ABSTRACT

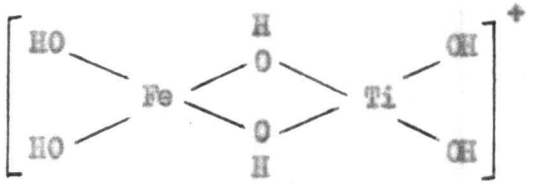
The chemical investigation of titanium containing minerals as ilmenite has attracted much interest. Ilmenite identified as a mixed metal oxide is formulated as $FeTiO_3$. It is characterised by a corrundum structure and is found to occur in nature corresponding to varying compositions of FeO, Fe_2O_3 and TiO_2. The Mössbauer spectroscopic study of the FeO and Fe_2O_3 contents of a large number of samples of ilmenite with titania contents ranging from 22 % to 61 % has been reported.

In solution, the most stable oxidation state, Titanium(IV) is formulated as the oxometal ion, titanyl ion (TiO^{2+}). The occurrence of such hydrolysed species of TiO^{2+} as $Ti(OH)_3^+$, $Ti(OH)_2^{2+}$, $Ti(OH)_3HSO_4$ and $Ti(OH)_2HSO_4^+$ has also been reported. The formation of ' hydroxo-bridged ' species involving Cr(III) and Zr(IV) is reported to account for the increased effect of combined Cr(III) - Zr(IV) sulphate solution for the tanning of hides and skins in leather processing as compared to the use of a solution of basic Chromium(III) Sulphate. The use of Zirconium(IV) sulphate however, is often limited by the ease of its hydrolytic polymerisation in aqueous solution. Studies of the hydrolytic phenomenon of the analogous titanyl ion, TiO^{2+} in the absence and presence of ligand systems are thus of particular significance.

Part 1 of this thesis records an investigation of the formation and hydrolysis of Titanyl chelates. TiO^{2+} is shown to form stable soluble complexes with a number of hydroxycarboxylic acids as malic acid, citric acid and salicylic acid. Potentiometric studies have shown the formation of titanyl chelates with metal to ligand ratios of 1 : 2. The formation constants of these chelates have been evaluated. The stabilities of the titanyl chelates with these ligands are found to be arranged in the order salicylic $>$ malic $>$ citric. Polarographic studies of these chelates also show that they are all characterised by reversible one electron reduction waves. The increase in diffusion current with time as observed for these chelates excluded the possibility of the formation of hydrolysed species. A yellow coloured species formed between TiO^{2+} and Tiron has been shown to involve the formation of a 1 : 2 chelate. No evidence has however been obtained for the hydrolysis of the Titanium(IV) - tiron chelate in contrast to the evidence reported for the hydrolysis of the analogous Zirconium(IV) - tiron chelate.

Mixed metal complex formation in solution is a continuing interest in our laboratories. However, little is reported on ' mixed metal interaction ' involving TiO^{2+}. Spectrophotometric evidence has been obtained in this study for an ' interaction absorption ' phenomenon involving Fe^{3+} and TiO^{2+}. No such ' interaction ' is found to occur in the presence of Fe^{2+}. The formation of this mixed metal species has also been studied in the presence of hydroxycarboxylic acids. The stoichiometry and formation of this species has been confirmed by both potentiometric and polarographic measurements. This section of the

thesis (Part II) also includes an investigation of the ion exchange characteristics of solutions containing Fe^{3+} and TiO^{2+} in dilute $HClO_4$. The results obtained have been used to postulate the existence of a hydroxy bridged ' interaction species ' involving these metal ions viz :



Procedures to enhance the titania content (TiO_2) of ilmenite are of much value in industry. Such ' beneficiation ' studies involving leaching of ilmenite samples with mineral acids under varied conditions, pretreatment and the use of reductants have been investigated under laboratory conditions. The results obtained indicate the optimum conditions for leaching with mineral acids as well as the effect of ' reductants ' and pretreatment in enhancing the TiO_2 content of ilmenite. Heating samples of ilmenite corresponding to 48.2 % TiO_2 in open vessels to about 1000° C followed by leaching with 11M HCl at 80° C for 4 hours was found to give a Titania beneficiated ' slag ' containing 87 % TiO_2. Laboratory studies have also been carried out with charcoal obtainable from local wood to indicate the use of varieties of uneconomical wood as ' reductants '. The significance of these studies are also discussed in Part III of this thesis.