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Synthesis, Characterization and Printing Application of Solvent Dyes Based on 2-Hydroxy-4-n-octyloxybenzophenone

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Abstract: Solvent dyes have been prepared by the coupling of diazo solution of different aromatic amines with 2-hydroxy-4-n-octyloxybenzophenone. The resultant dyes were characterized by elemental analysis as well as IR and ¹H NMR spectral studies. The UV-Visible spectral data have also been discussed in terms of structure property relationship. The printing of all the dyes on cotton fiber was monitored. The result shows that better hue was obtained on printing on cotton fiber and it is resulted in yellow to reddish brown colorations which showed a good fastness to light, with poor to good fastness to washing, perspiration and sublimation, however it shows poor rubbing fastness.

Keywords: Solvent dyes, Printing application, Cotton fibre, Light fastness, Washing fastness.

Introduction

Whilst phenols are well established intermediates for the syntheses of various commercial dyes¹⁻⁶, they are marketed in the form of azo disperse, azo-acid dyes *etc*. All of these dyes having phenolic moiety, containing hydroxyl group as an auxochrome group. Such auxochromic(-OH) and chromophoric(C=O) group containing compound *i.e.* 2-hydroxy-4-n-octyloxybenzophenone has shown wide applications as a polymer additives⁷⁻⁹. It is an excellent UV absorber¹⁰, which prevents the photo degradability of most of vinyl polymers¹¹⁻¹³. The area in which the acid azo dyes and mordent azo dyes formation based on this compound has not been developed except of few patents¹⁴⁻¹⁷.

The formation of solvent dyes based on this compound may yield the dyes with good hue properties. Hence, in continuation of our earlier work¹⁸, it was thought interesting to explore the field of acid azo dyes based on 2-hydroxy-4-*n*-octyloxybenzophenone. Thus, the present communication comprises the printing application of solvent dyes based on 2-hydroxy-4-*n*-octyloxybenzophenone.

Experimental

All the chemicals used were of analytical grade and were further purified as and when required. The aromatic amines listed in Scheme 1 were used for diazotization. Cotton fibers were gifted by color tax (Pvt) Ltd, Surat. Melting points were determined by open capillary method and are uncorrected. The visible absorption spectra were measured on a Carl Zeiss UV/VIS Specord spectrometer and elemental analysis was carried out on Perkin Elmer CHNS/O Analyzer 2400 Series II. Infrared spectra were recorded in KBr pellets on a Perkin-Elmer Spectrum GX FT-IR model, proton NMR spectra were recorded on Hitachi R-1500 in DMSO-D₆ solvent and TLC (Thin layer chromatography) was run on a aluminum sheets precoated with silica gel 60 F₂₄₅ (Merck, Germany) using methanol-water-acetic acid (12:3:7) solvent system. Colour spot was visualized by UV chamber. Printing machine (Process controller PC2F/R) was used for printing purpose.

Synthesis of solvent dyes

Diazotization

Diazotization of various aromatic amines 1(a-g) (Scheme 1) was carried out by the method reported in literature^{19,20}. Accordingly each of the aromatic amines 1(a-g) (3.19x10⁻³ kg, 0.01 mol) was mixed with HCl (2.5x10⁻⁵ m³, 37%) in a mortar, transferred to a 3-neck round bottom flask and additional HCl (2.0x10⁻⁵ m³, 37%) was added. To the resultant suspension crushed ice (25x10⁻³ kg) and NaNO₂ (2.5x10⁻⁵ m³, 4N) were added. Diazotization was carried out over 0.5 h at 5 0 C with constant stirring.

