Section III

Chapter 6: Summary and Conclusion

Summary

In the present dissertation we have reported the experimental details with corresponding results of synergistic extraction of several inorganic cations in chapters 3-5. As the inorganic cations, we have selected metal ions with incompletely filled subshells e.g., transition or d-block & f-block elements. Among d-block elements we have picked up Co (II), Zr (IV), Pd (II) & Au (III) while Ce (III), Pr (III), Th (IV), U (VI) & Np (IV) are the members of f-block elements which were included in our study. As the extracting agent we have used different chelating ligands among which 2,2$'$-dipyridyl and salicylaldoxime were procured. Both oxime and thiosemicarbazone derivatives of 2-hydroxy-1-naphthaldehyde were synthesised and characterised in our laboratory. We have also synthesised several other β-diketones e.g., isoxazolone adopting a previous method, reported by earlier workers and used as such after analysing their reported characteristic properties. Four distinct class of donors have been applied in out present dissertation work e.g., organophosphorus compounds i.e., alkyl or aryl substituted phosphates (TOPO), several substituted amides (long chain) and different classes of high molecular weight amines and some members of supramolecular chemistry like crown ethers and calix[n]arenes derivatives. Depending upon the specific case, we have adopted one or more than one set of donors. In addition, in few examples we have applied dimethyl sulphoxide as donor. Basic character of donor is a deciding factor for a given synergistic process and as the mechanism is explained by the formation of adduct in organic solvent, we may consider that the formation constant of adduct as the quantitative measure of the degree of the synergistic enhancement by the neutral base used as an additive. Hence, we have reported the experimental data in terms of formation constant of mixed adduct.

We can summarise our experimental results in connection with the metals taken up in this dissertation. When a particular metal is extracted by different sets of ligand donor combination we describe them under same heading.

Cobalt:-

Cobalt was extracted by the mixture of 2-hydroxy-1-naphthaldoxime and oxodonors like TOPO, TBPO, bis(2-ethyl)hexyl phosphonate and DMSO in o-xylene at aqueous pH 8-9. A composition of [Co(A)·Cl, S, 2H$_2$O] [A = ligand, S = donor] was determined for the adduct and the variation of S.C. was found to follow the trend DMSO > TOPO > Phosphonate > TBPO showing the electronic effect of donor. Fromation of strong TOPO-Co-ligand adduct was confirmed by I.R. data, e.g., $\nu_{P \to O}$ shifts from 1199 cm^{-1} to 1125 cm^{-1}. Values of log K$_S$ also are in same order. Results were applied in the determination of cobalt content in some drug samples and also in some ore bearing the metal. Experimental values are within the range of values obtained by the analysis of metal by direct AAS.

Zirconium:-

Use of a simpler oxime e.g., salicylaldoxime in the study of Zr (IV) extraction into dichloromethane in presence of both phospho donors and amine donors (high molecular weight amine) was made. This very important metal for nuclear technology is known to form oxygenated species in weakly acidic solution. Fall in extraction with increase in pH is obvious. In case of synergistic extraction the trend is TOPO > TBPO > TPPO > TBP for P-O compounds while for amine donors TOA > Amberlite LA-2. These results are in conformity with this basic character of donors. Results of overall equilibrium constant determination show same trend and nitrogen compounds have more profound influence than phosphorus donors. Here again

formation of ternary complex of metal involving both the oxime and donor was confirmed by the shift of $\nu_{P \to O}$ from 1199 cm^{-1} to 1149 cm^{-1}.

Palladium:-

This important transitional element was extracted by 2-OH-1-naphthaldehyde thiosemicarbazone and effects of several donors like phospho oxygen compounds and orgainic amines on its extraction were studied. We found only few limited solvents for the ligand and we choose ethyl acetate in preference to methyl benzoate because of higher solubility of the ligand itself. Synergic effects followed the trend of increasing basic character of donor and amines were found to be more effective than phosphine oxides, keeping other parameters unchanged. A species of composition [Pd A Cl S], A = ligand, S = donor was determined from slope ratio analysis and evaluation of equilibrium constants for ternary complexes indicated a similar trend with that of synergistic co-efficient values. Involvement of ligand and donor molecules in ternary complex was finally ascertained by the shift in C-S and P-O bond in the I.R. spectra of extracted species. Extrapolation of results into natural samples show good degree of recovery of the metal.

