PREFACE

The phenomena whereby two extractants when present together, extract a species, mostly metal ion – with greater efficiency than that corresponding to their additive action is called synergism. Rather much effort has been devoted to the synergistic extractions over the past two decades since the very nature of synergism offers interesting research possibilities of both the chemistry of these extractants and their practical applications.

The large enhancement of metal extraction has been widely investigated from the theoretical (mechanism), analytical as well as from the applied point of view. In the nuclear fuel industry synergistic extraction has been recommended for the recovery of the precious metal ions. The first careful study of this phenomenon in 1958 was carried out by Blake *et. al.* who found that U (VI) is extracted synergistically by a mixture of dialkyl-phosphonic acid and a neutral organophosphorus reagent. Later on, extensive works have been carried out on the synergistic extraction of di-, tri- and tetravalent metal ions with different combinations of reagents by two pioneer workers in this field namely H. Irving and T. V. Helay. The increasing interest in this subject can be seen from the large number of research papers and various reviews published in different journals.

When speaking about synergism, many extraction chemists will undoubtedly think immediately of the most common systems where a metal cation M^{n+} is extracted by a mixture of an acidic chelatating (HA) and a basic (S) reagent. Here the joint action of both extractants becomes very pronounced especially in those cases where the co-ordination capacity of MA_n chelate is not fully saturated by the ligand A. Then the extractant S brings about the formation of a mixed complex MA_nS_x which is extracted with much greater efficiency than the parent chelate.

The present dissertation is broadly divided in three sections. In section I. there is a general introduction related with the present study in Chapter 1. Section II (experimental) consists of three chapters. e.g.. Chapter 2 describes the materials and equipments used in the work. Chapter

3 contains the detailed experimental aspects of synergistic extraction of several d-block elements while chapter 4 & 5 include the identical aspects on several f-block elements including both lanthanide and actinide elements.

Finally in Section III, a brief and logical conclusion on overall results has been drawn in chapter 6 after summarization the outcome of chapters 3, 4 and 5.

In chapter 1, we have introduced the physico-chemical aspects of synergistic extraction, its success and its limitations with few selected examples of such extraction and their possible mechanism reported by earlier workers. Such a report is always necessary to search for the possibilities of further exploration of the process. In periodic table, both transitional elements and rare earths can exhibit variable oxidation states indicating the chance of expansion of co-ordination shell which can be the most popular mechanism of synergistic extraction. We have selected several members from all of these two families of metals (d & f block) depending upon their previous behaviour and also on their inclination towards hard or soft bases. A short review on recent works on such metals has been presented along with the earlier works reported on the different sorts of extracting agents, both ligands and donors, have been tabulated as far as possible systematically. Keeping in mind there may be omission of few latest works due to lack of informations. Finally, in this chapter we have presented our aim in a qualitative way. With an explanation of selection of few metals or few ligands over there.

In chapter 2, there is an attempt to describe the net organisation of whole work. Availability and quality of chemicals used, including radioisotopes and their measurement using different types of instruments e.g., UV/VIS spectrophotometer or γ-ray spectrophotometer, as the case demands have been reported. We have also described the methods of synthesis and characterization of all the ligands and donors used in this investigation, other than those we have procured. The characterisation of organic ligands include elemental analysis, IR & NMR data

and finally evaluation of pKa values of such systems in order to put a strong claim in favour of their use as extracting agents.

Chapter 3 includes the reports of our work on synergistic extraction of several d-block elements e.g., Co (II), Zr (IV), Pd (II) and Au (III). We have synthesized a ligand 2-hydroxy-1-naphthaldehyde thiosemicarbazone having three (O, N, S) donor sites. In this chapter, this ligand was applied in the study of extraction of Pd (II) & Au (III). Effects of oxodonors and long chain amines on such extraction have been studied in detail. It was possible to calculated the values of apparent formation constants of ternary adducts formed in such extraction. The dependence of such constants on different experimental parameters were systematically studied. Nature of metal complex responsible for mixed extraction was also ascertained by the study of distribution ratio against ligand and donor concentrations. For these two metals, ethyl acetate and MIBK were selected as organic media in which the metal was transferred in preference to methyl benzoate which was shown to exhibit slightly higher 'D' values in comparison to ethyl acetate and MIBK. The only practical reason is the better solubility of the ligand in ethyl acetate and MIBK. Synergistic extraction of Co (II) & Zr (IV) were followed by the use of two oxime ligands, e.g., 2-hydroxy-1-naphthaldoxime and salicylaldoxime. The former was synthesized, characterised and applied in the study of several metals in our laboratory in some earlier investigations. For both of these metals, we have reported the effects of several phosphorus-oxygen neutral donors on their binary extraction systems, the donors like DMSO were also used. In all these cases, the basic characters of donors were found to be crucial & deciding factor controlling the extent of extraction. Finally we have reported few applications of proposed methods to natural samples like ore, minerals, pharmaceutical drugs etc. for the respective metals like Pd (II), .   and Co (II). In absence of suitable matrix for the analysis of Zirconium, there is no such report on its determination although overall stability constants of all the four

transition metal-ternary complexes were evaluated. Results show Au (III) form stronger complexes than Pd (II) while among two oximes Co (II) complex is more stable.

