SOLVENT EXTRACTION OF COBALT (II), ZINC (II) AND EUROPIUM (III) WITH THIODERIVATIVES OF ACYLPYRAZOLONES AND β - DIKETONES

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TO

MY

BELOVED

PARENTS

C E R T I F I C A T E

This is to certify that the thesis entitled " Solvent Extraction of Cobalt (II), Zinc (II) and Europium(III) with Thioderivatives of Acylpyrazolones and β-diketones", being submitted by Mr.Vijay Singh Chouhan 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.Chouhan 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 B S T R A C T

The following chelating agents containing thiogroups have been prepared (a) 4-thiobenzoyl 2,4-dihydro 5-methyl 2-phenyl 3H-pyrazol-3-one (SBMPP) and thiobenzoyltrifluoroacetone (SBTA). Since heavy metals show a preference to coordinate to sulphur as compared to oxygen, such compounds appear to be very promising as selective analytical reagents. Solvent extraction of cobalt (II), zinc (II) and europium(III) from buffered aqueous media into benzene containing the ligands SBMPP, SBTA and benzoyltrifluoroacetone (BTA), have been investigated comprehensively. Radioactive tracers ^{60}Co, ^{65}Zn and $^{152+154}Eu$ were employed in these studies and the activity was counted in aqueous and nonaqueous phases to calculate the distribution coefficients. Mechanism of the extraction has been discussed on the basis of experimental evidence obtained and the relevant information available in the literature. Synergistic enhancement of extraction has been observed in these systems with auxiliary ligands like pyridine, γ-picoline, quinoline, tri-n-butyl phosphate (TBP), tri-n-octylphosphine oxide (TOPO), bipyridyl and ortho-phenanthroline. From the distribution data, extraction constants and the adduct formation constants have been calculated and the extracted species have been identified.

Analytical applications of SBMPP and SBTA apart from solvent extraction have been investigated. A qualitative survey for the colour reactions of thioligands with various metal ions has been made to assess the utility of these chelating agents for spectrophotometric determination of metals. Spectrophotometric methods for the determination of cobalt(II) and nickel (II) with SBMPP and uranium (VI) with SBTA have been developed. By shaking the nonaqueous phase with acid the estimation of cobalt(II) has been rendered highly selective. Thin layer chromatographic separation of various metal ions has been carried out employing SBMPP and SBTA as chelating agents in solvents of varying polarity and binary solvent mixtures. It has been observed that the mixed solvents are more useful for the separation of complexes, than pure solvents. Since the metal chelates are intensely coloured no additional reagent is needed in such separations.

Several metal complexes of SBMPP and SBTA have been synthesised and characterised employing following techniques (1) elemental analysis, (2) ultraviolet and visible spectroscopy, (3) infrared spectroscopy and (4) nuclear magnetic resonance spectroscopy.

C O N T E N T S

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