Dyes(D₁-D₇)

Dyes No	R_1	R ₂	R ₃	R_4	Amines (a-j)
D_1	NO_2	Н	Н	Н	2- Nitroaniline
D_2	Н	Н	NO_2	Н	4- Nitroaniline
D_3	Н	NO_2	Н	Η	3 -Nitroaniline
D_4	Cl	Н	NO_2	Cl	2,6 -Dichloro-4-nitroaniline
D_5	CH_3	Н	CH_3	Η	2,4-Dimethylaniline
D_6	Н	Cl	Н	Н	3-Chloroaniline
\mathbf{D}_7	Н	Н	Cl	Н	4-Chloroaniline

Scheme 1. Proposed synthetic rout for the preparation of solvent dyes

Coupling procedure

The coupling of above mentioned diazotized aromatic amines $\mathbf{1}(\mathbf{a}\mathbf{-g})$ was carried out in the similar manner. The general procedure followed is given below: 2-Hydroxy-4-n-octyloxybenzophenone (2.15×10^{-3} kg, 0.01 mol) was dissolved in sodium hydroxide (1.2×10^{-5} m 3 , 0.01 mol) solution. The clear solution was cooled in ice-bath and diazonium solution of aromatic amines $\mathbf{1}(\mathbf{a}\mathbf{-g})$ was added drop wise over a period of 30 min with vigorous stirring. The pH was maintained between 2.0 to 3.0 by simultaneous addition of 10% w/v sodium carbonate solution. Stirring was continued for 2 h, allowing the temperature to rise to ambient. The dyes was then filtered off and dissolved in distilled water after that solvent dyes were obtained by evaporation procedure and it was dried at room temperature. The dyes were designated as solvent dye (\mathbf{D}_{1-7}) and were recrystalised in acetone.

Printing on cotton fiber

Solvent dyes (D_1-D_7) used for printing of cotton fiber was carried out by the method reported in literature²¹.

Characteristic data of solvent dyes

1-[2-Hydroxy-4-n-octyloxy -5-(2-nitrophenylazo)phenyl]-1-phenylmethanone (D_1)

Calculated for $C_{27}H_{29}O_5N_3$: M. wt.: 475, % yield: 88, m. p.: 47-49 0 C, R_f value: 0.82; C, 68.21%; H, 6.10%; N, 8.84%. Found: C, 68.19%; H, 5.98%; N, 8.81%. IR: 3463 cm⁻¹ (-OH); 3072 cm⁻¹ (=CH, aromatic); 1628 cm⁻¹ (C=O, diaryl); 1521 cm⁻¹ (N=N); 1481 cm⁻¹ (C=C, aromatic); 1333 cm⁻¹ (C-N); 1101 cm⁻¹ (C-O); 1212-1024 cm⁻¹ (C-O-C, stretching); 732 cm⁻¹, 584 cm⁻¹, 481 cm⁻¹ (for substituted benzene). 1 H NMR: 10.7 δ (Ar-OH, singlet), 7.2-7.4 δ (Ar-H, multiplet), 3.6 δ (-OC₈H₁₇, singlet, 3H), 2.8 δ (-CH₂-, multiplet), 2.23 δ (-CH₃, singlet, 3H), 1.8 δ and 1.2 δ (triplet,-CH₃ and -CH₂-).

1-[2-Hydroxy-4-n-octyloxy -5-(4-nitrophenylazo)phenyl]-1-phenylmethanone (D₂)

Calculated for $C_{27}H_{29}O_5N_3$: M. wt.: 475, % yield: 92, m. p.: 52-54 0 C, R_f value: 0.80; C, 68.21%; H, 6.10%; N, 8.84%. Found: C, 68.17%; H, 5.94%; N, 8.78%. IR: 3450 cm⁻¹ (-OH); 3082 cm⁻¹ (=CH, aromatic); 1624 cm⁻¹ (C=O, diaryl); 1522 cm⁻¹ (N=N); 1490 cm⁻¹ (C=C, aromatic); 1345 cm⁻¹ (C-N); 1101 cm⁻¹ (C-O); 1032 cm⁻¹, 1211-1021 cm⁻¹ (C-O-C, stretching); 744 cm⁻¹, 564 cm⁻¹, 478 cm⁻¹ (for substituted benzene). 1 H NMR: 10.6 δ (Ar-OH, singlet), 7.1-7.3 δ (Ar-H, multiplet), 3.8 δ (-OC₈H₁₇, singlet, 3H), 2.4 δ (-CH₂-, multiplet), 2.13 δ (-CH₃, singlet, 3H), 1.6 δ and 1.4 δ (triplet,-CH₃ and -CH₂-).

1-[2-Hydroxy-4-n-octyloxy -5-(3-nitrophenylazo)phenyl]-1-phenylmethanone (D₃)

Calculated for $C_{27}H_{29}O_5N_3$: M. wt.: 475, % yield: 87, m. p.: 50-53 0 C, R_f value: 0.85; C, 68.21%; H, 6.10%; N, 8.84%. Found: C, 68.15%; H, 5.96%; N, 8.76%. IR: 3481 cm⁻¹ (-OH); 3070 cm⁻¹ (=CH, aromatic); 1632 cm⁻¹ (C=O, diaryl); 1542 cm⁻¹ (N=N); 1483 cm⁻¹ (C=C, aromatic); 1337 cm⁻¹ (C-N); 1103 cm⁻¹ (C-O); 1212-1020 cm⁻¹ (C-O-C, stretching); 1029 cm⁻¹, 737 cm⁻¹, 562 cm⁻¹, 472 cm⁻¹ (for substituted benzene). 1 H NMR: 10.9 δ (Ar-OH, singlet), 7.1-7.3 δ (Ar-H, multiplet), 3.7 δ (-OC₈H₁₇, singlet, 3H), 2.6 δ (-CH₂-, multiplet), 2.27 δ (-CH₃, singlet, 3H), 1.4 δ and 1.1 δ (triplet, -CH₃ and -CH₂-).

1-[2-Hydroxy-4-n-octyloxy-5-(2,5-dichloro-4-nitrophenylazo)phenyl]-1-phenylmethanone (D_4)

Calculated for $C_{27}H_{27}O_5N_3Cl_2$: M. wt.: 544, % yield: 78, m. p.: 66-69 0 C, R_f value: 0.87; C, 59.55%; H, 4.96%; N, 7.72%. Found: C, 59.49%; H, 4.92%; N, 7.68%. IR: 3633 cm⁻¹ (-OH); 3080 cm⁻¹ (=CH, aromatic); 1652 cm⁻¹ (C=O, diaryl); 1532 cm⁻¹ (N=N); 1473 cm⁻¹

(C=C, aromatic); 1338 cm⁻¹ (C-N); 1104 cm⁻¹ (C-O); 1210-1021 cm⁻¹ (C-O-C, stretching); 1032 cm⁻¹, 782 cm⁻¹, 741 cm⁻¹, 583 cm⁻¹, 485 cm⁻¹ (for substituted benzene). ¹H NMR: 10.6 δ (Ar-OH, singlet), 7.3-7.7 δ (Ar-H, multiplet), 3.5 δ (-OC₈H₁₇, singlet, 3H), 2.4 δ (-CH₂-multiplet), 2.24 δ (-CH₃, singlet, 3H), 1.6 δ and 1.4 δ (triplet,-CH₃ and -CH₂-).

1-[2-Hydroxy-4-n-octyloxy-5-(2,4-dimethylphenylazo)phenyl]-1-phenylmethanone (D_5)

Calculated for $C_{29}H_{34}O_3N_2$: M. wt.: 458, % yield: 82, m. p.: 45-47 0 C, R_f value: 0.86; C, 75.98%; H, 7.42%; N, 6.11%. Found: C, 75.94%; H, 7.39%; N, 6.08%. IR : 3580 cm⁻¹ (-OH, phenolic); 3070 cm⁻¹ (=CH, aromatic); 1621 cm⁻¹ (C=O, diaryl); 1531 cm⁻¹ (N = N); 1482 cm⁻¹ (C=C, aromatic); 1463 cm⁻¹ (C-N); 1338 cm⁻¹ (C-O); 1210-1023 cm⁻¹ (C-O-C, stretching), 1034 cm⁻¹, 1103 cm⁻¹, 732 cm⁻¹, 574 cm⁻¹, 473 cm⁻¹ (for substituted benzene). 1 H-NMR: 10.6 δ (Ar-OH, singlet), 7.2-7.6 δ (Ar-H, multiplet), 3.4 δ (-OC₈H₁₇, singlet, 3H), 2.5 δ (-CH₂-, multiplet), 2.21 δ (-CH₃, singlet, 3H), 1.6 δ and 1.3 δ (triplet,-CH₃ and -CH₂-).

