

ANALYTICAL STUDIES OF THE IRON AND MANGANESE COMPLEXES OF 7-NITROSO -8- HYDROXYQUINOLINE -5- SULPHONIC ACID

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ABSTRACT

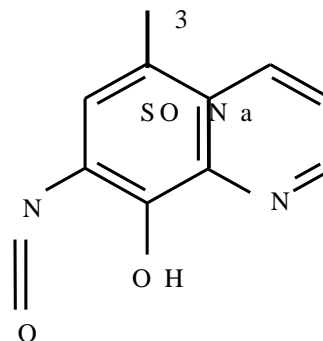
The ligand 7-nitroso-8-hydroxyquinoline-5-sulphonic acid (H_2L) possesses the coordination sites of 2-nitroso-1-naphthol and of 8-hydroxyquinoline, where the hydroxyl group is functional at either site. The absorption maximum of the complex formed with iron and Mn is at 700nm, at which wavelength the mole extinction coefficient of $Fe(H_2L)_3$ is $27,540 \text{ dm}^3 \text{ mol}^{-1}$ and $Mn(H_2L)_3$ is $44,500 \text{ dm}^3 \text{ mol}^{-1}$ respectively. The stoichiometry of H_2L reagent with the metal ions by the method of continuous variation gave the ratio of iron to ligand as 1:3 and manganese to Ligand as 1:3. Chemical analysis, and physicochemical evidence are compatible with formulating the Fe(II) and Mn (II) complexes as $H[M(HL)_3]$ where the 2-nitroso-1-naphthol site is involved in metal chelation.

Keywords: Analytical Studies, Iron, Manganese, Complexes, 7-nitroso -8, Hydroxyquinoline -5- Sulphonic acid

INTRODUCTION

The ligand 7-nitroso-8-hydroxyquinoline-5-sulphonic acid, denoted (H_2L) combines the characteristics of two of most reactive ligands, 2-nitroso-1-naphthol and 8-hydroxyquinoline. The existence of two coordination sites in this ligand is interesting and complex formation with this ligand should occur through only one site (Eugene and Belford, 1964).

This ligand is represented structurally as:



Nitrosonaphthols, 8-hydroxyquinoline and their sulphonated derivatives are known ligands, which react with metal ions to form neutral complexes with loss of a phenolic proton (Bajue *et al.*, 1975).

H₂L ligand can be regarded as 2-substituted 8-hydroxyquinoline in which the 2-substituent contains potential donor atom. The ligand possesses the additional feature that the quinoline ring system provides a completely rigid framework for the donor atom apart from combining the characteristics of two of the most reactive groups (Osimo and Niemi, 1972).

Nitrosonaphthol derivatives such as nitroso naphthols and sodium -1-1-nitroso-2-hydroxynaphthalene 3,6 disulphonates (nitroso-R-salts) are known to be selective and sensitive colorimetric reagents for cobalt and iron; while 2-nitroso-1-naphthol forms chelate complexes with a number of metal ions such as Cr(II), Cu(II), Fe(III), Ni(III), Pd(II) and U(VI) (Toei and Motomizu, 1976; Sugii and Ogawa, 1979).

The reacting group of oxine comprises a phenolic hydroxyl and a basic nitrogen in position to form a five-membered ring; which ring chelates are more stable than the 6-membered rings due to steric hindrance by the benzene portion. Oxine reacts with at least 43 metals, which usually form hydroxides with ammonia (Stary, 1964).

Eldawy and Eishabouri (1975) applied this ligand (H₂L) with significant success, to the determination of iron (II) in multicomponent pharmaceutical preparation; without prior separation from other mineral ions, vitamins, and hormones which occur along with Fe (II) in geriatric preparation.

Ring nitrosation used in the ligand preparation is an electrophilic substitution reaction in which the attacking reagent is either the nitrosonium ion, NO or some species like H₂O⁺ - NO or NOCl that can easily transfer NO to the ring. Nitration ordinarily occurs only in rings bearing the powerfully activating dialkylamino (-NR₂) or hydroxyl (OH) group (Morrison and Boyd, 1980).

MATERIALS AND METHODS

Experimental

Apparatus

Infrared spectra were obtained from hydrocarbon mulls utilizing, an ATI Matteson Genesis FTIR colorimeter.

Unicam 8625 UV/VIS spectrometer and Pye Unicam 929 AA atomic spectrometer were used to determine the absorbance values recorded as well as to obtain the spectra presented. pH measurement were made with a Philip PW 9408 pH meter with glass Calomel electrode.

The ¹H NMR spectra were scanned with a Varian mercury YH 200 spectrometer operating at 200 MHz.

