CHAPTER I

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Introduction

Analytical chemistry is as old and as new, as the science of Chemistry itself. There are various types of analytical researches, but the ultimate purpose of all is to improve the existing methods of analysis or to devise new ones.

For a very long time organic compounds have been applied in the most varied ways in analytical chemistry. However, the introduction of synthetic organic reagents was an obvious turning point in inorganic analysis. It is difficult to decide the very first application of synthetic organic reagents. The introduction of d-nitroso-\(\beta\)-naphthol for determining cobalt, by Il'inskii in 1884, may be considered as the first synthetic organic reagent applied in quantitative inorganic analysis. However, the beginning of extensive application of organic reagents may be attributed to the classical researches of Tschugaev, who proposed the reaction of nickel with dimethylglyoxime in 1905. During the decades which have elapsed since these discoveries, several thousand papers, and a large number of reviews and monographs have been published on the application of organic reagents in inorganic analysis.
The considerable interest taken in organic reagents may be attributed to the high analytical value of their properties. The formation of a great variety of metal complexes (notably chelate compounds) by organic reagents, the wider choice of chromogenic groups in organic compounds, and the possibility of suitably modifying organic molecules, all contribute to the more versatile character of organic reagents as compared to the inorganic ones. Their use greatly increases the specificity and the sensitivity of analytical reactions, introducing a simplification and rationalization of analytical methods, particularly in micro-analysis. The small solubility and large molecular weight of the metallic compounds formed by them, favour their use in gravimetric analysis. In addition, the high intensity of colouration of numerous reaction products of different ions with organic reagents, makes the latter irreplaceable for the determination of trace quantities of substances by colorimetry.

Rigid classification of the numerous organic reagents is difficult because of the diversified ways in which they are used. The most important are those which form chelate complexes, which involve the formation of one or more rings (generally five- or six-membered) incorporating the metal ion. These complexes, due to their non-ionic nature, are usually soluble in non-polar solvents and therefore, can be extracted from aqueous phase into immiscible solvents, making their separation and estimation possible.
In a survey of the analytical evaluation of new reagents and the improvement of activity of organic reagents already known, it was observed that certain atomic groupings (the so-called functional-analytical group) in the organic compounds exert a definite influence on the solubility, colour, etc., of the salts, so that it is safe to speak of the relation between these atomic groupings and specificity. In recent years, the knowledge of functional-analytical group has been considerably enriched. It has been observed that certain combination of groups are functional-analytical for certain metal ions giving specific reaction. Moreover, the introduction of substituents into the molecule of the reagent beyond the limit of the functional-analytical group have, usually, a favourable effect on the solubility, extractability, colour and stability of the reaction product of the organic compound with the ion determined. The introduction of such substituents, which Kulberg calls analytically active groups, widens the possibility of investigating reagents with more suitable analytical properties. It has also been noticed that sometimes substitution in the functional-analytical group reduced their specific action. For example, –NH – C (=NOH)-group is functional-analytical for Fe^{3+} ion, however, substitution of the hydrogen atom in this group by an alkyl group leads to the loss of its specific action on Fe^{3+} ion. Such examples emphasize on the specificity.
of a functional-analytical group and also indicate that only the presence of a functional-analytical group in an organic compound, still does not guarantee the analytical value of the latter.

Since there are only a few specific reagents, the quantitative approach to the selection of specific conditions for carrying out a chemical reaction facilitates the solution of a number of analytical problems and forms a tangible basis for the use of group-reagents for separating mixtures and for the determination of individual ions. Many factors influence the selectivity of a reaction.

Since a uniform mode of reaction does not always occur over all pH regions, many reactions which lead to the establishment of equilibrium conditions are pH dependent. Consequently, the reactions of the accompanying materials can be prevented or kept under control in many cases by proper adjustment of the pH. This objective can also be reached in some instances by adding appropriate masking agents.\(^5^5\)

Another way of obtaining a highly selective reagent is to combine selective coordinating groups, with groups imposing steric hindrance.\(^5^7-5^9\). For example, 1,10-phenanthroline reacts with Fe(II) and Cu(I) to form strongly coloured complexes, and is of no interest for the determination of Cu(I), in presence of iron, because of the
reaction with Fe(II). However, 2,9-dimethyl-1,10-
phenanthroline is a specific reagent for Cu(I)57.

Extraction of a metal complex from one solvent,
usually water, into another61-63, often permits a con-
siderable concentration of the complex to be achieved with
consequent increase in the effective sensitivity of an
analytical procedure. It is also sometimes, a very useful
means of securing separations from interfering substances.
The almost universal extractability of metal-organic
complexes into organic solvents contributes much to the
sensitivity and selectivity of organic reagents.

Another important approach towards the improvement
of selectivity of a reagent is the use of mixed
ligands49, 54-70. The complex compounds, formed by a
central ion with two or more different ligands are,
usually, termed as mixed-ligand complexes. Several metals
may react with a given reagent to form complexes having
almost identical spectra because in most cases, the chromo-
phore factor is electronic excitation within closely
spaced orbital-levels in the organic molecule70. Thus
colour modification within such a group of metal complexes
is, usually, only of minor nature due to variations in the
ionic covalent nature of the metal-ligand bonds, conse-
quently, there is considerable overlap of spectra and the
determination of one metal in presence of the others by
such a reagent, is not possible. If, however, the metal
ion is caused to react with two different ligands to produce mixed-ligand complex, the prospects of many ions producing near identical reaction is considerably decreased. In addition, the light capture cross-section of such a mixed complex is likely to be markedly great and hence the sensitivity of the determination may be considerably better than that of a binary complex. Furthermore, the formation of these complexes caused a change in properties, such as solubility in water and organic solvents, extraction rate, and others which are important in analytical chemistry.

