CHAPTER - I

A SHORT REVIEW OF ARYLAZO-QUINOLINOLS AND THEIR COMPLEXES:

IA. INTRODUCTION

IB. ANALYTICAL APPLICATIONS OF ARYLAZO QUINOLINOLS

IC. ELECTRONIC SPECTRAL PROPERTIES

ID. BIOLOGICAL PROPERTIES OF ARYLAZO QUINOLINOLS

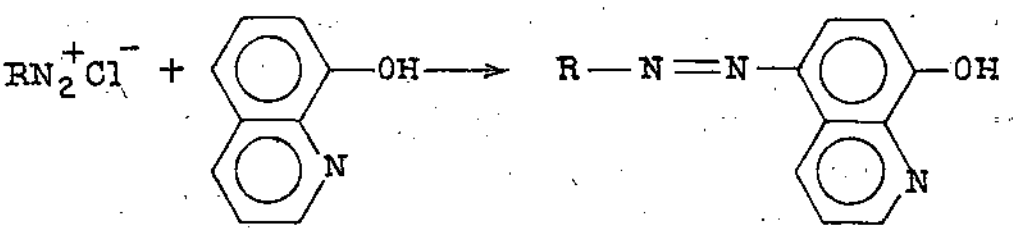
BIBLIOGRAPHY

1A. Introduction:

8-quinolinol, first described by R.Berg[1], is now one of the most versatile analytical reagents[2,3]. This reagent behaves as a weak acid[1] (pK = 9.7) and reacts with metal ions to form inner complexes which can be extracted at pH 1.6 - 14. Control of the pH of the solution, therefore, permits the extraction and estimation of individual metal ions[1-7]. In principle, it is possible to prepare more useful organic reagents by preparing compounds having the properties of 8-quinolinol together with other desired features, e.g., having an intense light absorption in the visible region for colorimetric applications. Azo derivatives of 8-quinolinols, commonly known as azoxines mentioned by Gherkasov[8] and first described by Gutzeit and Monnier[9-12], constitute one such group of reagents.

Azoxines can be prepared by coupling 8-quinolinol with diazonium component obtained by diazotising the appropriate diazoforming moiety:

$$RNH_2 \xrightarrow{HCl\ /\ KNO_2} RN_2^+Cl^-$$



Although 5-azo-derivatives are generally formed[9-12], 7-azo-derivatives are also formed in many cases. However, the resulting reagents exhibit such differences in their chemical properties that they can be used for specific tasks in analytical chemistry. For example, while 7-azo derivatives are, as a rule, good complexometric indicator[13-23], the 5-azo derivatives are used for mercurimetric titrations and spectrophotometric applications[24-26]. The relative yield of the 5- and 7- azo derivatives depend on the structure of the diazo forming moiety as well as the pH of the solution, addition of catalysts etc[27,28]. Methods for separation of the two isomers where both are simultaneously formed have also been reported[29,30].

IB. Analytical applications:

The analytical applications of the azo derivatives of 8-quinolinol have been recently reviewed by Ivanov and Rudometkina[31]. The presence of 8-quinolinol group, the reagents have high reactivity towards all metal ions which makes the reagents non selective. However, the presence of the hetero atoms in the diazo system often increases the selectivity of these reagents[13]. Cherkesov observed that 7-azoxines in acid media, unlike 8-azoxines form complexes with metal ions with the participation of the azo group[8,32]. While 8-azoxines, reacting via the 8-quinolinol group, form in neutral media yellow or greenish

yellow complexes, the 7-azoxines derivatives in acid media form red or red violet coloured complexes; these complexes are much less stable[8]. Azoxines are thus particularly useful for complexing easily hydrolyzable metal ions.

In addition, the shift of reactivity towards more acid conditions allows, in a number of cases, to increase the selectivity in determining elements, and has been utilized in complexometry where azoxines are used as metallochromic indicators[14-23,33-45]. However, an increase in the acidity of the reagent decreases the stability of the complex formed. It has been shown that the acidity of 8-quinolinol-5-sulphonic acid (I), 7-phenylazo-8-quinolinol-5-sulphonic acid (II), 7-(4-sulphophenyl azo-8-quinolinol-5-sulphonic acid (III), and 7-(4-sulphonapthyl azo-8-quinolinol-5-sulphonic acid (IV) increases in the sequence (I), (II), (III), (IV)[46]. The stability of the corresponding complex of Cr(IV), Mo(VI) and V(VI) with these reagents, as determined by potentiometry, decreases in all cases with the decreasing basicity of the reagent, i.e. in the sequence (I) > (II) > (III) > (IV)[46]. 8-quinolinol azo derivatives are used as complexometric indicators. The 7-azoxines are suitable for this purpose because only these derivatives give a sufficient contrast in the colour change near the titration end point[14]. It has been found that the presence of electrophilic groups (-COOH, -NO$_2$,

$-SO_3H$) in the structure of the reagent improves the sharpness of the colour change near the end point. The presence of the sulpho group improves the solubility of the reagent and the corresponding complexes in water[14-17]. In metal ions forming strongly dissociating complexes with the oxines, a gradual change in colour of the indicator is usually observed; the titration end point can be determined in this case by adding 1-2 ml. of 0.005M copper or zinc salt solutions. The ions of Al, Cd, Co, Fe(II), Pb, Ni, Mo(IV), Rare earth elements, V(V), Sc, Hg, Th and In can thus be titrated[14,41,42]. When 7-(1-naphthyl azo)-8-quinolinol-5-sulphonic acid (naphthylazoxines) and, particularly, 7-(6-sulpho-2-naphthyl azo)-8-quinolinol-5-sulphonic acid (naphthyl azoxines S), which is an indicator for both acids and bases, are used some of the metals can be determined by a direct titration[15,16,42]. The specificity of titration in neutral and basic media can be increased by employing a suitable masking compound. Some of the titration modifications are given in Table (1)[22].

Table (1) . Uses of Azoxines as Indicator in complexometric titration.

Metal ion estimated	Indicator	Conditions	Remarks	Ref.
Ca	MA	$pH_{2.2}(CH_3COOH)$, 70-80°	Ca, Mg, Mn, Cd, Zn; Al masked with fluoride	21
In	DNOX	$pH_{3.0-3.6}$ (CH_3COOH), 70-80°	Ca, Mg, Mn, Zn Cd; Al masked with fluoride	20
	MA	$pH \geqslant 2$	Cd, Al, Mg, Mn	18
	BNOX	$pH_{2.8-3.0}$ (CH_3COOH), 60-70°	The same	18
Bi(III)	DNOX	$pH \geqslant 2$ ($CH_2ClCOOH$)	Ca, Mg, Mn, Zn, Al, Fe, Bi	43
	PAOX	$pH_{1.8-3.5}$	Cd, Mn, Mg, Zn, Al, Bi	23
Cu	PAOX	$pH_{2.8-3.0}$	REE, Mg, Be and Al masked with fluoride	22

Contd..

Table 1 (Contd..)

Metal ion estimated	Indicator	Conditions	Remarks	Ref.
Co, Cd, Pb, Cu, Ni, Y, REE, Zn	NA	pH 5.5-6.6 (pyridine or CH_3COONH_4)	Th, Zr, and U(VI) masked with citrate; Be, Ti, Al, Nb masked with fluoride	41
Cu	NA	pH 4.0 (formate)	Th, Zr, U(VI) masked with citrate, Be, Nb, Ta, and Al masked with fluoride.	41
Mn(II)	NA	pH 6.5-7.0 (pyridine)	The same	41
Fe(III), Th	NA	pH 3.6-3.5 ($CH_2ClCOOH$)	The same	41
Zn	NA	pH 5.5-6.5 (CH_3COONH_4)	Masked with thiourea	41

Contd..

Table 1(Contd..)

