



## Studies on the Dyeing Properties of Zn(II) Complexes of 2-chloro-5-(2,4-Dihydroxy phenylazo)phenyl Phenylmethanone and 3-hydroxy-4-(1-Hydroxynaphthalene-2-ylazo) Naphthalene-1-Sulfonicacid

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Available online at: [www.isca.in](http://www.isca.in), [www.isca.me](http://www.isca.me)

Received 8<sup>th</sup> August 2016, revised 27<sup>th</sup> August 2016, accepted 30<sup>th</sup> August 2016

### Abstract

Two new zinc complexes were prepared from two different azodyes. They were characterized by various physico chemical methods. The dyes and their Zn(II) complexes were subjected to the dyeing property studies by dyeing on cotton fabrics. Colour fastness, fastness to light, perspiration, and sublimation fastness were analysed. The results show that the present dyes and their Zn(II) complexes have good affinity towards the fabric.

**Keywords:** Dyeing properties, azodyes, 2-chloro-5-(2,4-dihydroxy phenylazo)phenyl phenylmethanone, 3-hydroxy-4-(1-hydroxynaphthalene-2-ylazo)naphthalene-1-sulfonicacid, fastness to perspiration.

### Introduction

Before 1950 the dispersed dyes used were mostly amino anthraquinone derivatives. Though these dyes are bright in colour they have limitation of poor discharge-ability and are sensitive to the oxides of nitrogen<sup>1</sup>. Now a days, many research works have been done to replace these anthraquinone dyes with similar azodyes, for the protection of environment and for economical reasons<sup>2</sup>. The usual method adopted for the synthesis of azodyes consist of diazotization of primary aromatic amine followed by coupling with active mentylene group compound, amino and hydroxyl groups are commonly used coupling components. Aromatic azodyes may get converted to amines, which are carcinogenic and mutagenic and hazards to health<sup>3</sup>. Therefore the use of certain azodyes is prohibited all over the world<sup>4</sup>. A certain number of high stable poorly soluble complexes are known and used as pigments in dyeing process<sup>5</sup>.

The present work describes the dyeing properties of the azodyes RABP and ANSN and their Zn(II) complexes, on cotton fabrics. The dyeing properties of the dyes are compared with their complexes.

### Materials and Methods

All reagents and solvents for synthesis and analysis were Merck products and used as supplied.

**Synthesis of Azodyes:** The azodyes RABP (2-chloro-5-(2,4-dihydroxy phenylazo)phenyl phenylmethanone) and ANSN (3-hydroxy-4-(1-hydroxynaphthalene-2-ylazo)naphthalene-1-sulfonicacid) prepared by standard procedure of diazotization<sup>6</sup>.

RABP is synthesized by diazotising 2-amino-5-chlorobenzophenone and coupling with resorcinol<sup>7</sup>.

**Preparation of complexes:** Zinc acetate and the azodyes were dissolved separately in methanol and the mixture was heated to boil for 5-7 hours. The resulting solutions on cooling zinc complexes were precipitated. They were filtered and washed and recrystallised.

Based on the microanalytical data, metal estimation and mass spectral evidences the following formulae are suggested for the compounds which are given in Table-1.

**Table-1**  
**Analytical data of the newly synthesised compounds**

Compound	Mol formula	Mol Wt	M%
RABP	C <sub>19</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> Cl	352.5	-
ANSN	C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub> S	394.0	-
Z1	[Zn(C <sub>19</sub> H <sub>13</sub> N <sub>2</sub> O <sub>3</sub> Cl) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	805	8.1
Z3	[Zn(C <sub>20</sub> H <sub>14</sub> N <sub>2</sub> O <sub>5</sub> S)Ac(H <sub>2</sub> O) <sub>2</sub> ]	823	7.8

**Dyeing Procedure:** The general procedure for dyeing cotton fabrics with azodyes is given below. 2% dye (calculated as per the weight of the fabric) was used for dyeing the white cotton fabric. As a dispersing agent sodium chloride is added in the ratio 20:1. The dyeing process was started at 60°C and the temperature was raised to 100°C over 30 minutes and kept there for 1 hour. After cooling, the fabric was taken out and treated

with a solution of 2% sodiumbisulphite, 2% sodium hydroxide and 0.1% sodium chloride at 70°C for 30 minutes. Lastly the fabric was rinsed and dried at 60°C<sup>8</sup>.

