"*STUDIES ON THE EFFECTS OF MIXED EXTRACTANTS ON LIQUID - LIQUID EXTRACTION OF SOME METAL IONS*"

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This is to certify that the thesis entitled **'Studies on the effects of mixed extractants on liquid - liquid extraction of some metal ions'** is the result of work done by Pulak Dey, M.Sc., himself under my direct supervision and that he has fulfilled all the conditions necessary for the Ph.D degree examination of the University of Burdwan.

He has delivered a seminar lecture in the chemistry department of the University of Burdwan on 10th January, 2012 defending his dissertation. The lecture was highly appreciated by the audience.

It should be mentioned that either the thesis or any part thereof has never been submitted to any University or Institute for the purpose of any degree, diploma or award.

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Preface

The work embodied in the present dissertation entitled **"Studies on the effects of mixed extractants on liquid-liquid extraction of some metal ions"** was initiated to explore the consequences of extraction parameters on metal ion extraction in presence and absence of a basic donor. A wide range of metal ions were picked up from the periodic table in order to obtain a clear picture of such studies. As mixed extraction system, combination of a chelating agent with organic phosphorus compounds were used in most of the case with some different sorts of combinations have also been reported. Extraction parameters were thoroughly investigated in order to elucidate the mechanism of such processes.

This dissertation consists of three main sections. *Section- I* is the introductory part, *Section- II* contains the experimental part accompanied by analysis of experimental results and *Section- III* consists of summary and conclusion of the present investigation.

In ***Section- I,*** introductory part and background of present work have been described in **Chapters -1.** It includes a general introduction on the solvent extraction chemistry and covers the outlines of the general mechanism of solvent extraction, distributation law, separation factor etc. In present investigation, our prime interest is to study the synergistic extraction and their different parameters like synergistic coefficient (S.C), apparent stability constants (β),role of synergists, temperature, ligand etc. From the effect of temperature, using the Van't Hoff equation, the general mechanism of synergistic extraction can be explained from the change of thermodynamic parameters like enthalpy

(ΔH^0) entropy (ΔS^0) etc. Here, we present a brif review on the extraction properties of amide type ligand and organophosphorus donor, and a brief survey of the synergistic extraction of different metal like Co(II), U(VI), Cu(II), Ag(I), Au(III), Fe(III), Ni(II) and Cs(I) , which are of recent interest. Finally, objective of present investigation with planning of our work was explained in this Chapter.

Section II contains the experimental detail and results. In this section there are six chapters representing the wide application of synthesized and commercial substituted amide type ligand on the metal ion in presence and absence of donors. Among the six chapters, **Chapter-2** deals with the description of materials and equipments used in our experiments. Here, we also described the procedure of synthesis of the N-(thio acetyl) benzamide, N- acetyl benzamide and β-hydroxy-naphthaldoxime ligand and their characterization by various spectroscopic techniques and determination of their pK values by the use of Calvin-Wilson pH titration method. In this chapter we also discribe on the different quantitative methods of analysis employed in our present work which includes AAS technique, radiometric analysis and fluorescence spectroscopic techenique along with their instrumentation.

Chepter -3 describes the use of N-(thio acetyl) benzamide as a chelating extractant on the extraction of Group **11** metal ion in presence and absence of various neutral oxo-donors such as TOPO TBPO TBP and TPPO. Extraction behavior of Ag(I) and Au(III) ions were studied by the radiometric technique with use of ^{110m}Ag and ^{198}Au tracer respectively, where as Cu (II) has been determined by AAS technique. In each case different extraction parameters like effect of pH, effect of solvent, effect of concentration of ligand, effect of concentration of donor, effect of temperature etc were systematically

studied. The value of synergistic co-efficient (S.C), apparent stability constants (β), and equilibrium extraction constants of each metal ion was evaluated from distribution data under experimental condition. The extracted compound was also analysed for their IR spectra Finally study of temperture effect and evaluation of thermodynamic parameters were used to explore the extraction mechanism. Formation of either inner sphere or outersphere complex in ternary adduct was established from such study. It was observed that the extraction pathways for mixed extractions were not same for all of the there coinage metal ions.

Chapter 4 embodies the results of the studies carried out on the synergistic extraction of Fe(III) and Ni(II) ions with 2-Hydroxy-N-phenylbenzamide in the presence of various neutral oxo-donors from aqueous chloride medium to n-butanol solvent. Extraction behaviour of Fe(III) was studied by the radiometric technique with use of ^{59}Fe tracer, where as Ni(II) was studied by AAS technique. The correlation between distribution ratio of metal ions and different extraction parameter has been discussed in this chapter. Finally from temperature variation data the extraction mechanism were established and it was supported with IR data.

In the **Chepter- 5** of this section, we have reported the synergistic extraction of U (VI) using of N- acetyl benzamide and synergist donor (TOPO, DMSO and pyridine) in to chloroform at pH 3.0 adopting steady state fluorescence spectroscopic technique and Co(II) using of N- acetyl benzamide and oxodonor (TOPO, TBPO TPPO) in to toluene at pH 3.5 adopting radiotracer technique. In each case different extraction parameters like pH, effect of solvent, effect of concentration of ligand, effect of concentration of donor, effect of temperature etc have been systematically studied. In both the cases the

arithmetical sum of distribution ratio values are less than obtained when it was measured after the extraction by the mixture of ligand and donors. The results were used to calculate the synergistic co-efficient (S.C), apparent formation constant and net extraction equilibrium constants. Finally from temperature variation data the extraction mechanism were established and supported with IR studies.

