beth Colour Eye’ computer colour matching system with illuminants D55 with 10° observer. The results on colour coordinates of the samples are given in Table III, IV. Taking the various reactive dyes as standard, the reflectance measurements were made. The standard was selected on the basis of maximum match shade with the synthesized dyes. For
dyes I, II, III, and IV, Brown HE 2R, Mustard HE G, Brown HE G, and Acid brown R respectively were selected.

It should not be difficult to visualize the appearance of shade and draw some meaningful interference from the L, C, and H specification of the colour. The hue angle tells us about the colour itself i.e. whether the colour is yellow, green, red, purple, or blue. The chroma tells us about the purity of the colour, while the colour (light or dark) is reflected by the value L. The Table V-XII showed that ΔL value were negative for dye I and III on cotton fibre and dye I and II on wool fibre, which suggests that these compounds are darker than the standard taken against them. The chroma value (ΔC) was negative for all except dye II on cotton fibre as well as wool fibre, with duller effect, which suggests the leasing effect of these dyes

It can be further seen how L, a, b, c, H colour specifications are able to define any colour in a meaningful manner, which is very easy to understand, compared to the trichromatic coordinate.
### Fastness of the Synthesized Dyes on Cotton and Wool Fibres

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>I</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>II</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>3-4</td>
</tr>
<tr>
<td>III</td>
<td>4</td>
<td>4-5</td>
<td>4-5</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>IV</td>
<td>4</td>
<td>4</td>
<td>4-5</td>
<td>4</td>
<td>4</td>
</tr>
</tbody>
</table>

*a*: Alteration in shade of dyed fabric; *b*: Degree of staining cotton; *c*: Degree of staining wool.
<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>L*</th>
<th>A*</th>
<th>B*</th>
<th>C*</th>
<th>H</th>
<th>ΔL</th>
<th>ΔA</th>
<th>ΔB</th>
<th>ΔC</th>
<th>ΔH</th>
<th>ΔE</th>
<th>% strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>73.30</td>
<td>4.19</td>
<td>22.135</td>
<td>22.528</td>
<td>79.249</td>
<td>-0.056</td>
<td>-0.127</td>
<td>-0.14</td>
<td>-0.161</td>
<td>0.098</td>
<td>0.197</td>
<td>100.23</td>
</tr>
<tr>
<td></td>
<td>(73.356)</td>
<td>(4.317)</td>
<td>(22.275)</td>
<td>(22.689)</td>
<td>(79.00)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>52.794</td>
<td>25.495</td>
<td>49.401</td>
<td>55.592</td>
<td>62.677</td>
<td>0.060</td>
<td>0.079</td>
<td>0.175</td>
<td>0.192</td>
<td>0.010</td>
<td>0.201</td>
<td>98.74</td>
</tr>
<tr>
<td></td>
<td>(52.734)</td>
<td>(25.416)</td>
<td>(49.226)</td>
<td>(55.40)</td>
<td>(62.667)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>67.776</td>
<td>8.739</td>
<td>29.655</td>
<td>30.916</td>
<td>73.551</td>
<td>-0.018</td>
<td>0.028</td>
<td>-0.074</td>
<td>-0.063</td>
<td>-0.048</td>
<td>0.081</td>
<td>99.86</td>
</tr>
<tr>
<td></td>
<td>(67.794)</td>
<td>(8.711)</td>
<td>(29.729)</td>
<td>(30.979)</td>
<td>(73.639)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>60.057</td>
<td>10.137</td>
<td>19.909</td>
<td>22.341</td>
<td>62.991</td>
<td>0.046</td>
<td>-0.210</td>
<td>-0.088</td>
<td>-0.018</td>
<td>0.227</td>
<td>0.232</td>
<td>99.85</td>
</tr>
</tbody>
</table>
### Table IV