In chapter 4, we have reported synergistic extraction of Ce (III)-dipyridyl complex with oxodonors and effects of several crown ethers on the extraction of Pr (III)-benzoyl acetone into $CHCl_3$ medium. The mixed extraction results on Ce (III) was so encouraging that the procedure was adopted in the analysis of the metal in natural samples. Nature of extracted complex were well ascertained by slope ratio analysis and role of aromatic ring in deciding the relative basic characters of crown ethers which ultimately effects the degree of extraction of the Pr (III) were also investigated. The extraction of Pr^{3+} ion by the combination of benzoyl acetone and crown ethers is a very promising one in the field of solvent extraction chemistry because of every hydrophilic oxygen atom between a lipophilic ethylene moiety. crown ethers show a remarkable balance with regards to binding symmetry and polarity. Also due to large ionic diameter crown ethers can play the role of suitable host in presence of suitable guest. In the present dissertation work we have used two crown ethers, viz., 15-crown-5 and benzo-15-crown-5. These two crown ethers have ionic diameter around 170-220 pm. So Pr^{3+} ion can easily be encapsulated within the cavity of crown ether. Due to the presence of aromatic ring attached with the crown ether moiety in the present work, flexibility of the crown ether molecule seems to be different. By utilising this phenomena we have determined the equilibrium constant and also apparent formation constants for the Pr^{3+} - benzoyl acetone – crown ether ternary complexes. It has been found that benzo-15-crown-5 performs highest degree of extraction relative to 15-crown-5.

In chapter 5. extensive investigation on actinide extraction through ternary complex formation is reported. By using 2-hydroxy-1-naphthaldehyde thiosemicarbazone ligand we have studied the extraction of both Th (IV) and U (VI) and the effects of oxo donors and amines on such

extraction. Calix[3]OH[3]OMe[6]arene was used as one of the donor in Th^{4+} extraction. Studies on extraction of ternary complex of U (VI) in presence of several amide donors were also reported with respect to its extraction with HPBI, HPAI, HPMBP and HTTA. It has been found that binary formation constant (log k_{ex}), ternary adduct formation constant (log K) values were highest for UO_2^{2+} - HPBI – amide systems. It has been established in the present study that HPBI is a better extractant among the beta-diketones used. The effect of substituents in the monoamides on the adduct formation in the ternary complexes is explained on the basis of the molecular modeling. Foreign ions also play a very important role in synergistic extraction. Enhancement in the extraction for both binary as well as ternary complexes of UO_2^+ - HPBI – amide system is observed in the presence of $NaClO_4$. Here increased hydration of Na^+ cation is responsible for such enhancement in the extraction. Basic character of amides (K_H values) were found to have very strong effect on the extraction of metal. There is a gradual rise in K_S (overall formation constant) values with increase in K_H values of amides. The effects of temperature on ternary complex extraction of UO_2^{2+} with β-diketones and amides were studied and an enthalpy favoured mechanism was suggested. It has been found that the nature of substitution in the amide skeleton and stringent steric requirements govern the degree of extraction. This is well supported by the stabilization of the ternary complex through enthalpy favoured mechanism of the UO_2^{2+} - ligand – amide ternary complex. Thus D2EHAA is found to found to extract highest corresponding to other amides. The experimentally determined ΔH_f^0 and ΔS_f^0 values correspond well with that of typical ternary complexes value obtained earlier,   Although these studies were carried out with tracer uranium (U-233), macro scale extraction of uranium (VI) was also reported with dipyridyl-oxodonor adduct and the metal was determined colorimetrically.

Finally in an interesting study. Np (IV) was synergistically extracted by a mixture of HPBI and

TOPO. Perhaps. we can claim that this investigation cam be termed as the first synergistic

investigation of Np (IV) - β-diketones.

In a brief conclusion in Section III. we have summarized the overall experimental

results along with an attempt to explain such results in terms of some possible mechanism in

chapter 6. Since a particular explanation may not be the only alternate of our experimental data.

we can suggest a probable pathway in order to offer some explanation over the observations of

our investigation.