1-[2-Hydroxy-4-n-octyloxy -5-(3-chlorophenylazo)phenyl]-1-phenylmethanone (D_6) Calculated for C₂₇H₂₉O₃N₂Cl: M. wt.: 464, % yield: 76, m. p.: 55-58 0 C, R_f value: 0.83; C, 69.82%; H, 6.25%; N, 6.03%. Found: C, 69.78%; H, 6.21%; N, 5.97%. IR: 3430 cm⁻¹ (-OH, phenolic); 3540 cm⁻¹ (-OH, acidic); 3062 cm⁻¹ (=CH, aromatic); 1634 cm⁻¹ (C=O, diaryl); 1581 cm⁻¹ (N=N); 1483 cm⁻¹ (C=C, aromatic); 1352 cm⁻¹ (C-N); 1103 cm⁻¹ (C-O); 1210-1022 cm⁻¹ (C-O-C, stretching); 783 cm⁻¹, 741 cm⁻¹, 583 cm⁻¹, 482 cm⁻¹ (for substituted benzene). 1 H NMR: 10.8 δ (Ar-OH, singlet), 7.3-7.5 δ (Ar-H, multiplet), 3.7 δ (-OC₈H₁₇, singlet, 3H), 2.5 δ (-CH₂-, multiplet), 2.27 δ (-CH₃, singlet, 3H), 1.9 δ and 1.3 δ (triplet,-CH₃ and -CH₂-).

1-[2-Hydroxy-4-n-octyloxy-5-(4-chlorophenylazo)phenyl]-1-phenylmethanone (D_7) Calculated for C₂₈H₃₂O₃N₂: M. wt.: 444, % yield: 85, m. p.: 43-46 0 C, R_f value: 0.85; C, 75.67 %; H, 7.20 %; N, 6.30 %. Found: C, 75.62 %; H, 7.17 %; N, 6.27 %. IR : 3590 cm⁻¹ (-OH); 3063 cm⁻¹ (=CH, aromatic); 1632 cm⁻¹ (C=O, diaryl); 1533 cm⁻¹ (N=N); 1471 cm⁻¹ (C=C, aromatic); 1324 cm⁻¹ (C-N); 1103 cm⁻¹ (C-O); 1211-1023 cm⁻¹ (C-O-C, stretching);1031 cm⁻¹, 780 cm⁻¹, 744 cm⁻¹, 586 cm⁻¹, 475 cm⁻¹ (for substituted benzene). 1 H NMR: 10.6 δ (Ar-OH, singlet), 7.1-7.6 δ (Ar-H, multiplet), 3.8 δ (-OC₈H₁₇, singlet, 3H), 2.6 δ (-CH₂-, multiplet), 2.24 δ (-CH₃, singlet, 3H), 1.7 δ and 1.4 δ (triplet, -CH₃ and -CH₂-).

Fastness property

The fastness to light, sublimation and perspiration of dye pattern was assessed according to British standard: 1006-1978 and the wash fastness test according to Indian standard: IS: 765-1979. The rubbing fastness was tested by using Crock meter (Atlas) AATCC-1961, shown in Table 2.

Determination of the percentage exhaustion and fixation

The dye bath percentage exhaustion and fixation of the dyed fabric was determined according to the known method²² and is shown in Table 1.

Results and Discussion

Physical properties of solvent dyes

All the dyes are obtained as crystal powder ranging from yellow to reddish brown in colours. The purity of the dyes were checked by TLC using methanol-water-acetic acid (12:3:7) solvent system. The TLC results show that only single spot observed for each dye. The purified dyes have melting point measured by open capillary tube. The melting points were uncorrected.

