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Synthesis and Physical Characterization of Monofunctional Azo Reactive Dyes Derived from 2-Methyl-3-(2'-Methylphenyl)-6-Arylazo-4- Oxoquinazoline

Adedeji Olumide Adeniyi[1], D.E.A Boryo[2], Istifanus Yarkasuwa Chindo[2], A.A Mahmoud[2]

[1]Department of Primary Education. Federal College of Education, Kano

[2]Department of Chemistry, Abubakar Tafawa Balewa University, Bauchi

ABSTRACT

A series of quinazoline based mono azo reactive dyes (D_{1-6}) was prepared by coupling 2-methyl-3-(2'-methylphenyl)-6-arylazo-4-oxoquinazoline diazonium solution with six (6) cyanurated coupling components. The intermediates were white solids except IM4 which was yellow; IM 1 and IM 4 were powdery, IM 2 crystalline and IM 3 needle-like, also all the intermediates were insoluble in water. This may be due to the fact that they lack solubilizing group in their structure, they may however, be soluble in organic solvent. Their melting points range 82 – 124 ^{0}C and percentage yield above 50 %. The synthesized dyes gave bright colours of red, yellow, brown, reddish brown and dark blue. Percentage yield of the dyes is also above 50 % and their melting points well above 300 ^{0}C which is consistent with literatures. Their molar masses were calculated from molecular formulas of the dyes, all the synthesized dyes are soluble in water because of the presence of sulphonic, hydroxyl, and amine groups in their structure.

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Corresponding Author: Adedeji Olumide Adeniyi ✉ adedejiao68@gmail.com ✉ Department of Primary Education Federal College of Education, Kano

Introduction

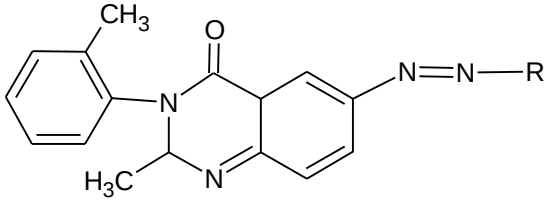
Synthetic dyes are extensively used in the textile and printing industries (Bassler *et al.,* 2018). Azo dyes are by far the most important group of synthetic colourants. They are the largest class of dyes, and more than half of the annually produced amounts of dyes (estimated for 1994 worldwide as 1million tonnes) are azo dyes (Patel *et al.,* 2018).

Reactive dyes are a class of highly coloured organic substances, primarily used for tinting textiles that attach themselves to their substrates by a chemical reaction that forms a covalent bond between the molecule of dye and that of the fibre. The dyestuff thus becomes a part of the fibre and is much less likely to be removed by washing than are dyestuffs that adhere by adsorption (Dermirbas *et al*., 2009).
The four characteristic features of a typical reactive dye molecule are a reactive group, chromophoric group, bridging group and solubilizing group. Among the triazine reactive dyes, azo derivatives have an important place and are applied for dyeing of various materials. The combination of unsaturated functional group and stabilizer residue in the dye molecule improves their light fastness, dyeing ability and possibility for application. Reactive dyes owe their covalent bond forming ability to the presence of the reactive groups in their structure which could be mono or bi-functional (Burkinshaw *et al.,* 2016).

Monofunctional reactive systems can react with one of the nucleophilic groups in the fibre, examples are halotriazine and vinylsulphone systems (Patel *et al.,* 2018). Also, the dichlorotriazine, difluoropyrimidine and dichloroquinoxaline heterocyclic ring systems, have two equivalent replaceable halogen substituents. However, when one of these halogen atoms is displaced by reaction with functional groups in the fibre or with alkali in the dye bath, the reactivity of the remaining halogen substituent is greatly decreased (Burkinshaw *et al.,* 2016).

Bifunctional reactive dyes contain two separate reactive centers for reaction with suitable groups in the fibre, they also have the potential to combine with more than one group in the fibre chain molecule. Such reactions may lead to covalent bond formation either within the same polymer chain or between two adjacent chains (Fadda *et al.,* 2014). Analytical techniques, viz. electron microscopy, surface area determination, and swelling in cadoxen solvent, have been used to obtain results which provide evidence for the formation of cross links between adjacent cellulose chains in cotton dyed with different types of bifunctional reactive dyes (Sekar and Swakumar*.,* 2013).