In **Chapter -6**, the extraction behaviour of Cu(II) from an aqueous nitrate medium employing β-hydroxy-naphthaldoxime (HL) in carbon-tetrachloride in presence of several organophosphorus donors like, tri-octyl phosphine oxide (TOPO), tri-butyl phosphine oxide (TBPO) and tri-butyl phosphate (TBP) at pH 1.5, adopting AAS techenoque have been described in detail. Variation of all the parameters were studied in terms of extraction efficiency, as before. The mechanism of extraction of ternary adduct were also analysed in terms of temperature effect.

In **Chapter -6**, we have described the antagonistic extraction of Cesium(I) by 18-Crown-6 in presence of organophosphorus compounds at pH 1.0 from perchlorate medium into nitrobenzene solvent adopting radio tracer techenique useing ^{137}Cs isotope. Antagonistic mechanism was established by the evaluation of binding constant values between 18-Crown-6 and organophosphorus compounds in organic phase with absorption spectro-photometric measurements employing Bensi-Hildebrand equation. Formation of electron donor accepter complex made the availability of crown ether bases, leading to less extraction of cesium. Antagonistic effects of different oxadonors were in accordance with their respective "*donor numbers*", establishing the relative trend of host guest complex formation with the synergist bases and neutral crown ether, making then less available for Cs-extraction. Use of strongly polar solvent nitrobenzene also hinders the extraction.

In ***Section III***, we have finally summarized our experimental results found in previous chapters and then offered a logical conclusion on the basis of such results. Wide variation of the extent of extraction with the nature of ligand and donor sets and their subsequent effects on the nature of both binary and ternary adducts were discussed in a conclusive way.

ABBREVIATIONS

acac	acetyl acetone
BA	Benzyl amine
BDSO	Butyldodecylsulfoxide
B2EHSO	Bis (2-ethylhexyl)sulphoxide
BHxSE	Bis (hexylsulfinyl)ethane
bipy	2,2' –bipyridine
bta	Benzoyltrifluoroacetone
bzac	1-phenyl-l,3-butanedione
B15C5	Benzo-l5-crown-5-ether
B18C6	Benzo-18-crown-6-ether
CE	Crown ether
CMPO	Octyl (phenyl)(N,Ndiisobutylcarbamoylmethyl) phosphine oxide
Cyanex- 272	Bis(2,4,4 trimethylpentyl) phosphinic acid
C18C6	Cyclohexano-18-crown-6
15C5	l5-crown-5-ether
18C6	18-crown-6-ether
DBA	Dibenzyl amine
DB15C5	Dibenzo-15-crown-5-ether

DBSO	Dibenzoylsulphoxide
DC18C6	Dicyclohexano-18-crown-6-ether
DDA	n-dodecylamine
D2EHPA	Di-2-ethylhexyl phosphoric acid
D2EHPrA	Di-2-ethylhexyl propanamide
D2EHiBA	Di-2-ethylhexyl isobutyramide
D2EHPvA	Di-2-ethylhexyl pivalamide
DMSO	Dimethyl solfoxide
DOSO	Dioctyl sulfoxide
EHEHPA	2-ethylhexylphosphonic acid mono 2-ethylhexyl ester, PC 88A
HDDNS	Didodecylnapthaenesulfonic Acid
HEHΦP	2ethylhexyl phenylphosphonic acid
HIPT	4- isopropyltropolone
HPA	Picrolonic acid
HNA	N-(2-hydroxy- 1-naphthalidene) aniline
HNN	N- (2-hydroxy-1-naphthalidene)-1-naphthylamine
HPAI	3-phenyl- 4-Acetyl-5-isoxazolon
HPBI	3-phenyl- 4-Benzoyl-5-isoxazolon
HPMAP	1-phenyl-3-methyl-4-acetyl-5-pyrazolone

HPMBP	1-Phenyl-3-methyl-4-benzoyl-5-pyrazolone
HPMDP	1-Phenyl-3-Methyl-4-Decanoyl-5-Pyrazolone
HPMSP	1-phenyl-3-methyl-4-stearoyl-5-hydroxypyrazole
Hq	8-hydroxyquinoline
HTTA	2- thenoyltrifluoroacetone
PSO	Petroleum sulfoxides
SA	N-salicylideneaniline
SAN	Salicylideneaniline
Saltn	N N disalicylidenetrimethylenediamine
SNN	Salicylidene-1-naphthylamine
TAA	Tri allyl amine
TBA	Tribenzyl amine
TBP	Tri butyl phosphate
TBPO	Tri butyl phosphine oxide
TDA	Tri dodecyl amine
TFA	Tri fluoroacety lacetone
TIBPS	Triisobutylphosphine sulphide
TOA	Tri-n-octyl amine
TOPO	Tri-n-octyl phosphine oxide
TPA	Tri propyl amine
TPPO	Tri-phenyl phosphine oxide