The same procedure is adopted for dyeing cotton fabric with RABP, ANSN,  $[\text{Zn}(\text{RABP})_2(\text{H}_2\text{O})_2]$  and  $[\text{Zn}(\text{ANSN})\text{AC}(\text{H}_2\text{O})_2]$ . The dyed cotton fabrics are shown in Figure-1-4.



Figure-1  
Cotton dyed with RABP



Figure-2  
Cotton dyed with  $[\text{Zn}(\text{C}_{19}\text{H}_{13}\text{N}_2\text{O}_3\text{Cl})_2(\text{H}_2\text{O})_2]$

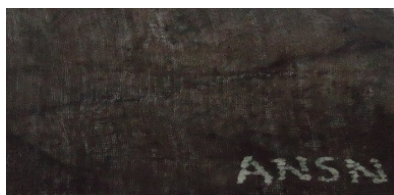


Figure-3  
Cotton dyed with ANSN

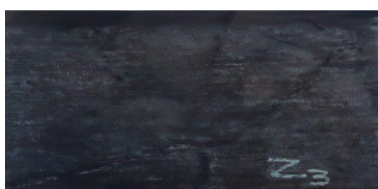


Figure-4  
Cotton dyed with  $[\text{Zn}(\text{C}_{20}\text{H}_{14}\text{N}_2\text{O}_5\text{S})\text{Ac}(\text{H}_2\text{O})_2]$

#### Methods used to study the properties of dyed fabrics:

Dyeing properties of cotton fabrics dyed with the azodyes and their Zn(II) complexes were studied at SITRA.

**Colour fastness tests: Rubbing fastness:** The specimen (cotton fabric dyed with the azodyes and zinc complexes) was lied flatly on the base of the crockmeter on the abrasive cloth with same dimension in the direction of rubbing. A Square of white testing cloth was allowed to slide on the specimen back and forth twenty times by making ten complete turns of the crank. For wet rubbing test, the testing cloths were immersed in

distilled water and the remaining procedure was same as in the dry test. The staining on the square of white testing cloth was examined in accordance the gray scale 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent<sup>9</sup>.

**Washing fastness:** Two undyed cotton fabrics of equal length were stitched on either side of dyed cotton fabric and then washed for 30 minutes at a temperature of 50°C. After treating with soap the dyed fabric is removed, and rinsed twice in cold running water. Squeezed and dried in air at 60°C. The staining on the undyed adjacent fabric was assessed according to the gray scale<sup>10</sup>. The washing fastness was tested on wool, acrylic, polyester, nylon, cotton and acetate clothes as adjacent clothes for staining.

**Light fastness:** The specimen cloth was exposed on a Xenotest 150 (original Hanau, Chamber temperature: 25-30°C, black panel temperature, 60°C, relative humidity 50-60%, dark glass UV filter system) for 40 hours. The variation in colour was assessed according to the following gray scale, 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent<sup>11</sup>.

**Perspiration fastness:** A piece of dyed cotton fabric was stitched between two pieces of undyed cotton fabric, having equal length and then immersed in acid or alkaline solution for 30 minutes. The staining on the undyed fabric was studied according to the following gray scale 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent.

The acid solution contains sodium chloride (10 g/dm<sup>3</sup>), Sodium orthophosphate (1 g/dm<sup>3</sup>), lactic acid (1 g/dm<sup>3</sup>) and histidine monohydrochloride (0.25 g/dm<sup>3</sup>). The pH of the solution is 3.5. The alkaline solution contains sodium chloride, ammonium chloride (4 g/dm<sup>3</sup>) disodium ortho phosphate (1 g/dm<sup>3</sup>), histidine monohydrochloride (0.25 g/dm<sup>3</sup>).

**Sublimation fastness:** Fastness to sublimation was determined with an iron tester (Yasuda N138). The specimen was prepared by stitching two pieces of undyed cotton fabrics of equal length on either sides of the dyed cotton, and then subjected to 180°C and 210°C for every 1 minute. Staining obtained on the undyed adjacent fabric was examined according to the gray scale.

## Results and Discussion

The prepared azodyes and their Zn(II) complexes were dyed on cotton fabric at 2% shade by high temperature technique. The dyed clothes and gave bright intense hues, ranging from dark grey to red.