Synthesis of the quinazolines based dyes have been reported by using quinazoline derivative as coupling components, improvement in the structure of chromogens and a variety of reactive group has led to its increase use as dye stuff (Rana *et al,* 2018)
Patel *et al*. (2018) had prepared 2-mercapto-3-aryl-quinazoline-4-one by condensation of anthranilamide with carbon disulphide or ammoniumthiocyanate. Cyclization of arylthiourea or arylisothiocyanate with anthranilic acid gives corresponding 2-mercapto-3-arylquinazoline-4-one. By the microwave induced dry media 2,3-dichloro-5,6-dicyano-1,4-benzaquinone (DDQ) oxidation of 2-amino-benzamides led to formation of 2-arylquinazoline-4-(3H)-ones.
Patel *et al.* (2019) also reported the synthesis and dyeing characteristics of dyes based on 2-methyl-3-(3'-aminophthalimido) - 4-(3H)-quinazolinone. These dyes were applied on nylon-6,6 and polyester fibers as disperse dyes which gave a variety of hues ranging from golden yellow and light brown to dark brown shades.
The present investigation reports the synthesis of series of reactive dyes from 2-methyl-3-(2'methylphenyl)-6-arylazo-4-oxoquinazoline
coupled with various cyanurated coupling components. The synthesiszed dyes were characterized using physical parameters of colour, melting point, solubility in water, appearance and percentage yield
The general structure of the dye is shown below.



Where R = Cyanurated coupling components D_1-D_6 (Mono-functional)

Structure 1: General structure of the dye.

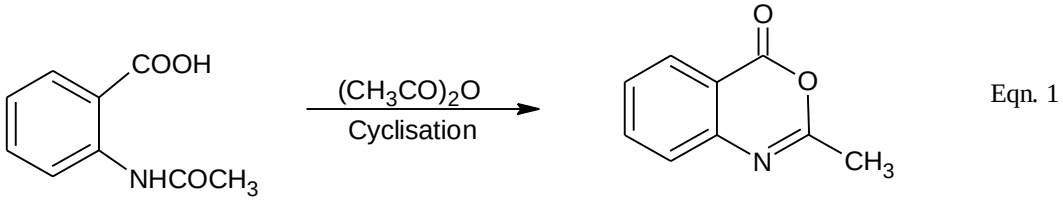
Experimental

Methods

The procedures used in the research are standard procedures as established by AATCC Test method, technical manual and standard (2018)

Preparation of 2-methyl-3, 1-benzoxazin-4-one:

A mixture of N-acetyl anthranilic acid (17.9 g, 0.1 mole) and acetic anhydride (36 ml) was refluxed for 30 minutes. The solid which separated on cooling the reaction mixture was filtered and washed thoroughly with dry petroleum ether.



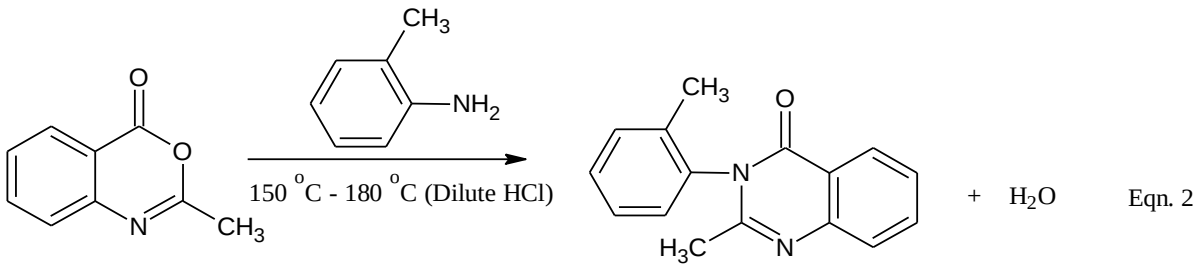
Eqn. 1

N-Acetyl Anthranilic acid

2-methyl-3,1-benzoxazin-4-one (IM 1)

Preparation of 2-methyl-3-(2'-methylphenyl-4-oxoquinazoline)

2-methyl-3,1-benzoxazin-4-one (16.1g, 0.1 mole) was suspended in o-toludine (10.7 g, 0.1 mole) and heated to 150 ^{0}C – 180 ^{0}C for 8 - 10 hours with vigorous, shaking. The reaction mass was decomposed with dilute hydrochloric acid. The solids separated out were filtered, dried and purified from methanol-water.