Gold:-

This novel metal was studied with identical sets of parameters like that of palladium. Solvent used in this case was MIBK and again amines are found to be more efficient synergic reagent than phosphine oxides due to lower electronegative character of nitrogen. Only difference is that TOPO is slightly better donor than phosphonate, while reverse is true for Pd. Calculation of S.C., log β (stability constant) and log K_S (adduct formation constant) also in accordance with the results. Among the amines, quarternary salts were the strongest while among the P-O compounds, TOPO was the best. Shift in I.R. stretching frequency of P$\to$O bond and C$\to$S bond in ternary complex established the involvement of both ligand and donor molecules in the mixed

adduct. The presence of halide group and water molecules have been assumed on the basis of slope ratio analysis of the adduct. Metal : Ligand : Donor = 1 : 1 : 1, the rest part of inner sphere in octahedral and tetra co-ordinate Au (III) & Pd (II) complexes are occupied by halide (2 for Au^{3+} & 1 for Pd^{2+}) and water molecules.

Lanthanides:- (Cerium & Praseodymium)

We have reported the synergistic effects of the extraction of only two lanthanoids e.g., Ce (III) & Pr (III). Although both of them belong to 4f-family the extraction chemistries adopted in the present investigation is quite different whier Ce (III) was extracted by bidentate chelating agent dipyridyl (DP), Pr (III) was extracted by a widely employed β-diketone i.e., benzoyl acetone.

Extraction of Ce (III) - DP into $CHCl_3$ and effects of amines and phospho-oxygen donor, as used in few previous cases, were studied radiometrically using Ce-141 isotope. Variation of S.C. and log β are in well accord to their basic character e.g., TOPO > TBPO > TPPO > TBP and TOA > Amberlite LA-2. A species of composition [Ce (DP)₃], TOPO was attributed for mixed extraction and appropriate shift in I.R. frequency of P-O bond (1196 → 1145) established the involvement of donor in ternary complex. Analysis of Ce (III) content in an ore and recovery of added Ce (III) from the analytes established the applicability of the method.

For, praseodymium however, we have used benzoyl acetone as extractant and effects of two crown ethers e.g., 15-crown-5 and benzo-15-crown-5 were studied in $CHCl_3$ solvent. The metal was determined by Arsenazo (III) reagent. Slope ratio analysis shows that ratio of metal : ligand : donor = 1 : 1 : 1 in mixed adduct. Trend in S.C. & β values follow the order benzo-15–crown-5 > 15-crown-5, perhaps due to presence of benzene ring. Enhances the donor ability of benzo-15-crown-5. In this extraction we have reported the variation of extraction with temperature and

evaluation of thermodynamic parameters established that extractions were found to be enthalpy favoured.

Actinides:-

Thorium and Neptunium (tetravalent)

These two quadrivalent cations of 5f-family in periodic table were extracted by two different chelating agents, e.g., Th (IV) by 2-hydroxy-1-naphthaldehyde and Np (IV) by HPBI in xylene. While Th (IV) was analysed colorimrtrically by Arsenazo (III), Np-238 was assayed radiometrically by γ counting NaI (Tl) detector.

The donors used in mixed extraction of Th (IV) was TOPO, DMSO, TOA and calix[3]OH[3]OMe[6]arene. The trend in S.C. and log β follow the order DMSO < TOPO < calix [3]OH[3]OMe[6]arene < TOA. Due to more availability of nitrogen lone pair, TOA acts as best donor but among the oxodonor fitting of metal complex into cavity of calixarene molecule becomes more dominant. I.R. data of ternary complex is also in accordance with it.

