

Synthesis, Characterization and Light Fastness Properties of Indigo Dye

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Abstract

A new violet indigo dye was synthesised from 2, 4- dinitroaniline which yielded a dark blue dye of indigo. 2, 4 dinitroaniline was treated with chloroacetic acid using a high boiling non polar solvent such as nitrobenzene at a temperature above 300⁰C in a base catalysed substitution nucleophilic bimolecular reaction. The resulted synthesized compound was purified and this in turn was treated with mixture of sodium hydroxide-potassium hydroxide - sodamide in a 5:5:1 ratio at a temperature of 130⁰C to yield an indoxyl, in an intramolecular cyclization reaction. Oxidation of the indoxyl into the indigo dye was take place by treating the indoxyl with acidified solution of ferric chloride. The yield of indigo dye was excellent. The synthesized dyes were applied on cotton fibre to asses their affinity of dye molecule with fibre with respect to time ,light fastness and wash fastness.

Keywords- indigo dye , dinitroaniline , Oxidation.

Introduction

Indigo is organic compounds that are useful as dyes.⁽¹⁻²⁾In modern industrial society, dyes are widely used in textiles, printing, dyeing and food.⁽³⁾Nearly all indigo dye produced today several thousand tone each year is synthetic. The synthetic industrial processes is employed for the preparation of indigo comprise forming an N-phenylglycine salt from aniline and chloroacetic acid, converting this salt into an indoxyl compound by alkali fusion at elevated temperature, and then oxidizing this compound with air.⁽⁴⁻¹⁰⁾in this paper, indigo dye, a vat dye was prepared by using 2, 4- dinitroaniline, chloroacetic acid to give an intermediate 2, 4- dinitrophenylglycine. This was fused with potassium hydroxide, sodium hydroxide and sodamide at a temperature between 110-120⁰C to give an indoxyl. This indoxyl was oxidized using acidified solution of ferric chloride to form a blue vat dye.⁽¹¹⁻¹²⁾

Material and Methods

All reagents were of analytical grade, melting point was taken and are reported uncorrected.

Synthesis of the Intermediate: 2, 4-Dinitrophenylglycine

18g, 0.11 moles of 2,4- dinitroaniline was introduced into a 500ml round bottomed flask, to this were added 30g, 0.32 moles of chloroacetic acid and 20g, 0.5 moles of sodium hydroxide. To this mixture was introduced 50ml of nitrobenzene and refluxed for six hrs at a temperature of approximately 300⁰C. The colour progressively changed from yellow, red to black as heating continued. The slurry that formed was cool and then washed with methanol. The crude product that was obtained, was a white amorphous powder. This compound was soluble in water but insoluble in organic solvents. It was then dissolved in water, treated with activated charcoal and filtered. A pure white powder weighing 20.4g crystallized out after distilling off the water. The melting point was 183-184⁰C.

Synthesis of 4, 4', 7, 7'-Tetranitroindigo Dye from 2, 4- Dinitrophenylglycine

5.0g, 0.025 mole of 2,4- dinitrophenylglycine, 30.0 g, 0.75 mole of sodium hydroxide , 30.0 g, 0.54 mole of potassium hydroxide and 6.0 g, 0.15 mole sod amide were ground intimately in a mortar and introduced into a 250ml beaker. The mixture was moistened with 20ml nitrobenzene, corked and heated for 1 hr.40 min. The colour changed progressed from colourless to light yellow to deep yellow and finally to orange. As the temperature increased, the mixture gradually melted, became molten and solidified. Then fused mixture was allowed to cool and dissolved in cold water, the solution was agitated for 1 hour and then treated with 120 ml of FeCl₃ solution acidified with concentrated HCl (60ml) to facilitate precipitation or oxidation of the dye. The dark blue dye that formed was recrystallized from acetone and dried. The melting point was >3900 .

Reduction of the Dye

1.0g dye was added in In four molar equivalents of sodium hydrosulphite(Na₂S₂O₄) and then 50 ml dimethylsulphoxide (DMSO) solution was added in it and the mixture heated under reflux for 2 hours, during which time the dye lost its colour as it is reduced to the dihydro derivative. The solution was poured into an iced cold solution of sodium hydrosulphite in 150 ml of water, the slurry was stirred and filtered. The yield of indigo dye was excellent.




Result and Discussion

Indigo dyes shows genral relation between the dye structure and fastness properties.

Action of Dye on the Dye Fibre with Respect to Time

Action of dye on the dye fibre with respect to different time was observed show various changes on the fibre colour. When the fibre was dipped in aqueous solution of indigo dye for 30 minutes. A slightly dark colour of indigo dye observed after 30 minutes. Similiarly when the same cotton fibre was dipped in aqueous solution of vat dyes for 1 hrs. A dark colour of indigo dye observed after 1 hrs. from this results it analysed that the colour fasten activity of indigo dye was observed with respect to the time. And also indicate the affinity of dye and fibre. molecule increases with increase in time more amount of dye absorbed on fibre as the time increases.

Table No 1 - Action Of Dye On Fibre With Respect To Time



Sr No	Time in minutes	Fibre	Colour
1	After 10 minutes		Faint Indigo
2	After 30 minutes		Slightly Faint Indigo
3	After 60 minutes		Dark Indigo

Action of UV Light on the Dye Fibre with Respect to Time

Action of light on the dye fibre with respect to time was observed shows various changes on the fibre colour. When the fibre undergoes UV light treatment for 1hr . the original colour of fibre 1 it remains same it means that colour of the fibre remains unaffected with light treatment. Similiarly when the same fibre is treated for 2hr in presence of uv light there is partial change in colour was observed on the fibre of indigo dye fibre this shows that dye prepared carried out dyeing activity of fibre in good condition also the same dye remains on fibre for long time in presence of UV light no more change on colour indigo dye fibre was observed therefore these dyes are less affected in presence of UV light no more change on the

colour of indigo dye fibre was observed therefore these dyes are less affected in presence of light they shows less light fasten activity within indigo dye fibre.