Reagents and solutions

All solutions were prepared with distilled water. Buffers were prepared in the usual manner using the appropriate salts as described elsewhere (James and Prichard (1974).

Manganese standard solution: 1.0g of 99.8% manganese metal was dissolved in 10ml of redistilled HNO₃ and diluted to 100ml with 1% (v/v) HCl such that 1ml = 1mg Mn.

Triethanolamine Buffer (pH 7-9): 70ml of triethanolamine was dissolved in 60ml of water. Between 4-30ml of concentrated nitric acid were added to the solution to adjust the pH to the desired value and the volume was made up to 1 litre.

Standard iron solution: 0.01g of pure iron was dissolved in 10ml of HCl (1:1) and 1ml of bromine water, and boiled to removed excess bromine. 200ml of HCl (1:1) were added, cooled and diluted to 1litre in a volumetric flask with water.

0.10 percent 7-Nitroso-8-hydroxyquinoline-5-sulphonic acid solution: 0.30g of the reagent were dissolved in a mixture of ethanol and water (1:4) and then made up to 100ml in a calibrated flask. Residue was filtered off.

7-Nitroso-8-hydroxyquinoline-5-sulphonic Acid as a ligand and its metal complexes were prepared according to reported methods (Aly *et al.*, 1973).

Chelate combining ratio was established by a modified method of Diehl and Lindstrom (1959), in Table 3.

pH and spectral studies

The spectra of H₂L were run at wavelengths of 400, 500, 600 and 700nm respectively with 5ml of 0.5 percent of the reagent in acid medium of pH 3 and alkaline medium of pH 8; in Table I below.

Table 1: pH effect on Spectra

Wavelength of measurement (nm)	pH 3	pH 8
700	0.001 ± 0.00	0.015 ± 0.00
600	0.016 ± 0.003	0.018 ± 0.00
500	0.050 ± 0.00	0.040 ± 0.00
400	0.060 ± 0.00	0.058 ± 0.01

Effect of acidity on Extraction

A solution containing 100 mg of iron (III) metal ion was added to 5ml of 0.15 percent H₂L ligand in a stoppered separating funnel. The effect of interfering ions was circumvented by the addition of 3ml excess of the reagent. The solution was diluted with water to 25ml and made 0.20 M in H₂SO₄; then extracted with two 10-ml portions of butanol for 2min. The two extracts were combined in a 25ml flask and made to mark with n-butanol. The absorbance was read at λ_{max} of 700nm, (Table 2).

Table 2: The effect of acidity on extraction

Percent Extraction	Acidity (pH)
0	0
98	1
60	2
36	3
22	4

Determination of the stoichiometry of 7-Nitroso-8 - Hydroxyquinolinol-5-Sulphonic Acid by the Method of Continuous Variation.

The variation of absorbance at a constant wavelength (λ_{max}) of 700nm was observed for a series of solution containing different volumetric ratio of metal – to ligand (reagent). A concentration of 0.1 M of each metal was used and various volumes of 0.1M NHQS solution ranging from 0 to 2 ml were added to the metal solution by means of a micrometer syringe. The optical densities of these solutions were measured at 700 nm against a similarly prepared reagent blank using the modified method of Diehl and Lindstrom (1959). The metal solutions were buffered with 2ml of McIlvaine's citric acid – phosphate buffer at the start of the experiment.

Absorption Spectra of Manganese (II) with variation in pH

A 10 ml portion of standard Mn (II) chloride (MnCl₂.4H₂O) solution, 2ml. 5 percent hydroxylamine hydrochloride solution, 1ml complexing reagent solution and 2 ml buffer were diluted to 50 ml in a calibrated flask with distilled water.

Table 3: Stoichiometric studies of Fe(II) and Mn(II) with 7-nitroso-8- Hydroxyquinoline – 5- Sulphonic Acid, by the method of continuous variation

0.1M metal ion (ml)	0	0.2	0.4	0.5	0.6	0.8	1	1.2	1.4
0.1M ligand solution (ml)	1	1	1	1	1	1	1	1	1
Buffer solution (pH 5)	2	2	2	2	2	2	2	2	2
Distilled water (ml)	2	1.8	1.6	1.5	1.4	1.2	1	0.8	0.6

The absorbance of the solution was measured between 400-750 nm at various pH values against a reagent blank similarly prepared. The maximum absorbance occurred at 700nm and at pH 5 ± 0.5 .

