CHAPTER 2
PAST WORK ON 2 HYDROXY 1 NAPHTHALDOXIME AND OBJECTIVES
Section (i) - Brief review of OXIMES as analytical spectrophotometric reagents.

Oximes are derived from aldehydes or ketone by replacement of the oxygen atom of the aldehyde group (aldoximes) or the keto group (ketoximes). The name oxime is an abbreviation of oxy-imines \( > C = N - OH \). This group is amphiprotic in nature, having a slightly basic nitrogen atom and a mildly acidic hydroxyl group.

The two main structures (A) and (B) are proposed for the oxime group with evidence for an equilibrium between them\(^1\)

\[
> C = N - OH \quad (A) \quad C = N \quad (B)
\]

The neutron diffraction work\(^2\) on dimethylglyoxime established the presence of O-H bands, favouring the structure (A). Oximes are usually associated\(^2-10\) with hydrogen bonding O-H - - - N in the solid state.
Isomerism in the oximes was first described by Werner\textsuperscript{11}. Owing to the restricted rotation around double bond geometrical isomerism. Occurrence of two\textsuperscript{12} isomers in monoximes and three\textsuperscript{13} in dioximes may be visualised as below.

\[ \begin{array}{c}
\text{H}_5\text{C}_6 -- \text{C} -- \text{C} -- \text{C}_6 \text{H}_5 \\
\text{N} \quad \text{N} \quad \alpha \text{ anti} \\
\text{H}_5\text{C}_6 -- \text{C} -- \text{C} -- \text{C}_6 \text{H}_5 \\
\text{N}-\text{CH} \quad \text{N}-\text{CH} \quad \beta \text{ (syn)} \\
\text{H}_5\text{C}_6 -- \text{C} -- \text{C} -- \text{C}_6 \text{H}_5 \\
\text{N}-\text{CH} \quad \text{N}-\text{CH} \quad \gamma \text{ amphi}
\end{array} \]

These isomers are usually identified by chromatographic or spectroscopic methods. TLC has successfully been used by Toul et al.\textsuperscript{14} to separate and identify benzil - \( \alpha \) monoxime, furil monoxime, furil dioxime and their isomers and dimethyl monoxime in dimethylglyoxime. Soules et al.\textsuperscript{15} separated and identified various isomers of 2, 2\textsuperscript{1} pyrsidiloximes.

It is interesting to note that the different geometrical isomers for the vic-dioximes have been isolated only in the aromatic series. There is little evidence that the \( \beta \) (syn) - or \( \gamma \) (amphi) - isomers exist in either aliphatic or alicyclic series\textsuperscript{16} of vic-dioximes.
**Modes of Bonding**

The oxime group has two donor atoms, N and O, and may co-ordinate to a metal atom through either or both, thus acting as unidentate or bidentate respectively. The following structure may arise from the different mode of co-ordination of an oxime.

\[
\text{O(H)} \quad \text{O----H----O}
\]

\[\text{C} \quad \text{M (a)} \quad \text{C} \quad \text{M (b)}\]

\[\text{O - M} \quad \text{C = N - O \ M (c) (d)}\]

The structural types (a) and (b) are quite common. The type C is known in polynuclear species, whereas only a few complexes belong to type (d).

The mode of co-ordination of the oxime group is greatly influenced by the other groups present in the ligand. The oxime group may be sole co-ordinating group present or accompanied by another donor group. On this basis the oximes may be grouped into the following main classes.
1. Simple oximes
2. Vic-dioxime
3. Carbonyl oximes
4. Nitroso phenols
5. Imine oximes
6. Pyridine oximes
7. Azo - oximes
8. Hydroxy oximes
9. Amine oximes
10. Amidoximes

**Structures of Metal oxime complexes**

It would be pertinent at this stage to mention, in brief, the structural aspects of the metal oxime complexes normally encountered. Simple oximes form complexes of the type (MLn)X where X represents a univalent anion and 'n' the oxidation number of the metal ion. These complexes assume varying structures and stereochemistries.

Hydroxy and vic-dioximes form square planar bis-chelates with most of the bivalent ions, with closed structures due to formation of additional rings by means of inter ligand and hydrogen bridges. Crystal structures of many of these complexes are known. Carbonyl oxime and Nitroso phenols form inner complexes.
of the type MLn where L represent the deprotonated ligand. Bis-chelates are usually square planar and tris-chelates are octahedral.

Pyridine oximes, imine oximes, amine oximes and amidoxime form complexes of varying composition and stereochemistries, governed by the properties of the central metal ion and steric requirements.

