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"SYNTHESIS AND STUDY OF CHELATING PROPERTIES OF POLY [AZO-(8-HYDROXY QUINOLINE)]"

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ARTICLE INFO	ABSTRACT
Article history Received 25/11/2019 Available online 31/12/2019 **Keywords** Poly [azo- (8-hydroxy Quinoline)] (PAHQ), Poly chelatcs of PAHQ.	Poly [azo(8—hydroxyquinoline)] (PAHQ) was synthesized by alcoholic alkaline reduction of 2, 4 dinitro1-napthol. The polymers synthesized at time intervals were characterized by elemental analysis, IR spectra and thermogravimetric analysis. The number Average molecular weight ($\overline{M_n}$) was determined by non-aqueous titration. Polymetric metal chelates of Cu^{+2}, Co^{+2}, Mn^{+2}, Zn^{+2}, Ni^{+2} with PAHQ polymer were prepared and characterized.

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INTRODUCTION

Polymers with azo groups are well known a class of aromatic azo polymers has been made of catalysed oxidative polymerization of aromatic diamines [1-3]. Ravve and fitko [4] have prepared azo polymers by coupling of various bisdiazonium salts to different poly phenols or phenol formaldehyde condonsales. The azo polynmers have also been prepared by decomposition of bisdiazonium salt [5], or by their pre cursors [6] by hydrogen abstraction from aromatic diamines by free radical [7], by poly conensation of azo benzene derivatives or by homo polymerization of dyes having [8-11] olefinic groups [12-14]. The azo polymers i.e. poly (azo arylenes) and azo poly chelates because of their infusible and insoluble nature make them difficult to apply for dyeing, pigmentation or to fabricate. The introduction of OH groups into these polymer chains may alter the properebes up to great extent. In recent years the study of electrical properties of organic polymers has made much progress. Several polymers, modified by dopping or by metal atoms, are classified us organic semi conductors [15, 16] well known olymers are poly acetylene, poly phenylene, polyaniline etc. [17-22] Most of the conducting polymers are of conjugated chain systems. Some dopents enhance the conductivity of the polymers, [23-26] one such are in which poly (azoarylenes) having conjugated system are reported [27], but their conducting properties has not been studied Hense so called are polymers and poly azo chelates has been thought to synthesis for its electrical conducting properties. The preparation of azo arylene polymers based on dinitro arylene has been reported (Desouza and Deoliveria 1978) hense it was thought to be of interest to study the polymers based on alcoholic alkaline reduction of 2, 4 dinitro 1-napthol. So the work described in the present communication is connected with the synthesis, study characterization and chelation with metal ion of poly [azo (8-hydroxyquinoline)] (PAHQ)

EXPERIMENTAL

All the chemicals used were of either analytical grade or laboratry grade.

Preparation of Poly [azo (8-hydroxy Quinoline)] polymers by self – polymerization of DNP (2,4, dinitro-napthol) self-polymerization of DNP was carried out by the method – reported for polymerization of dinitro arylenes (Desouza and Deoliveria 1978). The Polymerization was carried out for different intervals. A typical method of polymerization is given here.

To a solution of 2, 4 – dinitro-1-napthol (25.9 gms, 0.1 mole) in tri ethylene glycol (Trigol) (150 ml), KOH (44.8 gm, 0.8 mole) was added gradually and stirred well at room temperature up to complete dissolution of KOH. Then the reaction mixture, under mechanical stirring was warmed to $80 - 85^0C$ for 15 min. The temperature was then increased to $135 - 140^0C$ and the reaction was continued for 5h. The reaction was stopped by lowering to temperature to 100^0C and neutralized by adding a mixture of ethanol – HCL (50 : 50 V/v) the resulting neutralized mixture was then poured into ice water (500 ml) and the solid product was collected by filteration, washed with water and dried in an oven. Finally, it was purified by dissolving in DMF and repreciptating by addition of water. The yield of black powder was 82%.
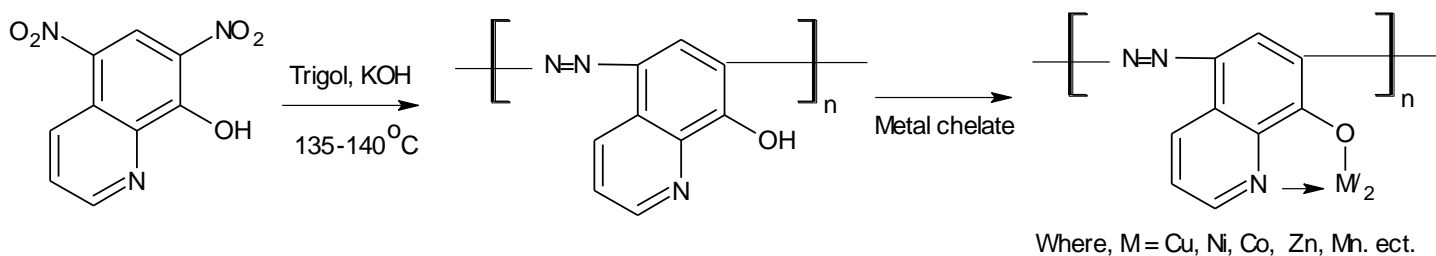

