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Original

New acid dyes and their metal complexes based on substituted phenols for leather: Synthesis, characterization and optical studies

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Abstract

The present investigation deals with synthesis of new acid dyes from 4-amino-1-(4-sulfophenyl)-3-methyl-5-pyrazolone and phenol derivatives and their metal complexes (Cu (II) and Fe (II)). The phenol derivatives include 4-chlorophenol, 4-nitrophenol, 4-hydroxybenzene sulfonic acid, 2-nitrophenol-4-sulfonic acid, resorcinol and bisphenol A and bisphenol S. The newly synthesized dyes were applied to crust leather to assess their dyeing properties. The fastness properties of unmetallized dyes were less as compared to metal complexes due to the strong interaction of metals with leather protein. The structures of these dyes were also confirmed by UV, FTIR and NMR studies.

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1. Introduction

Azo compounds are non-naturally occurring nitrogen compounds continuously receiving attention in scientific research (Kirkan & Gup, 2008; Otutu, 2013; Seferoğlu, 2009). Azo dyes constitute the largest group of Azo compounds and the most widely used colorants in the industry. Several derivatives of pyrazole (azo) were the subject of research because of a variety of applications. The applications of the azo dyes include their use in coloring fibers, due to their affinity for wool and silk (Patel & Patel, 2011), photoelectronics (Sekar, 1999), optical storage technology (Wang, Shen, & Xu, 2000), biological reactions (Weglarz-Tomczak & Gorecki, 2012), printing systems (Abe, Mano, Yamaya, & Tomotake, 1999; Dharmalingam, Ramasamy, & Balasuramanian, 2011) as well as in analytical

(Abdalla, El-Haty, Adam, & Hassan, 2013; Amin, Mohammed, & Mousa, 2003) and food chemistry (Almeida, Stephani, Dos Santos, & Oliveira, 2009). Beside these many azo compounds have been synthesized with an industrial and medical aim. The coordination complexes of transition metals with azo-ligands are also focus of the current attraction due to the interesting physical, chemical, photophysical and photochemical, catalytic and different material properties. Metal complex dyes play a very important role in the textile industry. Chromium, Cr (III) and cobalt Co (III) complexes are used most frequently for the dyeing of wool and synthetic polyamides (Kocaokutgen, Erdem, & Gümrükçüoğlu, 1998).

Photophysical and coloristic properties of the dyes are modified in the case of aggregate formation (molecular association) in solution. The self-association of dyes in solution is due to the interactions by Van der Waals forces, hydrogen bonds and hydrophobic interactions (Radulescu-Grad, Muntean, Todea, Verdes, & Andelescu, 2015). The dye aggregation is affected by parameters such as dye concentration, dye structure, pH, temperature, solvents and ionic strengths (Goftar, Moradi, & Kor, 2014).

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In the present work, two new series of azo-dyes, having Fe⁺² and Cu²⁺ as metalizing ion were synthesized, characterized and applied to leather. At the same time, spectrophotometric analysis was also performed for the qualitative study of ligand acid dyes and their metal complex.

2. Experimental

2.1. Materials and methods

All commercial products were purchased from Sigma-Aldrich. Solvents were purified and dried by the standard methods. Melting points were determined in open capillary tubes on a Stuart melting point apparatus. The FTIR spectra were run in the single beam Nicolet IR 100 (Fourier-Transform); while UV of all the samples were taken in water using UV-Genesys spectrophotometer. Their mass spectral data were obtained from waters GCT premier spectrometer. The ¹H NMR and ¹³C NMR spectra were recorded in DMSO-d₆ using NMR Bruker DPX 400 spectrophotometer operating at 300 and 75 MHz for ¹H and ¹³C NMR respectively. TMS was used as internal standard with the deuterium signal of the solvent as the lock and chemical shifts δ recorded in ppm. The elemental analysis (C, H, N, S) of the compounds was performed using Flash EA 1112 elemental analyzer while the pH was monitored using Portable pH Meter Model PHB4. Compounds were routinely checked by TLC on silica gel G plates using three different eluting solvents depending on the polarity disparity. The solvent systems are petroleum ether:chloroform (9:1, v/v), petroleum ether:chloroform (6:4, v/v) and chloroform:methanol (9:1, v/v). Also, the developed plates were visualized using a UV lamp for the presence of spots and R_f values were duly calculated. All of the crude products were isolated as solids and purified. Fastness to light was assessed in accordance with BS 1006-1978. Rubbing fastness was checked with an Atlas Crock meter in accordance with AATCC TM 8-1961 and the wash fastness was determined according to ISO: 765-1979 (Maradiya & Patel, 2002; Sakoma, Bello, & Yakubu, 2012).

2.2. General procedure for the synthesis of

1-(p-sulphophenyl)-3-methyl-5-pyrazolone based acid dyes

Synthesis of acid dyes and their metal complexes involves three-step procedure which is as follows.