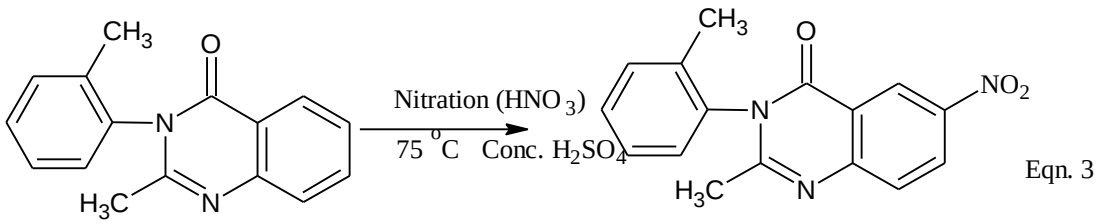
Eqn. 2

2-methyl-3,1-benzoxazin-4-one

2-methyl-3-(2'-methylphenyl)-4-oxoquinazoline (IM 2)

Preparation of 2-methyl-3-(2'methylphenyl)-6-nitro-4-oxoquinazoline

2-methyl-3-(2'-methylphenyl-4-oxoquinazoline) (7.53 g, 0.03 mole) was dissolved in concentrated sulphuric acid (20ml), forming nitric acid (10 ml, specific gravity 1.5) was then added in one portion keeping temperature below 75 ^{0}C by external cooling. The reaction mixture was poured on ice (200 g) and allowed to stand overnight. Tiny needles separated out of the liquor, it was collected, washed and crystallized from glacial acetic acid form colourless needle like solid.



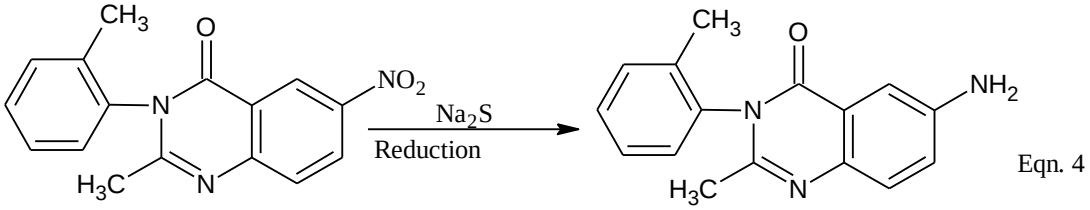
Eqn. 3

2-methyl-3-(2'-methylphenyl)-4-oxoquinazoline

2-methyl-3-(2'-methylphenyl)-6-nitro-4-oxoquinazoline (IM 3)

Preparation of 2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline:

2-methyl-3-(2'-methylphenyl)-6-nitro-4-oxoquinazoline (5.92 g, 0.0 2 mole) was suspended in a solution of sodium sulphide (14.4 g, 0.06 mole) in water (75 ml) was refluxed for 2 hours, yielding a deep reddish-brown solution after cooling. The cooled solution was then diluted with water acidified with hydrochloric acid (75 ml), boiled for 20 minutes and filtered. Sodium carbonate solution was added to precipitated free amines as pale-yellow compound. The product was crystallized from ethanol.



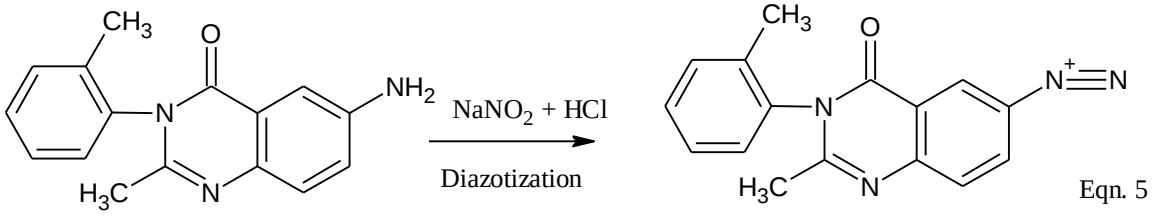
Eqn. 4

2-methyl-3-(2'-methylphenyl)-6-nitro-4-oxoquinazoline

2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline (IM 4)

Formation of diazonium chloride of 2-methyl-3-(2'-methylpheny)-6-amino-4-oxoquinazoline (Diazo solution A]

2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline (2.66 g, 0.01 mole) was suspended in water (60 ml). Hydrochloric acid (86 g, 0.024 mole) was added drop wise to this well stirred suspension. The mixture was gradually heated to 70 ^{0}C till clear solution obtained. The solution was cooled to 0-5 ^{0}C in an ice bath. A solution of $NaNO_2$ (0.6 g) in H_2O (4 ml) previously cooled to 0 ^{0}C was then added over a period of 5-minute with stirring and maintaining temperature at 0-5 ^{0}C, stirring was continued for 1hour maintaining the same temperature with positive test for nitrous acid on starch paper. After destroying excess of nitrous acid with required amount of a solution of sulphamic acid, the clear diazo solution at 0 - 5 ^{0}C was used for subsequent coupling reactions.



