CHAPTER 2

EXPERIMENTAL

2. EXPERIMENTAL

2:1. GENERAL

All the chemicals used were of A.R. or G.R. grades of B.D.H. or E.Merck respectively unless otherwise stated.

α-Naphthol (B.D.H.) was recrystalized from hot water and dried over P_2O_5, while 8-hydroxy quinoline was used without further purification. Commercially available aromatic amines were recrystallised (twice) from suitable solvents. Cyanuric chloride was generously supplied by M/S. Suhrid Geigy Ltd., Ranoli, and was used after crystallizing from benzene.

Melting points were recorded using Toshniwal melting point apparatus and are uncorrected. The i.r. spectra were scanned on a Beckmann IR-20 spectrophotometer as KBr pallets or nujol mulls. The ultra violet spectra were scanned using Beckmann Du-2 spectrophotometer, and the visible spectra were taken on Spekol spectrophotometer. The Elico pH meter model LI-10 equipped with glass electrode (pH range o-14) and fibre junction calomel electrode was used for pH measurements.

2:2. SYNTHESIS OF REACTIVE COUPLING COMPONENTS

Reactive coupling components were synthesised by Friedel-Crafts reaction. Cyanuric chloride undergoes the Friedel-Crafts reaction with hydrocarbons or phenols.

2:2:1. Synthesis of 2,4-dichloro-6-(4'-hydroxy-1'-naphthyl)-s-triazine.

4.25 g α-naphthol and 5.4 g cyanuric chloride were dissolved in 40 ml sodium dried benzene at 5-10°C in 250 ml flat bottom flask fitted with air condenser and guard tube. The content was continueously stirred on a magnetic stirrer. To this 3.9 g anhydrous aluminium chloride was added during 2 hr maintaining the same temperature. The temperature was then raised during a period of 2 hr to 25-30°C and was kept at this temperature for overnight. The mixture was filtered and the solid aluminium chloride complex was washed with benzene and dried. The aluminium chloride complex was then decomposed by stirring with a mixture of 10 ml conc HCl, 20 ml water and 40 g ice. The resulting mixture was filtered and the solid product was first washed with cold water until free from acid, then with a solution of 1.2 g sodium dihydrogen phosphate in 25 ml water, and was finally dried at 40°C under vaccum. The product, 2,4-dichloro-6-(4'-hydroxy-1'-naphthyl)-s-triazine (1-3), was crystallized from toluene. The purified compound was used as reactive naphthol for further study.

2:2:2. Synthesis of 2,4-dichloro-6-(4'-hydroxy-1'-anthracenyl)-s-triazine.

It was prepared from 1-anthracenol and cyanuric chloride. The starting compound 1-anthracenol was prepared by sulphonation of anthraquinone in presence of yellow mercuric oxide (4) followed by reduction to anthracene-1-sulphonic acid (5) and then fusion with potassium hydroxide to yield 1-~~n~~athracenol (6).

5.8 g 1-anthracenol was reacted with 5.4 g cyanuric chloride in presence of 3.9 g anhydrous aluminium chloride keeping all the conditions same as mentioned in section 2:2:1 for reactive naphthol. The product, after decomposing the aluminium complex, was crystallized from toluene and used as a reactive anthracenol for further study.

2:2:3. Synthesis of 2,4-dichloro-6-(8'-hydroxy-5'-quinolinyl)-s-triazine.

In 250 ml flat bottom flask fitted with a air condenser and guard tube 4.2 g 8-hydroxy quinoline and 5.4 g cyanuric chloride were dissolved in sodium dried benzene at 5-10°C. The content was stirred for two hours using magnetic stirrer. The contents temperature was raised to 25-30°C and kept for 12 hours. The mixture was filtered and the solid product was separated, dried and crystallized from carbon tetrachloride. The purified product was used as reactive 8-hydroxy quinoline for subsequent study.