2.2.1. Nitrosation of

p-sulphophenyl-3-methyl-5-pyrazolone (SPMP)

1-(p-sulphophenyl)-3-methyl-5-pyrazolone (**1**) (25.4 g, 0.1 mol) was suspended in H₂O (250 ml). Hydrochloric acid (45 ml) was added to this well stirred suspension. The reaction mixture was cooled to 0–5 °C in an ice bath. A solution of NaNO₂ (6.9 g, 0.1 mol) in H₂O (25 ml) previously cooled to 0 °C, was then added over a period of 35 min with stirring. The stirring was continued for an hour maintaining the same temperature, with a positive test for nitrous acid. Later on the excess of nitrous acid was destroyed with required amount of sulphamic

acid. The nitroso (oxime) was filtered after salting out. Then oxime was reduced by stirring in 200 ml water containing 85 ml HCl and 23 g zinc metal at boil for 4 h. On completion of reaction, pH of the reaction mixture was raised to 9 with 6 N NaOH, and precipitated the 1-(p-methylphenyl)-3-methyl-4-amino pyrazolones.

2.2.2. Diazotization and coupling with phenol derivatives

To the well stirred ice jacketed aqueous solution (2.69 g) of 1-(p-sulphophenyl)-3-methyl-4-amino pyrazolone (at 0–5 °C) was added conc. HCl (3.5 ml) and sodium nitrite solution (0.7 g in 2 ml H₂O). The reaction mixture was vigorously stirred for 1 h at the above mentioned temperature to obtain the diazonium salt of 1-(p-sulphophenyl)-3-methyl-4-amino pyrazolone. The diazonium compound formed in this way was coupled to various coupler mentioned previously to synthesize our dyes. Thus 1.285 g (0.010 mol) 4-chlorophenol (**5a**) was dissolved in 200 ml water containing 0.45 g NaOH and coupled with prepared diazo. The coupling was facilitated using sodium carbonate as an acid binding agent. The reaction mixture was given 4–5 h to complete the coupling at 30–35 °C. The dye was cooled to room temperature. Its pH was reduced to 4.5 by HCl and filtered. The cake was dried in oven at 70–75 °C till constant weight. By adopting the same procedure other dyes **6b–f** were prepared from couplers **5b–f** as shown in Scheme 1.

2.2.3. Metallization of acid dyes

For the synthesis of metal complexes (iron complex), pH of 25 ml (0.005 mol) of dye **6a** was reduced to 6.5 with HCl. Then it was heated to 70 °C and to it 5 ml (0.005 mol Fe²⁺) solution of ferrous sulfate (FeSO₄·7H₂O) was added drop wise. Mixing and heating at this temperature was continued for further 1.0 hour till the metallization was completed, as shown by the comparative TLC. The dye was cooled to room temperature; its pH was reduced to 1.0 with conc. HCl. Then it was salted out with sodium chloride, filtered and dried in oven at 80 °C till constant weight.

Similarly, copper (II) complexes of dye **6a** were prepared by treating dye with CuSO₄·5H₂O at 65–70 °C with metal to ligand mole ratio 1:1. In this way complexes **7a–l** were synthesized from respective dye ligands (see supplementary information).

2.2.3.1. **6a** (C₁₆H₁₃ClN₄O₅S). Orange, (76%). λ_{max} (nm): 460. FTIR (KBr, cm⁻¹) ν_{max}: 3255 (OH str.), 3050 (C=C–H str.), 2927 (CH₂ str.), 1653 (C=O str.), 1595, 1541 (C=C aromatic, C=N), 1498 (N=N str.), 1422, 1340 (SO₃H str., CH₂ bend.), 1236, 1155 (C–C, C–O str.), 1000 (S=O str.), 833 (Ar–H), 790 (C–Cl str.). ¹H NMR (300 MHz, DMSO-d₆) δ: 8.07 (1H, d, J=2.35 Hz), 7.95 (2H, d, J=8.6 Hz), 7.83–7.90 (1H, m), 7.68 (2H, d, J=8.6 Hz), 6.65 (1H, d, J=9.1 Hz), 2.20 (3H, s). ¹³C NMR (75 MHz DMSO-d₆) δ (ppm): 158.54, 156.64, 147.93, 147.37, 143.21, 139.93, 125.43, 124.41, 119.45, 118.06, 116.22, 12.45. Anal. Calcd. for C₁₆H₁₃ClN₄O₅S: C, 47.01; H, 3.21; N, 13.71; S, 7.84. Found: C, 47.05; H, 3.30; N, 13.59; S, 7.79.

2.2.3.2. **6b** (C₁₆H₁₃N₅O₇S). Dark Brown, (83%). λ_{max} (nm): 480. FTIR (KBr, cm⁻¹) ν_{max}: 3388 (OH str.), 2924 (CH₂ str.),

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