Table 4: Spectra of Manganese (II) with variation in pH

pH	Absorbance at λ_{max} (nm)
2	0.010
4	0.013
5	0.015
6	0.014
7	0.012
8	0.010
9	0.009
10	0.006

RESULTS AND DISCUSSION

Figure 1 shows the result of the spectrophotometric examination of H₂L reagent. It indicates a virtually identical spectra at pH 3 and 8 respectively. This implies that this ligand can be used over a wide pH range for various determinations.

Figure 2 shows the degree or extraction of iron (III) with this ligand. The extraction falls at lower acidity probably due to the dissociation of a proton from the sulphonic acid group. At higher acidity, an extractable iron – ligand complex is formed. The formed species were highly hydrophilic due to the sulphonic acid group, and were rendered hydrophobic by the addition of 6ml n-butanol to enhance the percent extraction.

Figure 3 shows the effect of pH on Manganese – ligand complex. Maximum absorption occurs at 480 nm. The absorption at this wavelength rises to a maximum at about pH 8 and decreases to almost zero after 520 nm. The maximum absorption of the complex occurs at 700nm; thus the colour of the excess reagent has very little effect on the detection. The maximum peak height for Mn (II) was attained at pH 5.0 being pH used for the experiment.

Stoichiometric studies were carried out using the modified method of Diehl and Lindstrom (1959). The amounts of reagents used in this work are indicated in Table 3. The predominant complexes formed are shown in figure 4 for manganese (II) as PX₃ (1:3) with ϵ value 44, 500dm³mol⁻¹cm⁻¹ and figure 5 for Iron (II) as PX₃ (1:3) with ϵ value of 27,540dm³mol⁻¹cm⁻¹ respectively.

Figures 6 and 7 respectively show the infrared spectra of the disodium salt of the manganese and iron complexes with the H₂L ligand. The absence of a weak absorption in metal–ligand complexes (Figures 8 and 9), characteristics of nitroso group at 1400cm⁻¹ points to molecular interactions with these metal ions; while the C-C bonds at about 1600cm⁻¹ may be due to tautomeric oxime group. The bands about 3368.74 to 3435.32cm⁻¹ are due to O-H stretching frequency of the phenol group as well as nitroso, C-N, N-O, C=O, C=N and NOH groups.

The band around 1200cm⁻¹ appears to be aromatic band of sodium salt of sulphonic acid complex and that between 700-800 cm⁻¹ due to the sulphur-oxygen bond. This agrees well with findings by Bajue *et al.*, (1975).

The intense visible band in Na₂FeL may be due to charge transfer involving reduction of the iron (III) to iron (II) at 705 nm and similar charge transfer is feasible in Na₂MnL complex in the UV/visible spectra of nitrosophthols.

The sharp band at 910-895cm⁻¹ is probably due to S-O stretching frequency in sulphonic acids while the coordinated metal-oxygen bonds are Mn-O (832.22-762.78cm⁻¹) and Fe-O(600.99-470.11cm⁻¹) respectively.

The ¹H NMR spectrum of NHQS in dimethylsulphoxide is presented in figure 6 with reference to tetramethyl silane (TMS). This assessment is made on the basis of earlier work by corsini and Louch (1974). The figure shows shifts of the H₃ and H₄ protons in the range 8.5- 8.7 ppm which are influenced by substitutions in the phenolic ring. The H₄, H₆ and H₈ and H₂₊₃₊₄₊₆ protons