The ever-growing interest in mixed-ligand complex, has stimulated development of new methods of research and led to the publication of a number of reviews on analytical applications on certain types of reactions. Researches, in the reaction mechanism of mixed-ligand complexes, stability and general conditions of formation, and kinetics of ligand interchange, have further promoted their use in analytical chemistry.

The use of mixed-ligand complexes in extraction methods has been developed considerably. The most extensively studied, are the extraction of anionic complexes with organic cations and of adducts (compounds with a mixed coordination sphere). The papers on synergistic effects, arising from metal extraction by chelate-forming reagents and on the extraction of anionic and cationic chelates are very interesting. Synergism in adduct formation can be of different origin,
however, it is connected with introduction of the neutral ligand into the inner sphere and displacement of water from the complex co-ordination sphere.

Mixed-ligand complexes have versatile application in photometric or extraction-photometric analysis. Organic reagents, particularly chelate-forming reagents, are widely used as electronegative ligand, which increases the specificity and sensitivity of reactions. Thus conversion of complexes with homogeneous co-ordination sphere into compounds containing several different ligands, is an effective means of solving one of the most important problems of analytical chemistry, i.e. to increase the sensitivity and selectivity of reactions. The use of mixed-ligand complex formation has several advantages.

(a) The sensitivity and specificity of reactions are enhanced.
(b) The degree of extraction of metal is increased.
(c) The hydrophilic nature of the complex is minimised.
(d) In some cases the hydrolysis of metal is prohibited.
(e) The decrease in solubility of the mixed-ligand complexes increases the accuracy of gravimetric determinations.

Thus, the recent line of approach for developing more sensitive and selective methods of determining ions, is the use of mixed ligands, besides the synthesis of new reagents of specific properties.
N-HYDROXY-N,N'-DIARYLBENZAMIDINES
AS ANALYTICAL REAGENTS

N-Hydroxy-N,N'-diarylbenzamidines, also called hydroxyemidine, are recently explored (potential analytical) organic reagents possessing the functional-analytical grouping, I,

\[
\begin{array}{c}
  - C = N - \\
  \mid \\
  - N - OH
\end{array}
\]

I

They have two possible sites for coordination with a metal ion i.e. \(- N -\) and \(- OH\) and are thus capable of forming five-membered ring on chelation with a metal ion. These compounds possess several distinct features important from analytical point of view. They are easy to synthesize, stable towards heat and light, appreciably soluble in various organic solvents, and their solutions can be stored for a long time without deterioration.

The reaction, involving the interaction of aromatic amines, II, with N-arylbenzimidoyl chloride, III, and producing amidines, IV, in high yields, is quite general. The synthetic chemistry of latter (amidines) has been extensively studied by various researchers\(^{92-97}\).
This reaction is capable of extension for the preparation of hydroxyamidines. Ley and others\textsuperscript{98-101}, worked on reaction of N-arylbenzimidoyl chloride, II, with N-arylhydroxylamine, V, in absolute ether medium at low temperature and obtained corresponding hydroxyamidine hydrochloride, VI, which on treatment of ammonia gave free base, VI.

Hydroxyamidines are sometimes confused with amidoximes\textsuperscript{102}, since hydroxylamine, VII, when condensed with imidoyl chloride, II, produce the hydroxyamidine, VIII, which tautomerises to the amidoxime, IX.
This tautomerism is not possible in \( N,N' \)-disubstituted hydroxyamidines and only hydroxyamidine forms can exist in them.

**Review of the Earlier Work**

Ley and Holzweissig\(^{98,99}\), reported the synthesis of seven hydroxyamidines in as early as 1901 of the general formula, VI. Their studies were principally concerned with the isomerism and reduction of these compounds. They also tried to study the hydrolysis of the hydrochloric salts of oxyamidine free bases by conductometric experiments but unfortunately, the analytical potentialities of this group of reagents had remained unexplored.
Recently, a number of analogues of hydroxysalidines have been synthesised by Mishra et al. Their analytical potentialities towards various metal ions have been tested and they have been found to be excellent reagents for gravimetric and spectrophotometric determination of various transition metals.

**PRELIMINARY INVESTIGATION**

It is apparent from the review of the earlier work that the synthesis and complexing properties of these compounds are not much studied. This group of compounds promises large field in analytical chemistry both of theoretical and of practical value. Consequently a systematic approach towards synthesis and applicability of these reagents, especially in presence of other complexing agents has been undertaken.

The present investigation reveals the preparation and properties of eleven new analogues of hydroxysalidines. These compounds are characterised in terms of their storage quality, melting points, elemental analysis, ultraviolet and infrared spectra.

These compounds have been named following the nomenclature described in literature. The reaction of these compounds with various metal ions have been studied with a view to explore analytical applicability of these reagents in the estimation of metal ions.
one of the most popular methods for trace analysis is colorimetry, which may be attributed to its modest apparatus requirements, the possibility of its use by the average analyst, a sensitivity adequate for present-day purposes, and an accuracy comparable to, if not better than that of any methods in its range. Accordingly, photometric methods based on reactions of hydroxyamidines with several metal ions (e.g., Fe³⁺, Y⁵⁺, Mo⁵⁺), in presence of other complexing agents, producing intensely coloured, organophilic mixed-ligand complexes, have been selected for determination of these metal ions.
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