Chapter 1.

Introduction to ion-pair complexes and metal catalysed reactions.
INTRODUCTION:

Coordination compounds have always been a challenge to the inorganic chemists. In the early days of chemistry they appeared unusual (hence the name “complex” ions) and seemed to defy the usual rules of valence. Today they comprise a large body of current inorganic research. Although the usual bonding theories can be extended to accommodate these compounds, they still provide stimulating problems to be resolved. In the synthetic work they continue to provide a challenge in the laboratory. The rapidly developing field of bioinorganic chemistry is centered on the presence of coordination compounds in living systems.

Classical complexes are of two types,


Neutral complexes are unchanged species, normally neither associate nor dissociate in solution. Ion-association complexes often termed as ion-pair complexes, or ternary complexes, which are uncharged species formed by association of pairing of ions through electrostatic force of attraction.

The concept of ion-pair was introduced in 1926 by Bjerrum. Ion-pair complexes are also neutral species in solid state containing cation and anion, either one or both may be complex. Ion-association complexes can be grouped in to two types, one which contains the metal ion in the complex anionic form and the other one contains the metal ion in the complex cationic form.
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The mode of formation of ion-pair complexes in the solution is described in detail in the series of papers. For example, Takayuki Nakai et al. have explained the ion-pair formation between dodecylsulfate and ammine-complexes of copper(II), nickel(II), zinc(II), palladium(II) and platinum(II), and the extraction behavior of the ammine-complexes by using sodium dodecylsulfate. D. Farscia and A. Vinslava have studied the formation of ion-pair from 2-fluoropropane and Lewis acids. Shoichi Katsuta et al. have explained the ion-pair formation in water and extraction into benzene of 18-crown-6-sodium ion complex with nitrated phenolate ions. Zheng-Zhi Zhang et al. have described the formation of an ion-pair complex. And some reviews are also reported on the ion-pair complexes.

The ion-pair complexes have excited great interest among chemists for the last few decades due to their wide variety of stereo-chemical features. Structural studies have demonstrated that the nature and size of the counter ion play an important role in the stereochemistry and the crystal packing of the kind of compounds. There are good numbers of papers dealing with the study of complex anions associated with different counter cations. Ion-pair complexes play very important role in organic and inorganic analyses. The ability of the organium ions to form ion-pair complexes with complex metal anion and with complex organo anions and the ability of drug molecules to form ion-pair complexes with various reagents are extensively being used in the determination of drugs in pharmaceutical analysis.
The use of high molecular amines, amine salts and quaternary ammonium salts as extracting reagents for various anionic metal halide species have been extensively investigated in recent years\(^3\). Number of authors has reported to applicability of quaternary ammonium ion in the isolation complex anion and in the estimation of drug or metal ion\(^3\). For example; solvent extraction of anionic silver(I) thiocyanate complex as ion-pairs with tetrabutylammonium ions into chloroform and 4-methyl-2-pentanone\(^{24}\). Solvent extraction of chromium(VI) in acid aqueous nitrate solutions into chloroform as ion-pairs with tetrabutylammonium ions\(^{25}\). Some observations on the extraction of triphenylmethane dyes by ion-pair formation with amines as counter-ions\(^{26}\). Based on the ion-pair concept, few analytical procedures have been established in the present work.

Chloramine-T, is an anti-microbial agent, has widespread use in a broad range of practices, including medical, dental, veterinary, food processing, and agricultural field. Chloramine-T is used as a synthetic reagent in the preparation of various organic compounds\(^{27}\). It is a good oxidizing agent\(^{28}\), hence used for the estimation of variety of reductants in solutions. Chloramine-T, having diverse properties, behaves as an haloginating agent and has been employed for the quantitative estimation of the magnitude of double bonds in oils and fats. It adds across double bonds of alkenes qualitatively, the reaction proceeds via an intermediate ion-pair complex formation\(^{29}\).
**Ion-pair halogens:**

Inter halogen compounds are also a class of ion-pairs which play important role in the synthesis and analysis. Due to the less electronegativity of iodine compared to the other halogens, iodine exists as iodinium ion in presence of other halogens. Ion-pairs of iodine with fluorine and bromine are finding importance in various synthetic and analytical reactions. Iodine forms number of ion-pairs with chlorine, such as $ICl_2^+$, $ICl_4^-$, etc. Inter halogens are also known to exist in the form of cation, $I(Cl)_2^+$ which is associated with $SbCl_6^-$. Ion-pair of iodine, iodinemonochloride (ICl) undergoes addition reactions with alkenes involving molecular or charge transfer complexation. There are number of reports, in which an ion-pair, iodinemonochloride has been applied in a variety of analytical applications. For example; in the determination of iodine value of oils, in the pharmaceutical analysis and in the spectrophotometric determination of Sb(III).