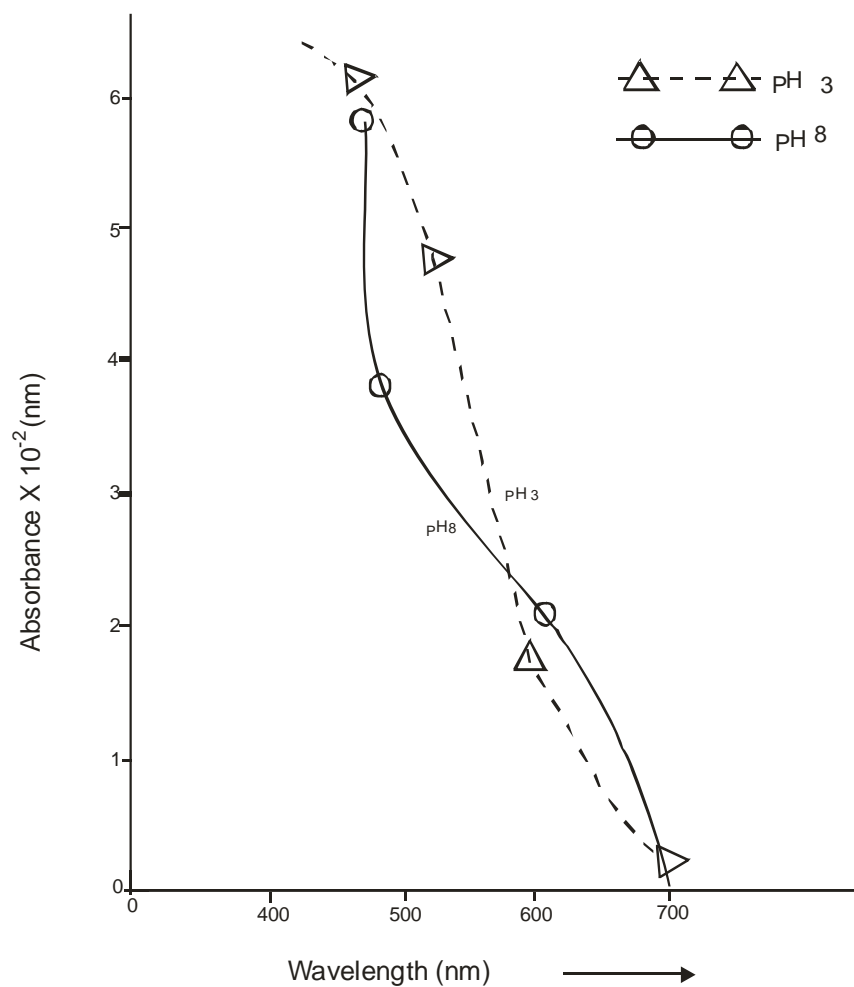


Fig. 1: pH Spectral curve for 5ml 1.5×10^{-1} percent NHQS ligand in Acid and Base media