Where, M = Cu, Ni, Co, Zn, Mn. ect.

Table:1 ELEMENTAL ANALYSIS.

% C		%H		%N	
Calculated	Found	Calculated	Found	Calculated	Found
54.27	54.2	2.51	2.5	35.17	35.2

Preparation of polychelates of PAHQ polymers;
As a typical Procedure, Polychelate of PAHQ is described below.
Formation of Cu^{2+} chelates i.e. PAC-1:

The Sodium salt solution (0.01M ligand) of ligand i.e. PAHQ was added drop wise to a solution of cupric nitrate hexahydrate (0.005 mole) in 100 ml of water with rapid stirring. The so called pH of the resultant solution was 4.5. A greenish blue solid precipitated out. It was allowed to settle. Then it was digested on water bath at 70ºC for about 2 hours. The solid mass was filtered, washed with 1:1 mixture of water:ethanol and finally with acetone, and air-dried, yield was 72%. The resulting complex was powdered well and further dried at 70ºC over a period of 24 hrs.

Formation of Co^{2+} chelates i.e. PAC-2:

It was obtained as black precipitate by mixing a solution of Sodium-salt of ligand i.e. PAHQ (0.01 mole) with that of cobalt nitrate hexahydrate (0.005 mole) in 100 ml of water. The final pH was 6.0. Complex was purified in the same manner described earlier. The purified chelate yielded 72%.

Formation of Mn^{2+} chelates i.e. PAC-3:

The Sodium salt solution (25ml) of each ligand i.e. PAHQ (0.01 mole) was stirred in a solution of manganese chloride hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The yield of chelate was 74%.

Formation of Zn^{2+} chelates i.e. PAC-4:

The Sodium solution of each ligand i.e. PAHQ (0.01 mole) was added to that of zinc nitrate hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The product was purified in the same manner described earlier. The dried chelate in black powder, yield 68%.

Formation of Ni^{2+} chelates i.e. PAC-5:

The Sodium solution of each ligand i.e. PAHQ (0.01 mole) was added to that of nickel chloride hexahydrate (0.005 mole) in 100 ml of water. The resultant pH was 5.6. The product was purified in the same manner described earlier. The dried chelate in balck powder, yield 74%.
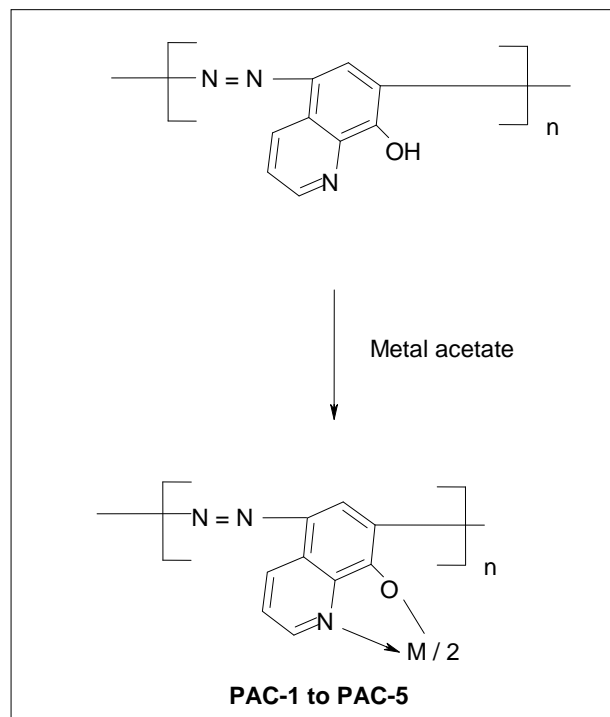
PAC-1 to PAC-5

Where, M= Cu, CO, Mn, Zn, Ni etc.