The results of elemental analysis content of each dyes are consistent with the predicted structure as shown in Scheme 1. The number of azo group is almost one for each dye. The nitrogen content and number of azo group for each dye are co-related with each other. The IR spectrum of each dye comprises the important features of aromatic, azo, hydroxyl, alkoxy and keto groups. The ¹H NMR spectra of all the diazo compounds based on 2-hydroxy-4-n-octyloxybenzophenone shows an important signals at their respective positions confirmed the structures of various dyes as shown in Scheme 1.

The visible absorption spectroscopic properties of dyes were recorded in double distilled water. The absorption maxima (λ_{max}) of all the dyes fall into the range of 346-410 nm in water, as shown in Table 1. The value of the logarithm of molar extinction coefficient (log ϵ) of all the dyes were in the range of 4.11 – 4.28, consistent with their high intensity of absorption.

Table 1. Absorption maxima (λ_{max}) , intensities (log ϵ), exhaustion (E) and fixation (F) of solvent dyes on cotton

Dyes	Absorption maxima	Intensities	Printing on Cotton		
No.	λ_{max} /nm In DMF	$\text{Log }\epsilon$	%E	%F	
D_1	346	4.216	80	89	
D_2	352	4.193	75	94	
D_3	385	4.167	72	90	
D_4	349	4.280	85	89	
D_5	385	4.117	74	86	
D_6	410	4.172	71	88	
D_7	397	4.185	85	92	

Moreover, the presence of electron donating or electron attracting groups did not bring about any marked increase or decreased in λ_{max} in the visible region and that $\log \epsilon$ remained nearly constant. However, electron attracting substituents like $-NO_2$ and -Cl in the substituent group of the coupler increase polarizability, and will results in bathochromic shifts. This leads to decrease in energy between the highest occupied molecular orbital and lowest unoccupied molecular orbital and thus $\pi \to \pi^*$ electronic transition takes place at lower frequency photon, resulting in the bathochromic shift of the visible absorption band.

Dyeing properties of dyes

The solvent dyes were applied at 2% depth on cotton fabric respectively. Their printing properties are given in Table 2. These dyes gave a wide range of colours varying from yellow to reddish brown shades with good levelness, brightness and depth on the fabrics.

Table 2. Results of solvent dyes on printing and various fastness properties of dyes on cotton

Dyes No.	Color shades on cotton	Light fastness	Washing fastness	Perspiration fastness		Sublimation	Rubbing fastness	
				Acid	Alkaline	- fastness	Dry	Wet
D_1	Orange brown	5	5	4	5	4	4	4
D_2	Reddish brown	5	4	4	4	4	4	4
D_3	Reddish orange	5	5	5	5	5	4	4
D_4	Light yellow	4	5	4	5	4	4	3
D_5	Chocolate brown	4	4	5	5	4	4	4
D_6	Yellow	5	5	5	5	5	4	3
\mathbf{D}_7	Yellow	5	4	5	5	4	4	4

The variation in the shades of the dye fabric results from both the nature and position of the substituent present on the diazotized compound. The dyeing showed an excellent fastness to light, with very good to excellent fastness to washing, perspiration and sublimation, however it shows poor rubbing fastness. A remarkable degree of levelness after washing is observed. This may be attributed to good penetration and affinity of the dye molecule in to fiber structure.

Conclusion

Produced solvent dyes have good fastness to light but show poor sublimation and rubbing fastness properties. The nature of the substituent in the coupling components has a little influence on the visible absorption and shade of the printing. All the solvent dyes show a good solubility in various organic solvents therefore, they may be useful as fuel dye and in printing ink.

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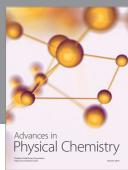
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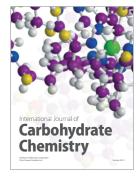
















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