INTRODUCTION

1. INTRODUCTION

1.1. Chemistry of Azo Dyes

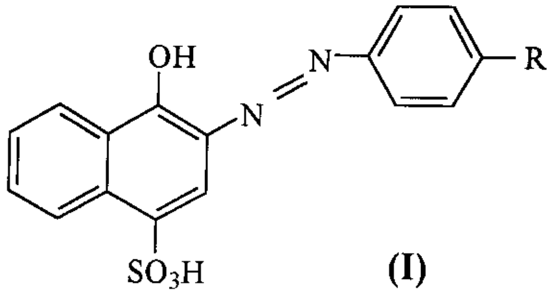
Azo dyes are the largest class of synthetic dyes. Their chromophore is an aromatic system joined to the azo group, and the common auxochromes are NR_2, NH_2 or OH. The usual method for preparation of azo dyes is the direct coupling of diazonium salts with phenolic, enolic and amino compounds. The structure of an azo dye is readily determined by reduction with stannous chloride and hydrochloric acid or with sodium hyposulphite where upon the azo group is ruptured with the formation of primary amines which are then easily identified(1).

Azo dyes are classified according to the number of azo group in the molecule to monoazo, bisazo, triazo, etc. and are also subclassified as basic (cationic) dyes, acidic (anionic) dyes, etc. The parent substance for this class of compounds is the diimide, $NH = NH$; a fugitive material(2) about which a relatively little is known, compared to the isoelectronic system ethylene and formaldehyde. Azo compounds are more stable than hydrazo compounds and therefore a good number of different structures of azo compounds has been determined. Most azo molecules are plannar with a reference for the transform(3). The geometry and electronic spectra of azo compounds can easily be understood on the basis of a simple MO treatment(4). The two nitrogen atoms are assumed to be sp^2-hybridized and remaining p-electrons are used to build up a π-orbital between the two nitrogen atoms. This leads to coplanar but non-linear arrangement.

Naphthol dyes are widely used as analytical chromogenic reagents for metal ions. The formation of such chelates is accompanied by changes in colour and absorption spectra. The formed chelates are characterised by their stability due to formation of five or six-membered chelate ring. From the structural point of view, these are considered as metal indicators since they possess functional groups capable of chelate formation with the groups joined directly to the central metal ions. Many naphthol azo derivatives are used as analytical reagents in spectrophotometry and compleximetry. The wide application of these reagents has promoted the study of the composition and stability of these metal complexes.

1.2. Literature Survey on Absorption Spectra of Azo Compounds

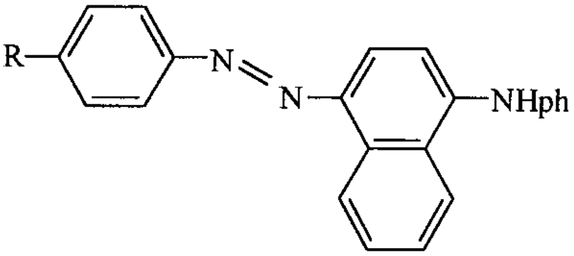
Khalifa et al(5) studied the acid-base properties of some acid azo dye derivatives. The electronic absorption spectra of 2-(azophenyl)-1-naphthol-4-sulfonic acid, 2-(azophenyl-p-methoxy, p-nitro and p-sulfo)-1-naphthol-4-sulfonic acid (I) were studied in aqueous buffer solutions having various pH values. The dissociation constant of the naphthoic OH group was determined spectrophotometrically and the dissociation constant for SO_3H group was detected potentiometrically.



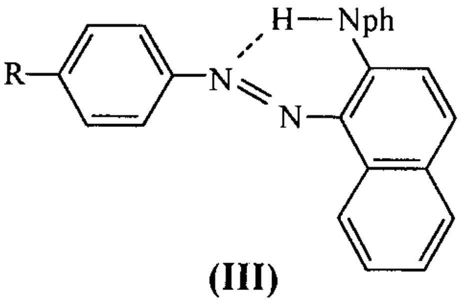
(I)

R = H, MeO, Cl, SO_3H, NO_2

Kostyuchinko et al(6) studied the visible spectra of monoazo dyes (II) (R = H, OMe, Br, NEt_2, NO_2) and their 2-phNH-isomer (III) and found that all compounds exist in the azo form in neutral solvents such as dioxan and also in acetic acid, but they exist in the quinone-hydrazone form in 30-90% aqueous-acid mixtures. The azo form of (III) is stabilized by intramolecular H-bonding.

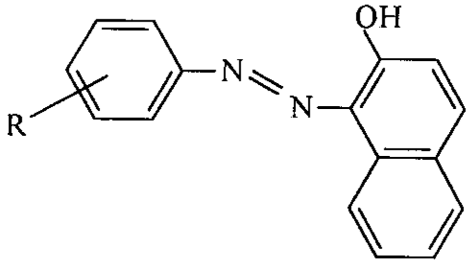


(II)

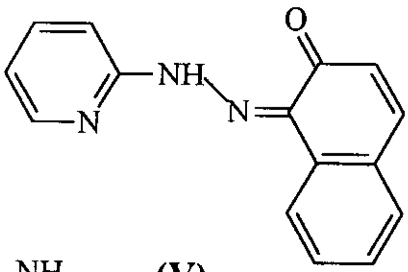


(III)

Haessner et al(7) studied the azo-hydrazo tautomerism in substituted 1-phenylazo-2-naphthols (IV) (R = 2- NO_2, 4-F, 3-OCH_3, 4-OH, 4-NH_2) from the ^{1}H-NMR shifts of using the pyridylazonaphthol (V) and phenylazonaphthylamine (VI) as model compounds. The equilibrium constant for (IV) tautomerization gave a linear free energy relationship with σ. The studied reaction entropy for the conversion of the azo form into hydrazo form was always negative and was substituent effect free. The quinone-hydrazone form has a higher tendency to aggregate than does its tautomer.



(IV)



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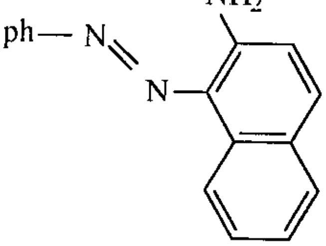
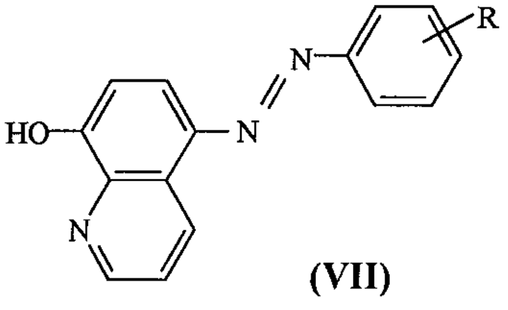


(VI)

Gaber et al(8) studied the electronic absorption spectra of some phenylazohydrazone derivatives in some organic solvents of different polarities and in buffer solutions of varying pH values. The variation of the absorbance with pH was utilized for the determination of pk_a. The IR-spectra and ^1H-NMR spectra of these compounds were also discussed in relation to their molecular structure.

Mohamed(9) studied the electronic absorption spectra of some 1- and 3-hydroxy-2-naphthoic acid azo dyes in organic solvents of different polarities. The absorption bands were assigned to the electronic transitions in the molecules, the effect of the solvent polarity on the absorption band was also discussed. The structures of the hydroxy naphthoic acid azo dyes were confirmed by IR and ^1H-NMR spectroscopy.

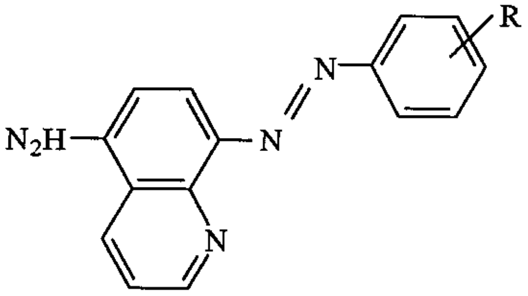
The solvent and substituent effects on the absorption spectra of 5-arylazo-8-quinolinols (VII) (R = H, Cl, Br, OEt, $N(Me)_2$, $AsO(OH)_2$, SO_3H, OMe, Ac, Me, OH and NO_2) were studied by El-Ansary et al(10) in organic solvents of different polarities. The effect of the solvent polarity on the band shift was interpreted in terms of the functions of the dielectric constant of the medium. Deviation in highly polar solvents was attributed to H-bond formation between the solute and solvent molecules. The IR absorption bands were also identified fcr each dye.



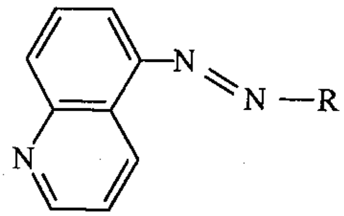
(VII)

Kamel et al(11) investigated the absorption spectra of some azo dyes containing the quinoline nucleus in ethanolic solutions. The authors pointed out that the λ_{max} and ε_{max} values for the band due to the π-π^* transition of the N=N center were influenced by the intramolecular charge transfer and essentially depended on the type of aromatic moities attached to the azo group. The band shift in comparison to the non-substituted compound, 2-amino-6-quinolinyl-4-hydroxyphenylazobenzene was explained in terms of additive or counter effects of the substituents present on the aromatic system.

