



ISSN 2278 – 0211 (Online)

Synthesis and Application of Monoazo Acid Dyes Based on 3-[(2-methyl-6-ethoxy-4 quinoliny) amino] phenol

Dr. Jitendra H. Tandel

Associate Professor, Department of Chemistry, B.P. Baria Science Institute, Navsari, Gujarat India

Dr. Arvind G. MehtaEx. Principal, Department of Chemistry, P.T. Sarvajani College of Science, Surat, India
Ex. Dean, Faculty of Science, Veer Narmad South Gujarat University, Gujarat, India**Abstract:**

Colour has been playing a dominant role in the life of man from time immemorial. Even in the prehistoric times, the ancestors of man must have noticed (perhaps with or without understanding) the abundance of multitude of colours worn by nature. In my work study and synthesise of 3-[(2-methyl-6-ethoxy-4-quinoliny) amino] phenol (II) used as a coupling component was prepared by the condensation of 2-methyl-6-ethoxy-4-chloroquinoline (I) and 3-aminophenol. Fourteen Acid dyes (III a-n) were prepared by coupling (II) with various diazo components (R= a -n). study of application of acid dyes, determine their absorbance at specified λ_{max} (nm), exhaustion, wash fastness and light fastness of these dyes. These dyes were applied on silk, wool and nylon fabrics

Keywords: Silk, Wool and Nylon fabrics, diazotization**1. Introduction**

The synthesis and application of azo acid dyes derived from 4-oxoquinazoline [1] , mercaptoquinazoline [2] and quinoline [3] systems are reported to have excellent dyeing properties including low sublimation and high thermal stability [4]. Synthesis of acid dyes based on 4-hydroxy-1-methyl-2-oxoquinoline , 4-hydroxy-1-phenyl-2-oxoquinoline [5] , 4-hydroxyquinoline-[1,2-b]-4-oxoquinazoline , N-[3-hydroxyphenyl]-8-quinolinesulfonamide, 3-[(2,6-dimethyl-4-quinoliny)amino]phenol systems [6] have been very recently reported. A study of the fastness of dyed patterns showed that dyes were good on silk and wool and fair on nylon.

2. Problem of the Study

The method of extraction of these dyes from natural sources and the subsequent processes of application to textile materials were lengthy, laborious and tiresome. Further these dyes being natural products could not be obtained in as much quantity as one wanted and man had to depend on the slow and time-consuming natural processes for obtaining these dyestuffs. As a result, the dyes were very costly. Indigo has been in use in the textile industry for the last several thousand years. It is one of the earliest dyestuffs recorded in history and yet retaining its supreme importance even today. India has been credited with the discovery and use of Indigo in the distant past, when the art of producing blue dyeing was practiced in this country. The name Indigo, itself owes its origin to this country.

3. Review of Literature

The art of dyeing textile materials has been practiced for nearly 5000 years. Natural dyes, such as indigo, tyrian purple, alizarin and logwood were used exclusively until the discovery of Mauve or Mauveine by W. H. Perkin in 1856. Although the structure of the compound was not known at the time, the discovery is of particular importance. It marked the beginning of the dye manufacturing industry, from which many of the major chemical companies of today, and provided impetus to the study of organic chemistry. The elucidation of the structure of benzene by Kekule in 1865 laid the foundation for the present concepts of structural organic chemistry.

4. Materials and Methods**4.1. Preparation of 3- [(2-methyl-6- ethoxy-4- quinoliny) amino] phenol (I)**

A mixture of 2-methyl-6-ethoxy-4-chloroquinoline (2.076g, 0.01 mole) and 3-aminophenol (1.09g, 0.01 mole) was refluxed in glacial acetic acid (40 ml) on a sand bath using an air condenser for four hours. The reaction mixture was cooled to room temperature and

poured over ice and was neutralized with ammonia solution (20%). The product was filtered, washed with water, dried and crystallized from aqueous alcohol, yield 68% m.p. >300°C

4.2. Preparation of 4-R-azo-3-[(2-methyl-6-ethoxy-4-quinolnyl) amino] phenol (II a-n)

A clear solution of (II) (1.24 g, 0.005 mole) in acetone (30 ml) and sodium hydroxide (15 ml, 10%) was cooled below 5°C in an ice-bath. To this well stirred solution diazo-solution was added drop wise over a period of 10-15 minutes, maintaining the pH between 7.5 and 8.0. The stirring was continued for two hours at 0 to 50°C. The reaction mixture was heated at 60°C, and sodium chloride was added until the coupled mass was precipitated. It was stirred for an hour, filtered and washed with a small amount of sodium chloride solution (5% w/v). The dye was dried at 80°C to 90°C, extracted with DMF. A yellow dye thus obtained was filtered, washed with acetone and dried to 60°C, yield 86 % m.p. >300°C.

