ABSTRACT

Nitrilotriacetic acid (NTA), \(N(CH_2COOH)_3\), is a tribasic acid with three carboxylic acid groups. It is known to form simple and complex salts with either single or more metal ions. Since its isolation in 1862, syntheses of different metal salts of this acid have been reported. Metal salts of this acid find various applications. In fact its uses as a detergent builder or as a complexing agent in plating industry is well known. Chelation of NTA with different metal ions has been investigated through stability studies with both single as well as ternary system. However, the ternary system with NTA and hydrazine (\(N_2H_4\)) ligand has not been investigated so far as revealed from literature survey. Secondly, in plating industry, since the temperature of the working bath is fairly high, the knowledge of thermal stability of M-NTA complex becomes essential. The objective in the present study is to understand the thermoanalytical properties of metal - NTA and metal - NTA hydrazinates.

Alkaline earth metals Mg, Ca and Sr and transition metals Ni and Zn are used in present study. Metal NTA is synthesized by known method. The hydrazinates of these salts are prepared under different preparative conditions, especially with respect to the pH. The composition of these product salts and complexes are fixed with the help of chemical analysis and infrared spectra. It is then confirmed with the help of thermal analysis. Whereas, simple salts decompose above 200°C, the hydrazinates do so ~ 170°C. Hydrazinates are found to decompose through simple salts to carbonates to oxides. The kinetic parameters of these complexes are calculated from the TG data by known methods. In the case of hydrazinates, the initial decomposition of hydrazine is confirmed from the activation energy value for the decomposition step. The details of the present investigation is presented in five chapters.
CHAPTER I.

Chapter I, presents the literature survey on nitrilotriacetic acid (NTA) and hydrazine with respect to the synthesis, spectral and thermal properties. Similarly various methods of synthesis, spectral and stability studies of metal-nitrilotriacetate salts are also reviewed in this chapter. Tribasic acid NTA has three different dissociation constants with large difference between the first two. Consequently, pH plays important role in the reaction between NTA and aqueous metal ion.

The scope for the present investigation and its objective is briefly given at the end of this chapter.

CHAPTER II.

In chapter II, various analytical procedures and instrumental methods, used in the present study are described. The instrumental techniques employed include thermogravimetric analysis (TGA), differential thermal analysis (DTA), infrared spectroscopy (IR) and magnetic susceptibility measurements by Gouy's balance.

The use of the thermal data to obtain the kinetic parameters which is used in this study is also described in this chapter.

CHAPTER III.

Chapter III, contains the results of the study on metal ion-NTA hydrazine system. The products obtained depend on the preparative conditions and are tabulated here.
The compositions of these organo metallic complexes obtained under different preparative conditions, are assigned on the basis of chemical analysis and spectral studies. The infrared spectra show typical carboxylic (-COO⁻) and metal nitrogen (M-N), metal oxygen (M-O) absorptions. Shifting of the -COO⁻ absorption to ~ 1680 cm⁻¹ indicates the presence of ionic carboxylic group. The stretching N - N absorption 950 - 1000 cm⁻¹ is used as the criteria for assuming the presence of N₂H₄ ligand or ionic N₂H₅⁺. The magnetic susceptibility values and densities of these complexes are tabulated and briefly discussed at the end of this chapter. Two carboxylic acid groups in NTA are co-ordinated to divalent Ni whereas the third is preferentially neutralized by N₂H₄.H₂O (i.e. N₂H₅OH).

CHAPTER IV.

Chapter IV, deals with the thermal analyses of metal nitrilotriacetates, metal - nitritoltriacetate hydrazinates and mixed metals nitrilotriacetate hydrazinates. Decomposition steps are given on the basis of the weight loss observed in the TG. The interpretation of the thermal data is described in this chapter. These salts decompose through dehydrated salt to carbonate to oxide as intermediates. The decomposition of products includes ammonia (NH₃) carbon dioxide (CO₂) and acetone (CH₃COCH₃). For some of the salts, the residue obtained on heating to ~ 700°C is found to be the mixture of oxide and metal (mostly metal). Ni - NTA hydrazinates are found to be good precursor for fine powder Ni.

\[ \text{N(CH₂COO)}₃\text{M(N₂H₅)} \rightarrow \text{N(CH₂COO)}₃\text{MH} \rightarrow (\text{MCO₃}) \rightarrow \text{M/O} \]
CHAPTER V.

Thermogravimetric data is used to evaluate the kinetic parameters involved in different decomposition reactions. Chapter V highlights the activation energy values obtained from the dynamic TG data of the samples. The three different methods used are as given by 1.) Freeman - Carroll, 2.) Coats - Redfern, 3.) Metzger - Horowitz. The comparison and interpretation of activation energy values of simple salts and hydrazinate complexes are also discussed. Activation energy values for hydrazine decomposition are found to be lower in case of salts in comparison to its hydrazinates which may be due to co-ordinated hydrazine in the latter.