CHAPTER I

INTRODUCTION

Oxidation of a substance can be defined as a loss of electrons by the substance, and reduction as a gain of electrons. When an electrochemical cell is working, a reduction process is taking place at the cathode, and an oxidation process at the anode. The term oxidation-reduction potential or "redox potential" is the potential for processes in which the electrolyte contains two oxidation states of a substance in equilibrium with each other. Suppose a platinum wire is inserted in a solution containing both ferrous ions and ferric ions. The processes that are liable to occur are

$$Fe^{3+}+e \quad = \quad Fe^{2+}$$

$$Fe^{2+}-e \quad = \quad Fe^{3+}$$

Thallium is an element in group III of the periodic table. It possesses two oxidation states-thallous and thallic compounds-in which the element is respectively uni and ter-valent. In aqueous solution unipositive state is more stable than ter-valent state. The electron exchange reactions in the Tl(I) - Tl(III) have been intensively studied and appear to be two-electron transfer processes (1). The potential of the Tl(I) - Tl(III) electrode is - 1.25 volts (E_f = -0.77, 1 M HCl.,
-1.26, 1 M $HClO_4$)

The oxidation potential is naturally raised by the presence of substances which form complexes with the Tl(III) ion. As indicated by the above potentials, the presence of Cl^- stabilizes Tl(III) ion more (by the formation of complexes) than Tl(I) ion and the potential is thereby greater. Hence oxidation of thallium (I) to thallium (III) compounds is most readily effected in the presence of complexing agents.

Thallous sulphate, nitrate, acetate are soluble in water, but-except for the very soluble TlF, - the halides are sparingly soluble. Incoporation of Tl(I) halides into the alkali halides gives rise to a new absorption and emission band due to the formation of complexes of the type that exist also in solutions, notably mainly TlX_2^- and TlX_4^{3-}.

The ease of oxidation of thallous to thallic salt varies greatly with the nature of the anion present. It was found that thallous chloride in hydrochloric acid solution is much more easily oxidised than is thallous sulphate or thallous nitrate in solutions of sulphuric or nitric acid (2). This difference is due mainly to the fact that the thallic ion, which is the primary oxidation product of thallous ion, is more or less converted in to a complex anion with a consequent displacement of the equilibrium conditions of the thallous-thallic ion reaction of oxidation. The extent of such complex ion formation, and hence the magnitude of the effect, varies with the nature of the anion of the salt and the acid present. These effects of some of the thallous-thallic systems have been studied through the measurement of the redox potentials using potentiometric and polarographic methods. But none have been reported on such a study of the acetates of thallium.

Moreover, the previous workers showed more interest in the potential measurements in aqueous electrolyte solutions than those in the so called nonaqueous solutions. This may be attributed to the inefficiency of the equipments and the inadequacy of the theory of the electrolytes in nonaqueous media. The nonaqueous system can be classified into three classes according to the media in the measurement. The following media are usually met.

1. Organic nonaqueous solvents including are inert organic solvents, acidic organic solvents, and basic organic solvents e.g., hydrocarbon, acetic acid, formamide.

2. Inorganic nonaqueous solvents. The very popular ones are hydrogen cyanide, sulphur dioxide, ammonia, hydrogen fluoride.

3. Fused salts. Fused salts are regarded as a novel class of electrolyte and they also have been employed as media in the measurement of e.m.f.. In the electrochemical of fused salts, the equilibrium potential of a metal at a given temperature is determined by the thermodynamic activity of its ions in the melt which depends on the composition of the solution, the interaction between the ions, and the processes of formation and breakdown of complex ions. In determining electrode potentials, there is as yet no widely accepted reference electrode similar to the hydrogen electrode in aqueous solution whose potential would be equal to zero.

In the present work the potentiometric measurement of the redox potential of Tl(III) / Tl(I) in acetic acid formed a major part of the work with the primary intention of making some contribution to the e.m.f. work in nonaqueous media which is still progressing. Acetic acid was chosen because it is readily available and is inexpensive. The acetates of thallium of either oxidation states were found to be completely soluble in this solvent. Besides, acetic acid is of particular interest because of its "super acid function" CH_3COOH is a weaker base than H_2O and $CH_3COOH_2^+$ is a stronger acid than H_3O^+. This solvent is therefore a differentiating solvent since it changes the relative strength of the electrolytes.

The pre and the post stages of the e.m.f. measurement can also be regarded as the important contribution to the academic value of this work. Prior to the commencing of the measurement, a suitable reference electrode had to be chosen, prepared and calibrated. A problem of liquid junctions had to be solved. The method of preparation and the stability of the thallous and thallic acetate had to be found. The potentiometric measurement yields an electrode potential and Nernst equation is used in the computation of the standard electrode potential. In order to solve this equation the term ionic activity coefficient of each ion which is a non-measurable quantity must be known and these involved other quantities such as dielectric constant of the media, the dissociation constant of the electrolytes in such media. The methods of the computation are presented in the Appendix II

It is worth pointed out here that in the past before the IUPAC meeting at Stockholm in 1953 there were two conventions regarding sign of the measured potential i.e., the oxidation potential which was used frequently by the U.S. scientists whereas the reduction potential was the preference of the Europeons. In the work reported in this thesis, otherwise mentioned, the IUPAC convention is adopted.