Metal ion estimated	Indicator	Conditions	Remarks	Ref.
Al	HAS	$pH_{6.4}$; BT with copper salts		42
Bi	HAS	$pH_{6.0}$; BT, with copper salts		42
Ca	HAS	pH 10 (TEA) 50-70 Vol. % acetone		42
Co,Cu,Cd, Hg,Fe(III)	HAS	$pH_{6.0}$	All masked with citrate	42
Mn(II),Pb, Cu,Cd	HAS	$pH_{8.5}$;50 vol. % acetone	Fe masked with citrate, W(VI) masked with tartrate	42
V(IV)	BOAQ or SFA	$pH_{3.6-4.3}$	F⁻,Phosphates and fluorides; Cu,Cd,Hg,Mn,Co and Ni masked with cyanide; Al, Ti and Th masked with fluoride.	16

Note: HA); 6-(1-napthyl azo)-3-quinolinol-5-sulphonic acid; DHQS); 7-(5,7-disulpho-2-napthyl azo)-8-quinoline sulphonic acid; SHQS); 7-(4-sulpho-1-napthyl azo)-8-quinolinol-5-sulphonic acid; PAQ); 7-(2-pyridyl azo)-8-quinolinol; HAS); 7-(6-sulpho-2-napthyl azo)-8-quinolinol-5-sulphonic

(Contd..)

Interestingly the complex formation between metal ions and 7-azoxine not containing heteroatoms in the diazo forming moiety changes the colour of solution in reverse to the usually observed change on complexing with other heterocyclic hydroxy azo compounds. The colour changes from violet or crimson to yellow or lemon yellow usually; complexing with azo compounds containing heteroatoms in the diazo-forming moiety results in deepening of the colour of the solution; the reagent in its dissociated form has the deepest colour.

The dissociated form of 7-azoxines and of some 5-azoxines is orange or red in colour, as compare to its protonated form (in acid media) that is rose coloured or violet. The colour of complexes of these reagents is usually less deep than the colour of the uncomplexed reagent at the same pH value. During direct complexometric titration the colour of the titrated solution thus changes from yellow (the colour of the complex with an indicator) to bright crimson (the colour of the free reagent). The more acid is the medium during titration the brighter is the colour of the free reagent.

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acid; BAOQ); 7-(benzene azo)-8-quinolinol-5-sulphonic acid; SPA); 7-(4-sulphophenyl azo)-8-quinolinol-5-sulphonic acid; TEA); Triethanolamine; BT); back titration; REE); rare earth elements.

The azoderivatives of 8-quinolinols are used in mercurimeter. The formation of brightly coloured complexes between Hg (II) ions and azoxines is very convenient for detecting mercury ions in solution. The ability of mercury (II) to form stable complexes with halogens or thiocyanides and cyanides has been utilized for quantitative determination of these ions by titrating with mercury salts and indicating the end point with azoxines. Silver salts instead of mercury salts have also been used.

The ions of Hg or Ag bind chlorides less fully than bromides and iodides. All ions capable of binding to mercury more strongly than halogen will interfere with the determination. The reaction is, therefore, more sensitive to cyanide and thiocyanide. For the same reason, sulphides, thiosulphate, nitrilotriacetate and cations capable of binding the 8-quinolinol group more strongly than the mercury and silver ion also interfere with the determination. The specificity of these reaction can be increased by carrying out the titration in an acid medium. However, only mercury salts can be used since silver reacts with azoxines only in neutral media. Microquantities of mercury can be determined by titrating with iodides[47]. The reaction can be best followed by using the sodium salt of stilbene-4,4'-bis [(azo-5)-8-quinolinol]-3-3'-disulphonic acid as the titration indicator. The ions of Pb, Cu, Ag, Co, Ni, Cd and Zn also give colour reactions with this reagents, forming compounds of various

violet shades at weakly acid pH.

Its already mentioned azoxines are widely used as photometric reagents for the estimation of large number of metal ions[31]. Depending on the structure and position of the diazoforming moiety, the complexes results either via the 8-quinolinol group or via the participation of the heteroatoms or groups in a sterically suitable position in the diazo forming moiety. Almost all the complexes are formed in acid or weakly acid media. The difference between the absorption maxima of the reagent and the complex varies from 70 to 105 nm[48]. The high molar absorptimity of the complexes[31]($\epsilon \sim 10^4$) allows the determination of trace amounts of elements. Ions of Cu, Cd, Co and Ni can be masked with cyanide[16,49], while those of Al, Ti(IV) and Th can be masked with fluoride. Introduction of a thiazo ring into azoxines increases considerably the selectivity of the reagent. 5-(2'-(4', 5', 6', 7' -tetrahydrobenzothiazolyl)-azo)-8-quinolinol reacts with Cu, Ag, Sn, Cd, Hg, Ga, In, Ya, La, Ce, Nd, Gd, Dy, Yb, Sn, Pb, Zr, Th, V, Ta, Mo, Fe, Co and Ni ions[37]. The reagent is very sensitive to Ni[50].

Efforts to obtain azoxine analogs of PAR led to the synthesis of 7-(2-pyridylazo)-5-methyl-8-quinolinol[51]. This reagent gives violet and blue violet chelates with Co, Ni, Cu, Cd, Zn, Pb, Bi, In, U(IV), Y, V(V) and Pb. Some of the

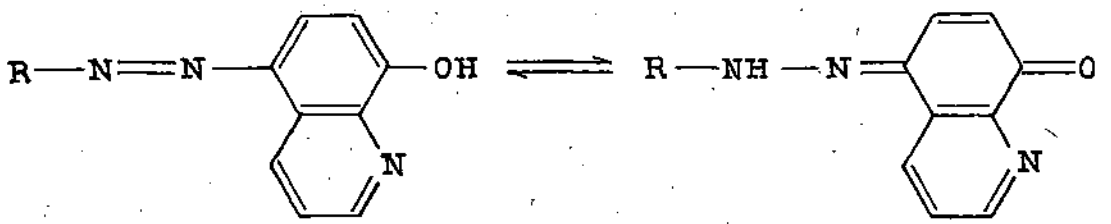
complexes can be extracted with organic solvents. In a number of cases the sensitivity is higher than that obtained with PAR.

7-(2-Quinolylazo)-8-quinolinol[58] was found very reactive toward the Fe(II,III), Ni, Co, Zn, Cd, Pb, Hg, Ge(III), In, Ga, Tl(III), V(V), Bi, As(III,V), Th, U(VI), Pd, Cr(III), Cu, and Ag(I) ions at pH 1-5, and toward Mn (II) and Al ions at pH 3-7. The colour of the resulting complexes varies from red (Mn, Pd) to red violet [As(V), Ge] and dark blue-violet [U(VI), Zn, Co, Fe, In, Tl, Bi, V, Hg and others].

The absorption maxima, reaction condition and the sensitivity of the various types of azoxines are given in reference[31].

10. Electronic Spectral Properties:

Despite the wide use of 5-phenylazo-8-quinolinol for spectrophotometric estimation of metal ions, the electronic absorption spectra of these compounds and their complexes have not been investigated in detail. The studies that have so far been made concern mainly azo-hydrazone tautomerism (I) exhibited by azo dyes containing -OH group in ortho - or para-position to the azo group[53].



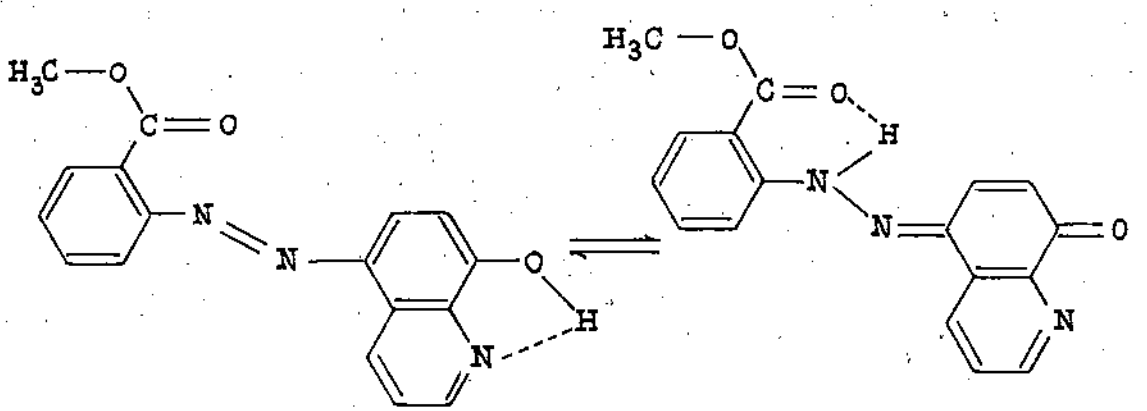
[Azo-Form] [Hydrozone-Form]

(I)

For example, 4-phenyl azo-1-napthol is know to exist in absolute alcohol as an equilibrium mixture of the azo and phenyl hydrazone tautomer, the absorption curve consisting of two broad bands at 403 nm (azo form) and 462 nm (hydrazone form)[54]. It has been well established that the hydrazone form always absorbs at longer wave-lengths compared to the azo form[53,55].

The existence of intramolecular hydrogen bonding in 8-quinolinol is shown by its high melting point, small wet m.p. depression (3^{0}C), steam volatility and IR spectrum[54]. The intramolecular H-bonding involves the formation of a 5-membered ring between the heterocyclic nitrogen and the hydroxylic hydrogen. In the case of 8-quinolinol - N-oxide, such intramolecular H-bonding is much more extensive due to formation of a 6-membered ring[54]. It has been demonstrated that the existence of intramolecular H-bonding in the 8-quinolinol moiety influences the azo-hydrazone tautomeric equilibria in the azo dyes of 8-quinolinol. For example, 5-phenyl azo-8-quinolinol in absolute alcohol shows two regions of absorption at 337 nm (ϵ = 21.1 x 10^{3}) and 462 nm (ϵ = 5.5 x 10^{3}) but the longest wave length absorption appears only as an inflexion[56]. The intramolecular H-bond tends to stabilise the azo tautomer, ratio of the concentrations of hydrazone to azo tautomer being 0.26. In other solvents, only small difference in the relative intensities of the two absorption bands are observed, the absorption due to the phenyl hydrazone

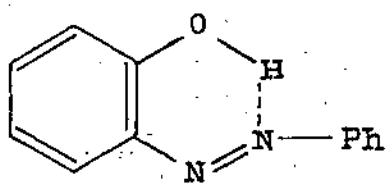
tautomer increasing in the order: CCl_4 $CHCl_3$ C_2H_5OH CH_3COOH. This shows that the greater the possibility of intramolecular H-bonding with the solvent, the smaller would be the influence of weak intramolecular H-bonding on the position of the equilibrium[54]. The spectra of 5-phenyl azo-8-quinolinol-N-oxide shows that the molecule exists almost completely in the azo form in ethanol. The spectra are identical in a series of solvents except for small shifts in λ_{max} which means that the intramolecular H-bonding is so strong the intramolecular H-bonding with the solvent is without effect on the equilibrium[54]. Similarly, in 5-(2'-carbomethoxy phenyl azo)-8-quinolinol, the intramolecular H-bond involving a 6-membered ring in the azo form (IIA) is pitted against the intramolecular H-bond involving a 6-membered ring of the hydrazone form (IIB).



(II A) (II B)

The spectrum of 5-(2'-carbomethoxy phenyl azo)-8-quinolinol consists of two broad bands (λ_{max} at 395 nm and 460 nm), the ratio of the concentrations of hydrazone to azo tautomers as deduced from the relative intensities of the bands is 1:1. The hydrazone form is, thus, stabilized to a greater extent than the azo form[56].

The situation is analogous to that prevailing in 1-phenyl azo napthol (III) which exists exclusively in the azo form. The azo form is stabilized by intramolecular H-bond due to formation of a 6-membered ring[57].



(III)

Matsunaga, in an attempt to study thermochromism in 5-arylazo-8-quinolinols, have shown that the molecules exhibit azo-hydrazone tautomeric equilibria in the solid state also[63].

Acid base transformations in solutions often lead to a change in the electronic absorption of the azoxines. Spectrophotometric studies of solutions of azoxines at various acidity

show the existence of a number of equilibria. Introduction of an arylazo group into 8-quinolinol generally increases the acidity of the hydroxy group. At pH 1-3, protonation of the quinolinol N-atom occurs and in conc. H_2SO_4, azo group N-atom is protonated [31]. It has been observed that for 8-arylazo-8-quinolinols, the absorption spectra exhibit intense maxima in the long wave length region that decreases with decreasing acidity with an appearance of a maximum in the 400 nm region. The presence of a sharp isobestic is consistent with the existence of equilibrium (1). deprotonation of the azo-group nitrogen:

$$H_3R^{+2} \rightleftharpoons H_2R^{+} + H^{+} \qquad \ldots (1)$$

deprotonation of the hetero atom nitrogen:

$$H_2R \rightleftharpoons HR + H^{+} \qquad \ldots (2)$$

the hydroxy - group dissociation:

$$HR \rightleftharpoons R^{-} + H^{+} \qquad \ldots (3)$$

At pH > 1, the absorption maximum moves bathochromically. The equilibrium is shifted toward the more deeply coloured form of the reagent (neutral form) as shown in equilibrium (2). With further increase in pH, the molecule dissociate and a sharp

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bathochromic shift of the absorption maximum is observed [equilibrium (3)][39].

The colour deepening, particularly in a basic medium, is characteristic only for 8-azoxines and is due to the formation of a longer conjugated chain. Usually, all the 7-arylazo-8-quinolinols show just the reverse behaviour i.e. the deepest colour (λ_{max} = 530-550 nm) is observed for solutions of azoxines in acid media (pH < 2) and with increasing pH the colour becomes lighter, the dissociated form of the molecules being yellow or orange in colour[31].

The primary interest in the azoxines being due to their potential use as analytical reagent, no theoretical studies on the electronic transitions in these molecules in terms of the molecular orbitals are still available. Although in the absence of such studies it is hazardous to make any conjecture about the nature of transitions responsible for the light absorption properties of the azoxines, their spectra may be understood, at least in part, by comparison with other azo compounds which have investigated in detail by several workers

In simple azo-dye, like substituted azobenzene, strong $\Pi - \Pi^*$ transition is responsible for the visible absorption[63]. The comparatively weak n-Π^* bands are fully masked in the trans-configurations in which the azo-dyes normally exist. The n-Π^* transition may, however, be observed in cis-form where the first Π-Π^* transition occurs at shorter wave lengths[60,61]. According to MO descriptions, the upper MO for the longest wave length

π-π^* transition is the perturbed orbital originating from the anti bonding π-orbital of the azo group, while the lower one is the orbital arising from the perturbation of the highest bonding π-orbital of the aryl residue[60,62]. The electronic spectra of metal and organometallic derivatives of simple azo dyes have also been interpreted in terms of π-π^* transitions, the coordination of metal ion or organometal group exerting a bathochromic shift of the absorption maxima[53,60-63].

II. Biological Properties:

In the last decade there has been increasing interest in the biological properties of the azoxines which were so far used only as analytical reagents. Azoxines have received attention presumably for their stability and reactivity[46].

The survey of literature reveals that the biological effect is very dependent upon the nature of the reagents. Shreve and Bennett[66] prepared 5-R-8-quinolinols (R = substituted aryl azo groups) and studied their bacteriostatic power (B.P.) towards E. Coli and S. aureus. The testing solution in gm/100 ml. is given for the base in 95% ethanol at 25°C and for the HCl -salt in glycol at 24°C and in 0.1 N HCl at 24°C. In some cases the standard solution was diluted. Observation shows that the lowest dilution supported some growth and the water dilution of HCl-salt just prevent the growth.

The azoxine derivatives were tested for the properties of diabetes[67] which shows no better results but induced diabetes and stained the Langerhans island cells. The reagents caused diabetes during chelation with metallic ions[68] in the β-cells of the pancreatic islets of Langerhans and, otherwise, did not cause diabetes.

A series of azoxines metal derivatives, tested by Rao and Hirear[69], shows low antibacterial activity. Some new fungistatic compounds of azoxines[70] were investigated on liquid mash containing 10% cattle-serum and on solid media containing 5% agar. A relation was sought between the chelate complex forming ability and fungistatic activity of these compounds. These compounds exercise their fungistatic activity by means of intercellular chelation of the heavy metal components in certain enzyme of fungus cells. These enzyme were inactivated and this prevented multiplication.

Mycobacterium phlei and Staphylococcus aureus SG'G 6342 shows possible anti-microbial activity[71] against many aryl-azoquinolinol derivatives. The water soluble copper salt of azoxines shows some fungicidal properties[72]. Azoxines derivatives of Cu^{++}, Cd^{++}, Fe^{++}, Ni^{++} and Co^{++} complexes[73] exhibits antibacterial activity and found to be useful in the treatment of dysentery.

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