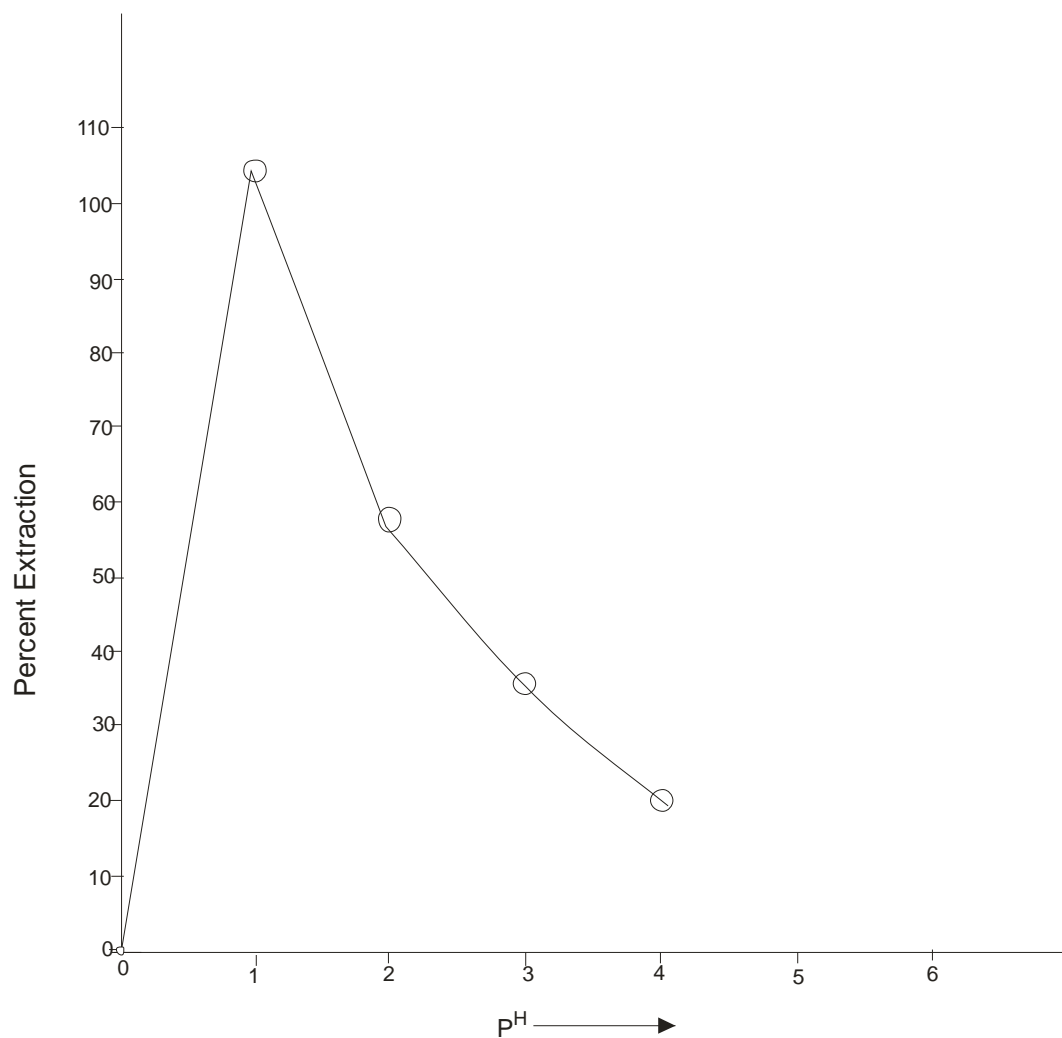


Fig. 2: The Effect of Acidity on percent Extraction of NHQS liqand

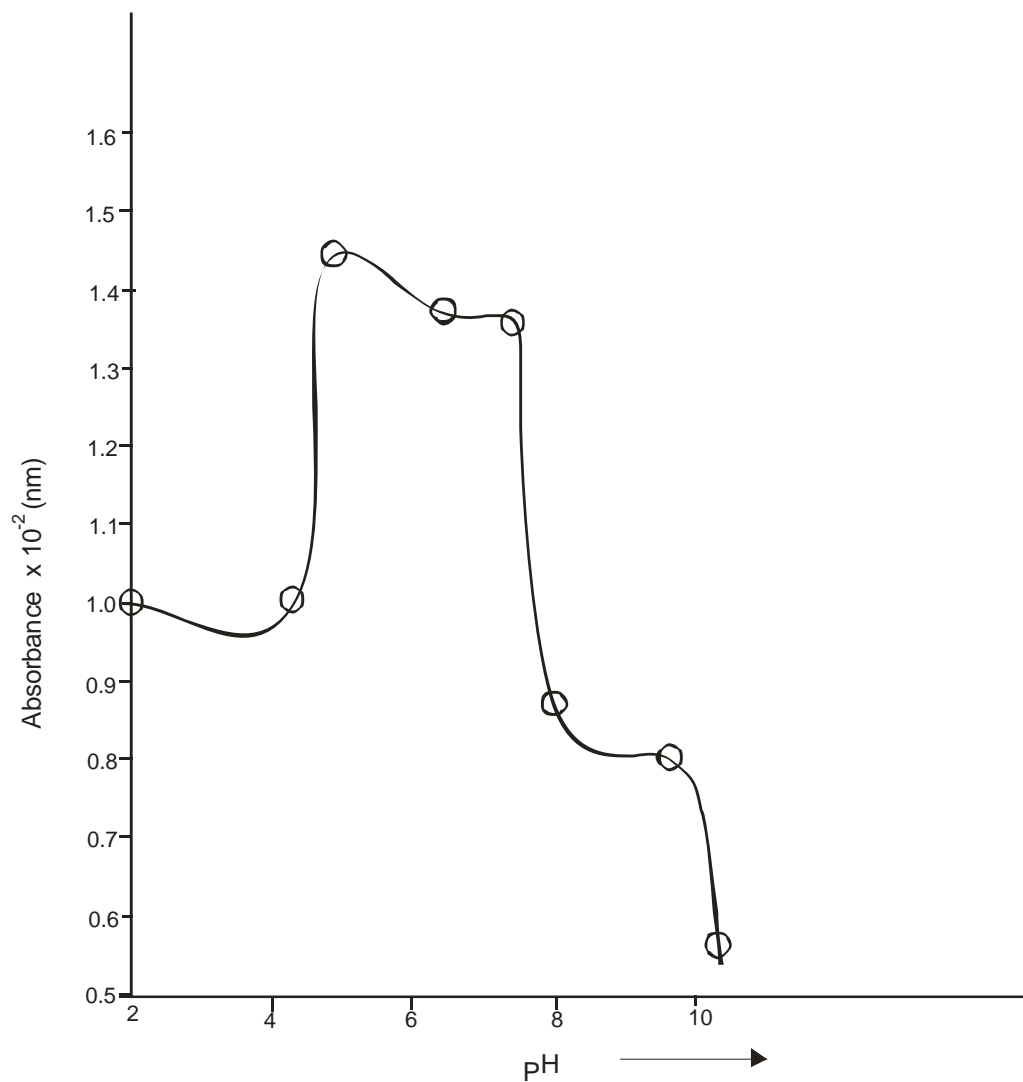


Fig. 3: Variation of Absorption spectra of Manganese (II) - NHQS Complex with variation in pH