**Colour Coordinate Values for Calix[4]resorcinarene-Dyes on Wool Fibre**

<table>
<thead>
<tr>
<th>Compd. No.</th>
<th>L*</th>
<th>A*</th>
<th>B*</th>
<th>C*</th>
<th>H</th>
<th>ΔL</th>
<th>ΔA</th>
<th>ΔB</th>
<th>ΔC</th>
<th>ΔH</th>
<th>ΔE</th>
<th>% strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>73.128</td>
<td>4.224</td>
<td>22.22</td>
<td>22.618</td>
<td>79.205</td>
<td>-0.2208</td>
<td>-0.093</td>
<td>-0.055</td>
<td>-0.072</td>
<td>0.081</td>
<td>0.252</td>
<td>98.67</td>
</tr>
<tr>
<td></td>
<td>(73.356)</td>
<td>(4.317)</td>
<td>(22.275)</td>
<td>(22.689)</td>
<td>(79.00)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>52.362</td>
<td>25.616</td>
<td>49.343</td>
<td>55.596</td>
<td>62.539</td>
<td>-0.372</td>
<td>0.200</td>
<td>0.117</td>
<td>0.196</td>
<td>-0.124</td>
<td>0.434</td>
<td>95.58</td>
</tr>
<tr>
<td></td>
<td>(52.734)</td>
<td>(25.416)</td>
<td>(49.226)</td>
<td>(55.40)</td>
<td>(62.667)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>68.092</td>
<td>8.645</td>
<td>29.523</td>
<td>30.763</td>
<td>73.649</td>
<td>0.298</td>
<td>-0.066</td>
<td>-0.206</td>
<td>-0.216</td>
<td>0.005</td>
<td>0.368</td>
<td>102.5</td>
</tr>
<tr>
<td></td>
<td>(67.794)</td>
<td>(8.711)</td>
<td>(29.729)</td>
<td>(30.979)</td>
<td>(73.639)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>60.283</td>
<td>10.096</td>
<td>19.871</td>
<td>22.289</td>
<td>63.041</td>
<td>0.272</td>
<td>-0.251</td>
<td>0.050</td>
<td>-0.070</td>
<td>0.246</td>
<td>0.373</td>
<td>101.501</td>
</tr>
</tbody>
</table>
STRENGTH CALCULATION REPORT

Table V: Strength Calculation of Dye I on Cotton Fibre

<table>
<thead>
<tr>
<th></th>
<th>STANDARD</th>
<th>BATCH</th>
<th>DIFFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>75.556</td>
<td>73.300</td>
<td>DL* = -0.056</td>
</tr>
<tr>
<td>a*</td>
<td>4317</td>
<td>4189</td>
<td>Da* = -0.127</td>
</tr>
<tr>
<td>b*</td>
<td>22.275</td>
<td>22.135</td>
<td>Db* = -0.140</td>
</tr>
<tr>
<td>C*</td>
<td>22.869</td>
<td>22.528</td>
<td>DC* = -0.161</td>
</tr>
<tr>
<td>E*</td>
<td>79.000</td>
<td>79.248</td>
<td>DLH* = 0.098</td>
</tr>
<tr>
<td>E* S*</td>
<td>2.49</td>
<td>2.51</td>
<td>dE* = 0.0197</td>
</tr>
<tr>
<td>RFL</td>
<td>24.27</td>
<td>24.47</td>
<td>Strength : 100.23 %</td>
</tr>
</tbody>
</table>

COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%

Observer : 10 Degree  Mode : Reflectance
Colorspace : CIELAB(1976) Spectro : 5100
Illuminant : D65  Wavelength : Integrated

Normal
Table VI: Strength Calculation of Dye II on Cotton Fibre

<table>
<thead>
<tr>
<th></th>
<th>Standard</th>
<th>Batch</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>52.734</td>
<td>52.794</td>
<td>DL* = 0.060 Lighter</td>
</tr>
<tr>
<td>a*</td>
<td>25.416</td>
<td>25.495</td>
<td>Da* = 0.079 More Redder</td>
</tr>
<tr>
<td>b*</td>
<td>49.226</td>
<td>49.401</td>
<td>Db* = 0.175 More Yellower</td>
</tr>
<tr>
<td>C*</td>
<td>55.400</td>
<td>55.582</td>
<td>DC* = 0.192 Brighter</td>
</tr>
<tr>
<td>H*</td>
<td>62.667</td>
<td>52.677</td>
<td>DH* = 0.010</td>
</tr>
<tr>
<td>Z/S</td>
<td>99.94</td>
<td>98.69</td>
<td>dE* = 0.201</td>
</tr>
<tr>
<td>BFL</td>
<td>3.51</td>
<td>3.66</td>
<td>Strength : 98.74 %</td>
</tr>
</tbody>
</table>

COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%

Normal

Observer: 10 Degree
Colorspace: CIELAB(1976)
Fluorescent: D65

Mode: Reflectance
Spectro: 5100
Wavelength: Integrated
### Table VII: Strength Calculation of Dye III on Cotton Fibre

<table>
<thead>
<tr>
<th></th>
<th>Standard</th>
<th>Batch</th>
<th>Difference</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>77.75</td>
<td>67.77</td>
<td>DL* = -0.98</td>
<td>Darker</td>
</tr>
<tr>
<td>a*</td>
<td>2.71</td>
<td>2.73</td>
<td>Da* = 0.02</td>
<td>More Redder</td>
</tr>
<tr>
<td>b*</td>
<td>25.29</td>
<td>39.65</td>
<td>Db* = -0.07</td>
<td>Less Yellow</td>
</tr>
<tr>
<td>C*</td>
<td>30.95</td>
<td>30.91</td>
<td>DC* = -0.06</td>
<td>Duller</td>
</tr>
<tr>
<td>H*</td>
<td>73.63</td>
<td>73.51</td>
<td>DH* = -0.04</td>
<td></td>
</tr>
<tr>
<td>E*</td>
<td>17.42</td>
<td>17.39</td>
<td>dE* = 0.02</td>
<td></td>
</tr>
<tr>
<td>RFL</td>
<td>16.81</td>
<td>16.52</td>
<td>Strength : 99.86</td>
<td>Normal</td>
</tr>
</tbody>
</table>

**COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%**

- **Observer**: 10 Degree
- **Colorsce**: CIELAB (1976)
- **Illuminant**: D65
- **Mode**: Reflectance
- **Spectra**: 5190
- **Wavelength**: Integrated

**Strength Calculation Report**

- **2004.04.04 04:57 PM**
- **Batch**: BATCH2
- **Dye**: Dye III
- **Fibre**: Cotton
- **Eulab, VATVA, AHMEDABAD, PH: 5834499**
STRENGTH CALCULATION REPORT

Table VIII: Strength Calculation of Dye IV on Cotton Fibre

<table>
<thead>
<tr>
<th></th>
<th>STANDARD</th>
<th>BATCH</th>
<th>DIFFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>63.041</td>
<td>60.057</td>
<td>DL* = 0.046</td>
</tr>
<tr>
<td>a*</td>
<td>10.247</td>
<td>10.137</td>
<td>Da* = -0.210</td>
</tr>
<tr>
<td>b*</td>
<td>19.521</td>
<td>19.909</td>
<td>Db* = 0.088</td>
</tr>
<tr>
<td>C*</td>
<td>22.359</td>
<td>22.341</td>
<td>DC* = -0.018</td>
</tr>
<tr>
<td>H*</td>
<td>62.409</td>
<td>62.991</td>
<td>DH* = 0.227</td>
</tr>
<tr>
<td>K/S</td>
<td>22.73</td>
<td>22.69</td>
<td>dE* = 0.232</td>
</tr>
<tr>
<td>KFL</td>
<td>16.35</td>
<td>16.17</td>
<td>Strength : 99.85 %</td>
</tr>
</tbody>
</table>

COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%

Observer : 10 Degree
ColorSpace : CIELAB(1976)
Illuminant : D65
Mode : Reflectance
Spectro : 5100
Wavelength : Integrated
COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%    Normal

Observer : 10 Degree      Mode : Reflectance
Colorspace : CIELAB(1976)  Spectro : 5100
Illuminant : D55  Wavelength : Maximum (420)

Table IX: Strength Calculation of Dye I on Wool Fibre

<table>
<thead>
<tr>
<th>STANDARD</th>
<th>BATCH</th>
<th>DIFFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>L* = 73 356</td>
<td>73 128</td>
<td>DL* = -0.228</td>
</tr>
<tr>
<td>a* = 4.217</td>
<td>4.224</td>
<td>Da* = -0.093</td>
</tr>
<tr>
<td>b* = 22.275</td>
<td>22.220</td>
<td>Db* = -0.055</td>
</tr>
<tr>
<td>C* = 22.689</td>
<td>22.615</td>
<td>DC* = -0.073</td>
</tr>
<tr>
<td>E* = 27.500</td>
<td>27.205</td>
<td>DH* = 0.081</td>
</tr>
<tr>
<td>NS = 1.18</td>
<td>1.17</td>
<td>dE* = 0.252</td>
</tr>
<tr>
<td>RFL = 24.27</td>
<td>24.47</td>
<td></td>
</tr>
</tbody>
</table>

