CHAPTER 4

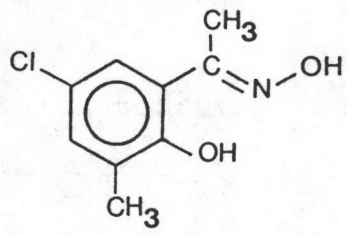
CONCLUSION AND SUGGESTION FOR FUTURE WORK

In this work, 5-chloro-2-hydroxy-3-methyl acetophenoxime and 2,5-dihydroxy acetophenoxime were synthesised and their possibilities of being use as spectrometric reagents were also investigated. Both of them are suggested as being syn-acetophenoximes because the other isomers (anti) are unlikely to exist according to the calculations with CNDO approximation (by Reoungpornvisuti, V., Group Theoretical Reserch, Department of Chemistry, Faculty of Science, Chulalongkorn University) Some conformations of syn-and anti-isomers of 5-chloro-2-hydroxy-3-methyl acetophenoxime were proposed and their total energies, binding energies and dipole moments were determined through computerized calculation (shown in Appendix). All the conformation of anti-forms have much higher values of total energy, binding energy and dipolemoment and are reported not to exist. The syn-isomers, themselves, in solid state show the intramolecular hydrogen-bonding between ortho positioned hydroxy groups and nitrogen atoms of the oxime groups according to their low melting points and IR spectrometric results. Because of the non-polar benzene nucleous, the oximes are slightly soluble in water but can easily dissolved in less polar ethanol-water mixture in which the intramolecular hydrogen bonds are replaced by extrahydrogen bonds with the solvent molecules. Other functional group(s) attached on the phenyl ring also plays the important role on solubility. 2,5-Dihydroxy acetophenoxime contained another polar hydroxy group (meta hydroxyl position) is more soluble in aqueous solution than 5-chloro-2-hydroxy-3-

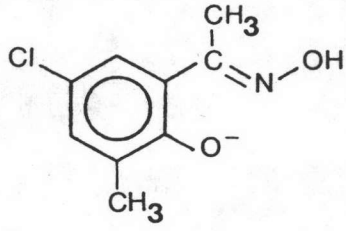
methyl acetophenoxime contained less polar chlorine and methyl group. The same result occurs on their Ni complex. 5-Chloro-2-hydroxy-3-methyl acetophenoxime -Ni (II) complex can be readily extracted in chloroform with high distribution ratio between chloroform and water whereas 2,5-dihydroxy acetophenoxime-Ni (II) complex is much less extractable into chloroform but being a flake concentrated between the immiscible water and chloroform contact.

Both oximes can react with the same group of metal ions like other o-hydroxy acetophenoximes do. It is believed that the auxochromic group of the oximes for binding with the bivalent metal are oxygen atom of ortho positioned hydroxyl group and nitrogen atom of oxime group. The metal ions, Mn (II), Co (II), Ni (II) and Cu (II), characterized suitable charge/ionic radius ratio in the formation of closed structure complexes, All bivalent metal-oxime complexes are formed in basic or slightly basic medium. It can be assumed that the more acidic phenyl hydroxy hydrogen is neutrallized causing the oxime anion presents in the solution and then combines with bivalent metal yeilding neutral 1:2 metal-oxime complex. Among these metal-oxime complexes, Ni (II)-oxime and Cu (II)- oxime complex are less polar and present as precipitates in solution.

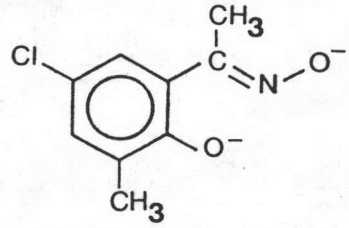
On the study of Ni-bis (5-chloro-2-hydroxy-3-methyl acetophenoxime)complex, it is formed at pH 6-9, not at lower or higher value of pH. In acidic or neutral medium, the more acidic phenyl hydroxy hydrogen and less acidic oxime hydrogen of the oxime do still attach to the molecule whereas in strong basic medium, both acidic hydrogens are loosen. The oxime molecules at various pH are probably assigned as Fig. 4.1.



At pH lower than 6



At pH 6-9



At pH higher than 9

Fig. 4.1

Owing to the visible absorption spectra at various pH (in the range of 6-9) showing the same maximal wavelength of 607.0 nm, it is suggested that only one species of Ni (II) - oxime complex is formed. The metal-oxime ratio of the complex is 1:2 determined by various methods. The Ni-bis (5-chloro-2-hydroxy-3-methyl acetophenoxime) complex can be assigned in Fig. 4.2. The proposed square planar complex is quite stable because five-and six-membered rings are formed since these have minimum strain.

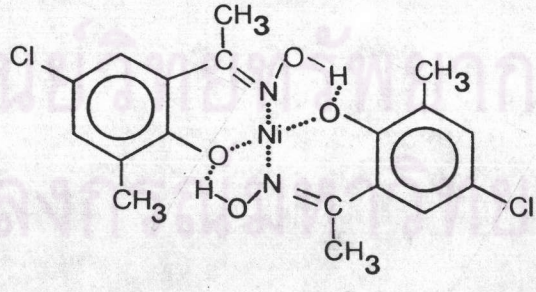


Fig. 4.2

In the case of 2,5-dihydroxy acetophenoxime, it is also assumed that the complex formation with Ni (II) occurs in the similar manner. The meta phenyl hydroxy group can effect on the complex forming pH but the distance of the meta phenyl hydroxyl oxygen atom, a doner atom, is far from the nitrogen atom and ortho hydroxyl oxygen atom so the bis-chelate-Ni (II) complex using it as an auxochromic group are quite impossible.

Unfortunately, the meta hydroxy group makes the complex modurately polar so it can slightly dissolve in aqueous solution and partially be extracted into chloroform. The sensitivity of the Ni-2,5-dihydroxy acetophenoxime is much lower than the one of 5-chloro-2-hydroxy-3-methyl acetophenoxime. It may be relevant to give suggestion for further study that if a series of o-hydroxy acetophenoxime compounds are synthesised by fixing the central muclei of the system but changing the substituents which are less polar considering inductive effect, large, hydrophobic and (or) electron donating (sigma or pi-electrons can be valid), if another solvents (pure or mix solvents) are applied in extraction, higher sensitivity or some spectroscopic properties of the Ni (II) or other previously mentioned metal ions using the solvent extraction spectrometric method for determining the metals may be obtained.

It is also seen from this research work that 5-chloro-2-hydroxy-3-methyl acetophenoxime can act as an indicator for determination of Fe (III) by direct EDTA titration method. The metal-oxime ratio of this complex was not determined. Fe (III) gives intense colour complex by adding very small amount of the indicator however the end point is rather difficult to obtain.

It is suggested to used 5-chloro-2-hydroxy-3-methyl acetophenoxime as precipitating agent for Ni (II) for future studies. This complex is effectively insoluble in water and in ethanol while the excess oxime can be washed out with ethanol. The complex is so thermally stable that can be dried at 150^{o}C without melting or decomposing. High sensitivity of this precipitation method is expected to be obtained because of the high molecular weight of the complex. The usefulness of oximes has been discussed widely and is considered to be multipurpose reagents in metal analyses.