Analysis of PAHQ polymers and polymeric chelates.
The details and the results of analyses of these polychelates are presented in table below.

Table:2 Characterization of Poly Azo Chelates i.e. PAC-1 to PAC-5.

Poly azo Chelates	Molecular Formula	M.Wt Gm/mole	Yield %
PAC-1	$C_{18}H_8N_{10}O_2\ Cu^{+2}.2H_2O$	495.5	72
PAC-2	$C_{18}H_8N_{10}O_2Co^{+2}.2H_2O$	491	72
PAC-3	$C_{18}H_8N_{10}O_2Mn^{+2}.2H_2O$	487	74
PAC-4	$C_{18}H_8N_{10}O_2Zn^{+2}.2H_2O$	497	68
PAC-5	$C_{18}H_8N_{10}O_2Ni^{+2}.2H_2O$	491	74

The elemental analysis of polymers and their polychelates were carried out on a C, H. N, O, S elemental analyzer, carlo Erba, Italy. The analysis of metal ions in the polymetric chelates were carried out by the decomposition of unknown amount of chelate by mineral acids. The metal content was estimated by a method reported in literature (Vogel 1979).

Table:3 Elemental analysis of PAC-1 to PAC-5.

Poly azo Chelates	% Metal Analysis		Elemental analysis					
			%C		%H		%N	
	Cald.	Found	Cald.	Found	Cald.	Found	Cald.	Found
PAC-1	12.81	12.80	43.59	43.60	2.45	2.45	28.25	28.25
PAC-2	12.01	12.00	43.99	44.00	2.47	2.45	28.51	28.50
PAC-3	11.29	11.25	44.35	44.34	2.48	2.45	28.74	28.75
PAC-4	13.07	13.00	43.46	43.45	2.44	2.44	28.16	28.15
PAC-5	12.01	12.00	43.99	44.00	2.47	2.46	28.51	28.50

IR Spectral Data

IR Spectra were performed by using KBr pellets on Nicolet FTIR – 760 spectro photometer. PAHQ polymers and polychelates were characterized by infra-red spectra.

Table:4 Anticipated IR spectrum for Azo Polymers i.e. Poly [azo (8-hydroxy Quinoline)] & Poly Chelates 1 to 5.

Sr. No.	GROUPS	IR frequencies (Cm^{-1})
1.	-N=N-	1406 ± 14
2.	Aromatic.	3050, 1600, 1010
3.	-OH of Quinoline moieties	3400-3360, 1420
		1090, 1280
4.	-CH$_2$-	2780-2820
5.	-CH$_3$-	3200-3650

Thermo gravimetric analysis of polymers and poly chelates were carried out on a PERKIN ELEMER PYRIS in air at a heating rate of 10^0C/min.

Experimental (TGA)

The thermogravimetric analyses (TGA) of sample have been carried out by using "PERKIN ELMER PYRIS 1 TGA" in a slow stream of air. The boat prepared from platinum foil would hold the sample for analysis. It is properly washed and dried. It was suspended on the quartz rod in the TG balance. The powdered sample (about 5 mg) was placed in the boat. The sample in the boat is covered by a quartz tube in which the flow of air was maintained. The weight of sample was noted on TGA balance. The whole assembly was brought down in the furnace. It was ascertained that the boat was hanging on quartz rod. The experiment was started by the heating the system at a constant rate of 10°C/min. Simultaneously change in the weight was recorded automatically with time (temperature). This will reveal percentage weight loss of material s a function of the time and also of temperature. The experiment was stopped at about 650 °C, when there was no further decrease in weight.

Table:5 *Thermogravimetric analysis of metal chelates of PAHQ.*

Chelate	% wt loss at temperature			
	250	300	350	400
PAC-1 (Cu^{+2})	6.5	8.0	14	76
PAC-2 (Co^{+2})	3.2	5.5	23	70
PAC-3 (Mn^{+2})	6.7	14.6	21	76
PAC-4 (Zn^{+2})	6.5	19.2	64	75
PAC-5 (Ni^{+2})	7.3	25.0	78	86

The reflection spectra of the poly chelates were recorded on a Beckmann Du spectro meter with reflectance attachment using M$_g$O as the reference.

Table:6 *Reflectance spectrum data of Cu^{2+} chelates.*

Metal Chelates	Observed transition energies (cm-1)	
	CT	2B1g$\rightarrow$ 2A1g
PAC-1	23990	15765

Table:7 *Reflectance spectrum data of Co^{2+} chelates.*

Metal Chelates	Observed transition energies (cm-1)		
	4T1g(F) → 6T2g(u1)	4A2g(u2)	4T1g(P)
PAC-2	23957	18122	8742

Table:8 *Reflectance spectrum data of Mn^{2+} chelates.*

Metal Chelates	Observed transition energies (cm-1)		
	6A1g→ 6A1g(4Eg)	4T2g(4G)	4T1g(4G)
PAC-3	23888	18343	16850
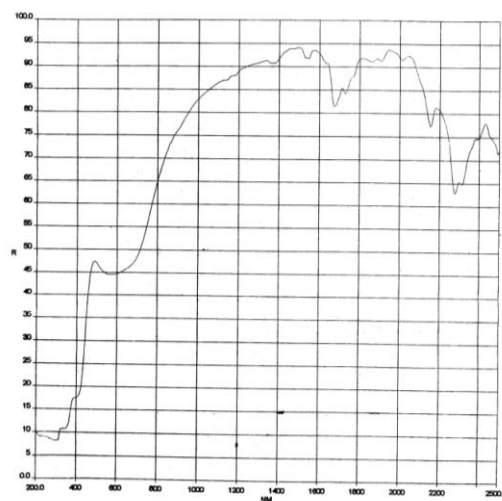
Fig. 1 Reflectance spectrum of PAC-8 chelate.

Conductometric Titration of PAHQ polymer were carried out in pyridine against sodium methoxide (MgOme) in pyridine as standard. The valur of the number average molecular weight (M_n^-) was calculated following a method of conductometric titration reported by chatterjee 1970.
Conductance measurements was METROHM KONDUCTO SKOP E 365.

Experimental and Calculations :-
The azo polymer (50 mg) was dissolved in pyridine (50 ml). the solution was introduce into the conductivity cell. The solution was stirred well throughout the titration with the help of a magnetic stirrer. Standard sodium methoxide solution (0.1 N prepared in pyridine) was taken in a microburette and was added to the solution in the conductivity cell in amounts as shown below.
(a) 0.05 ml upto 1.0 ml
(b) 0.1 ml upto 3.0 ml
(c) 0.20 ml upto the end
About 1 to 2 min time lapse was allowed after each addition of sodium methoxide solution and before addition of new lot of the titrant. 1.0 equivalent of the dye would require 1.0 equivalent (1000 milliequivalents) of the base for compete neutralization since out of the hydroxyl group present on repeat unit only hydroxyl group will be neutralized. Hence total moleequivalents (X) of the base required to neutralize 100 gm of the polymer would be,

$$= \frac{1000 \times 100}{\text{Mol. wt. of the repeating unit}} = X$$

Let "Y" be the milliequivalents of the base used up in the shortest break (first break) in the titration curve. Then by principle the degree of polymerization   would be,

$$\overline{P} = \frac{X}{Y}$$

And the number average molecular weight of polymer would be,

The assumption in which the degree of polymerization is calculated would be invalid firstly. If some of the chains do not contribute any hydroxyl group during the shortest interval and secondly. If some of the chains contribute more than one group during the first interval.

The results of the conductormetric study are presented in table. the selected curves for conductormetric titrations are shown in figure.

Table:9 *Results of conductometric study of azo polymers (PAHQ).*

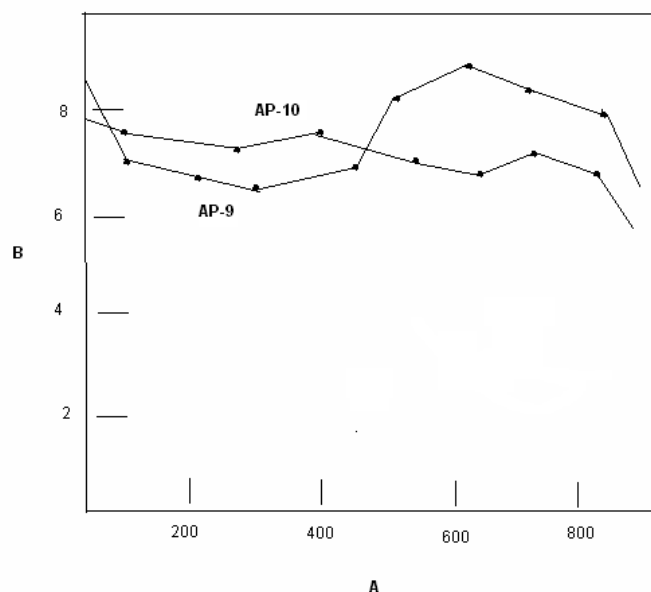| Polymer	Milliequivalents of base required for neutralization of one OH Group (First Break) (Y)	Milliequivalents of base required for Complete neutralization (X)	Degree of polymerization Dp = X/Y	Number average molecular weight Mn
PAHQ	60	835	14.0	1655

Fig. 2 Conductometric titration curve of (PAHQ).

RESULTS AND DISCUSSIONS

The brief account of the thermal behavior of samples in air is given below:

(I)   Each chelate degradation in two steps.

(II)   The degradation of all the chelates start in the temperature Range of 200 to 350^0C depending upon the natures of chelate.

(iii)   The wt. loss amount in this first stage is in between 4.5 to 7 % this may be due to water molecules associated in to the chelates. This is supported by Nikolaev et al. [28].

(IV) The second stage of decomposition of all chelates is rapid with the loss of mass about 50%. This is due to "in situ" formation of metal oxide during degradation. Which accelerate the rapid degradation of chelate.

(V)   The last stage of digression cause a mass loss of about 80%. This is due to loss molecular fragments of polymers.

Reflectance spectroscopy is specially useful technique in the study of geometric & electronics structure of metal chelates of transition metal complexes. [29] The diffuse electronic spectrum of Cu^{+2} complex shows two broad bands 15765 cm^{-1} and 23990 cm-1, $^2B_{19} \rightarrow A_{19}$ translation and charge transfer respectively. This indicates the octahedral structure. These findings are in agreement with data reported by several research works. [30-34].

Electronic spectral data of Co^{+2} indicates that transition observed in the 8742 cm^{-1} are assigned to $^4T_{19}(F) \rightarrow \, ^4T_{29}(F)(V_1)$ and another bands 18122 cm^{-1} and 23975 cm^{-1} may be attributed to $^4T_{19}(F) \rightarrow \, ^4A_{29}(F)(V_2)$ and $^4T_{19}(F) \rightarrow \, ^4T_{19}(P)(V_3)$ transitions. This indicates the octahedral structure. Similar observations are also reported in the literature. [35, 36]

The Mn^{+2} complex also the bands at 16850 cm^{-1}, 18343 cm^{-1}, 23888 cm^{-1} suggest the $^6A_{19} \rightarrow \, ^4T_{19}(^4G)$, $^6A_{19} \rightarrow ^4E_9(^4G)$ and $^6A_{19} \rightarrow ^4T_{29}(G)$ Transition. This indicates the octahedral structure. Similar observations are also reported in the literature [37]

This indicates the octahedral structure.

The values of $\overline{M}_n$ of the azo polymers estimated by the above said methods agree well. Within limits of experimental errors. The degree of polymerization of polymers varies from 10 to 14 depending upon the nature of monomer used. The result shows that the degree of polymerization increase with increases in reaction time.

CONCLUSION

Structures of Polyazo [8 –hydroxy quinoline] is confirmed by elemental analysis, IR spectra, TGA and reflectance spectra. PAHQ complexes exhibit octahedral structure by reflectance spectra, conductometric study of azo polymers (PAHQ) shows that the degree of polymerization increases with increase in reaction time. This study may afford good electrical conducting properties of complexes and good electrical conducting material.

ABBREVIATIONS

$\overline{M}_n$ - molecular weight

PAHQ   - Poly [azo- (8-hydroxy Quinoline)]
DNP   - 2,4, dinitro-napthol

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