4.3. Application of Acid Dyes

The acid dyes form a big class comprising compounds with various chemical constitutions. A majority of acid dyestuffs are sulfonic acid derivatives of azo dyes. They are applied from a dye-bath rendered acidic by addition of mineral acid or organic acid. The free dye acids are difficult to isolate and hygroscopic making it difficult to pack and store them. These dyes are invariably isolated as sodium salts. The most significant assistance in the application of acid dyes is provided by the acid added to the dye-bath. Many acid dyes will not exhaust at all on polyamide fibres unless the dye-bath has been acidified.

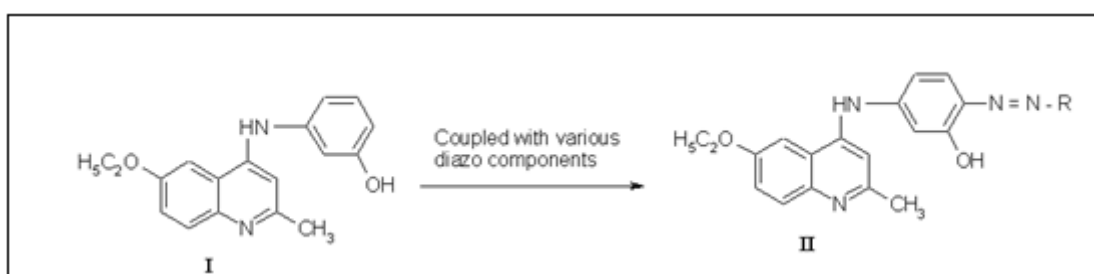


Figure 1

For Compounds II a-n R=

- | | |
|--|-----------------|
| a. T-acid | h. S-acid |
| b. H-acid | i. Peri acid |
| c. Gamma acid | j. K-acid |
| d. 1,7-Cleaves acid | k. C-acid |
| e. J-acid | l. Tobias acid |
| f. 1-Amino-2-naphthol-4-sulphonic acid | m. Chicago acid |
| g. Bronner acid | n. Laurent acid |

It has been accepted in practice that commercial exhaustion of dye-bath (about 90%) is attained in about an hour time which is known as economic time for dyeing.

4.4. Calibration Study

4.4.1. Preparation of the Dye Solution

The solution of the dye was prepared in water. The solution contained 0.1 g of dye in 100 ml of solution. Details of preparing solutions are given below.

The dye (0.1g) was made into a paste in minimum quantity of water. To this paste, boiling water was added with stirring to obtain a clear solution. The cooled solution was diluted to 100 ml with water. The concentration of the dye solution was estimated colourimetry.

4.4.2. Colourimetric Estimation

This would require a calibration curve for the dye. Calibration curve was prepared by plotting respective absorbance against known concentration of dye in solution.

Five solutions of known concentration of a given dye were prepared as described here. A dye solution (40 ml; 0.1% w/v) was diluted with distilled water to 100 ml, 5 ml, 10 ml, 15 ml, 20 ml and 25 ml of diluted solutions of the dye would now contain 4×10^{-3} , 8×10^{-3} , 12×10^{-3} , 16×10^{-3} and 20×10^{-3} mg of dye per ml of solution.

From the absorption spectrum of the solution of a given dye, the position of λ_{\max} absorption was noted. At this wavelength absorbance of different solutions containing 4×10^{-3} , 8×10^{-3} , 12×10^{-3} , 16×10^{-3} and 20×10^{-3} mg of dye per ml of solution were measured. The relevant data for different dyes (D-43 to D-84) are presented in Tables 1 to 2.

→ Calibration of Acid Dyes & Absorbance at Specified λ_{\max} (nm).

DyeNo.	λ_{\max} (nm)	Absorbance of the dye solution Concentration x 10^{-3} (mg. ml ⁻¹)				
D - a	550	0.045	0.09	0.135	0.18	0.225
D - b	559	0.19	0.38	0.57	0.76	0.95
D - c	420	0.09	0.18	0.27	0.36	0.45
D - d	490	0.08	0.16	0.24	0.32	0.4
D - e	500	0.04	0.08	0.12	0.16	0.2
D - f	424	0.191	0.382	0.573	0.764	0.955
D - g	422	0.121	0.242	0.363	0.484	0.605
D - h	420	0.13	0.26	0.39	0.52	0.65
D - i	540	0.036	0.072	0.108	0.144	0.18
D - j	532	0.093	0.186	0.279	0.372	0.465
D - k	423	0.068	0.136	0.204	0.272	0.34
D - l	420	0.055	0.11	0.165	0.22	0.275
D - m	504	0.075	0.15	0.225	0.3	0.375
D - n	546	0.085	0.17	0.255	0.34	0.425