For Neptunium (IV), we have reported the extraction with HPBI (pKa = 1.12) and effect of TOPO on such extraction into xylene. Variation of several extraction parameters and study of corresponding formation constants indicated a species of composition $Np(PBI)_4TOPO$ was responsible for enhancement of extraction. Determination of thermodynamic parameters show that the ternary complex is both enthalpy and entropy favoured. The method provides a possible separation of Np (IV) from two tetravalent actinides Th (IV) and Pu (IV).

Uranium:-

This actinide element in hexavalent state with f^0 configuration exhibit peculiar chemical characteristic which partly resembles with that of transition element. Therefore we have provided

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an extensive support on the study of uranyl extraction with different type of ligand-donor combination with a possible attempt to study different parameters.

A very simple and widely used ligand dipyridyl (DP) was utilised in our present report in which effect of donors TOPO, TPPO, TBP and of two amines e.g., tertiary and secondary were studied. Preferential solvent was $CHCl_3$ and metal was determined colorimetrically by oxime reagent. The values of S.C., log β and log K_S are found to be in same sequence e.g.,

TOPO > TBPO > TPPO > TBP; TOA > Amberlite LA-2; and also N-donor > O-donor. Changes in I.R. frequency are also in right agreement.

For the ligand 2-hydroxy-1-naphthaldehyde thiosemicarbazone, synthesis of which has been described in chapter 2, ethyl acetate was used as solvent and metal was determined with Arsenazo (III) colorimetrically. We have used only three donors for this study. Synergistic coefficient, log β and log K_S for mixed adduct are in following sequence, DMSO < TOPO < TOA. Shifts in I.R. stretching frequency of C-S ligand, P-O of TOPO established the involvement of both of them in ternary complex with stoichiometry, metal : ligand : donor = 1 : 1 : 1.

Among the β-diketones, HTTA (pKa = 6.24) is well known extracting agent for actinide. We have reported the use of HPBI in the extraction of the metal in toluene solvent as it has got lower pKa value (pKa = 1.1). Effects of several amide donors like di-2-ethylhexyl acetamide (D2EHAA), di-2-ethylhexyl propanamide (D2EHPrA), di-2-ethylhexyl isobutylamide (D2EHiBA) and di-2-ethylhexyl pivalamide (D2EHPvA) were studied in detail. A mixed chelate $UO_2(PBI)_2S$, where S = donor was attributed for synergism. Not only the temperature, but the effect of several foreign electrolytes on the degree of synergism were studied. All the amides result in exothermic extraction (enthalpy favoured) and a trend is as follows:

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D2EHAA > D2EHPrA > D2EHiBA > D2EHPvA. D2EHAA is both enthalpy and entropy favoured, due to lesser branching. Again, effect of added donor shows high changes in free energy indicating the synergism is very important aspect of this sort of extraction.

Conclusions

The experimental findings related to synergistic extraction of different metal complexes obtained in the present dissertation work clearly indicate that a remarkable synergistic enhancement takes place in each of the systems chosen for our present study. Such investigation is particularly valuable from different point of view. The practical applicability of the present synergistic extraction technique for the recovery of the metals from complex matrices show that the experimental values are in close proximity with the theoretical values. For example, by applying synergistic extraction technique, we have estimated Co content in some pharmaceutical drug samples and also in some ore bearing the metal. The experimental values are within the range of values obtained by analysis of metal by direct AAS. Similar to cobalt, a good degree of recovery of Pd metal in several ore samples are obtained in present dissertation work. One more application of our present synergistic extraction technique is employed for estimation of cerium in an ore containing cerium. The reported data shows the applicability of the proposed method in some natural samples. However, we were unable to show the similar sort of applications for all other metals used in present dissertation work. This is mainly due to non availability of the suitable matrix. However, we are of opinion that the method of extraction could be well applied for the analysis of these metals from complex matrices too. Besides application in quantitative analysis this method can also be applied for separation and recovery studies from much higher acidic and complexing media in ternary phase.