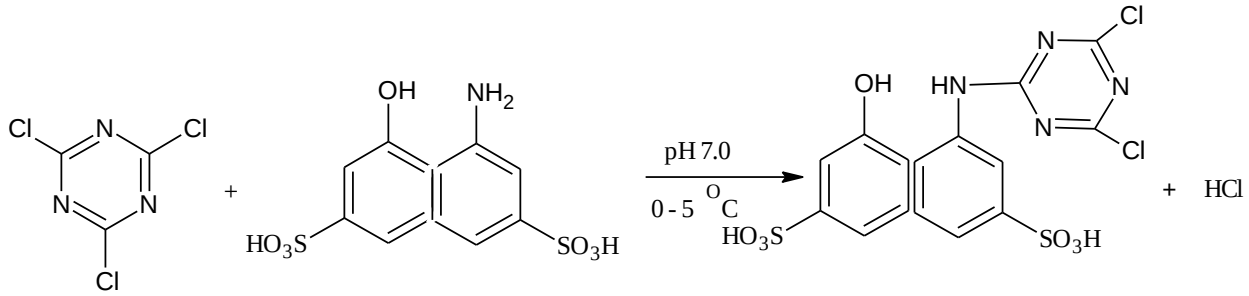
Eqn. 5

2-methyl-3-(2'-methylphenyl)-6-amino-4-oxoquinazoline

Diazonium solution

Preparation of Coupling Components

A total of six coupling components were used in this research. The coupling components (DM_1-DM_6) were treated with Trichlorotriazine (2.0 g) Eqn. 6.



Trichlorotriazine H - acid Cyanurated H - acid

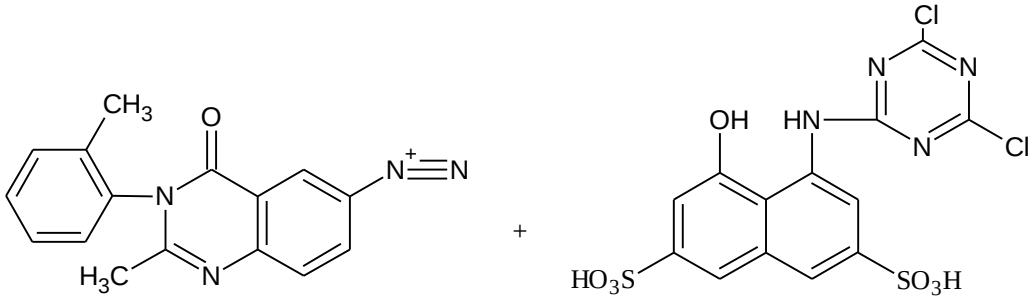
Table 1: Coupling Components

Dye No.	Coupling Components	Molecular Formula	Mol. Mass
CC_1	H-acid	$C_{26}H_{20}O_8N_5S_2Na_2$	616
CC_2	J-acid	$C_{26}H_{21}O_5N_5SNa$	526
CC_3	K-acid	$C_{26}H_{20}O_8N_5S_2Na_2$	616
CC_4	Tobias acid	$C_{26}H_{22}ON_5$	420
CC_5	N-phenyl J-acid	$C_{32}H_{25}O_5N_5SNa$	602
CC_6	N-methyl Gamma acid	$C_{27}H_{23}O_5N_5SNa$	540

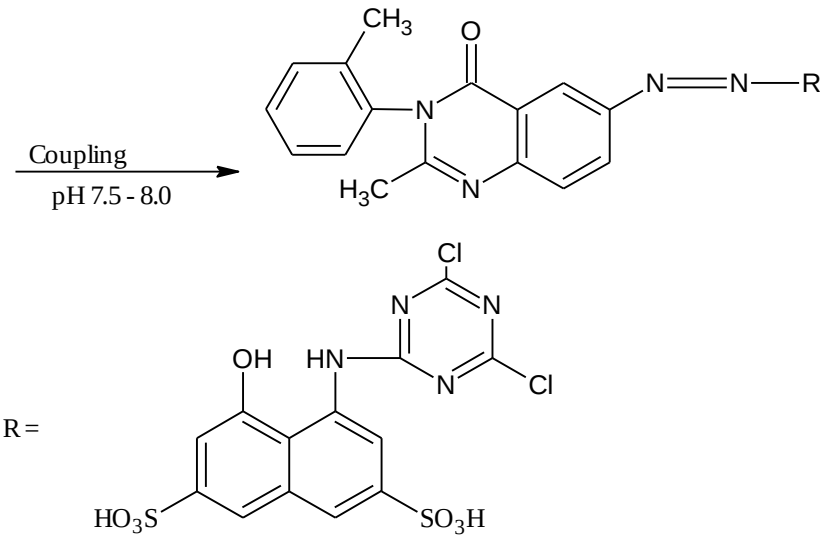
Coupling Reactions

Mono-functional Reactive Dye

Cyanurated H-acid (3.19 g, 0.01 moles) was suspended in water (20 ml) and cooled below 5 ^{0}C in an ice bath. The diazoniun solution was then added in drops over a 10 - 15 minutes period maintaining the pH 7.5 - 8.0 by simultaneously addition of sodium carbonate solution (10 % w/v) The reaction mixture was continuously stirred for between 2 - 3 hours and heated up to 60 ^{0}C, solution of sodium chloride (5 % w/v) was then added until coloured precipitate was obtained. The precipitate was filtered and washed with small amount of dilute sodium chloride, the solid was dried at 80 - 90 ^{0}C and extracted with dimethylformamide (DMF). A purple dye was precipitated by diluting the DMF extract with excess chloroform, the dye was then filtered, washed and dried at 60 ^{0}C. This was repeated for all the other coupling components (Patel *et al.,* 2019). Eqn. 8



Diazonium Compound Cyanurated Coupling Component



Coupling Reaction of Mono-functional Reactive Dye (DM_1-DM_6) – Equation 8

Purification of the Intermediates and Synthesized Dyes

The intermediates and synthesized dyes were purified through the process of re-crystallization. Some of the intermediates and synthesized dyes required the mixed solvent of ethanol, methanol /DMF (9/1 solvent mixture) according to a procedure suggested by (Patel *et al*., 2018). The purity of each synthesized dyes were confirmed by melting point.

Percentage Yield of Synthesized Dyes and Intermediates

The percentage yield of the synthesized dyes and intermediates were determined using the formula given bellow

$$\text{Percentage yield} = {}^{\text{Actual Yield}}/_{\text{TheoreticalYield}} \text{ X } {}^{100}/_{1}$$

Results and Discussion

The results obtained are shown in Tables 2 and 3.

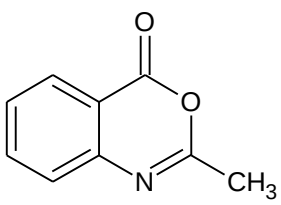
Table 2: Physical Properties of the Intermediates

Physical Characteristics of the Intermediates

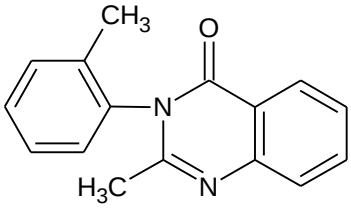
The results of the physical characteristics of the intermediates are given in Table 2. The result indicated the

Intermediate No	Solubility in Water	Molar Mass	Melting Point ^{0}C	Colour	Appearance	Percentage Yield %
IM 1	Insoluble	161	79 – 82	White	Powder	55
IM 2	Insoluble	250	115 – 120	White	Crystalline	60
IM 3	Insoluble	296	130 – 136	White	Needle like	62
IM 4	Insoluble	266	124 – 130	Yellow	Powder	65

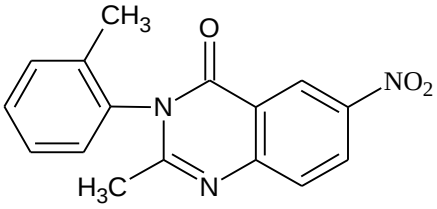
percentage yields, solubility in water, molar mass, melting point, colour and appearance of the intermediates. The percentage yield of the intermediates was satisfactory, and consistent with values in literatures. Also, their molar masses were calculated from molecular formula. The intermediates are white solid except IM4 which is yellow. The results showed that their melting points and molar masses gradually increase from IM 1to IM 3 except for IM 4 where there was a decrease. This may be as a result of the building up of molecules from IM 1- IM3. In IM 4 the drop in molar mass and melting point may be due to reduction of -NO_2 to –NH_2 group. However, the melting points were within acceptable range of above 50 %.



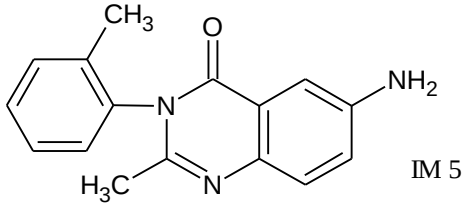
IM (2)



IM 2 (3)



IM 3 (4)



IM 5

Structures of the Intermediates (IM 2-5)

Furthermore, the entire intermediate is insoluble in water on account of lack of solubilizing groups. First of all, a careful examination of the intermediate molecules must be undertaken in order to identify the parts of the molecule that present adequate chemical activity and are suitable as attachment points for the solubilizing group. Functions such as -OH, -CL, -F, NH, -CO_2H, -SO_3Na and so on are reactive sites that furnish nucleophilic or basic entities are lacking.

Physical Characteristics of the Synthesized Dyes

The results of the physical characteristics of the Synthesized Dyes are given in Table 3

Table 3: Physical Characteristics of Mono-functional Reactive Dyes

Dye No	Colour	Molar Mass	Melting Point ^{0}C	Solubility in water	Appearance	Percentage yield (%)
DM_1	Dark Blue	616	>300	Soluble	Crystalline	60
DM_2	Reddish brown	529	>300	Soluble	Powder	65
DM_3	Yellow	616	>300	Soluble	Powder	68
DM_4	Brown	420	>300	Soluble	Powder	50
DM_5	Brown	602	>300	Soluble	Powder	55
DM_6	Red	540	>300	Soluble	Powder	69

The physical characteristics of the dyes showed percentage yield of the dyes are over 50% and their melting points are well above 300 ^{0}C, the exert value could not be found because of the inability of the instrument to measure above 300 ^{0}C these are in agreement with Patel *et al.* (2018). The molar masses of the dyes were also calculated from their molecular formula. The dyes gave wide range of shade like red, yellow, brown, reddish brown and dark blue (Table 3) The synthesized dyes are all soluble in water on account of high solubilizing groups present as auxochromes/substituent on the heterocyclic ring of the dye molecule. In a study, by Burkinshaw *et al.* (2016) on the solubilization of two organic dyes, Sudan I (1-phenylazo-2-naphtol) and Quinizarin (1,4-dihydroxyanthraquinone), in the presence of different types of surfactants. The effects of ionic group the dye molecule, temperature, pH and electrolyte on dye solubilization were investigated. . The results showed that the solubilization of both dyes increased with increase in temperature and addition of salt and availability ionic groups (auxochromes) on the dye molecules.

Furthermore, in support of the high solubility of the synthesized dyes Halla and choi (2019) in solubility and mono-functional reactive dyes submitted that the higher the number of solubilizing groups in the dye the higher the solubility as the solubilizing group molecules in the micelles form colloidal aggregation at critical micelle concentration where solubilization begins. Thus, increase in the concentration of this micelles lead to increase in dye solubility.

Conclusion

The present investigation reported the synthesis of six (6) mono azo reactive dyes derived from 2-methyl-3-(2'- methylphenyl)-6-arylazo-4-oxoquinazoline coupled with six (6) cyanurated coupling component (DM). The following conclusion can be drawn from the physical characteristics of the synthesized dyes; wide range of colours can be obtained by increasing the conjugation in the heterocyclic ring system and the number of substituents on coupling component. The synthesized dyes have high melting point and are all soluble in water obviously due to the presence of solubilizing substituents in all the coupling components

Recommendation

Activity in the area of synthesis of new colourant is fluid and dynamic therefore it is necessary to continue further work until desired properties is obtained. It is in the light of this that the following recommendations are made:

- Further studies could be carried out on reactive dye with multiple reactive groups
- UV-VIS and FTIR test could be carried out to further characterizes the synthesized dyes spectroscopically
- The use of G.C, Mass spectrometer and N.M.R spectroscopy can as well be undertaken to further confirm the structure of the dyes.
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