Strength : 98.67 %

RFL = 24.27 24.47

Table IX: Strength Calculation of Dye I on Wool Fibre

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### STRENGTH CALCULATION REPORT

**HuELAB**, VATVA, AHMEDABAD, PH: 5834490.

**STRENGTH CALCULATION REPORT**

**01/04/2004, 04:42 PM**

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#### Table X: Strength Calculation of Dye II on Wool Fibre

<table>
<thead>
<tr>
<th></th>
<th>STANDARD</th>
<th>BATCH</th>
<th>DIFFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>52.734</td>
<td>52.362</td>
<td>DL* = -0.372</td>
</tr>
<tr>
<td>a*</td>
<td>25.416</td>
<td>25.616</td>
<td>Da* = 0.200</td>
</tr>
<tr>
<td>b*</td>
<td>49.226</td>
<td>49.343</td>
<td>Db* = 0.117</td>
</tr>
<tr>
<td>C*</td>
<td>55.460</td>
<td>55.596</td>
<td>DC* = 0.196</td>
</tr>
<tr>
<td>H*</td>
<td>62.56°</td>
<td>62.529</td>
<td>DH* = -0.124</td>
</tr>
<tr>
<td>K/S</td>
<td>12.25</td>
<td>12.67</td>
<td>dE* = 0.438</td>
</tr>
<tr>
<td>RFL</td>
<td>3.31</td>
<td>3.56</td>
<td>Strength . 95.88 %</td>
</tr>
</tbody>
</table>

**COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%**

<table>
<thead>
<tr>
<th></th>
<th>Normal</th>
</tr>
</thead>
</table>

**Observer** : 10 Degree

**Color space** : CIELAB (1976)

**Illuminant** : D65

**Mode** : Reflectance

**Spectra** : 5100

**Wavelength** : Maximum (430)

---

**Graph**

1. **RFL % Wavelength**
2. **Yellower +Db 3 00**
3. **Greener -Da 3 00**
4. **Darker -DL 3 00**
5. **Bluer -Db -3 00**
6. **Lighter +DL 3 00**

---
**STRENGTH CALCULATION REPORT**

---

**Table XI: Strength Calculation of Dye III on Wool Fibre**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard (3)</th>
<th>Batch (3)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>L*</td>
<td>87.94</td>
<td>88.992</td>
<td>+0.048</td>
</tr>
<tr>
<td>a*</td>
<td>8.711</td>
<td>8.545</td>
<td>-0.166</td>
</tr>
<tr>
<td>b*</td>
<td>29.729</td>
<td>29.523</td>
<td>-0.206</td>
</tr>
<tr>
<td>C*</td>
<td>30.979</td>
<td>30.763</td>
<td>-0.216</td>
</tr>
<tr>
<td>H*</td>
<td>73.615</td>
<td>73.649</td>
<td>+0.035</td>
</tr>
<tr>
<td>K/S</td>
<td>2.05</td>
<td>2.11</td>
<td>+0.06</td>
</tr>
<tr>
<td>RFL</td>
<td>1681</td>
<td>1652</td>
<td>-29</td>
</tr>
</tbody>
</table>

**COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100%**

- Normal
- Mode: Reflectance
- Colorspace: CIELAB(1976)
- Illuminant: D65
- Wavelength: Maximum (420)

---

RFL vs. Wavelength

Greener: Da = -0.066
Less Redder: Da* = -0.206
Less Yellower: Db* = -0.216
Duller: DH* = 0.005
Darker: DL* = 0.368
Lighter: DE* = 0.368

Strength: 102.50%
COLOR DIFFERENCE ON STRENGTH ADJUSTED TO 100% Normal

Observer: 10 Degree
Mode: Reflectance
Colorspace: CIELAB(1976)
Spectro: 5100
Illuminant: D55
Wavelength: Maximum (420)

Table XII: Strength Calculation of Dye IV on Wool Fibre