Addition of halogens across double bonds takes place more readily in presence of iodine halides than those of more active halogens, as iodine halides are found to lower the activation energy. This forms the basis for the use of iodine as an halogenation catalyst. In this context compared to hazardous chemicals used in the previous methods for the generation of ion-pair, iodinemonochloride generated in the present work using chloramine-T with iodine in acetic acid are relatively safe chemicals, has been successfully employed for the quantitative determination of sulfur dioxide and ascorbic acid. Similarly, iodinemonochloride generated in the present work using N-chlorosuccinimide with iodine in acetic acid, has also been
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successfully employed for the quantitative spectrophotometric determination of some phenothiazines involving ion-pair formation.

Manganese:

Manganese metal was isolated by Gahn in 1774. This can be prepared commercially either by the electric furnace process, the thermite method in which manganese oxide is treated with the metallic aluminium or by the electro-deposition from a solution of the manganese sulphate solution. Manganese is a gray-white metal, resembling iron. It is a hard metal and is very brittle, fusible with difficulty, but easily oxidized. The oxidation states of manganese are from +1 to +7. Oxidation state, +3 is known in the compound such as manganese(III) acetate, this is also a powerful oxidizing agent. 

Mn(III) ion can be obtained by the electrolytic or peroxosulfate oxidation of Mn(II) solution, or by reduction of MnO₄⁻. The ion plays central role in the complex redox reactions of the higher oxidation states of manganese in aqueous solutions. It is most stable in acid solutions, since it is very readily hydrolysed. Mn(III) has been used as catalyst in the synthesis and in the chemical oxygen demand determination of some organic compounds. It is also an used in redox reactions for the determination of organic and inorganic ions. In the present work, electrolytically generated Mn(III) in the acidic condition is used as an oxidant for the spectrophotometric determination of benzidine and trace amounts of nitrite in various samples involving ion-pair complexation.

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CATALYSIS:

The term catalysis was first used in 1835 by the Swedish chemist Jons Jacob Berzelius to characterize phenomena observed by chemists in the late 18th and early 19th centuries. Catalyst is a substance which alters the rate of reaction without undergoing any chemical change. Catalysis is a process whereby the rate of a particular chemical reaction is altered by the presence of small quantities of a substance which does not itself seem to take part in the reaction.

Adsorption behaviour of metal ions on the oxide surfaces of water is becoming better understood in terms of coordination chemistry framework. For example, metal oxide catalysts generally exhibit a "ligand effect" in the selective oxidation of methanol to formaldehyde. Inhibition effect of SO$_2$ on NO$_x$ and VOCs during the photodegradation of synchronous indoor air pollutants at parts per billion (ppb) level by TiO$_2$. Metal ions are also finding lot of catalytic applications in air pollution abatement. For example in controlling organic compounds which are the most troublesome pollutants in industrial processes and combine with oxides of nitrogen in the presence of nitrogen in the sunlight to form ozone. Transition metals have been recognized as convenient substrates in a variety of catalytic transformation. L. I. Fedorina et al. have studied the catalytic activity of rhodium solutions in oxidation reactions of azo dyes with sodium periodate. Z.Y. Yu et al. have developed a flow-injection-photometric method for the sub-nanogram amounts of cobalt by its catalysis of the oxidative coupling of 3-methylbenzothiazolin-2-one hydrazone with NN-dimethylaniline in a micellar medium. A. Keshavaraja et al. have studied the effect of surface modification due to super acid species in controlling
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the sensitivity and selectivity of tin oxide gas sensors. R. R Himebaugh and Michael J. Smith, have developed a semi-micro tube method for chemical oxygen demand using silver as catalyst. In addition, electrolytically generated Mn(III) has been employed as a catalyst and oxidant for some organic compounds. A. G. Anshits et al., have studied the physicochemical and catalytic properties of glass crystal catalysts for the oxidation of methane. Akimasa Iwado et al., have studied the catalytic activity of glass beads, silica gels and anion-exchange resins modified with metal-porphines in oxidative reactions of ascorbic acid.

Therefore, in the present work catalytic the effect of cadmium(II), manganese(III) metal ions and glass surface of the container on the determination of chemical oxygen demand has been studied.

SCOPE OF THE PRESENT WORK:

Over the past few years, increasing interest has been given to the ion-pair complexes due to their wide variety of application in analytical, pharmaceutical and food quality analyses. And also metal ions and complexes are finding lot of catalytic applications in air pollution abatement. Considering these significance, in the present work some analytical procedures have been established for the determination of sulfur dioxide, ascorbic acid and some phenothiazines using iodinemonochloride via ion-pair formation and also benzidine and trace amounts of nitrite in various samples using Mn(III) as an oxidizing agent through ion-pair complexation. Finally, the catalytic effect of
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cadmium(II), manganese(III) metal ions and also the glass surface of the container on the decomposition of the organic compounds, for example; thiourea, salicylic acid and sulfosalicylic acid followed by chemical oxygen demand determination volumetrically are studied along with the comparison to a standard uncatalyzed reaction.
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References:


