



MORDANT DYES DERIVED FROM 4-(2-PHENYL-4-OXO-3-QUINAZOLINYL)-4'-AMINO DIPHENYL SULFONE AND ITS M (II) - SCHIFF BASE COMPLEXES

S. B. MEHTA^a, RAKSHA V. ZALA^b and P. N. DAVE^c

^aDepartment of Chemistry, Bhavnagar University, BHAVNAGAR - 364002 (Guj.) INDIA

^bKamani Sc. College, AMRELI - 365601 (Guj.) INDIA

^cSir P. P. Institute of Science, I. C. Dept, BHAVNAGAR - 364002 (Guj.) INDIA

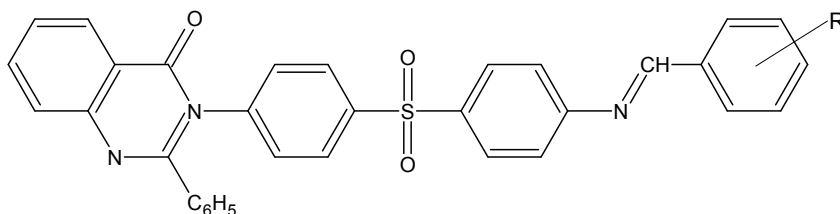
ABSTRACT

The aim of this study is to determine the stability constant and dyeing characteristics of some quinazoline metal complexes as M (II) - Schiff base complex systems. The Schiff bases derived from condensation of 4-(2-phenyl-4-oxo-3-quinazolinyl)-4'-aminodiphenyl sulfone with different aldehydes are, 4-(2-phenyl-4-oxo-3-quinazolinyl) -4' (benzylidene)-amino diphenyl sulfone [PBADS]; 4-(2-phenyl-4-oxo-3"-quinazolinyl)-4'(2-chloro benzylidene)-amino diphenyl sulfone [P-2- CBADS]; 4-(2-phenyl-4-oxo-3-quinazolinyl)-4' (2-hydroxy-1- naphthylmethine)-amino diphenyl sulfone [P-2- HNMADS] and 4-(2-phenyl-4-oxo-3-quinazolinyl)-4'(2- hydroxy benzylidene)-amino diphenyl sulfone [P-2- HBADS].

Key words : Mordant dye, Schiff base, Complex, Quinazolinyl, Sulfone

INTRODUCTION

The literature survey of the mordant dyes based on metal-Schiff base complex reveals that these dyes possess good dyeing and fastness properties. Hence, it was thought interesting to undertake the solution studies of M (II) - Schiff base complexes of quinazolines¹⁻⁶. The 4-oxo-quinazoline is a versatile nucleus yielding a variety of dyes and medicinally important compounds. The Schiff bases of the following general structure were synthesised.



Where R = Cl, OH

The stability constants of M (II)-Schiff base complexes of Cu (II), Ni (II), Co(II) and Mn (II) were calculated using Calvin - Bjerrum pH-metric titration technique adopted by Irving and Rossotti^{7,8}.

Metal complexes obtained by chelation contain a heterocyclic or aromatic ring and such compounds form mordant dyes. This type of compounds containing chelate group often exhibit abnormal colour, sparing solubility in water, solubility in organic solvents and volatility without decomposition⁹. Mordant dyes are the most important class of compounds used in dyeing different fibers and provide a wide range of hues, good buildup and fastness properties adequate for most purposes.

EXPERIMENTAL

Experimental procedure follows preparation of amine, preparation and characterisation of Schiff bases, preparation of standard solutions for titrimetry to determine the stability constant of M (II) - Schiff base systems and the preparation of metal- complex dyes. The primary amine 4-(2-phenyl-4-oxo-3-4 quinazoliny)-4'-amino diphenyl sulfone was prepared by following the method adopted from literature⁴. Schiff bases were synthesised by following a general method. Methanolic solution of amine and aldehyde in 1 : 1 molar ratio were refluxed at 70-80⁰C for 4-5 hours and cooled at room temperature, the solid product i.e. Schiff bases were filtered, purified and characterised by elemental analysis, I.R. and H NMR spectral studies.

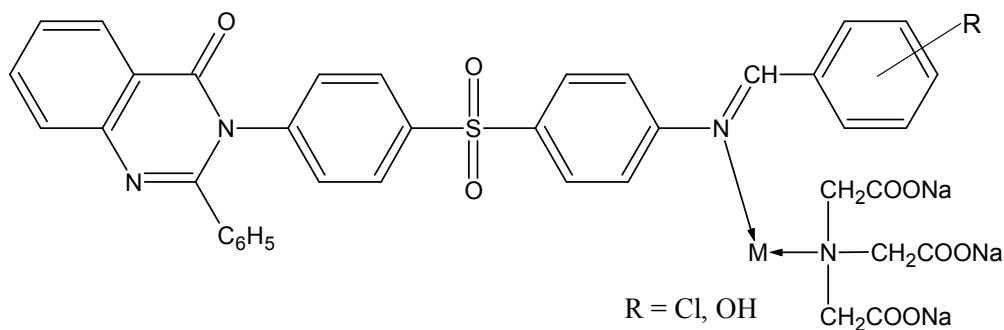
Table 1. Characteristic physical data of Schiff bases

Schiff base	M.F.	M.W.	M.P. (°C)	%C	%H	%N
PBADS	C ₃₃ H ₂₃ O ₃ N ₃ S	541	201	73.14	4.05	7.60
P-2-CBADS	C ₃₃ H ₂₂ O ₃ N ₃ SCl	575.5	190	68.75	3.80	7.28
P-2-HNMADS	C ₃₇ H ₂₅ O ₄ N ₃ S	607	198	73.10	4.10	6.86
P-2-HBADS	C ₃₃ H ₂₃ O ₄ N ₃ S	557	203	71.05	4.10	7.50

Preparation of metal-complex dyes: The metal complex dyes have been prepared by following the method adopted from literature¹¹⁻¹⁵. The method was divided into two steps.

Step 1: To prepare the complex of metal with NTA (Nitrilo triacetic acid) in the form of sodium salt.

Step 2: 0.5 M solution of Schiff base was prepared in triethanol amine and then mixed with M (II) -NTA complex solution at 7.5 pH. The pH was maintained by using NH_4OH . The resulting solid product i.e. metal complex was separated and dried in vacuum. The general formula of metal complex dye is as follows.



Where M = Cu (II), Ni (II), Co (II) and Mn (II)

Method

All chemicals used were of A.R. Grade. The ligands under study are water insoluble and hence, a mixed solvent consisting 60 : 40% v/v 1,4-dioxane-water medium has been used to maintain the homogeneity during pH titration. The following three sets of solutions were prepared. (i) HNO_3 (0.2 M, 5 mL) + KNO_3 (1 M, 9 mL) + 6 mL D.D.W. + 30 mL 1, 4 - dioxane. (ii) HNO_3 (0.2 M, 5 mL) + KNO_3 , (1 M, 8.9 mL) + Schiff base solution (0.02M, 5 mL) + 6.1 mL D.D.W. + 25 mL 1,4-Dioxane (iii) HNO_3 (0.2 M, 5 mL) + KNO_3 (1 M, 8.8 mL) + Schiff base solution (0.02 M, 5 mL) + Metal nitrate solution (0.02 M, 5 mL) + 1.2 mL D.D.W. + 25 mL 1,4-dioxane.

The total initial volume was kept at 50 mL for all the sets. The titrations were performed at $27 \pm 0.1^\circ\text{C}$ and 0.2 M ionic strength (KNO_3). All sets were titrated against standard 0.2 M KOH solution. Titration curves were obtained by plotting pH v/s volume of alkali added.

Application of dye: Dyeing of nylon fabric with all the metal complex dyes follow the steps (i) Pretreatment of the fabric (ii) Preparation of dye bath and (iii) Dyeing process and after treatment. The conditions for dyeing nylon fabric are as follows : fabric 2.0 g; dye, 40 mg; dispersing agent (Dadamol), 40 mg; Wetting agent tween-80, 5 mg;

material to liquor ratio (MLR), 1 : 50; volume of dye bath, 100 mL; pH, 4.0. High temperature dyeing technique was used at 90°C for 1 hour.

RESULTS AND DISCUSSION

Using Irving-Rossotti formula, various computations were made to evaluate \bar{n}_H , \bar{n} and pL. For each ligand, pK_1^H value was obtained from the graph $pH \rightarrow \log \frac{\bar{n}_H}{(1 - \bar{n}_H)}$. The plots were found to be linear with intercept equal to $\log pK$, which is known as proton ligand stability constant. The stability of metal complex is proportional to the proton ligand stability constant.

Table 2. Proton-ligand stability constants at $27 \pm 0.10^\circ\text{C}$, ($M = 0.2 \text{ M KNO}_3$)

Ligand	PBADS	P-2-CBADS	P-2-HNMADS	P-2-HBADS
$\log pK_1^H$	4.06	5.06	4.12	5.00

From the data of $\log pK_1^H$, the order of proton- ligand stability in referred ligands is PBADS < P-2-HNMADS < P-2-HBADS < P-2-CBADS. The influencing factors for $\log pK_1^H$ are mainly inductive and electrostatic effects¹⁶.

Table 3. Metal - ligand stability constants of binary systems at $27 \pm 0.1^\circ\text{C}$, $\mu = 0.2 \text{ M (KNO}_3)$.

Ligand	$\log K_1$			
	Cu (II)	Ni (II)	Co (II)	Mn (II)
PBADS	5.28	4.34	3.93	3.38
P-2-CBADS	3.97	3.76	3.65	3.55
P-2-HNMADS	5.21	4.28	3.63	3.34
P-2-HBADS	3.84	3.12	2.65	2.27

The metal-ligand ratio was maintained at 1 : 1 through out the study and hence the discussion is mainly restricted to the values of $\log K_1$. The point wise calculation method^{17, 18} has been incorporated in the present study. The values $\log K_1$ have been

evaluated by constructing a plot of $pL \rightarrow \log \frac{(1 - \bar{n})}{n}$. The values $\log K_1$ obtained from other methods agree with those obtained using point wise calculation method. With all the ligands studied, the order of the stability constants for different binary systems is $Cu > Ni > Co > Mn$, which confirm the well established Irving - Williams order¹⁹.

Table 4. Physical data of metal - complex dyes

Dye No.	Metal complex dye	Colour of dye		λ_{\max} in DMF	% Exhaustion	% Fixation
		Aqueous media	Acidic media			
1	Cu-L ₁ -NTA	Parrot Green	Lemon Green	660	52.5	82
2	Cu-L ₂ -NTA	Pista Green	Ming Green	715	60.0	75
3	Cu-L ₃ -NTA	Tea Green	Lime Green	703	97.48	67
4	Cu-L ₄ NTA	Sea Green	Lime Green	725	45.0	80
5	Ni-L ₁ -NTA	Aqua Blue	Sky Blue	575	50.0	78
6	Ni-L ₂ -NTA	German Blue	Sky Blue	642	58.75	70
7	Ni-L ₃ -NTA	Indigo Blue	Light Blue	672	97.00	67
8	Ni-L ₄ -NTA	Aqua Blue	Sky Blue	572	37.5	70
9	Co-L ₁ -NTA	Brown	Red	490	52.5	84
10	Co-L ₂ -NTA	Brownish Red	Reddish Pink	487	62.0	79
11	Co-L ₃ -NTA	Reddish	Brown	523	89.25	88
12	Co-L ₄ -NTA	Dark Red	Orange	520	47.5	85
13	Mn-L ₁ -NTA	Rose Pink	Light Pink	516	55.0	50
14	Mn-L ₂ -NTA	Rose Pink	Pink	517	57.5	66
15	Mn-L ₃ -NTA	Candy Pink	Light Pink	485	83.33	48
16	Mn-L ₄ NTA	Reddish Brown	Rose Pink	489	53.75	52

Where L₁ = PBADS ; L₂ = P-2-CBADS; L₃ = P-2- HNMADS; L₄ = P-2- HBADS

The general dye bath exhaustion was assessed by spectrophotometric evaluation of the exhaust liquors using Perkin-Elmer Lamda - 2 UV-visible spectrophotometer. The

percentage exhaustion of the 2% dyeing on nylon fabric was found good to excellent.

The dye content of the dyed fabric can also be determined by a spectrophotometric method using reflectance of dyed fabric or yarn, which depends not only on concentration but also on distribution and physical state of the dye in the fabric and on dye-fabric interactions^{20, 21}. The fixation study was carried out with all dyed samples using dissolution method in which a weighed dyed sample was dissolved in A.R. Grade conc. H₂SO₄ and the optical densities were measured at various wave lengths in the range from 350 to 750 nm. Calibration curves were obtained by plotting concentration versus absorbance and using these calibration curves, the concentration of dyes were measured to find the fixation values of various dyes on nylon fabrics. The values, % fixation varies from 45 to 85 % with various metal complex dyes.

Fastness to light, sublimation and acid and alkaline perspiration were analysed by standard methods of testing. The rubbing fastness test was carried out by using a crockmeter. The washing fastness test was also carried out and the results were found to be good to excellent.

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