Etaiw and Elmorsy(12) studied the UV-visible spectra of azo dyes containing the quinoline nuclues, (VIII) (R = H, MeO, OH, Me, Cl, NO_2) and (IX) (R = substituted ph or naphthalene, or aminoquinolinyl) in organic solvents, H_2O and HCl. The observed bands were assigned to different π-π^* and charge transfer transition. Spectral structure correlations were considered. The ir-spectra of VIII and IX were discussed in relation to molecular structure.

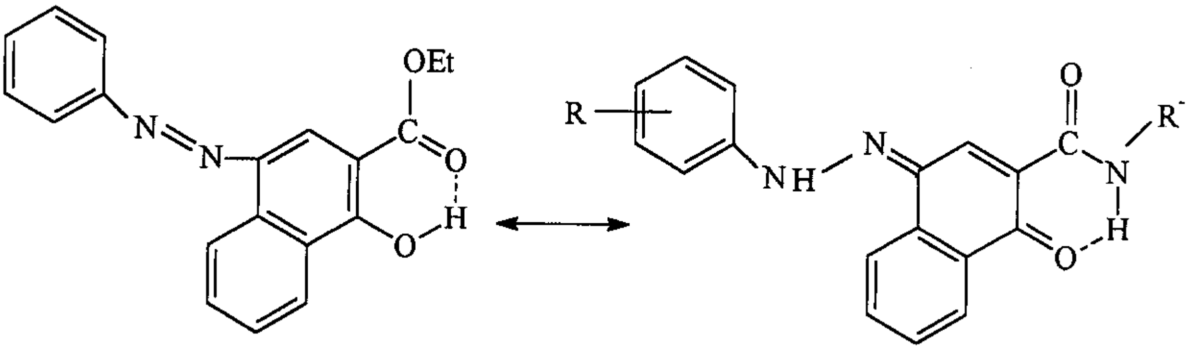


(VIII)



(IX)

Traven et al(13) studied the tautomerization and colour of monoazo dyes of 4-(arylazo)-1-naphthols (X) in solution. A group in position 2 stabilized the azo tautomer by hydrogen bonding, whereas o-COOH or o-CONHR stabilized the quinone-hydrazone tautomer by similar mechanism in both cases as shown by mass spectroscopy. A strongly electron-donating substituent tends to stabilize the azo tautomer regardless of the functionality of the substituent in o-position of the naphthyl ring.

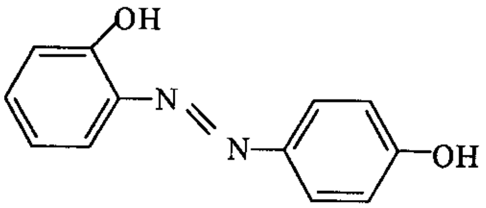


(X)

Azo tautomer

quinone hydrazone tautomer

Issa and Harfoush(14) investigated the UV-visible absorption spectra of some hydroxymono-azo compounds containing more than one hydroxy group (XI) in organic solvents. The absorption bands were assigned to definite electronic transitions. The effect of solvent and molecular structure on band position were discussed. The formation constant for the molecular complexes formed in ethanol was determined.



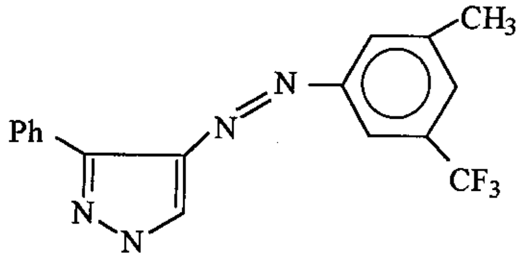
(XI)

Dessouki et al(15) studied the electronic absorption spectra of some azo-azomethine dyes (XII) in organic solvents of different polarities and in buffer solutions of different pH values, the change of absorbance with pH was utilized for the determination of pk_a. The important bands in the absorption spectra have been investigated. The important IR bands and ^{1}H-nmr signals are assigned and discussed in relation to molecular structure. The presence of intermolecular hydrogen bonding and quinone-hydrazone tautomerism within the molecules have been demonstrated from the IR-spectra. The biological activities of the azo compound towards some filamentous microscopic fungi, yeasts and bacteria have also been studied.

1.3.Literature Survey on Studies of the Metal Chelates of Azo Compounds

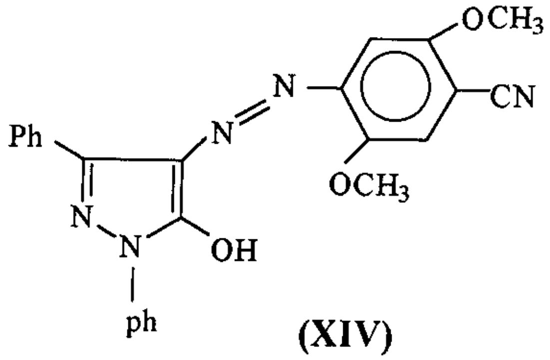
Moustafa et al.(18) studied the complexes of Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} with six azo compounds based on substituted 8-arylazo-6,7-dihydroxy-4-methylcoumarin; the solids have been synthesized and characterized by elemental and thermal analysis magnetic susceptibility. Molar conductance as well as IR spectroscopy, indicated that metal ions are surrounded by coordinated water molecules and one ligand molecule bonded in a bidentate O and N fashion in the case of ligand 1 (X=H) and in tridentate ONO fashion in the case of all the remaining ligands forming a coordination number of six in all cases. The potentiality of the prepared azo compounds as new chromophoric reagents for the spectrophotometric determination of the metal ions is studied by extensive investigation of the optimum conditions favouring the formation of coloured complexes in solution.

Mostafa(19) studied the complexes of 1-(2-pyridylazo)-2-naphthol with ZrO^{+2}, Nb^{+5}, Pb^{+2} and Cd^{+2} ions using different techniques. The ionization constant of the ligand and the formation constants of its complexes were determined potentiometrically. The stoichiometry of the complexes was determined using spectrophotometric as well as

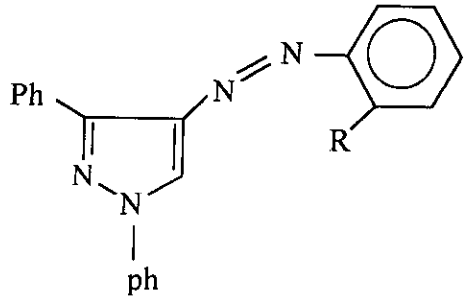


(XIII)

R = H(I), ph(II)



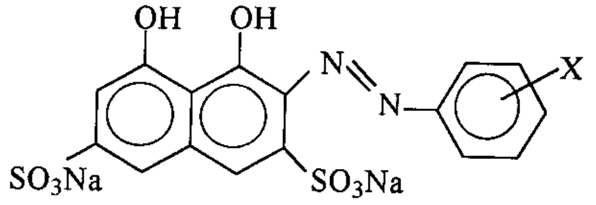
(XIV)



(XV)

R = COOH, OH

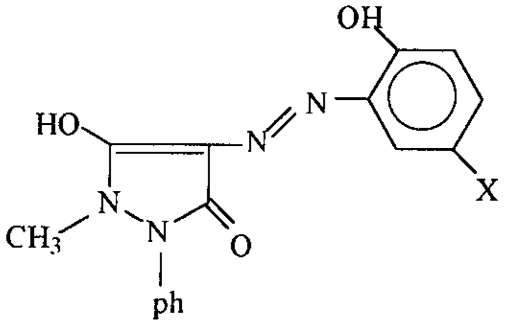
The IR-spectra of some chromotropic acid azo dyes (XVI) and their complexes with Cr, Mn, Co, Ni and Cu ions have been investigated to elucidate their molecular structure by Issa et al(22). The solid complexes were prepared and subjected to elemental analysis, TGA and magnetic susceptibility measurements to throw more light on the coordination nature and magnetic properties of such complexes. The chelates formed have the stoichiometric ratios 1 : 1 and 1 : 2 (M : L). Chromotrophic acid dyes acted as mono-basic in the formation of these chelates.



(XVI)

X = H, p-NO_2, o-AsO $(OH)_2$, p-SO_3H

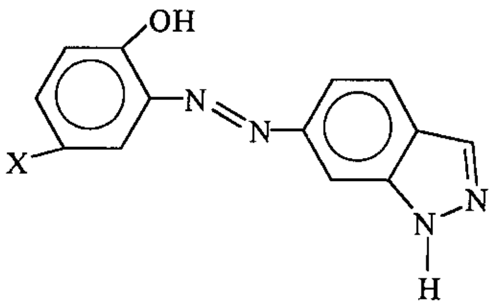
Spectrophotometric studies and analytical applications of the complexes of Fe(III), Ni(II) and Cu(II) with some 4-aminoantipyrene azo derivatives (XVII) were studied by Moustafa et al(23). Extensive study of the composition, stability constants and optimum conditions for the formation of Fe(III), Ni(II) and Cu(II) complexes with four azo compounds based on 4-aminoantipyrene were studied. The coloured complexes formed under the optimum conditions mentioned were successfully used in the microdetermination of metal ions in synthetic solution as well as in incoloy 800 alloy.