2:3. REACTIVE AZOIC DYEING OF COTTON

The dyeing was carried out in the usual way. The reactive naphthol (0.1 g) was dissolved at 10 to 15°C in aqueous sodium hydroxide (Ca.5 ml 10%) in a dye pot and the volume of solution was made to 100 ml with demineralised water. The cotton hank (5.0 g) was wetted with water. It was impregnated in the solution after squeezing and kept for 30 min at room temperature. The dye pot was placed in a water bath for further 30 min at 60-65°C. For more exhaustion of the naphthol, 20 ml 10% aqueous sodium chloride solution was added in small portions during dyeing. The hank was squeezed, dried and heated for 3 min at 155°C in jet drier.

In case of reactive anthracenol, 0.1 g reactive anthracenol was dissolved in 5 ml of aqueous sodium hydroxide (10%) and 2.5 ml of ethanol at 10 to 15°C. The dyeing was carried out by the same method as described for reactive naphthol.

The hank was developed in 3% neutral solution of diazotised base. The dyed hank was rinsed with cold water followed by boiling with 1% soap solution for half an hr. Again it was rinsed with cold water and dried. Several aromatic amines were used for developing purpose.

2:4. REACTIVE AZOIC DYEING OF WOOL

As wool is very sensitive to alkali, sodium carbonate was used instead of sodium hydroxide for dissolving the naphthol or anthracenol. While dyeing the wool, the general instructions given by Everest and Wallwork were followed (7).

The reactive naphthol or reactive anthracenol (0.1 g) was dissolved in aqueous sodium carbonate (Ca 10 ml 10%) and ethanol (5 ml) in a dye pot. The solution was made upto 100 ml with demineralised water. The wool hank (5.0 g) was wetted with water, squeezed, impregnated in the solution and kept for 30 min at room temperature. Further it was kept for 30 min at 50 to 55°C on water bath. For maximum exhaustion of the naphthol, 20 ml of 10% aqueous sodium chloride solution was added in small aliquot during dyeing. The hank was squeezed, dried and heated for 3 min at 110°C in jet drier.

The hank was developed in 3% neutral solution of diazotised base. Different aromatic amines were used for developing purpose. The dyed hank was rinsed with cold water followed with 1% soap solution (50 to 60°C, 30 min) and cold water. Then it was treated with dilute acetic acid and dried.

2:5. VISIBLE SPECTRA OF DYED FIBRES.

2:5:1. Spectra of Dyed Cotton

20 mg of dyed cotton was dissolved in 2.5 ml of

conc sulphuric acid at 5 to 10°C. After an hr, the solution was diluted with 20 ml of cold distilled water. The solution was allowed to stand at room temperature for 10 min. The dye was extracted with chloroform (ethanol free). The extract was diluted to 25 ml with chloroform. A solution of the same amount of undyed cotton was used as the reference for absorbance measurement. The spectra were taken on a Spekol spectrophotometer with 10 mm cell.

2:5:2. Spectra of Dyed Wool

20 mg of dyed wool was dissolved in 20 ml sodium hydroxide (10%) at room temperature by keeping it overnight. The solution was acidified with cold dilute hydrochloric acid and the dye was extracted with n-butanol, and diluted 25 ml with n-butanol. A solution of the same amount of undyed wool was used as the reference solution for absorbance measurement.

2:6. SYNTHESIS OF REACTIVE DYES

Reactive dyes were synthesized by coupling diazotised aromatic amino sulphonic acids to reactive naphthol, reactive anthracenol and reactive 8-hydroxy quinoline in alkaline medium.

2:6:1. Synthesis of Monoazo Reactive Dyes

0.86 g (0.005 mole) sulphanilic acid was diazotised in the usual way (8). The diazo solution was neutrallised to Congo Red test paper with sodium bicarbonate. The diazo solution was added to a mixture of 1.46 g (0.005 mole) reactive naphthol and 2.0 g sodium bicarbonate in 75 ml of acetone at 0-5°C. The mixture was stirred for 1 hr and then 2.5 g sodium dihydrogen phosphate, 2.5 g disodium hydrogen phosphate and 20 g sodium chloride were added. The mixture was stirred for further 1 hr. The solid dyestuff was filtered off, washed with a solution of 6.0 g disodium hydrogen phosphate and 6.0 g sodium dihydrogen phosphate in 50 ml of water, and dried at 40°C under reduce pressure. Different aromatic amino sulphonic acids were taken, diazotised and coupled with reactive naphthol, reactive anthracenol and reactive 8-hydroxy quinoline.