Table No 2- Action Of UV Light On The Dye Fibre With Respect To Time.

Sr No	Time in minutes	Fibre	Colour
1	After 1 hour		Faint Indigo
2	After 2 hour		Slightly Faint Indigo

Washing With Water at Different Temperature on Indigo Dye Fibre

When indigo dye fibre 1 was washed at room temperature with cold water there was no change in coloured was observed similarly when indigo dye fibre 2 was washed with hot water there was no change in coloured was observed but when indigo dye fibre 3 was washed with boil water small change in the colour of fibre was observed indigo dye fibre 3 get faint when washing carried out at very high temperature. These means that indigo dye prepared with washing fasten activities at different temperature.




Table No 3 - Effect Of Washing With Water At Different Temperature On Indigo Dye Fibre.

Sr No	Water	Fibre	Colour
1	Cold Water		Dark Indigo
2	Hot Water		Slightly Dark Indigo

Action of different detergent on indigo dye fibre

Action of different detergent on indigo dye fibre also shows poor changes in the fibre colour when indigo dye fibre 1 is treated with detergent rin for 30 min the colour of the fibre 1 gets slightly faint on the coloured was observed . similarly indigo dye fibre 2 is treated for 30 min with detergent tide the colour of the fibre 2 also gets slightly faint on the coloured was observed same result was observed in this case also when indigo dye fibre 3 is treated with wheel detergent the colour of the indigofibre 3 also gets slightly faint on the coloured was observed. This shows that the dyes prepared are better with respect to washing with various detergents that means indigo dyes are very stable with various detergent.

Table No 4-ActionOf Different Detergent On Indigo Dye Fibre.




Sr No	Name of detergent	Fibre	Colour
1	Rin		Dark Indigo
2	Tide		Slightly Dark Indigo
3	Wheel		Faint indigo colour

Action of different chemical solvents on indigo dye fibre

Action of different chemical solvents on indigo dye fibre show changes in fibre colour when indigo dye fibre 1 is treated with ethanol for 10 minutes the colour of the fibre 1 gets faint on coloured was observed. Similarly when indigo fibre 2 is treated with petrol for 10 minutes the colour of the fibre gets faint on the coloured was observed but in case of indigo dye fibre 3 when undergoes treatment with ether for

10 minutes there is partial colour change is observed. This shows that the indigo dye is stable with chemical solvents like ethanol, petrol and ether.

Table No 5 - Action Of Different Chemical Solvents On Indigo Dye Fibre.

Sr No	Different Solvent	Fibre	Colour
1	Ethanol		Faint indigo colour
2	Petrol		Dark Indigo colour
3	Ether		Dark Indigo

Conclusion

From the above result and dissection, it is clear that indigo dye which produce violet colour and on dyeing with fibre showed very slight changes with different parameters. When dyes are more time in contact with fibre produces more dark colour on the fibre. This shows the affinity between vat dyes molecules and fibre molecule increases with the time, these also conclude that the superioerfastness is due to the ability of dye molecule to associated into large aggregate in fibre which then how low diffusin rate. When light fasten activities was observed with vat dyes with respect to time it conclude that after 2 hrsintraction with uv light very small changes on the fibre colour was observed violet colour of fibreslightly faint after 2 hrsintraction with UV light very small change on the fibre colour was observed violet colour of fibreslightly faint after 2 hrs UV light very small change on fibre colour was observed violet colour of vibre slightly faint after 2 hrs. UV light treatment or otherwise the indigo dyes are very stable with UV light fasten activity when indigo dye fibre on treatment with different detergents. It is found that on treatment with rin detergent. After 1 hrs the violet colour of indigo dyes slightly faint but the othe detergent do not change the colour of the fibre shows the indigodyefibre are partially stable with washing fasten activity with detergents. Similarly when this fibres treated with water at different temperature there is slight change in colour was observed at very high temperature these indicated indigo dye fibre are stable in cold and hot conditions. When the fibre was traeated with different solvent the violet dye fibre remains stable with some solvent like petrol and ether.

References

- [1]. Serrano A.L. and Roos B.O., The Theoretical Study of Indigoid Dyes and Their Chromophore, European Journal of Chem., 3, (5), 717-725 (1996).
- [2]. Baeyer, A. Ber., 1296 (1878).
- [3]. C.C. Wang, C.K. Lee, M.D. Lyu and L.C. Juang, Dyes Pigments, 76, 817 (2008).
- [4]. Kos C, Process for the Preparation of Indigo U.S. Patent 5, 686,625 (1997).
- [5]. Sachs F. and Kempf R., Ber., Dtsch. Chem. Ges, 36 (1903).
- [6]. Posner T. Ber., Dtsch.Chem. 59, 1799-1833
- [7]. Golding, B.T. and Pierpont, C., Indigo Blue, Educ. Chem, 71-73 (1986).
- [8]. Heumann K. Ber., 23, 3043 (1890).
- [9]. Heumann K. Ber., 27, 2657 (1894).
- [10]. Baeyer, A. Ber., 456 (1879)
- [11]. Smith W.A., Floods A., Bochkov D. and Caple R. Organic Synthesis, Royal Soc. Chemists, 4 (2006).
- [12]. Otutu J.O. Ukponmwan D.O. and Oviawe A.P. Synthesis and Fastness Properties of Diazo Disperse Dyes from 4- Aminophenol, J. Chem. Soc. Nig., 32 (2), 65-71 (2007).