STUDIES ON SELENITO COMPLEXES OF MANGANESE(II) AND MANGANESE(III) AND ELECTROANALYTICAL APPLICATION OF MANGANESE(III) PYROPHOSPHATE

by

MALLELA SIVA PRASAD

DEPARTMENT OF CHEMISTRY

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Certificate

This is to certify that the thesis entitled " Studies on Selenito Complexes of Manganese(II) and Manganese(III) and Electroanalytical Application of Manganese(III) pyrophosphate", being submitted by Mr.Mallela Siva Prasad to the Indian Institute of Technology Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr.Mallela has worked with my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

B. L. Khandelwal
Thesis Supervisor

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Mallela Siva Prasad

Department of Chemistry
Indian Institute of Technology
New Delhi 110029

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Abstract

The thesis consists of two parts. Part A deals with the studies on selenito complexes of manganese(II) and manganese(III) and part B includes polarographic, amperometric and ion exchange studies on manganese(III) pyrophosphate.

The recent literature on manganese complexes of oxygen and sulphur donor ligands is presented in the first chapter of the thesis. The literature survey shows that only few metal selenito complexes have been reported.

The second chapter is devoted to the preparation of manganese(II) selenite monohydrate, sodium bis-selenito manganese(II) dihydrate and potassium tris-pyroselenito manganese(II) trihydrate. The composition of these complexes has been established by chemical analysis. All the compounds show magnetic moment (μ_{eff}) value of 5.90 BM expected for a high spin manganese(II). Their thermal decomposition processes have been established by thermogravimetric and differential thermal analyses supplemented by chemical and spectral analyses of the products formed at various temperatures. The interplanar spacings (d-values) of these compounds have been calculated from the diffractograms. Attempt has been made to elucidate their structure by spectral analysis.

Third chapter of the dissertation deals with the preparation of manganese(III) compounds of the type $Mn(SeO_3)_3 \cdot 4H_2O$ and $M\ Mn(SeO_3)_2 x\ H_2O$ (where $M = H^+$, NH_4^+, K^+, Rb^+ - Cs^+

All these compounds are very stable and show μ_{eff} value of 4.90 BM, which corresponds to the high spin d^4 manganese(III) ion. Based on the results of thermogravimetry and differential thermal analyses their decomposition transitions have been proposed, supported by the chemical, spectral and X-ray analyses of the products fomred at various temperatures. The d-values of these compounds have been calculated. The structures of these compound have been proposed by the spectral analyses. Electronic spectra of all these complexes showed Jahn-Teller disortions.

Fourth chapter of the thesis includes a brief introduction to polarography and amperometry. Analytical applications of manganese(III) solutions, with particular emphasis on manganese(III) pyrophosphate, is also discussed in this chapter.

The fifth chapter embodies results of polarographic studies of manganese(III) pyrophosphate and the utilisation of these results for amperometric determination of micro quantities of arsenic(II), iron(II), tin(II), hydrazine, hydroxylamine, nitrite, ascorbic acid, oxalic acid, thiourea, thiosulphate, thiocyanate and hydrogen peroxide. Rotating platinum electrode is used as indicator electrode at an applied potential of 0.00 V vs SCE. Effect of number of diverse ions on these determinations has also been discussed.

Chapter sixth of the thesis is devoted to the preliminary introduction to the ion exchange process. Ion exchange properties of manganese(III) pyrophosphate is studied and its separation from several cations has also been described.

In the last and the seventh chapter of the thesis the summary and further scope have been presented.

Contents

PART B