Besides, starting with some known compound, we have synthesised a new chelating ligand compound as 2-hydroxy-1-naphthaldehyde thiosemicarbazone. Having three different types of donor centers, viz., O, N and S it can binds with hard, soft and borderline metal ions. This unique property of 2-hydroy-1-naphthaldehyde thiosemicarbazone makes it very much instrumental to be used as a successful chelating extractant in the syneregistic extraction study of gold (borderline metal), palladium (soft metal) and thorium and uranium (both are hard metals). It has been seen in chapters 3 and 5 tha the binary extraction constant, $\log k_{ex}$, value is higher for Au^{3+} compared to Pd^{2+} (chapter 3) and those for Th^{4+} are larger compared to UO_2^{2+} (chapter 5) using 2-hydroxy-1-napthaldehyde thiosemicarbazone as ligand. This may be explained considering charge of the cations. Our ligand prefers Th^{4+} compared to UO_2^{2+} (the later having smaller effective charge), Au^{3+} compared to Pd^{2+} (due to the same reason).

One of our main striking feature in the present dissertation work is that we have sum up the total synergistic extraction processes by setting up of a mathematical model. Instead of using a common mathematical derivation, we have set up different sets of mathematical equations for different metal ions used in the present dissertation work. These metals belong to different categories (like Co (II) belongs to transition elements, Ce (III) belongs to lanthanide elements, U (VI) belongs to actinide series etc), they possess different electronic configurations. For this reason outer sphere charges are different for different metal ions. So different charge of metal ions resulted different stoichiometry of the extracted species.

The results obtained in the present dissertation work is also important from the viewpoint of metal – ligand – donor bonding characteristics. This phenomenon is well supported by using IR experimental technique. For example in the extraction of palladium by 2-hydroxy-1-naphthaldehyde thiosemicarbazone and neutral donor, the stoichiometry is found to be PdAXS,

where A = ligand, X =solvent and S = Donor. From IR data it has been found that stretching frequency of C=N in the free ligand was at 1471 cm^{-1} but it was shifted to 1463 cm^{-1} in case of Pd^{2+} - 2-hydroy-1-naphthaldehyde thiosemicarbazone – TOPO complex.

One important finding in our present dissertation work is that by applying calix[3]OH[3]OMe [6]arene we have successfully extracted Th^{4+} in preference to TOPO and DMSO. Calix[3]OH[3]OMe[6]arene adopts a conical configuration in solution thus facilitating its upper rim to open up. Thus Th^{4+} is included into the caity of the calixarene molecule indicating clearly a host – guest phenomena. This well supported by IR data.

We have also used crown ethers as donor molecules in the synergistic extraction study of praseodymium. It has been found that benzo-15-crown-5 extracts Pr (III) higher in compared to 15-crown-5.. Here ionic diameter of the crown ether used fits very well with that of the Pr^{3+} ion. Thus we have shown that 2nd and 3rd generation supramolecualr novel compounds like crown ether and calixarene respectively can be used successfully as donor or host molecules capturing the metal ion entity within its own cavity and by this way facilitating the synergistic extraction process.

Throughout investigating the dissertation work it has been found that TOPO generally forms the stronger complex in keeping with its highest donor ability. For amine derivatives, TOA generally extracts highest compared to Adogen 464 and Amberlite LA-2. The amide donors used in the present dissertation work obey the following trend: D2EHAA > D2EHPrA > D2EHiBA > D2EHPvA. It clearly reflects that the increased branching requires greater conformational changes during adduct formation. The effect of substituents in the monoamides on the ternary adduct formation is explained on the basis of molecular modeling.

One point should be highlighted before drawing concluding remark. Up to now much attention has been paid to the synergistic extraction of trivalent actinide ions. But no such investigation is being reported regarding synergistic extraction of tetravalent actinide ions like neptunium. Thus it will be fascinating to see what type of stringent steric requirements would be necessary for such high oxidation state ions with small size. The present dissertation work thus comprises of a detailed investigation on the extraction of ternary complexes of Np (IV) with HPBI and TOPO. Thus as concluding remark we can say that by picking up metals starting from transition elements to lanthanides and going down to actinides we have established the fact that synergistic extraction technique can effectively be employed throughout the entire periodic table. This is not only important for analytical chemists point of view but also for the solution of nuclear waste disposal problem and recovery of trace and ultra trace precious metals studied in the present investigation.