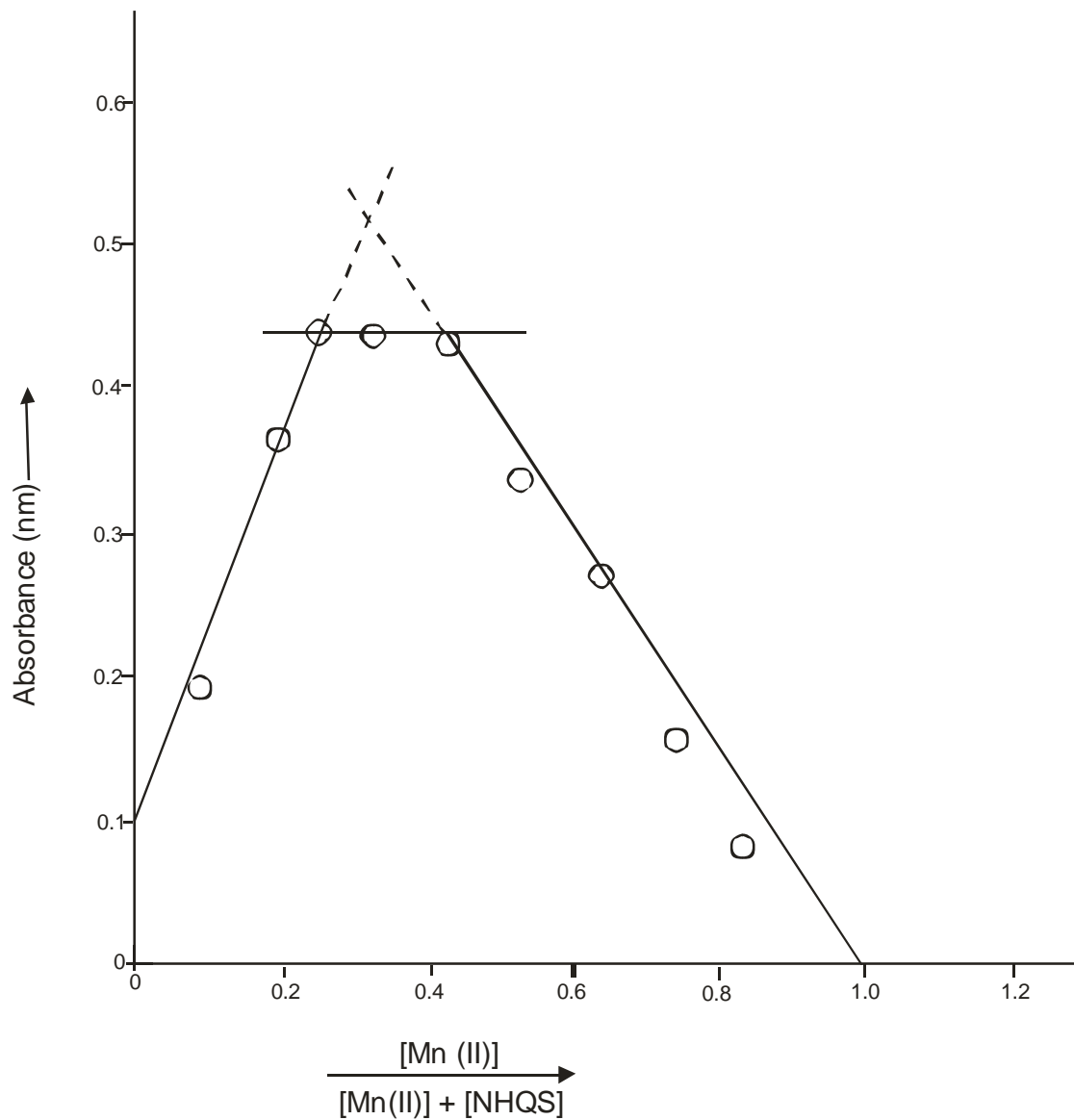


Fig. 4: Job's plot for Manganese - NHQS Complex

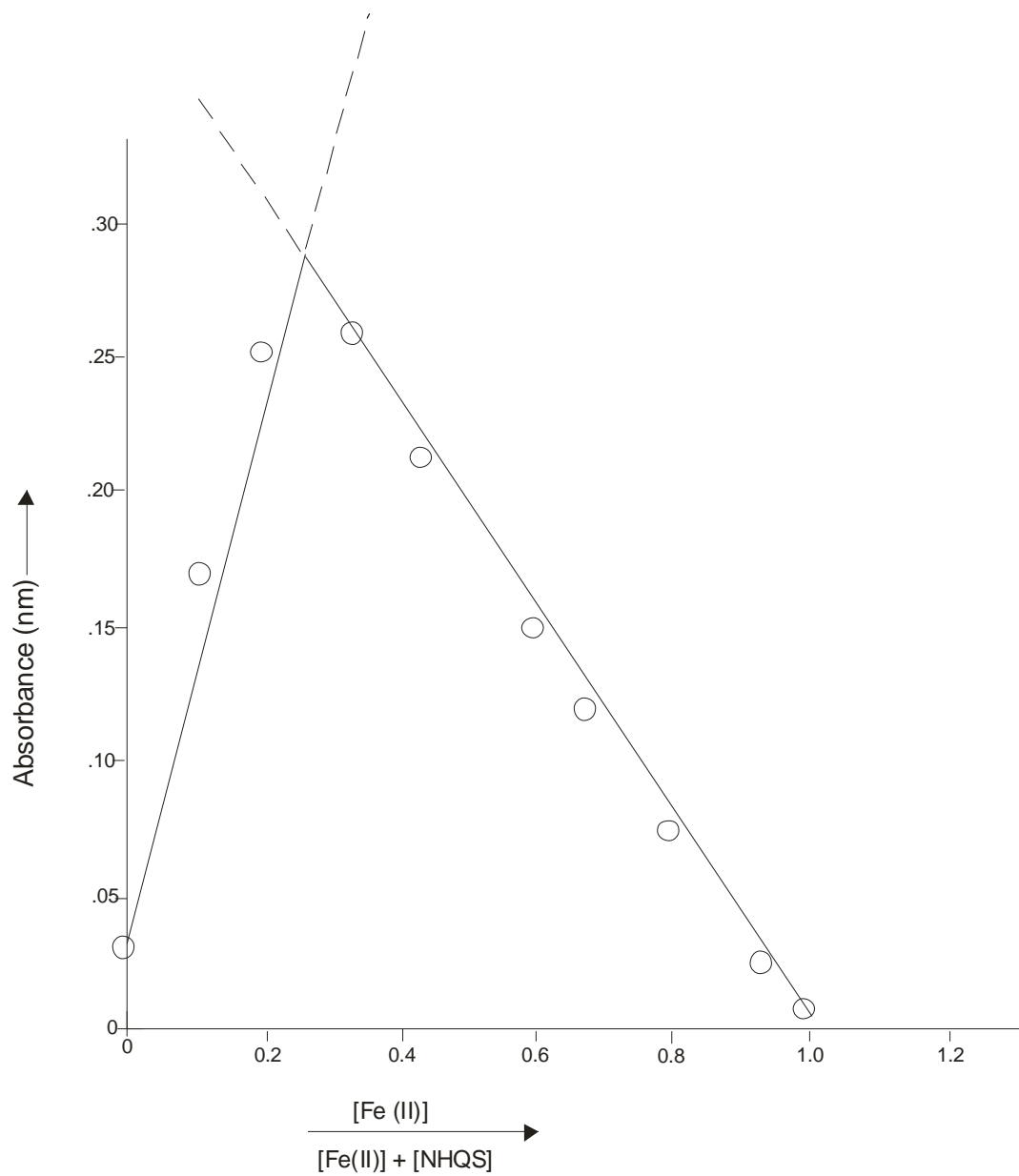


Fig. 5: Job's plot for Iron - NHQS complex

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Sample directory:
File: PROTON

Pulse Sequence: s2pul

Solvent: DMSO
Ambient temperature
Mercury-200BB "oauife"

Relax delay 1.000 sec.
Pulse 45.0 degrees
Acq. Time 1.997 sec.
Width 3194.9 Hz
16 repetitions
OBSERVE H1, 199.9700451 MHz
DATA PROCESSING
FT size 16384
Total time 0 min, 49 sec.