**Evaluation of fastness to colour:** On comparing with the commercial dyes used under the same condition, our dyes also gave satisfactory colour yields; at 2% depth and exhaustion of dyes were also achieved. The dyed fibers showed only small colour unevenness.

**Fastness to washing:** The washing fastness of the azodyes and their complexes are given in Table 2. Good behavior is shown by the azodye ANSN and its  $[Zn(ANSN)Ac(H_2O)_2]$  complex shows excellent behavior in the fastness to washing at  $50^\circ C$ . The azodye RABP shows moderate behavior and its  $[Zn(RABP)_2(H_2O)_2]$  complex shows good behavior in the fastness to washing at  $50^\circ C$ .

**Fastness to rubbing:** The behavior of the azodyes and their Zn (II) complexes to dry and wet rubbing is shown in Table-2 along with the results of washing fastness. The azodyes RABP and ANSN shows moderate behavior in dry dubbing and their complexes also shows similar behavior. Both the dyes shows poor behavior towards wet rubbing but  $[Zn(ANSN)Ac(H_2O)_2]$  complex shows good behavior and  $[Zn(RABP)_2(H_2O)_2]$  complex shows moderate behavior.

**Table-2**  
**Fastness properties of the azodyes and their Zn(II) complexes**

Colour fastness	ANSN	RABP	$[Zn(ANSN)Ac(H_2O)_2]$	$[Zn(RABP)_2(H_2O)_2]$
Dry rubbing	3	3	3	3
Wet rubbing	2-3	2	3-4	2-3
Washing Change in colour	1	2	1	2
Staining on				
Wool	3-4	2-3	4-5	3-4
Acrylic	4	4	4-5	4
Polyester	4	3-4	5	4-5
Cotton	3-4	3	4-5	4
Acetate	3-4	3-4	5	4-5

Gray scale 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent

**Fastness to light:** The results of fastness to light shown by the azodyes and Zn(II) complexes are shown in Table-3. The azodye ANSN shows moderate light fastness, RABP shows fair light fastness. The complex  $[Zn(ANSN)Ac(H_2O)_2]$  shows good and  $[Zn(RABP)_2(H_2O)_2]$  complex shows greater than moderate behavior of light fastness.

**Fastness to perspiration:** The azodyes ANSN and RABP shows gray scale values between 4-5 towards perspiration (both in acid and alkali) but their complexes shows good and excellent behavior in acid and alkali.

**Fastness to sublimation:** The dyes and their Zn(II) complexes exhibits good sublimation fastness. Staining at  $180^\circ C$  and  $210^\circ C$

the azodyes shows good and excellent behavior and their Zn(II) complexes exhibits excellent behavior. The results of fastness to light, sublimation and perspiration are given in Table-3.

**Table-3**  
**Response to light perspiration and sublimation of azodyes and Zn(II) complexes**

	ANSN	RABP	$[Zn(ANSN)Ac(H_2O)_2]$	$[Zn(RABP)_2(H_2O)_2]$
Colour fastness to light	3	2-3	2	3
Light fading				
Fastness to perspiration	4-5	4-5	5	4
Acid				
Alkali	4-5	3-4	5	4
Fastness to sublimation Change in tone	4	4	4-5	4-5
Staining at $180^\circ C$	4-5	4	4-5	4
Staining at $210^\circ C$	4-5	3-4	4-5	5

Gray scale 1-poor, 2-fair, 3-moderate, 4-good, 5-excellent

## Conclusion

The two new azodyes [2-Chloro-5-(2,4-dihydroxy phenylazo) phenyl] phenylmethanone (RABP) and 3-Hydroxy-4-(1-hydroxynaphthalen-2-ylazo) naphthalene - 1 - sulfonicacid (ANSN) and their Zn(II) complexes were subjected to study their dyeing properties. The dye bath exhaustion in cotton fabric was about 60-70%. The dyes give grey to red colour to the fabrics. The change in the colour of the dyed cotton is due to the coordination with the metal ion. The results obtained shows moderate to good gray scale values to wash fastness, light fastness, rubbing, perspiration and sublimation. The results show that the present dyes and their Zn(II) complexes have good affinity towards the fabric.

## Acknowledgements

We express our sincere thanks to Department of Chemistry, University College, Trivandrum for providing instrumental facilities, STIC, Cochin University of science and Technology and SITRA, Coimbatore for analytical facilities.

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