Table 1

→ Exhaustion Study of Acid Dyes on Nylon

Substrate of dyeing : Nylon (2g)
 Amount of dye under study : 40 mg
 Medium for spectral study : Aqueous

sDye No.	Wavelength for absorbance measurement λ_{\max} (nm)	Amount of dye remained in the dye-bath (X mg)	Amount of dye exhausted from dye- bath (40-X) = Y mg	% Exhaustion = (Y / 40) 100
D-a	550	8.93	31.07	77.675
D-b	559	4.48	35.52	88.800
D-c	420	6.45	33.55	83.875
D-d	490	7.46	32.54	81.350
D-e	500	6.50	33.50	83.750
D-f	424	11.45	28.55	71.375
D-g	422	9.10	30.90	77.250
D-h	420	9.39	30.61	76.525
D-i	540	7.33	32.67	81.675
D-j	532	8.93	31.07	77.675
D-k	423	4.37	35.63	89.075
D-l	420	7.08	32.92	82.300
D-m	504	6.45	33.55	83.875
D-n	546	5.46	34.54	86.350

Table 2

4.4.3. Study of Wash Fastness

Fastness to washing is dependent on the substantivity and polarity of the dye molecule and also on the fibre morphology. In the case of polyester and other newer synthetic fibres, the dyeing is carried out at 100-130°C and washing at relatively lower temperature. One of the methods of improving the wash fastness is to increase the molecular size of the dye; however, this reduces the permeability and substantivity of the dye.

A soap solution, which is recommended for ISO test, was prepared by dissolving the soap (5 gm) in distilled water (1000 ml). For the test, the dyed pattern was then treated with 20 ml of soap solution for 30 minutes at 40°C. After treatment, the test pattern was squeezed and dried at 50°C. Loss in depth of shade of the pattern was assessed with Grey Scale. Grey Scale for alteration of colour, consisting of grade 1 to 5 defines the following:

Grey Scale in light of I. S. O. recommendation:

Observation	Grade	Qualitative Assessment
Shade unaltered	5	Excellent
Very slight loss in depth or alteration	4	Very good
Appreciable loss in depth or alteration	3	Good
Distinct loss in depth or alteration	2	Fair
Great loss in depth or much alteration	1	Poor

Table 3

Following the above procedure, the wash fastness properties of all the test patterns were evaluated and assessed.

4.4.4. Study of Light Fastness

Fastness to natural day-light is only important, where as artificial light employed for domestic and industrial purpose does not cause serious fading.

In light fastness determination, use of Grey Scale is not made, but the test sample is exposed to light along with standard dyed material.

When day-light is used, fading is slow and therefore, artificial lamp is used for a quick result. The spectral distribution of artificial lamp is similar to day-light. Xenon-test is one such apparatus in which Xenon lamp is used. A Xenon lamp of colour, temperature between 5500⁰ K to 6500⁰ K is used along with filters to cut-off UV.

The test pattern showing such a behaviour is considered to have light fastness between 3 and 4. In this way, the dyed patterns were classified as regards the rating of light fastness as shown below.

Grade	Quantitative assessment
8	Outstanding fastness
7	Excellent fastness
6	Very good fastness
5	Good fastness
4	Fairly good fastness
3	Fair fastness
2	Poor fastness
1	Very poor fastness

Table 4

Following the above procedure, the light fastness properties of all the test patterns were evaluated and assessed.

5. Result and Discussion

Mono azo acid dyes using 3-[(2-methyl-6-ethoxy-4-quinoliny) amino] phenol as coupling component have been synthesized and their dyeing performance on silk, wool and nylon has been evaluated.

The percentage dye-bath exhaustion of monoazo dyes based on 3-[(2-methyl-6-ethoxy-4-quinoliny) amino] phenol is between 75-89%. Visual observation of the dyed patterns mounted on shade cards shows a variation in shades like yellow, brown, orange etc. The light fastness of the dyes can be ranked fair to good and wash fastness can be ranked very good to excellent.

6. Acknowledgement

I express my heartfelt thanks and sincere gratitude to my guide Dr A.G. Mehta (Former Dean Faculty of Science, Veer Narmad South Gujarat University, Surat, I express my deepest gratitude to Dr. H.F. Mogal, Former Principal, B.P. Baria Science Institute, Navsari. I would like to thanks to my friend Dr. C. R. De for his never-ending guidance and direction through valuable suggestions along with enthusiastic encouragement through-out the period of my work. The authors are thankful to the principal, P.T. Sarvajanic College of Science for providing research facilities and Atul Ltd., Atul for dyeing facilities.

7. References

- i. Mehta, H. T., Mehta, A.G., (2000) Asian J. Chem., 12(2), 389-93.
- ii. Desai, V.A., Patel, V.S., (1985) Ind.J.Tex.Res.10(2),72-74.; Chem.Abstr.103, 197361.
- iii. Desai, K.R. Naik, D. N., (1990) Dyes and Pigments,14,1.
- iv. Naik, N.M., Desai, K.R., (1994) J.Ind.Chem.Soc.,67,84.
- v. Joshi, S.A., Mehta, A.G., (2004) Oriental J.Chem.,20(1),173.
- vi. Malankar, U.V., Desai, K.R., (1994) Oriental J.Chem.;10(2),171.