2:6:2. Synthesis of Disazo Reactive Dyes

Aromatic amino monoazo suphonic acid-diazo component-, was prepared by diazotising aromatic diamine and coupling with H-acid or 7-amino-1-naphthol-3-sulphanoc acid. A typical procedure is described below.

1.1 g (0.01 mole) p-phenylene diamine was dissolved in conc hydrochloric acid. It was cooled to 0-5°C. To this cold solution of 0.86 g (0.01 mole) sodium nitrate in water was added. The mixture was kept at 0-5°C for 1 hr. It was added to the 3.1 g (0.01 mole) H-acid in aqueous sodium hydroxide maintaining the same temperature. The dye was isolated in the usual way. The compound was purified and was used for further diazotizing and coupling to reactive coupling components for the synthesis of disazo reactive dyes.

2:6:3. Purification of Reactive Dyes

The synthesised reactive dyes were purified by solvent-non-solvent technique (9,10).

The reactive dye was dissolved in dimethylformamide and filtered. To the filtrate acetone was added to precipitate the dye. The precipitated dye was filtered and washed with acetone, chloroform and solvent ether. The procedure repeated thrice and the purified dye was subjected for determination of hydrolysable chlorine atoms present in a dye molecule.

2.7. DYEING PROCEDURE

2.7.1. Dyeing of Cellulose Fibres

Cellulose fibres in the hank form were dyed by exhaust method using 20:1 liquor to material ratio. Dyeing was carried out for 1 hr at 30-60°C using soda ash - bicarbonate. 4 to 5% electrolyte solution was added during dyeing. After this, the samples were removed from the dye bath, washed thoroughly first with ample cold water (20°C) and then with hot water (90°C), soaped at boil using nonionic detergent and finally washed with distilled water. The samples were treated in 50% aqueous pyridine solution for 2 hr at 30°C to remove unfixed dye, followed by through washing and air drying at room temperature (30°C). The dyed samples were conditioned under 65% R.H. at 30°C.

2.7.2. Dyeing of Wool Fibres

Wool fibres in the hank form were dyed in solutions (50:1 liquor: Wool ratio) containing 0.5 - 3% O.W.F dye, 10% O.W.F. sodium sulphate and 1-2% O.W.F. sodium acetate. The dyebaths were adjusted to the required pH by the addition of sulphuric acid, acetic acid or sodium hydroxide. The samples were entered at 30°C and the temperature was raised to 30-50°C during 20 min, and after 30 min to 60° and then finally after 10 min to 70°C for fixation of dye. The dyed samples were first washed with cold water and then with hot water (60°C), soaped at the same temperature using non-ionic detergent and finally washed with distilled water. Acid pyridine (10 parts pyridine, 20 parts formic acid (90%) and 70 parts water) at the boil was used to remove non-covalently bound dye. The dyed samples were conditioned under 65% R.H. at 30°C.

2.8. COLOUR FASTNESS OF DYED FIBRES

2.8.1. Colour Fastness to Washing

Washing fastness of the dyed samples was determined on Launder-Ometer according to ISO Test No.5. The test samples for washing fastness were prepared by interweaving the hank of dyed test sample (2.5 g) with a undyed sample (1.25 g).

Launder-Ometer was adjusted to 95 ± 2°C and wash liquior was prepared by dissolving 1 g lux soap chips in 200 ml water in a stainless steel cylinder. The composite specimen was treated for 30 min at this temperature. The specimen was removed and rinsed twice in cold distilled water and then for 10 min in cold running tap-water and squeezed. The specimen was dried and compared with grey scale for washing fastness.

