ANALYTICAL APPLICATIONS OF SCHIFFBASE LIGANDS AND STUDIES IN SYNERGISTIC EXTRACTION

By

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C E R T I F I C A T E

This is to certify that the thesis entitled " Analytical Applications of Schiffbase Ligands and Studies in Synergistic Extractions" being submitted by Mr.A.Varadarajulu to the Indian Institute of Technology, Delhi for the award of Degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr.Varadarajulu has worked under 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 thesis have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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A C K N O W L E D G E M E N T S

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(A. VARADARAJULU)

A B S T R A C T

This thesis describes the results of studies relating to analytical applications of schiff base ligands and synergistic extraction of metals. In the first part of the thesis, the solvent extraction studies of copper (II), nickel(II) and cobalt(II) as representative transition metals with (a) salicylidene aminothiophenol (b) salicylidene aminopyridine (c) naphthalidene aminophenol and (d) naphthalidene aminothiophenol are presented. A general survey of the extraction of various metals with salicylidene aminothiophenol indicates that Pb(II), Cd(II), Hg(II), Co(II), Zn(II), Ce(IV) and V(V) are extracted completely under certain conditions while Ag(I), Ca(II), Cu(II), Mn(II), Fe(II), Be(II), La(III) Al(III), Fe(III), Cr(III), Th(IV), Zr(IV), U(VI), Mo(VI) and W(VI) are incompletely extracted under all conditions employed. Salicylidene and naphthalidene aminothiophenol are comparable to thenoyl trifluoroacetone for the extraction while salicylidene aminopyridine is much weaker as extractant than TTA. Spectrophotometric methods for the determination of copper(II), cobalt(II) and nickel(II) with naphthalidene aminothiophenol have been developed based on the extraction studies. The schiff bases with sulphur as one of the donor atoms seem to be attractive for the estimation of other metals. Effect of various factors such as pH variation, excess of ligand

concentrations, changes in the volume of phases, the presence of foreign ions etc. have also been studied. In addition, this ligand has been shown to be a promising agent for the gravimetric estimation of lead(II) as well as for the spot test of uranium(VI) Further, inorder to understand the nature of the bonding involved, physico-chemical studies in the solid complexes isolated from solution has been carried out.

In the second part of the thesis, synergistic extraction of metals using N-benzoylphenylhydroxylamine and salicylaldoxime as chelating agents while tributyl-n-phosphate, trioctylphosphine-oxide, tricapril tertiary amine, pyridine, β-picoline, γ-piccline as synergents are presented. The adduct formation constants, log K_s , calculated for these adducts are comparable to those obtained with β-diketones and corresponding synergents. Spectrophotometric determination of uranium(VI) with mixtures of N-benzoylphenylhydroxylamine and tributyl phosphate, salicylaldoxime and tricapril tertiary amine and salicylidene aminothiophenol and morpholine have been developed taking advantage of the synergistic extraction.

Equilibrium constants for the formation of adducts in copper-β-diketonate- heterocyclic base systems (β-diketones- thenoyl trifluoroacetone, benzoyl trifluoroacetone and acetylacetone Heterocyclic bases- piperidine, morpholine, quinoline and pyridine) have been determined spectrophotometrically and some of adducts have been isolated as solids and investigated. The data are correlated with the characteristics of the ligands employed.

C O N T E N T S

PART-B - SECTION-I

SECTION-II

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