APPLICATION OF REGULAR SOLUTION THEORY TO THE SOLVENT EXTRACTION OF METAL COMPLEXES USING CHELATING LIGANDS

BY

S. NARAYANAN

DEPARTMENT OF CHEMISTRY

SUBMITTED IN

FULFILMENT OF THE REQUIREMENTS OF
THE DEGREE OF DOCTOR OF PHILOSOPHY

TO THE

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

JULY 1980

DEDICATED

TO MY DEAR PARENTS

AND

TO THE FOND MEMORY OF MY BELOVED UNCLE

PROF. N. VENKATASUBRAMANIAN

CERTIFICATE

This is to certify that the thesis entitled, "Application of Regular Solution Theory to the Solvent Extraction of Metal Complexes using Chelating Ligands," being submitted by Mr. S. Narayanan 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. S. Narayanan 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.

(G.N. RAO)
Thesis Supervisor
Assistant Professor
Department of Chemistry
Indian Institute of Technology
New Delhi-110016, INDIA

ACKNOWLEDGEMENTS

At this moment of exultance, I find words to be inadequate to express my deep sense of gratitude to Dr. G.N. Rao, Assistant Professor, Department of Chemistry, I.I.T. Delhi, 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 a informative & lively discussions throughout the course of this programme.

I am grateful to Prof. R.P. Gandhi and Prof. J.C. Ahluwalia for providing all the necessary facilities in the department of Chemistry during my research work. I am thankful to Dr. M.M. Bhutani for extending the facilities in the Radiochemistry laboratory.

I acknowledge the assistance rendered by Mr. Bala Dutt and Mr. L.C. Sharma in taking the spectra. I wish to express my appreciation to my colleagues for their pleasant association and co-operation and I particularly thank Dr. V.S. Chouhan, Mr. M.K. Gupta and Mr. C.S.R. Murthy, who helped me in many ways during my tenure.

I am grateful to University Grants Commission for the fellowship under the Faculty Improvement Programme scheme and to Principal, Deshbandhu College, Delhi University, for deputing me to pursue this programme.

I reminisce with deep appreciation the affectionate forbearance of my wife during the tenure of this programme.

I am thankful to Mr. Arora for the neat tracing of figures and to Mr. Jagdish Kumar for the excellent typing of the thesis.

S. Narayanan

(S. NARAYANAN)

ABSTRACT

In the present work, a systematic and detailed studies of extraction of metal complexes using different chelating ligands into different types of solvents have been made and regular solution theory has been applied to investigate the regularity in the distribution on the basis of solubility parameter concept. The correlation between the experimentally determined distribution coefficient of the ligand and that of its metal chelate has been shown by plots and the regularity in the distribution established. From the above plots the ratio between the molar volume of the chelate and that of the ligand have been shown to be in conformity with the predicted extraction mechanisms . The theory has been applied to the synergistic studies also.

The molar volume and the solubility parameter of the ligands have also been determined experimentally and the values confirmed by plots and from the equations derived from regular solution theory. The correlation between the distribution ratio of the ligand and the solubility parameter of the solvent have also been established satisfactorily. In the synergistic studies, good correlation has been shown between the adduct formation constant and activity coefficient on the basis of regular solution theory.

In the first chapter of the thesis a brief review of the previous work done on the solubility parameter concept has been made followed by discussion on the scope of present work.

The second chapter describes studies using benzoyltrifluoroacetone with 'inert' solvents and oxygenated solvents with Cu(II), Co(II), Zn(II). The results indicate that BTA is a better extractant than thenoyl trifluoro acetone. The solubility parameter and molar volume of BTA have been found to be 10.6 and 150 respectively.

The third chapter describes extraction studies of Co(II), Zn(II) and Eu(III) with 4-Benzoyl 2,4-dihydro 5-Methyl 2-Phenyl 3H-Pyrazol-3-one (BMPP). Co(II) and Zn(II) form the predicted complex of the type MA_2. Eu(III) does not form the anticipated simple complex EuA_3. Eu(III) definitely shows different behaviour and forms mixed and ion pair chelates in all the inert solvents studied. Detailed methods of determining the solubility parameter and molar volume of BMPP have been described and these are found to be 9.4 and 430 respectively. The synergistic studies using BMPP and Tributyl Phosphate Mixtures have been described with Co(II), Zn(II) and Eu(III). Again Co(II) and Zn(II) show the normal behaviour while Eu(III) indicates the probable formation of mixed adducts. The solubility parameter of the adduct evaluated is around 9.5 in the studies with Co(II) and Zn(II). Due to the unusual behaviour of Eu(III) solubility parameter value of adduct could not be ascertained.

In the last chapter, extraction studies employing Salicylaldoxime, as the chelating ligand, have been described.

The extraction pattern follows the order Cu > Co/Zn, with these three metals studied, in different inert solvents. Hexane and cyclohexane show abnormal behaviour with Cu(II) while in the case of Zn(II) no extraction was possible to the desired level with these two solvents. The solubility parameter and molar volume of salicylaldoxime were estimated to be 13 and 100 respectively.

The correlation between the distribution coefficient of the ligand and that of its metal chelate, on the basis of regular solution theory was found to be satisfactory with all the three ligands, with all metals and in most of the different types of solvents.

CONTENTS