2.8.2. Colour Fastness to Light

Light fastness of the dyed samples have been determined on ATLAS FADE-OMETER according to AATCC test method (11). The results were evaluated by comparing the test specimens with grey scale.

2.8.3. Colour Fastness to Crocking

Crocking fastness of the dyed samples was determined on crock-meter of ATLAS ELECTRIC DEVICES CO. MODEL-1 according to AATCC test method by dry and wet crocking test (12). Ten to and fro movements in 10 sec were made. The white test squares were evaluated for the amount of colour transferred from the specimen to the white test square under examination by means of grey scale for staining with intermediate steps.

2.9. SOLVENT DYEING OF COTTON

2.9.1. Solvents

Standard laboratory grade dimethyl formamide (DMF) and trichloroethylene (TCE) supplied by E.Merck were used.

2.9.2. Sample Preparation for Dyeing

Conditioned cotton yarn weighing 0.2 g in the form of small hank was pre-swollen overnight with aqueous sodium hydroxide solution at room temperature. The samples were dried with the folds of the filter papers and hung on rubber bungs by means of small pins. Each rubber bung alongwith the samples was then placed in centrifuge tube containing small pieces of filter paper at the bottom to avoid the respraying of the centrifuged liquid, and centrifuged at 4000 rpm. The samples were transferred immediately into the dyebaths without giving any chance to dry in the air.

2.9.3. Dyeing

The dyeing of alkali pre-swollen centrifuged samples was carried out in 25 ml measuring glass cylinders fitted with water condensor. All the dyeings were carried out at the desired temperature using liquor ratio 75:1. Initially the dyebath was set only with required quantity of dye in DMF (stock solution) and the required volume of DMF. The sample was first treated in this bath at room temperature for 10 min. Then required volume of TCE was added in three instalments with an interval of 5 min. The addition of TCE in intervals was essential to get level dyeings. After the initial exhaustion the temperature of the dye bath was raised as desired. The dye fixation was carried out for the required time.

At the end of dyeing period the samples were taken out, pressed between folds of filter papers, rinsed, and soaped twice at boil before dye analysis.

2.9.4. Dye Estimation

The dye estimation was carried out by dissolving the known weight of dyed samples in cold conc sulphuric acid and measuring the optical density on Metzer Spectra 75 spectrophotometer at the wavelength of the maximum absorbance. The percent exhaustion and fixation values were calculated by the difference.

2.9.5. Alkali Estimation

The estimation of NaOH on samples before dyeing, after treatment in blank dyebath was carried out by titration with standard HCl using phenolphathalein as an indicator. However, for estimation of NaOH on dyed samples electrometric method was used. This was essential due to colouration of solution because of unfixed dye and thus making it impossible to determine the end point by direct titration method with phenolphathalein indicator.

2.9.6. Estimation of Dye Hydrolysis

The presence of hydrolysed dye on dyed sample was estimated by using caustic soda pyridine test (13). Dichloro-s-triazinyl compounds show a characteristic colour change when treated with a mixture of pyridine and sodium hydroxide, which is indicated by a characteristic peak in the absorption spectrum, the height of this peak is proportional to the amount of unreacted dye present. The dye sample (1.0 ml) was removed and added to 8.5 ml of a mixture of pyridine and sodium hydroxide, and made up with water to 10 ml. The pyridine-sodium hydroxide mixture was prepared by mixing sodium hydroxide (0.5 g) with pyridine (55.0 ml) and diluting with water to 100 ml. After an interval of time to allow the characteristic peak to develop its maximum value, the height of the peak was measured.

2.10. RATE OF HYDROLYSIS

0.01 M solution of reactive naphthol in different buffer solutions prepared from sodium carbonate-sodium bicarbonate were prepared at 25°C. At various intervals of time 10 ml solution was removed, immediately acidified with dil nitric acid and titrated with silver nitrate to determine the concentration of liberated chloride ion (14).

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