(XVII)

$X = H, NO_2, COOH$ and NH_2

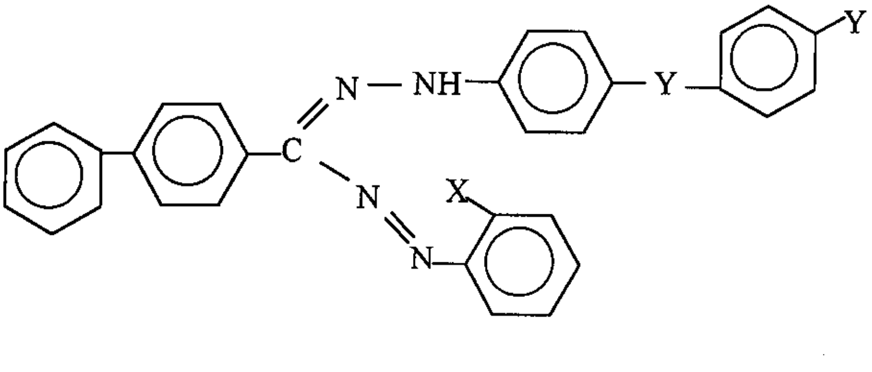
Four azo compounds based on 5-aminoindazole (XVIII) had been synthesized and characterized using elemental analysis as well as different spectroscopic techniques by Moustafa et al(24). The potentiality of the prepared azo compounds as new chromogenic reagents for the spectroscopic determination of VO_2^+ was studied by extensive investigation of the optimum conditions favouring the formation of the coloured complexes.



(XVIII)

X = OH, COOH, CHO, NH_2

Investigation of some lanthanide complexes with 1,3,5-triphenylformazan derivatives (XIX) applying potentiometric, TGA, DTGA, IR and PMR methods was carried out by Abdel-Ghani et al(25). The stability constants of trivalent La, Nb, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu ions with some 1,3,5-triphenylformazan derivatives were determined in 70% ethanol-water medium at 25°C and 0.1M $NaClO_4$ ionic strength. The solid complexes were prepared and subjected to elemental analysis, TGA, DTA, IR and PMR techniques. Relations between the basicity of the ligand and ionization potential, electron affinity, ionic radius and coordination number of lanthanide (III) ions were studied.



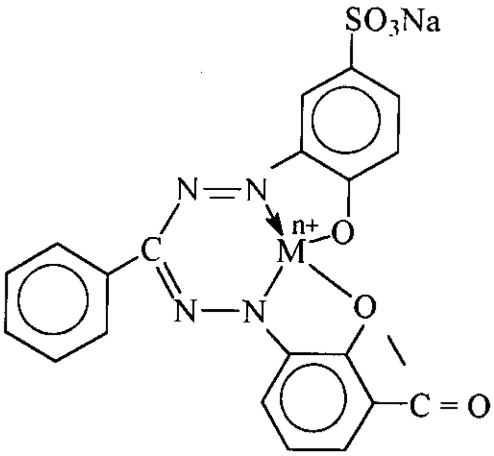
(XIX)

(X,Y) = (OH, H), (OH,Cl), (OH, NO_2), (COOH, NO_2), (COOH, Cl).

Gaber et al(26) studied the chelates of Co(II), Ni(II) and Cu(II) with some 3-arylazo-1,2,4-triazole dyes by conductometric titration, IR and

ESR spectra. The formation of 1:1 and 1:2 (M:L) complexes established by elemental analysis and conductometric titration.

Gaber <u>et</u> <u>al</u>(27) studied the thermal behaviour of 2-hydroxy-5-sulphonyl-azobenzylidene hydrazine benzoic acid (Zincon) complexes with Mg^{+2}, Ca^{+2}, Sr^{+2}, Ba^{+2} and Bi^{+3} ions. The structures of the complexes (XX) were characterized by elemental analysis and IR-spectra. The bonding between metal and ligand was represented as follows:



(XX)

where $(n^+) = 0$ for Mg, Ca, Ba, Sr; $(n^+) = 1$ for Bi.

The thermal stability of the prepared complexes was investigated in terms of the type of metal ions. The kinetics of the thermal decomposition were discussed. The activation energies were determined and the electrical resistivities were measured.

Masoud <u>et</u> <u>al</u>(28) reported the acid dissociation constant of some 2-hydroxy-5-methyl-4-substituted azobenzenes and the formation constants of their chelates with Fe(III), Co(II), Ni(II) and Cu(II) ions. The substituent and the solvent beside the pH value affect the tautomeric phenomenon in the ligands. The ligand formed 1 : 1 and 1 : 2 complexes in solution. The pK values of the complexes were evaluated spectophotometrically. The solid complexes were found to have octahedral spatial configuration.

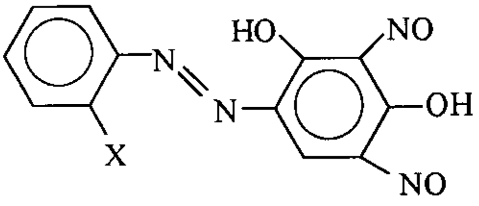
Dessouki et al(29) studied the complex formation of Co(II), Ni(II) and Cu(II) with o-carboxyphenylazosalicyladehyde by potentiometric and conductometric titrations. The stoichiometry of the complexes was also studied spectrophotometrically, the proton-reagent ionisation constant and conditional formation constants were determined. DTA and IR-spectra for the binuclear complexes were reported. This study showed that the ligand in the case of binuclear metal chelates functions as a dibasic tetradentate group.

Abd El-Mottaleb et al(30) synthesized a series of complexes of the type $[ML].nH_2O$ in which M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions and L is 2-hydroxy-5-sulphonylazobenzylidenehydrazino benzoic acid (Zincon). These complexes were characterized by elemental analysis, IR, ^{1}H-NMR and electronic spectra. TGA and room temperature magnetic susceptibility were measured. The stability constants were determined by the potentiometric technique and discussed in relation to ionic potentials.

Aref(31) synthesised a series of 5-phenylazo-8-hydroxquinoline derivatives (XAHQ) and their metal complexes with hexacyano ferrates and picric acid (pic). The first series included $(HXAHQ)_4[Fe(CN)_2].H_2O$ (X=H, o-Me, m-Cl, p-OMe) and $(HXAHQ)[Fe(CN)_6].7H_2O$(X = o-Cl, o-Me) and the second series included M $(XAQ)_2$. pic [M=Co(II), Ni(II), Cu(II), (X=o-Me, p-OMe)]. The nature of bonding in both series is

H-bonding. The complexes were characterised by elemental analysis, IR, electronic spectra and thermal analysis.

Masoud et al(32) studied the electrical conductivity of 2-(substituted phenylazo)-2,4-dinitrosoresorcinol (XXI) and their transition metal complexes measured in the temperature range (293-433 K). The data indicated slight semiconducting behaviour for these compounds. A discontinuity in the conductivity curve was observed. Different activation energies were calculated due to the change in the magnitude of the energy gap in both the ligands and their complexes. The data were explained based on the electronic character of the transition metal ions Fe(II), Co(II), Ni(II) and Cu(II) and the molecular structure of the compounds.

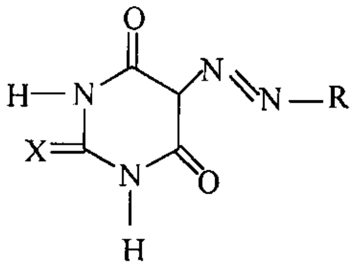


(XXI)

X = H, OH, COOH

Gaber et al(33) studied the reaction of Cu(II) with azo dyes derived from 3-aminotrizole (XXII) in solutions of varying H^+ ion concentration and composition by spectrophotometric methods as well as by conductometric one. The results revealed the formation of different types of complexes. The effect of pH, time, sequence of addition and selection of suitable wavelength and Beer's law were studied. The stability constants of the complexes were determined and the chelating behaviour of the titled azo dyes were confirmed by preparing the solid complexes which were characterized by different methods.

between oxygen and sulphur atoms, indicating more conjugated and stable structure for the former complexes.



(XXIII)

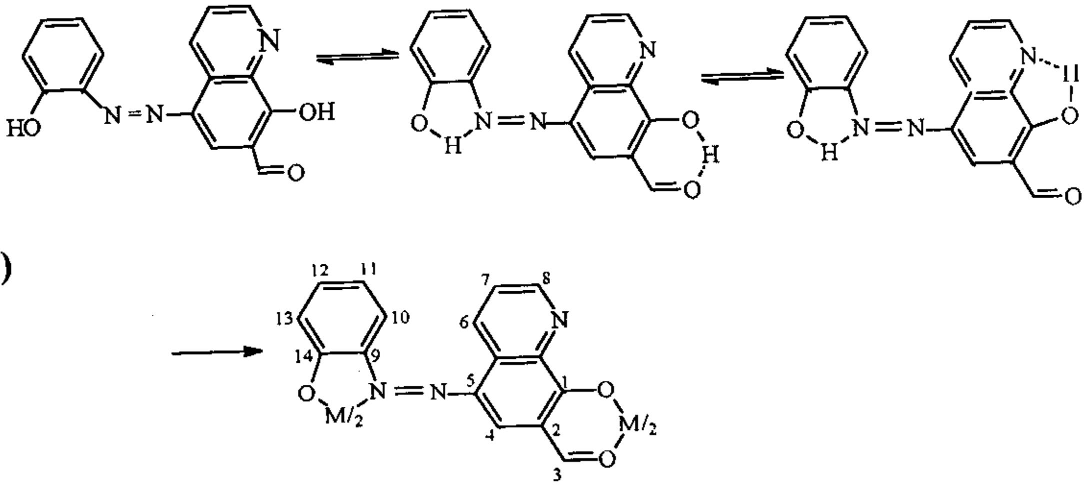
R = pyrimidine, pyrazine, adenine, 1,3,4-thiadiazol-2-thiol, benzothiazol.
X = O or S.

Mahapatra and Sukhendu(35) synthesised new complexes of azo dye ligands giving $[M_2L_2(H_2O)_4]$, $[M^1{}_2L_2]$, $[ML^1(H_2O)_2]_n$ and $[M^1L^1]$ where [H_2L = 2-hydroxy-1-(hydroxyphenylazo)-naphthalene; H_2L^1=3-(hydroxyphenylazo)-2,4-pentanedione, 2-(3-hydroxyphenylazo)-1-(phenylamino)-1,3-butanedione, and 8-hydroxy-5-(3-hydroxyphenylazo)-quinoline; M= Co, Ni and Cu; M^1 = Zn, Cd and Hg]. From elemental analysis, conductance, magnitic, electronic, IR and ESR spectral data, the Co(II), Ni(II) and Cu(II) complexes were six-coordinate with an octahedral or distorted octahedral configuration, while Zn(II), Cd(II) and Hg(II) complexes were four coordinate with a tetrahedral geometry around the metal ions.

Omar et al(36) studied the complexation of 2-(4-benzimidazolylazo)-R-acid (R-acid = 2-hydroxynaphthalene-3,6-disulfonic acid) and 5-(4-benzimidazolylazo)-8-hydroxyquinoline with Mn(II), Co(II), Ni(II) and Cu(II) using the potentiometric titration method. The protonation constant of the ligands and stability constants of the metal complexes were determined at a constant temperature (25°C). The order of stability constants was Mn(II) < Co(II) < Ni(II) < Cu(II). The structure of the complexes were assigned using elemental analysis, IR spectroscopy and conductometric titrations.

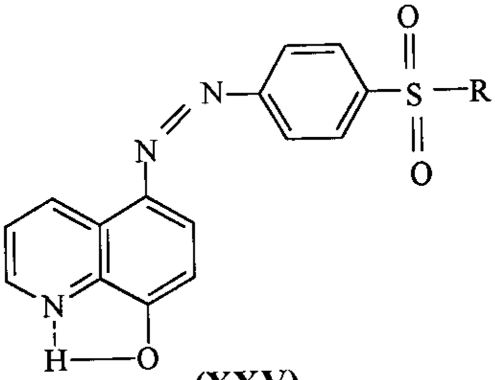
The chelates of some arsenazo compounds derived from 1- and 2-naphthol and 1-hydroxy-2-naphthoic acid as ligands with Sc(III), Y(III), La(III), Th(IV) and uranyl (II) ions were investigated in solution by Abdel-Badei et al(37) using spectrophotometric and conductometric titration methods. The studies revealed the formation of ML and ML_2 complexes. The solid chelates have been characterized by chemical analysis, thermal methods (DTA & TGA), IR and electronic spectra.

New polymeric complexes of Co(II), Ni(II), Cu(II), Fe(II), Fe(III), Zn(II), Cd(II) and UO_2(II) with 5-(2-hydroxyphenyldiazo)-8-hydroxy-7-quinolinecarboxaldehyde (LH_2) (XXIV) have been synthesized and characterized by analytical, thermal, magnetic, infrared, electronic, ^{1}H-NMR, ^{13}C-NMR and EPR spectral studies(38). The infrared spectral data of the metal complexes indicated that LH_2 acts as bis-bidentate towards the metal ions. The electronic spectral data suggested that Co(II) and Mn(II) complexes are octahedral, while Ni(II) complex is square planar. The complexes of Zn(II) and Cd(II) are tetrahedral. The chelating ligand around the copper was expected to be distorted square planar for Cu(II). The electronic aborption and a g/A value were indicative for the beginning of tetrahedral distortion. The coupling constants of various coordinated nuclei with copper (II) were estimated from EPR spectrum of copper(II) complex.



(XXIV)

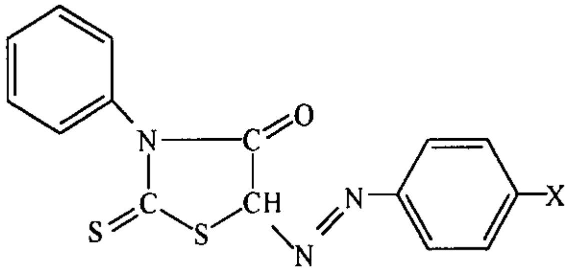
Some new azo sulphonamide derivatives containing 8-hydroxyquinoline moiety (XXV) and their complexes with some transition metal ions vz. Fe^{+3}, Co^{+2}, Ni^{+2}, Cu^{+2}, and Hg^{+2} have been prepared and characterized(39). The stereochemistry as well as the type of bonding around the metal ions were determined on the basis of microanalysis, IR and UV-VIS spectra, conductivity and magnetic moment measurements. The thermal behaviour of the complexes was also studied. The metal ions coordinate exclusively to the 8-hydroxyquinoline moiety. The biological activity of the complexes was tested against a number of bacteria. Chelation of the metal ions to the ligands induces a remarkable increase in their antimicrobacteral activity.



(XXV)

R = anilino, benzylamino, butylamino, dimethylamino, piperidino and m-chloroaniline.

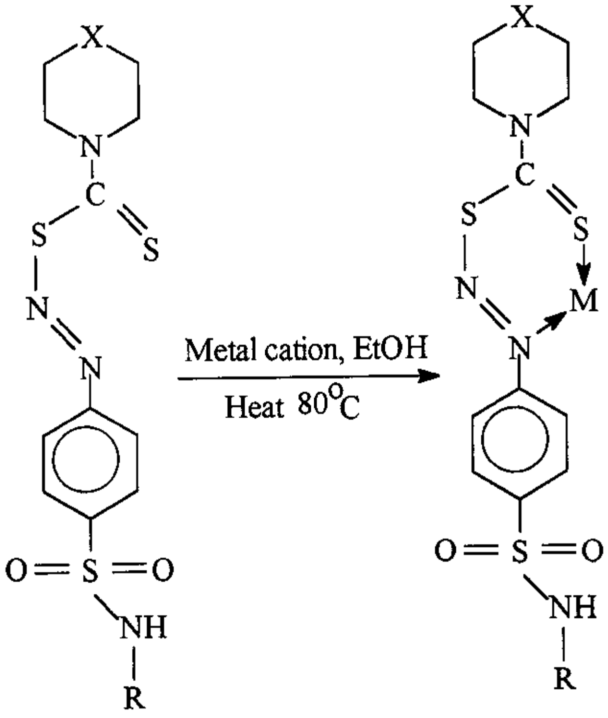
Stability constant of the complexes of bivalent Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} metal ions with 5-azorhodanine derivaties (XXVI) have been determined potentiometrically in 0.1M KCl and 50% (v/v) ethanol-water mixture(40). The order of the stability constants of the formed complexes was found to be = $Mn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+}$. The influence of substituents on the stabillity of the complexes was examined on the basis of electron- repelling property of the substituent. The effect of temperature on the stability of the complexes formed was studied and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed. The stoichiometries of these complexes were determined conductometrically and indicated the formation of 1 : 1 and 1 : 2 (metal : ligand) complexes.



(XXVI)

X = H (PR), Cl(CPR),NO_2(NPR), CH_3(CPR),OCH_3(TPR)

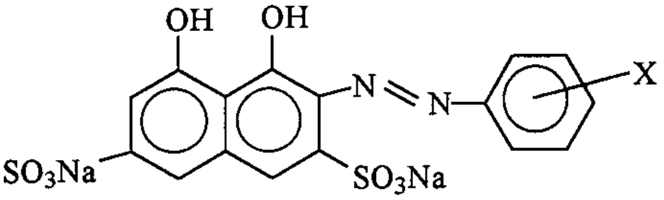
A series of novel azo-sulfa drugs of piperidino-morpholino, mono- and bis-piperazino-N-dithiocarbamylazo dyes (XXVII) were synthesiezed(41) via a reaction of 4-[(4`-heterocyclo-substituted)sulfamoyl and/or sulfonyl] benzenediazonium salts with N-piperidino, N-morpholinomono and bis-N-piperazino-dithiocarbamate sodium salts in acid medium to afford the corresponding azo dye ligands. Interaction of these ligands with metal salts; iron(III), copper (II) and mercury(II) chlorides in ethanolic solution afforded the corresponding metal chelates. Ligands and their metal chelates were characterized by microanalysis, IR, UV-VIS, ^{1}H-NMR spectroscopy and were screened in vitro for their antimicrobial activities. Chelation of ligands induced a remarkable increase in their antimicrobial activity.