Structures of some oxime chelates have been elucidated by infrared, NMR, X-ray and magnetic measurements etc. 17 - 19

Solubility

In analytical chemistry the solubilities of metal complexes are of vital importance. For instance, the analytical selectivity of dimethylglyoxime arises from the low solubilities of its complexes with nickel and palladium, where as the corresponding complexes of all the other transition metals are quite soluble in water. The strong hydrogen-bonding of the OH groups in the planar bis-(dimethylglyoxime) nickel (II) complex makes it relatively difficult to co-ordinate water molecules and this explains its ready extractability into chloroform. In the corresponding, but non-planar, cobalt (II) complex, the -OH groups are available for
bonding to solvent water molecules, thereby preventing extraction into chloroform and making possible the separation of nickel from cobalt.

Formation of mixed-ligand complexes also plays an important role in solubility. This is clearly illustrated by the palladium-DMG complex.

**Nomenclature of the oximes**

In oxime chemistry the terms syn and anti are used instead of the terms cis and trans. In the case of the aldoximes the syn-form is the one in which both the hydrogen atom and the hydroxyl group are on the same side. When these groups are on opposite sides, the configuration is anti. Thus I is syn- and II is anti-benzaldoxime. With ketoximes, the prefix indicates the spatial relationship between the first groups names and the hydroxyl group. Thus III may be names as syn-p-tolyphenyl ketoxime or anti-phenyl-p-tolylketoxime.

\[
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C} \\
\text{N} - \text{OH}
\end{array}
\quad
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C} \\
\text{N}
\end{array}
\quad
\begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{C} \\
\text{N} \\
\text{HO}
\end{array}
\]

1 Syn

II Anti
General method for preparation

Vogel\textsuperscript{20} has outlined the general method for the preparation of aliphatic and aromatic oximes. Preparation of monoximes is simple but that of dioximes is slightly difficult because a mixture of isomers is formed and a special procedure is employed for their separation.

Analytical applications in spectrophotometry

A large number of oximes are used as spectrophotometric reagents in analytical chemistry. The analytical applications of oximes in spectrophotometry are reviewed by Singh et al\textsuperscript{21}. They have presented the data on spectrophotometric application of various oximes for different metal ions.

Of the various types of oximes aldoximes are easy to prepare and more soluble in common organic solvents. 2 Hydroxy 1-naphthaldoxime was first
employed by G.R. Reddy \textsuperscript{22} for the colorimetric determination of U (VI) in the pH range 9-11. Willard et al.\textsuperscript{23} found that Co OHNAO complex is extractable into organic solvents. Gultzeit et al.\textsuperscript{24} determined nickel (II) after extraction into an organic solvent.

It has also been extensively used for the determination of several metal ions\textsuperscript{25 - 28}. Using the reagent Krishna Reddy et al.\textsuperscript{29} determined Mo (VI) spectrophotometrically at pH 3. The Molar absorptivity is $1.75 \times 10^3$ lt mol$^{-1}$ cm$^{-1}$. Shantalakshmi et al.\textsuperscript{30} determined iron using OHNAO colorimetrically. Paria et al.\textsuperscript{31} carried out extractive spectro photometric determination of nickel with OHNAO. Cobalt\textsuperscript{32} was determined by extractive spectrophotometric technique with OHNAO.
Section II:

Objectives of the Present Investigations

The above review shows that oximes are important analytical spectrophotometric reagents and that OHNAO has been employed for the spectrophotometric determination of several metal ions. However, no attempt has so far been made to carry out derivative spectrophotometric determination of metal ions, inspite of its advantages over the normal spectrophotometric technique using oximes in general and OHNAO in particular. Thus in view of the importance of molybdenum in industry and biological process the author has undertaken derivative spectrophotometric determination of Mo(VI) using OHNAO. Further as it is noticed in present studies that the sensitivity of the determination of Mo(VI) using OHNAO is more than the method reported earlier. Thus a reinvestigation of the direct spectrophotometric determination of Mo(VI) is also carried out.
REFERENCES


  Rai, A.K., Singh, A. And Bohra, R.
  (1973) 721.
23. Willard, H.H. and Hall, D., TAM Chem. Soc. 44(1922), 2219, 2226
  15 (1960), 180.
28. Raja Reddy, G. Oximes as Inorganic analytical, reagents Ph.D. Thesis,
  S.V. University, Tirupathi 1970.
  19 No. 9 (1980) 928 929
30. K.S. Santha Lakshmi, R.R. Naidu and V.R. Krishnan

   J Indian Chem. Soc. (1992), 734, 430

32. P.K. Paria, A. Sarkar, S.K. Majumdar