EXTRACTION STUDIES OF METALS WITH SOME SELECTED LIGANDS

BY

RUCHI SHUKLA

Department of chemistry

Submitted
in fulfilment of the requirements
of the degree of

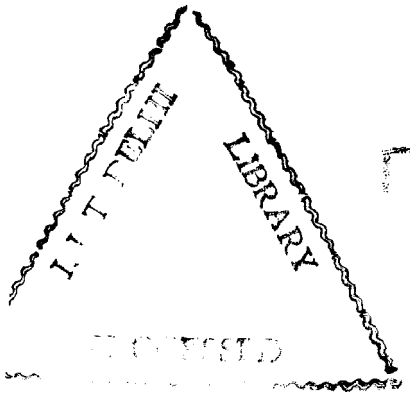
DOCTOR OF PHILOSOPHY

to the

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

INDIA

JUNE, 2001



Ligand

Dedicated to

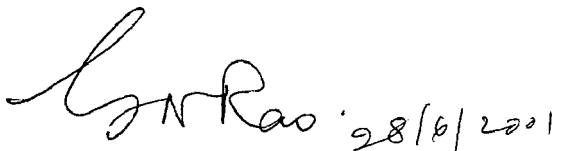
my

Parents

CERTIFICATE

This is to certify that the thesis entitled **"EXTRACTION STUDIES OF METALS WITH SOME SELECTED LIGANDS"** being submitted by **Ruchi Shukla** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** in Chemistry, is an account of bonafide research work carried out by her. Ruchi Shukla 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 result 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.



(G. N. Rao)

Professor, Department of Chemistry,

Indian Institute of Technology,

New Delhi-110016

ACKNOWLEDGEMENTS

At this moment of exultance, I find words to be inadequate to express my deep sense of gratitude to Prof. G. N. Rao, for his help in achieving my goal. It was a pleasure to work under him and my sincere and heartfelt thanks are due to him for his excellent guidance, kind and sustained co-operation and for many informative discussions throughout the course of this programme.

I am grateful to the Head of the Chemistry Department, Prof. M. N. Gupta and former Head of department Prof. A. S. Brar for providing me the necessary facilities to carry out the research work. Thanks are also due to all supporting staff for their kind help and cooperation.

It gives me immense pleasure to thank my friends Gunjan, Sampriya, Preeti, Thirumal, Sadia, Indu and Sonal for their help and encouragement during the course of this work.

I am thankful to Anupama, Vibha, Pankaj, Sooriya, Kadal, Parvesh, Charles, Sanjeev, Marilyn, Pooja, Roopali, Mukesh, Achintya, Nina, Nabin, Srinivas, Anamika, Rashmi and Anubhav for their help in various forms at different stages of this work.

The financial assistance given by Indian Institute of Technology Delhi is gratefully acknowledged.

I, thank Neeloo, Gudia and Surabhi for their affection and support that has kept me up.

Ruchi Shukla

Ruchi Shukla

ABSTRACT

A brief introduction of solvent extraction of metal ions including a) types of extraction systems, b) types of ligands used and c) synergistic extraction using auxiliary ligands is presented in the chapter first. The scope of present work has been indicated at the end of this chapter.

In chapter two efficacy of potassium-dihydrobis-pyrazolyl-borate in the extraction of selected metal ions (e.g. copper (II), cadmium (II), cobalt (II), lead (II), manganese (II), nickel (II) and zinc(II)) has been described. The method of preparation of ligand and the experimental techniques used in the study of extraction of the metal ions have also been given. From the distribution data $pH_{1/2}$ (pH at which 50% extraction of metal occurs using 0.005M ligand) and log K_{ex} (equilibrium constant in the two phase extraction system) values have been calculated. The order of extraction of metals with potassium-dihydrobis-pyrazolyl-borate in dichloromethane as a function of $pH_{1/2}$ value is as follows:

Cu(II) < Ni(II) < Co(II) < Zn(II) < Cd(II) < Pb(II) < Mn(II)

The efficiency of potassium-dihydrobis-pyrazolyl-borate for the extraction of metals studied here has been compared with that of other well known chelating ligands like thenoyltrifluoroacetone (HTTA), dibenzoylmethane (DBM) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP). Separations of pairs of metals (eg. Cu-Mn, Ni-Mn) which are

feasible using potassium-dihydrobis-pyrazolyl-borate have been indicated. The extractant has also been studied for the possible applications in a) determination of metal ion concentration in standard samples b) preconcentration and group extraction of metals.

Chapter three describes the preparation and characterisation of potassium-hydrotris-pyrazolyl-borate and its utility in metal ion extraction.. Extraction of some selected metal ions like copper(II), cadmium(II), cobalt(II), lead(II), iron(II),manganese(II), nickel(II), zinc(II) with potassium-hydrotris-pyrazolyl-borate has been studied. Mechanism of extraction has been discussed on the basis of experimental evidence obtained. $pH_{1/2}$ and log K_{ex} values have been calculated for all the systems. The order of extraction of metals with potassium-hydrotris-pyrazolyl-borate in dichloromethane as a function of $pH_{1/2}$ value is:

Cu(II) < Ni(II) < Co(II) < Zn(II) < Cd(II) < Fe(II) < Mn(II) < Pb(II)

log K_{ex} values obtained with potassium-hydrotris-pyrazolyl-borate have been compared with those obtained with thenoyltrifluoroacetone (HTTA), 3-phenyl-4-benzoyl-5-isoxazolone (HPBI), oxine (HOx) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP). Separations of pairs of metals (eg.Cu-Mn, Ni-Mn) which are feasible have been described. The extractant has also been studied for the possible applications in a) determination of metal ion concentration in standard samples and b) preconcentration and group extraction of metals.

Chapter four describes the synergistic extraction work done with potassium-dihydro-bispyrazolyl-borate as primary ligand and trioctylphosphineoxide (TOPO) as auxiliary ligand. Mechanism of synergistic extraction has been discussed on the basis of experimental evidence obtained; $pH_{1/2}$, log K_{ex}' and log K_s values have been calculated for all the systems. The log K_s values obtained with potassium-dihydro-bispyrazolyl-borate and TOPO are compared with those obtained with other chelating ligands and TOPO.

Chapter five deals with preparation and characterisation of Octaacetate of calix(8)arene and its applicability in the extraction of lanthanides. Solvent extraction of some selected metal ions La(III), Nd(III), Sm(III) and Eu(III) with Octaacetate of calix(8)arene has been described. Mechanism of extraction has been discussed on the basis of experimental evidence obtained. $pH_{1/2}$ and log K_{ex} values have been calculated for all the systems The order of extraction of metals with octaacetate of calix(8)arene as a function of $pH_{1/2}$ value is : Eu(III) < La(III) < Sm(III) < Nd(III).

Chapter six describes the synergistic extraction of some selected metal ions like cadmium(II), lead(II), manganese(II) and zinc(II) with a commercial extractant LIX26 (Henkel corporation) and tributylphosphate (TBP). Mechanism of extraction has been discussed on the basis of experimental evidence obtained. $pH_{1/2}$ and log K_{ex}' and log K_s values have been calculated for all the systems. The log K_s values obtained with LIX26 and TBP are compared with those obtained with other chelating ligands and TBP.

Table of Contents