(XXVII)

1.4. Literature Survey on Polarographic and Cyclic Voltammetric Studies of Azo Compounds

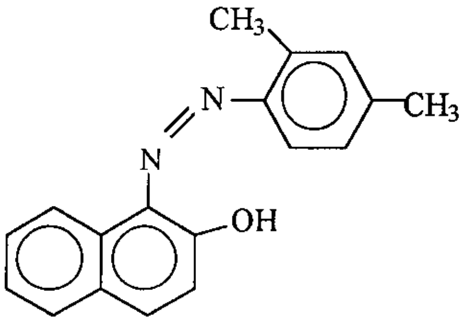
Ghoneim et al$^{(42)}$ studied the polarographic behaviour of phenylazochromotropic acid dyes (XXVIII) in aqueous B.R. buffer solutions within the pH range (2-12). The polarograms of these compounds consisted of a single 4-electron reduction wave within the entire pH range which corresponded to the reduction of the azo center to the amine group. The kinetic parameters of the electrode reaction were determined. Introducing different substituents in m- or p-position with respects to N = N center causes a shift in $E_{1/2}$ of these compounds to more or to less negative values depending on their donor or acceptor character. The plots of $E_{1/2}$ as a function of σ_X yielded a linear relationship with negative slope ($\rho_{\pi,R}$) amounting to – 0.1V. The negative value indicated that the reduction of N = N center was hindered by the presence of electron donor substituents and corresponding to electrophilic attack in the potential-determining step.



(XXVIII)

X=H, o-Cl, p-Cl, m-Cl, o,p-diCl, m-COOH, m-OCH_3, p-NH_2SO_2, p-SO_3Na

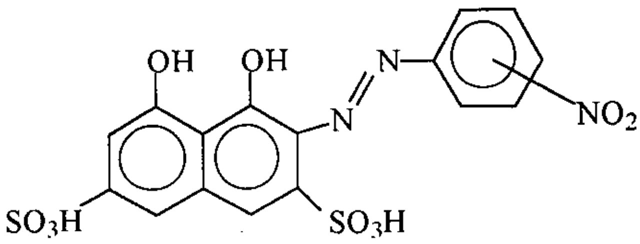
The electrochemical reduction of Sudan II azo dye (XXIX) in 60% hydrochloric acid medium was studied by Yaguez et al(43) using different polarographic techniques. Sudan II showed a well-defined irreversible diffusion-controlled polarographic wave covers the all pH range studied. The $E_{1/2}$ was strongly pH-dependent but i_l was not. Slope changes are due to acid-base equilibria involving the oxidized and reduced forms. The number of electrons involved in the reduction process in both acidic and alkaline solutions was four electrons leading to the formation of 1-amino-2-naphthol and 2,4-dimethylaniline. Normal dc and ac-polarography showed the irreversibility of Sudan II reduction process.



(XXIX)

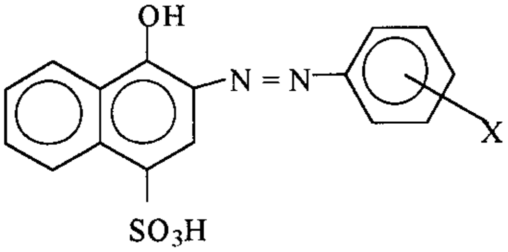
Malik et al(44) studied the electroreduction of fast sulphone Black-F in phosphate buffers within the pH range 2-11 at the dme and pyrolytic graphite electrode. It was observed that the reduction of the azo group attached to the naphthaline ring having electron-donating groups occurred more easily than that of the azo group attached to the naphthaline ring with electron-withdrawing ones. Cyclic voltammetry confirmed the formation of 1-amino-2-naphthol by 4e, $4H^+$ transfer, which revealed that the cleavage of N=N group attached to the naphthol ring took place at the beginning, followed by 2e, $2H^+$ transfer affecting the reduction of the second azo group to give the hydrazo product. The cleavage would form an amine and quinone-imine, the latter was then reduced in a 2-electron transfer process immediately at the electrode or by the hydrazine to give the final products.

Mabrouk et al(45) studied the reduction behaviour of o-, m- and p-nitrochromotropic acid dyes (XXX) using dc-polarography and cyclic voltammetry measurements. At $pH > 3.5$, the m- and p-derivatives were reduced through two 4- electron, diffusion-controlled irreversible waves. The first wave corresponded to the cleavage of N = N bond, while the second one was due to the reduction of the NO_2 to NHOH stage. For m-nitro compound, a single 8-electron diffusion-controlled irreversible wave was obtained in the entire pH range and corresponded to the reduction of N=N and NO_2 centers in one step. At $pH > 9$, the polarograms showed two waves of equal heights. At different sweep rates, the voltammograms of these compounds showed two cathodic peaks within the entire pH range, corresponding to two different reduction steps. The kinetic parameters were calculated and in discussed in the absence and presence of anionic or nonionic surfactants.



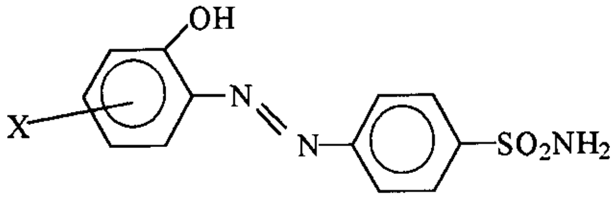
(XXX)

Mabrouk et al(46) studied the polarographic and cyclic voltammetric behaviour of some azo dyes (XXXI) in B.R. buffer solutions of pH 2-12. The polarograms of these azo compounds showed an irreversible 4-electron wave corresponding to the reduction of the azo group to the amine stage within the range 2-9, while at pH > 9 the reduction wave of some derivatives splitted into two waves of unequal heights. The half-wave potential was shifted to more negative potential on increasing the pH of the solution. The total limiting current was pH-independent and corresponding to four electrons. The voltammograms showed one or two cathodic peaks at different scan rates, depending on the nature of the substituent and pH of the medium. The kinetic parameters of the electrode reaction were calculated and the effect of substituents on the reduction mechanism was discussed.



(XXXI)

X = H, m-Cl, p-Cl, m-COOH, p-COOH, p-SO_3H, m-OH, p-OCH_3, p-C_2H_5, p-SO_2NH_2, m-NO_2



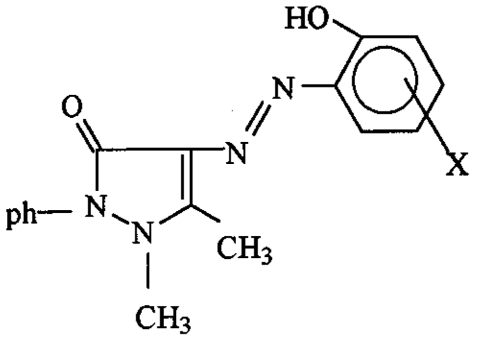
(XXXII)

X = 4-OH, 5-OCH_3, 4-$N(CH_3)_2$, 5-Br, 5-COOH, 5-CHO

Mabrouk et al(47) studied the polargraphic and cyclic voltammetric behaviour of some azo compounds (XXXII) derived from sulphonamide in DMF-aqueous solutions. Within the pH range 2-12, the polarograms of all compounds exhibited a single 4-electron, diffusion-controlled and irreversible wave. The cyclic voltammograms of all compounds exhibited a single cathodic peak in both acidic and alkaline solutions. Also, a small anodic peak appeared in the reverse scan which may be attributed to the formation of hydrazo intermediate. The kinetic parameters of the electrode reaction were calculated and discussed.

El-Mossalamy and Mabrouk(48) studied the polarographic and cyclic voltammetric behaviour of some bisazo compounds derived from 4,4`-oxydianiline in B.R. buffer solutions of pH 2-10 as well as electronic absorption spectra of this bisazo compound in organic solvents of varying polarities. It was found that, the bisazo compound exhibited a single reduction wave corresponding to eight electrons at pH < 6, whereas in the pH range 6-8 the wave splits into two waves of equal height. In alkaline solutions (pH>10), the second wave disappeared and a well-defined wave corresponding to four electrons was observed. The $E_{1/2}$ of the reduction wave was shifted to more negative potential with increasing pH, denoting the involvement of protons in the reduction propcess. The cyclic voltammograms of the bisazo compound under study exhibited a single cathodic peak. The absence of any peaks in the reverse scan as well as the shift of peak potential (E_p) to more negative values on increasing the scan rates indicated the irreversible nature of the reduction wave.