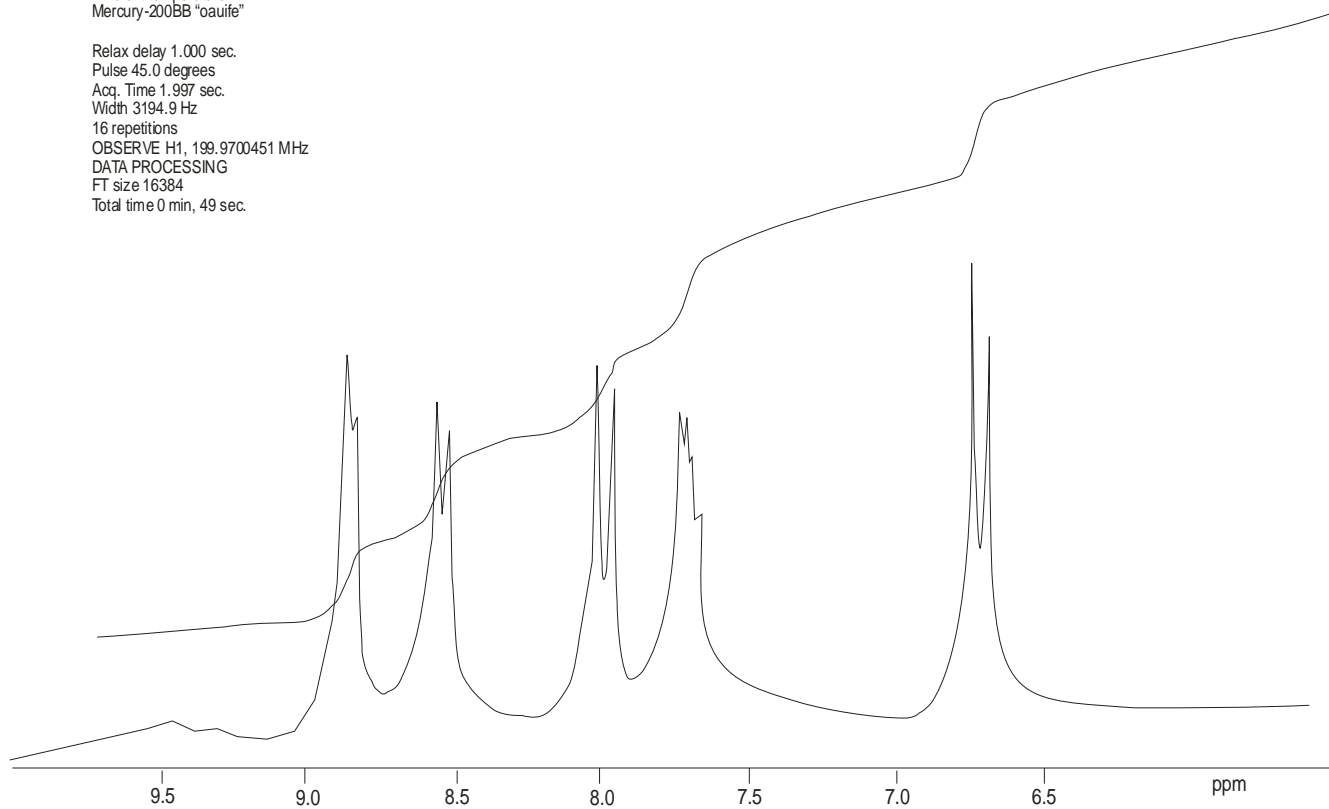


Fig. 6: Nuclear magnetic resonance graph of 7-Nitroso-8 Hydroquinoline - 5-sulphonic acid (NHQS) ligand

have chemical shifts in the range 7.6 – 7.90. The proton ortho to an aromatic ring is deshielded and the greatest deshielding is exhibited by electron withdrawing groups in the 5 - position.

The nitroso form of the ligand tends to be dominant and bonds through the lone pair on the nitroso oxygen rather than nitroso nitrogen with little rotation about the N-C bond of the nitroso group due to close proximity of ortho proton.

In the preliminary work, an attempted reaction of Iron (III) ion with the monosodium salt of the ligand produced a brown solution without precipitation. It is expected that the coordination of the third ligand molecule would result in the formation of Iron (II) complex. The resulting complex anion could attach a proton from the acidic medium, having an octahedral structure. This observation is consistent with that by Takashi *et al*; (1973) who reported that iron (II) formed a large monovalent complex anion with nitrosophenols and nitrosonaphthols as



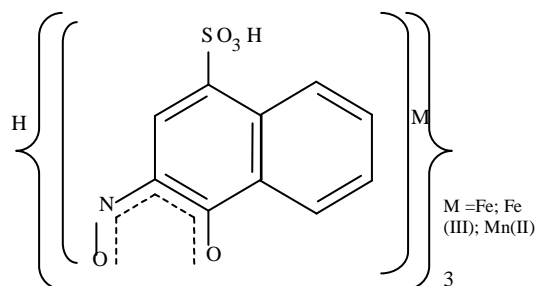
The binding of the nitroso group to these metal ions may take place either through the nitrogen or the oxygen atom (Eugene and Belford 1964). The shift of the N=O frequency according to Bellamy (1966) from 1530cm^{-1} to higher frequency in the complexes is indicative of coordination involving the 2-nitroso-1-naphthol site. This trend was observed in figures 7-9 where 1613.70 increases to 1654.62 and 1842.33 cm^{-1} respectively; confirming the binding through the oxygen atom;



CONCLUSION

From the evidence provided in this study, the binding of the nitroso group to iron and manganese is probably through the oxygen atom as shown in the structure below.

Suggested structure of NHQS – metal Bonding via Oxygen atoms:



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