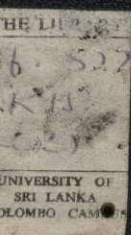


# STUDIES WITH THE OXOMETAL ION OF VANADIUM

A THESIS SUBMITTED FOR THE DEGREE OF  
MASTER OF SCIENCE OF THE  
UNIVERSITY OF SRI LANKA, COLOMBO CAMPUS

BY

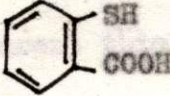
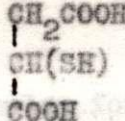
M. KANAGARATNAM



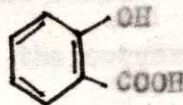
AUGUST 1974

ABSTRACT

Much interest has been shown in the coordination chemistry of vanadium. Of the oxidation states available to this element, the oxometal ion, vanadyl ion ( $VO^{2+}$ ) has been identified as the most stable species for the oxidation number four. The V - O bond is known to persist as a discrete unit in most of the reactions involving the vanadyl ion. Although the 'acceptor' characteristics of this ion have been studied with the 'hard' ligand atoms of groups V<sup>B</sup> and VI<sup>B</sup>, little is known of its behaviour with the heavier donor atoms of group VI B.

Mercapto carboxylic acids such as thiosalicylic acid,  and thiomalic acid,  are

known to be important both as analytical reagents as well as therapeutically promising ligand systems. The study of the metal complexes with these ligands has been a continuing interest in our laboratories. However, an attempt to investigate the coordination chemistry of vanadyl ion with the analogous oxygen containing ligands as salicylic acid,



and malic acid,  $\begin{array}{c} \text{CH}_2\text{COOH} \\ | \\ \text{CH}(\text{OH}) \\ | \\ \text{COOH} \end{array}$  have presented some experimental

difficulties.

Part I of this thesis reports an investigation of the use of vanadium(V) as a metal ion oxidant for thiol compounds. This section describes the reaction of a series of thiol compounds with vanadium(V). Arising out of this study a photometric procedure for the estimation of vanadium(V) in the presence of vanadium(IV) as well as in the presence of other interfering ions is presented.

The reaction products of a series of thiols have all been isolated and identified as their respective disulphides by polarographic, U.V./visible and infra-red studies. The nature of these products have also been confirmed by the use of conventional oxidants for obtaining disulphides from their parent thiols.

The reported observations of complex formation between selenium(IV) and thioalicyclic acid and that of the formation of equimolar mixtures of  $\text{RSSeSR}$  and  $\text{RSSR}$  from reactions of  $\text{Se(IV)}$  in 4 - 8 M  $\text{HCl}$  with  $\text{RSH}$  compounds have also been reinvestigated. The results indicate no evidence of the presence of elemental selenium in the oxidation product of  $\text{RSH}$  with  $\text{Se(IV)}$  in 4 - 8 M  $\text{HCl}$ , and confirms the role of  $\text{Se(IV)}$  purely as an oxidant to yield the corresponding disulphide ( an  $\text{RSSR}$  type compound ) rather than its ability

to complex with RSH compounds - a finding compatible with the redox potential data of Se(IV) in acid media. Spectroscopic and polarographic data are presented in support of this observation. The dissociation constants of the SH group of the thiols have also been evaluated using a polarographic procedure. The results of the studies presented in Part I of this thesis indicate that (i) thiols are oxidised to the corresponding disulphides with vanadium(V) - a reaction not affected by the presence of vanadium(IV) and foreign ions. This has been the basis of an analytical procedure for the estimation of vanadium(V) in a mixture containing vanadium(IV) and diverse ions. (ii) Disulphides are also formed from their corresponding thiols with Se(IV)/ 6 - 8 N HCl. The products of oxidation of SH groups by vanadium(V), Se(IV) and conventional oxidants as  $Pb(OAc)_4$  have been shown to be identical.

A potentiometric study of the complexes of vanadyl ion with salicylic acid, sulphosalicylic acid and malic acid and the evaluation of thermodynamic constants are described in Part II of this thesis.  $VO^{2+}$  is shown to form a 1:1 chelate with sulphosalicylic acid with a log K of 11.29 at 30°C. Potentiometric measurements were also carried out at varying temperatures with this system and this has enabled the evaluation of  $\Delta H$  and  $\Delta S$  for this system at 35°C as -8.754 K.cals/mole and 22.95 cal.deg<sup>-1</sup>.mole<sup>-1</sup> respectively. Potentiometric studies with sodium salicylate and malic acid are also reported in this

part of the thesis.

Mixed metal complex formation is known to be induced in the presence of hydroxy carboxylic acids as citric acid and tartaric acid. The tendency of vanadyl ion to enter into mixed metal complex formation with ions normally found associated with vanadium has been investigated. The reaction of vanadyl citrate with  $Al^{3+}$  is shown to give spectrophotometric evidence for the binding of  $Al^{3+}$  to vanadyl citrate, whereas its reaction with the kinetically inert  $Cr^{3+}$  is found to be controlled by the temperature of the reaction. Displacement reactions of vanadyl citrate with  $Fe^{3+}$  and EDTA and studies of the spectral variation of uranyl citrate in the presence of  $Al^{3+}$  to form the reported ternary species have been used as additional evidence for the formation of the  $VO^{2+} - citrate - Al^{3+}$  species. The results of these studies form Part III of this thesis.

The reaction of vanadyl diketonates with bases has also been studied to distinguish between the formation of base adducts as against coordination of base to the diketonates.

This part of the thesis also reports the reaction of vanadium(V) with  $SCN^{-}$  in the presence of ligands as oxine. Thiocyanate ion is shown to function as a reductant with vanadium(V). The composition of these species have been studied by isolation of solids and study of their infra-red spectra. The spectral observations for the reactions of these mixed

ligand complexes of vanadium in the presence of alcohols suggests the possible replacement of the coordinated base by alcohols in these species.