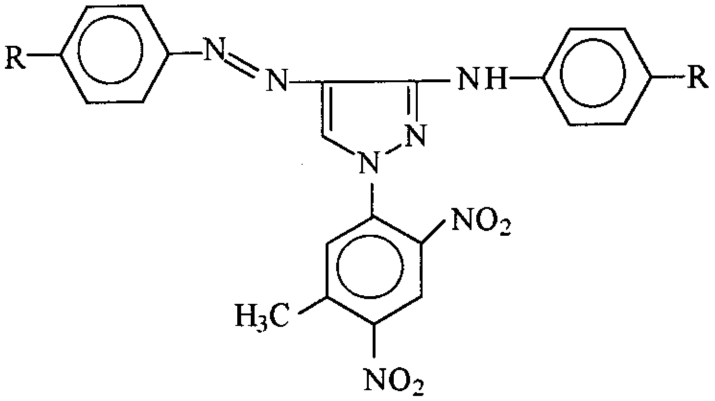
Killa et al(49) studied the electrochemical behaviour of some azo compounds of 4-aminoantipyrine (XXXIII) using dc-polarography and cyclic voltammetry techniques. The dc-polarograms exhibited a single 4-electron diffusion-controlled irreversible wave in the pH range 2-12. The polarograms of 5-NO_2 derivative showed two waves of unequal heights. The second wave corresponded to the uptake of six electrons as confirmed by controlled potential coulometry. The cyclic voltammograms of all compounds (except the 5-NO_2 derivative) exhibited a single cathodic peak in solutions of pH 3.3, 6.7 and 10.1. For the 5-NO_2 derivative, two cathodic peaks were observed. Both $E_{1/2}$ and E_p are pH-dependent and E_p was shifted to more negative potentials on increasing scan rates which confirmed the irreversibility of the reduction waves. The values of the kinetic parameters were evaluated and discussed.



(XXXIII)

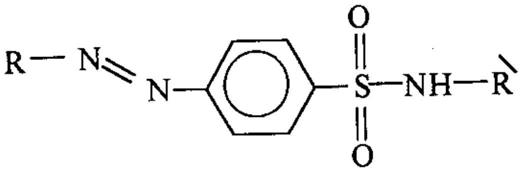
X= 5-NH_2, 5-CH_3, 4-OH, 5-Br, 5-NO_2

The electrochemical behaviour of some 1-(2,4-dinitrophenyl)-3-phenylamine-5-methyl-4-arylazopyrazdes (XXXIV) was studied by Jain and Jain(50) over a wide range of pH at DME and GCE. It was found that these compounds gave two well-separated polarographic waves corresponding to the reduction of NO_2 and N = N groups. Coulometric measurements confirmed that the first wave involved 8 electrons which corresponded to the reduction of the two nitro groups to the hydroxylamine stage, whereas the second wave involving two electrons represented the reduction of the N = N center to hydrazo group. Cyclic voltammograms of these compounds exhibited two well-defined cathodic peaks. The peak potential (E_p) of these compounds was found to shift cathodically with increasing the scan rate (v) and with increasing concentration of the depolarizer. Also, in the reverse scan no anodic peak was noticed even at higher sweep rates indicating that the electrode reaction was totally irreversible. Also, peak current (i_p) of both peaks were proportional to the concentration of the depolarizer as well as $v^{½}$ suggesting that these peaks should corresponded to a diffusion-controlled process. The effect of substituents, cations, anions, ionic strength and organic solvents on the reduction waves was studied and discussed.



(XXXIV)

The electrochemical behaviour of some pharmcodynamically significant 2-sulphonamoly azo imidazoles (XXXV) was studied by Pandey and Dav(51) in B.R. buffers of pH 2-12 containing 30% DMF at the DME. It was found that these compounds exhibited a single well-defined, diffusion-controlled reduction wave. The $E_{1/2}$ shifted towards more negative potentials on increasing the pH of solution. The pK value of all compounds was evaluated from the $E_{1/2}$ – pH curves and found to be 8. The total number of electrons involved in the reduction process amounted to two and the number of electrons involved in the rate-determining step is four. The effect of the cation size of the supporting electrolyte on the nature and shape of the wave was also studied. The effect of different solvents viz, DMF, CH_3OH, DMSO as well as effect of Triton X-100 on the reduction wave were also investigated and discussed. Generally, it was found that the $E_{1/2}$ shifted to more negative potential and i_l decreased with increasing concentration of the organic solvents.

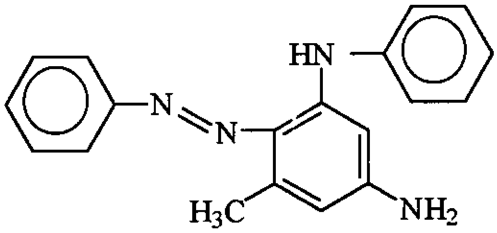


(XXXV)

The polarographic behaviour of 4-(4`-nitrophenylazo)-resorsinol in B-R buffers over a wide range of pH was studied by Husain et al (52). The ionic strength (μ) was adjusted at 0.4 M with KCl. The results showed that the compound exhibits a well-defined 2-electron wave in acidic solutions. Within the pH range 4-7, two 1-electron reduction waves were observed whereas in neutral and slightly alkaline medial (pH 6.9-9.0) three waves of different heights were obtained. In alkaline solutions (pH > 11), only one 2-electron wave was observed. The overall reduction process was diffusion-controlled and irreversible. The $E_{1/2}$ was shifted cathodically with increasing the pH denoting the involvement of protons in the reduction process. The same results were obtained by using differential pulse polarography (dpp). It was found that the first two waves observed in the pH range 7-9 are due to the reduction of the N = N centre involving two electrons and the third wave represents the reduction of the NO_2 group to NHOH consuming 4 electrons.

Jain and Pandey(53) studied the electroreduction of N-(4,6-dimethyl-pyrimidinyl-3-phenylamino-5-methyl-4-arylazoles. The polarographic reduction showed a single 2-electron wave in B.R. buffer solutions corresponding to the reduction of the azo group to the hydrazo stage. The reduction process was diffusion-controlled. Effect of various anions, cations and solvent composition on the reduction process was discussed.

Jain and Dua(54) studied the electrochemical reduction of 2-amino-5-aryl-4-phenylamino-6-methylpyrimidine (XXXVI). The polarograms showed a single 2-electron, diffusion-controlled, irreversible wave corresponding to the reduction of the azo group. Based on dc-polarography, cyclic voltammetry, coulometry and products of electrolysis, a reaction mechanism was proposed for the reduction. Effects of cations, anions, ionic strength and different solvents on the electrode process have also been discussed.

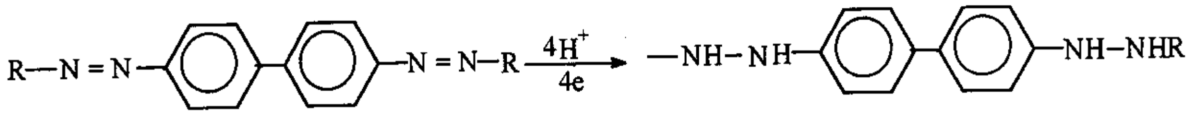


(XXXVI)

The polarographic and cycilic voltammetric behaviour of N-aryl-N`-2-(4-p-anisyl-5-arylazothiazolyl)thiocarbamides (XXXVII) was investigated at DME and HMDE in Britton-Robinson buffers of pH 2-10, containing 60% (v/v) dimethylformamide(55). The polrograms exhibited a single reduction 4-electron diffusion-controlled and irreversible polarographic wave corresponding to the leavage of the N=N group. The cyclic voltammograms showed a single cathodic peak in the forward scan and no anodic peak is observed in the reverse one. The product of electrolysis have been characterised and a possible mechanisms was suggested.

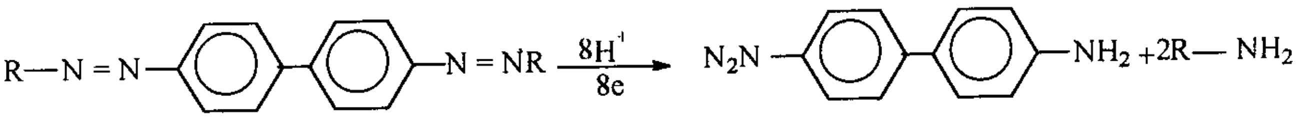
Polarographic behaviour of 4,4`-bisazobenzene (XXXVIII) was studied by Temerk et al(56). The polarograms of the dye in aqueous buffered solutions and aqueous-alcohol mixtures of different pH consist of a single irreversible diffusion controlled reduction wave. The height of the wave in alkaline solutions was almost half its value in moderate acidic media, whereas at intermediate pH, the wave height lies between the two values, indicating that the electrons involved in the electrode reaction in weakly acidic media are double those in alkaline ones, since the overall electrode reaction involved the uptake of 8 and 4 electrons in acidic and alkaline solutions, respectively. With respect to the effect of solvent on $E_{1/2}$ it was found that the solvent increased the shift in $E_{1/2}$ to more negative potentials and the shift became more apparent with rise of the molecular weight of alcohol. The total limiting current decreased more in the presence of alcohols than in aqueous medium due to the increase of viscosity of the medium and effective size of molecules of reducible species. The reduction mechanism can be represented as follows:

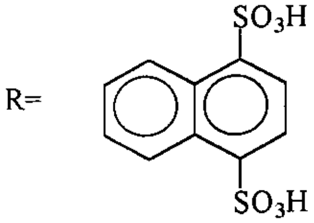
In alkaline solutions:



(XXXVIII)

In acidic solutions





Issa et al (57) studied the polarographic behaviour of some azo-azomethine compounds in solutions of varying pH at DME. The polarographic reduction of these compounds comprising two diffusion-controlled irreversible waves of almost equal heights. The two waves obtained corresponded to the reduction of the N = N and C = N centers, respectively. The wave height decreased tremendously with increasing pH till it attained in neutral and alkaline solutions almost half its height in acid media. It was concluded that the number of electrons involved in the electrode reaction in acid media is double that consumed in alkaline ones. The behaviour observed for both waves was quite identical with that of compounds containing either the N = N or C = N centre only, indicating that each center consumes four or two electrons in acid and alkaline solutions, respectively. The reduction mechanism can be re presented as follows

In acid solutions:

$$R_1-N=N-R_2 + 4H^+ + 4\bar{e} \longrightarrow R_1-NH_2 + NH_2-R_2$$

$$R_1-CH=N-R_2 + 4H^+ + 4\bar{e} \longrightarrow R_1-CH_3 + NH_2-R_2$$

In alkaline solutions

$$R_1-N=N-R_2 + 2H^+ + 2\bar{e} \longrightarrow R_1-NH-NH-R_2$$

$$R_1-CH=N-R_2 + 2H^+ + 2\bar{e} \longrightarrow R_1-CH_2-NH-R_2$$

The reductive polarographic behaviour of 3,5-dimethyl-4-phenyl azo(2H)-1,2,6-thiazine-1,1-dioxides (1) and some of its derivatives in aqueous B.R. buffers solutions of pH 2.5-11.4 containing 30% (v/v) DMF at DME was studied by Maharran et al(58). The polarograms in all pH consist of a single 2-electron takes place in a single 2e transfer, giving a diffusion-controlled irreversible wave corresponding to the reduction of azo group. The cyclic voltammograms of all compounds showed a single unidirectional cathodic peak at a platinum electrode. The symmetry coefficient (α) and the heterogeneous rate constant (K_s) of the electron transfer were evaluated. The diffusion coefficient (D) for all compounds under examination was determined using chronoamperometric, chronopotentiometric techniques. Convolution-deconvolution analysis of the recorded cyclic voltammetric current data was used to confirm the mechanism of electrode reaction.

The electrochemical properties of a number of azosalicylic acid derivatives have been studied by Eriksson and Nyholm(59) compared at glassy carbon electrodes using cyclic and hydrodynamic voltammetry. The reduction of all studied compounds, except one, was found to be irreversible giving rise to disruption of the azo bridge and formation of the corresponding amines. It was found that the rate of cleavage of the azo bridge depended on the position of the hydroxy substituents on the aromatic rings of the azosalicylic compounds. A reoxidation wave, most likely due to the oxidation of a hydrazo intermediate, was observed for compounds with either only one hydroxyl group, or hydroxyl groups in the meta-para or meta-meta positions relative to the azo bridge. The oxidation of the azosalicylic compounds with no, or only one, hydroxyl group in the para position was generally found to be irreversible yielding poorly defined oxidation waves. Azosalicylic acids with two hydroxyl groups, either in the para position of both rings or in the ortho position of one ring and para position of the other, gave rise to well-defined oxidation peaks at significantly less positive potentials. For the compounds with the hydroxyl groups in the para position of both rings, rereduction waves were also seen on the return scan, indicating that the oxidation products were stable on the voltammetric time scale.

Sharma et al(60) studied the electrochemical behaviour of the medicinally important 4-(4`-sulphonamoyl)hydrazono-1-phenyl-3-methyl-2-pyrazolin-5-ones at dropping mercury (dm) and glassy carbon electrodes. At DME, all six compounds exhibited a single, well-defined, 4-electron wave in the pH range 2.5-12.0. Polarographic 4-electron wave was found to be diffusion-controlled and irreversible. Similary, cyclic voltammetry of these compounds at glassy carbon electrode exhibited a single peak. Peak potentials showed shifts towards negative potential with pH with linear segments up to pH 8.2 and are practically pH-independent at higher pH values. An anolic peak at positive potential was observed in the reverse scan. Controlled potential electrolysis and coulometric studies gave the value of the n as 4.0±0.1 in the pH range 2.5 to 10.0 and two major end products were formed, one was identified as sulphanilamide and the other as 1-phenyl-3-methyl-4-amino-2-pyrazolin-5-one on the basis of IR and NMR studies. On the basis of DCP, LSV, CV, CPE, coulometry and spectral analysis, a mechanism has been postulated for the reduction of these compounds at dm and glassy carbon electrodes.

Aly(61) applied the cyclic voltammetry for studying the cathodic reduction behaviour of 3-azo-[4-(diazin-2-yl)-benzene-sulphonamido-]-1-oxo-4-thia-spiro(4,5)decan-2-one sodium salt, as azo dye sulpha drug, at the hanging mercury electrode in different supporting electrolytes. viz., perchlorate, acetic acid-acetate buffer, nitrate and phosphate, at different pH values ranged from 1 to 11 and different ionic strengths (0.01 -0.15M). The two related compounds for the sodium salt of azo dye sulpha drug have been also studied in acetic acid - sodium acetate buffer (pH - 3.45). Direct current sweeping voltammetry (DCSV) has been used for the determination of the drug under investigation. The effect of the different parameters, e.g. initial potential, scan rate, ...etc has been tested. The detection limit has been determined for azo dye sulpha drug and its related compounds. The method was applied to the determination of the compounds in urine sample.

Jain et al(62) studied the electrochemical behaviour of 2-(4-sulphonamoyl) hydrazonobutyrate-1,3-dions and sulphonamoylazo-aminobenzenes over a wide range of pH at dropping mercury as well as glassy carbon electrodes. Both types of compounds exhibited a 4-electron reduction reaction at both electrodes. At pH >4.5, 2-(4-sulphonamoyl)-hydrazonobytrate-1,3-dions exhibited a 2e-reduction wave at higher potentials. Both compounds undergo a 2e-oxidation reaction. On the basis of polarogaphy, linear and cyclic voltammetry, controlled potential electrolysis, coulometry, and spectral analysis, a detailed mechanism has been postulated for the reduction as well as the oxidation.

Gupta et al(63) studied the reduction mechanism of some azo-compounds in various buffer of pH ranging between 2 and 12. In acid and alkaline media, the products of reduction were not identical. The reduction is primarily acid catalyzed at low and high pH values. At high pH values a part of the reduction is in the homogeneous solution. Consequently, the following different pathways are possible:

(i) The 2e wave of azo compound at pH < 7 appears at less negative potential and is pH-independent. In acid media, the uptake of H^+, 2e was followed by fast proton attack. This protonated hydrazo derivative may undergo cleavage of N-N to form diimine derivative which is reduced to 2,4-dihydroxyaniline derivative by further consuming $2H^+$ and 2e, thereby totaling 4e for the entire process.

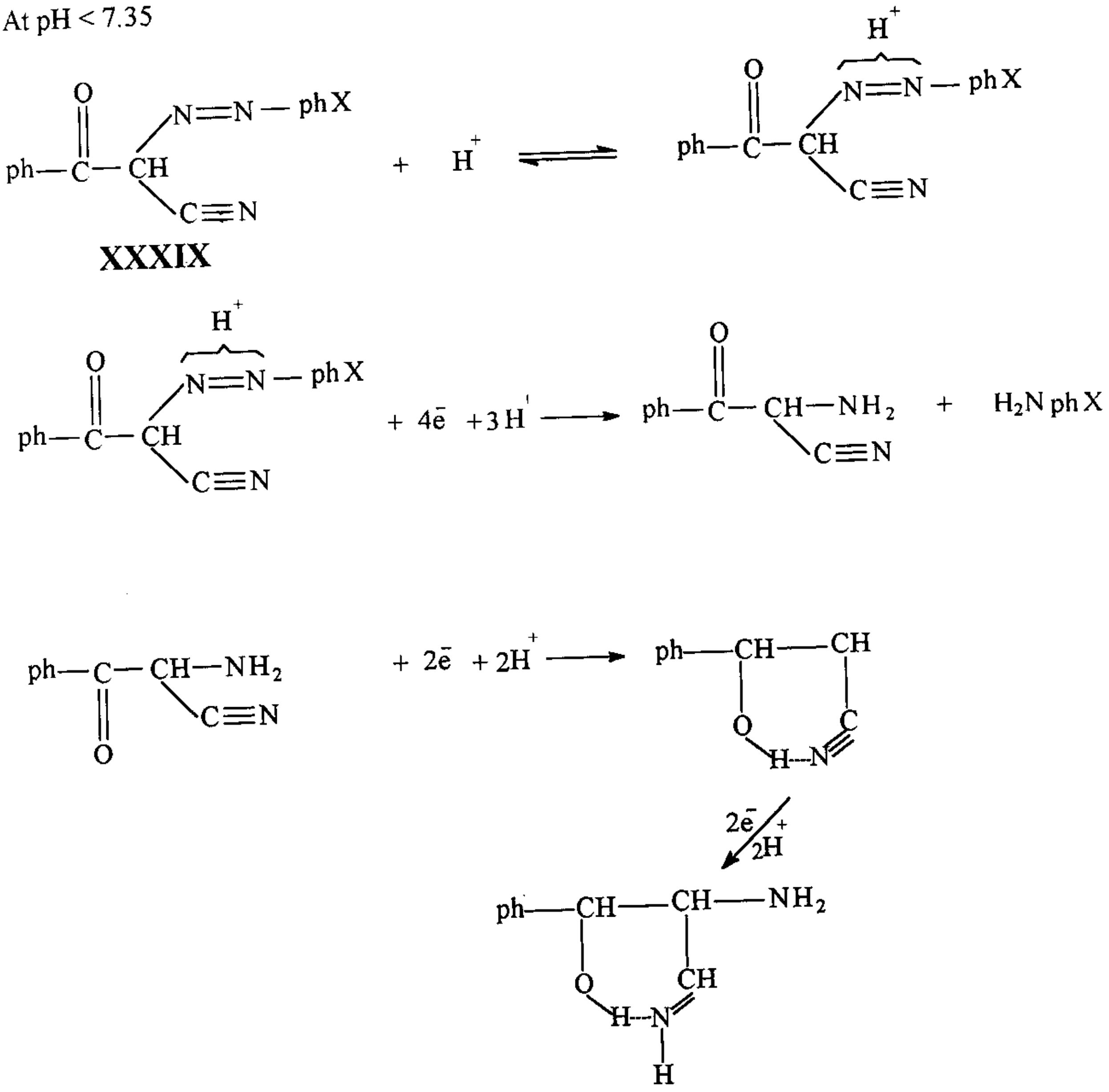
ii) At $7 < pH < 12$, the height of the wave is less than that observed in acidic medimn. The first step seems to be $2H^+$, 2e resulting in the formation of hydrazo derivative, followed by a fast base (OH^-) attack and simultaneusly undergoing hydolysis to produce diimine.

Husain et al(64) studied the polarographic behaviour of 4-(4`-nitrophenylazo) resorcinol in B.R. buffer solutions over a wide range of pH. The ionic strength (μ) is adjusted to 0.4 M with KCl. The results showed that the compound exhibited a well-defined 2-electron wave in acidic solutions of pH < 4.0. Within the pH range 4.0-6.7, two 1-electon reduction waves were observed whereas in neutral and slightly alkaline media (pH = 6.9 – 9.0) three waves of different heights were observed. In strongly alkaline solutions (pH > 11) only 2-electron wave is observed.

The $E_{1/2}$ is shifted cathodically with increasing the pH indicating that proton is involved in the electrode process. The same results were obtained by using differential pulse polarography. It was found that the first two waves observed in the pH range 7-9 are due to the reducton of the N=N center involving two electrons and the third wave represents the reduction of the NO_2 group to the NHOH consuming four electrons.

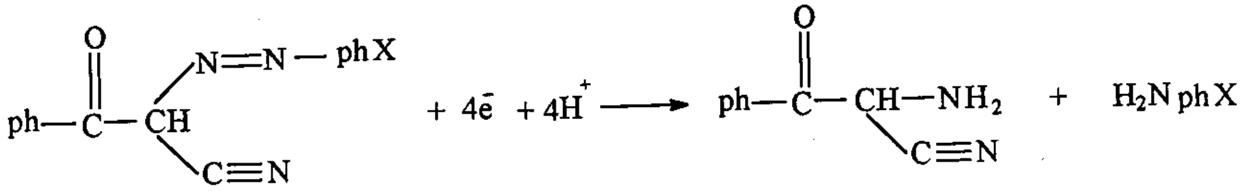
Moharram(65) studied the polarographic behaviour of α-cayano-acrylazoacetophenone (XXXIX) and some of its derivatives in aqueous B. R. buffer solutions of pH 2.6-11.4 containing 40% (v/v) ethanol at DME. The medium and substituent effects on the electrode reaction are classified. Values of symmetry coefficient (α) and heterogeneous rate constant (k_s) of the electron transfer are evaluated. The half-wave potential ($E_{1/2}$) value is determined by a fitting procedure using digital simulation CONDECON software. Chronoamperometric and chronopotentiometric techniques and convolution-deconvolution analysis of the recorded CV data allowed measurement of the diffusion coefficieats (D) for the compounds examined. The electrochemical reaction mechanism was suggested to be as the following:

At pH < 7.35



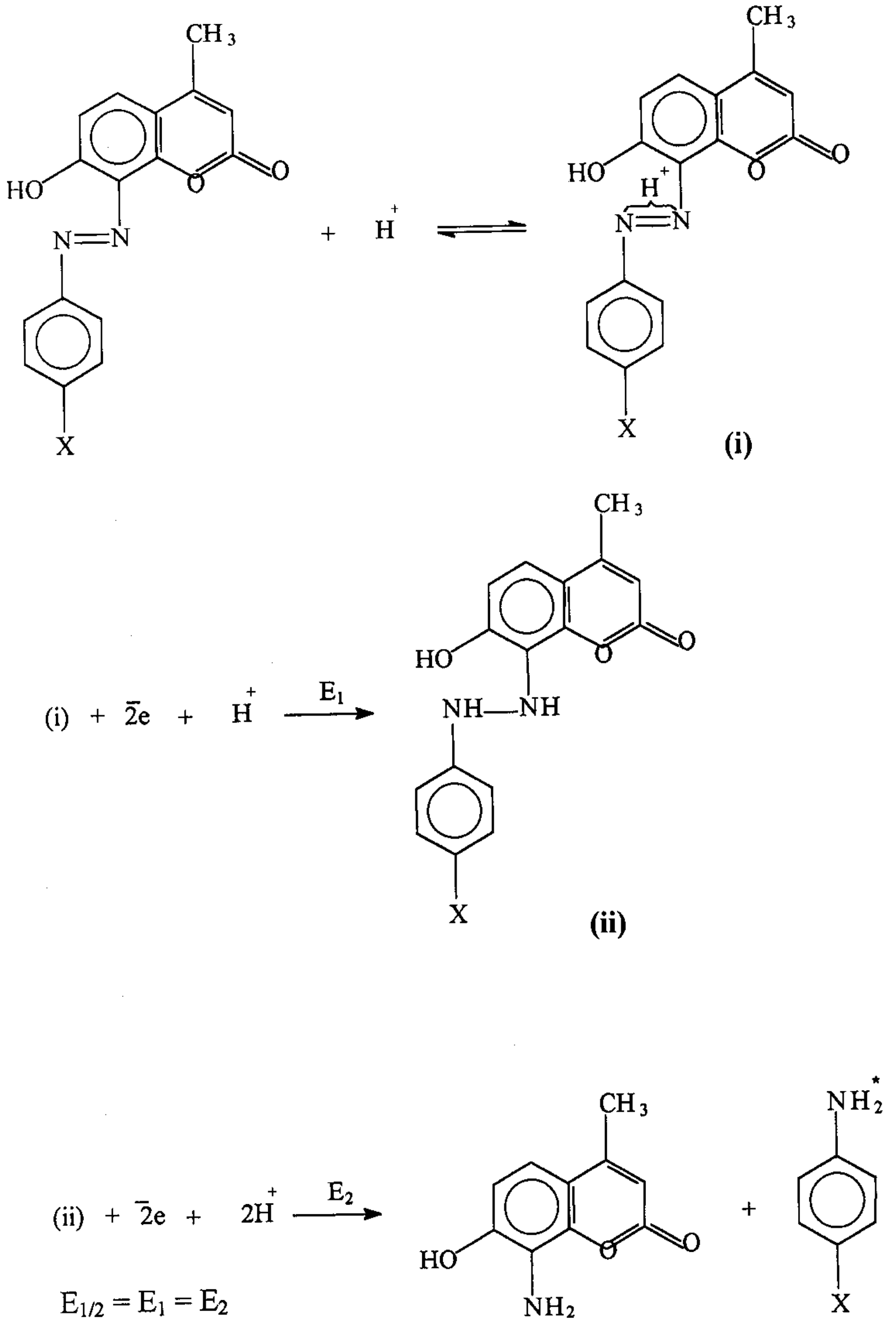
XXXIX

At pH > 7.35



Jain et al.(66) studied the electrochemical reduction of 1-(2,4-dinitrophenyl)-3-phenylamine-5-methyl-4-arylazopyrazoles (XXXX) over a wide pH range at DME and GCE. These compounds give two

El-Hallag et al.(68) studied the electrochemical behaviour of 2-one-4-methyl-7-hydroxy-8-arylazo coumarine and its substituted derivatives in 40% ethanolic aqueous buffer solutions of pH 2.3-11.5 by dc-polarography, dp-polarography, cyclic voltammetry, controlled potential electrolysis and digital simulation methods. These compounds were reduced in a single 4-electron reduction wave which assigned to the reduction cleavage of the azo group. The wave height was practically constant over the entire pH range studied. $E_{1/2}$ of these compounds shifted towards more negative potential with increasing pH indicating thereby the involvement of protons in the reuction process. One cathodic peak was obtained by cyclic voltammetry. The peak potential of the cathodic peak shifted to more negative potentials as the pH of the solution and the sweep rates are increased. The absence of anodic peak indicated the irreversible nature of the electrode process. The evaulated kinetic parameters were verified by digital simulation using the CONDECON software and then compared with the experimental ones. The reduction step took place for the azo group via the saturation of the N=N by two electrons and cleavage of the N-N bond by another two electrons according to the following pathway :



$E_{1/2} = E_1 = E_2$

* identified product