SYNERGISTIC SOLVENT EXTRACTION OF THORIUM(IV) AND URANIUM(VI) WITH β-DIKETONES IN PRESENCE OF OXO-DONORS

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BY

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CERTIFICATE

This is to certify that the work embodied in the thesis entitled **"SYNERGISTIC SOLVENT EXTRACTION OF THORIUM(IV) AND URANIUM(VI) WITH β-DIKETONES IN THE PRESENCE OF OXO-DONORS"** is the result of the investigations carried out by Mrs. MEERA R. under my supervision in the Chemical Sciences Division of Regional Research Laboratory (CSIR), Thiruvananthapuram, and the same has not been submitted elsewhere for any other degree.

Dr. M.L.P. Reddy
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CONTENTS

PREFACE

The thesis entitled "**SYNERGISTIC SOLVENT EXTRACTION OF THORIUM(IV) AND URANIUM(VI) WITH β-DIKETONES IN THE PRESENCE OF OXO-DONORS**" embodies the results of the investigations carried out on the extraction of thorium(IV) and uranium(VI) with heterocyclic β-diketones in the presence and absence of various macrocyclic ligands and neutral organophosphorus extractants. The objective of this work is to generate the knowledge base to achieve better selectivity between thorium(IV) and uranium(VI) by understanding the interactions of crown ethers or neutral organophosphorus extractants with metal-heterocyclic β-diketonate complexes. The thesis is comprised of six chapters.

The introductory chapter highlights the need for development of new synergistic solvent extraction systems for the separation of thorium(IV) and uranium(VI) in the reprocessing of spent thorium based nuclear fuels as exemplified by THOREX Process and also from mineral resources. A general introduction to the solvent extraction chemistry has also been presented in chapter 1.

The second chapter deals with a comprehensive review of literature on the recent developments in the synergistic solvent extraction of thorium(IV) and uranium(VI) with various β-diketones in the presence of neutral oxo-donors.

The synthesis of various para-substituted derivatives of 4-aroyl-5-pyrazolones and their characterization by various spectroscopic techniques has been described in chapter 3. The investigations on the extraction of thorium(IV) and uranium(VI) with para-substituted 4-aroyl-5-pyrazolones in the presence and absence of macrocyclic crown ethers, benzo-15-crown-5, 18-crown-6, dicyclohexano-18-crown-6 and dibenzo-18-crown-6, have also been included in this chapter.

Chapter 4 describes the results of the investigations on the synergistic extraction of thorium(IV) and uranium(VI) with sterically hindered 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone in the presence of various mono- and bi-functional organophosphorus extractants.

The synthesis, characterization of various para-substituted 4-aroyl-5-isoxazolones and their extraction behavior towards thorium(IV) and uranium(VI) in the presence of various crown ethers has been detailed in chapter 5.

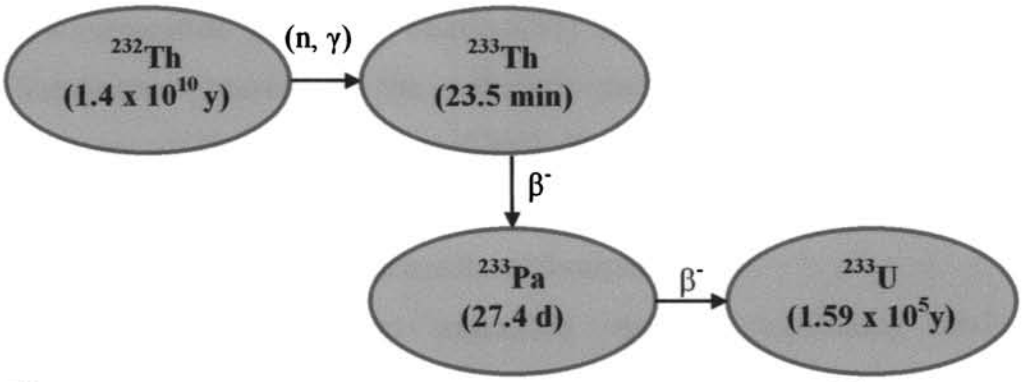
The contributions to the new knowledge arising out of this thesis have been highlighted in the concluding chapter. The relevant references of the work have been cited towards the end of the thesis.

Chapter 1

Introduction

In the context of growing world population with increasing energy demands, and the threat of global warming due to CO_2 emission (caused by coal and hydrocarbon burning), the nuclear technology may be an attractive option particularly in the developing countries [Manchanda 2004]. The nuclear power production at present is based broadly on the uranium fuel cycle. Natural uranium contains only 0.7% of ^{235}U (of fissile isotope). However, a large number of power reactors in the world are based on the enriched uranium fuel (^{235}U content > 2%) and are referred to as *Light Water Reactors*. Another fissile isotope particularly suitable for thermal reactors is ^{233}U which is obtained by the neutron irradiation of ^{232}Th. Due to their significant abundance in the earth's crust, uranium (4 ppm) and thorium (10-20 ppm) represent a large potential source of power [Seaborg and Katz 1954]. Thorium is recovered from monazite, which is a complex phosphate mineral containing phosphates of thorium and rare earths (about 9% ThO_2, 60% rare earth oxides, 0.4% UO_2 and 27% P_2O_5).

The third phase of the Indian Atomic Energy Programme is based on the Thorium-Uranium Fuel Cycle.



^{232}Th (a fertile material) when irradiated in a reactor forms ^{233}Th ($t_{1/2}$ = 23.5 min) which on successive β-decays is converted to ^{233}Pa ($t_{1/2}$ = 27.4 days) and the fissile isotope, ^{233}U ($t_{1/2}$ = 1.59 x 10^5 y) respectively. Reprocessing of irradiated thorium to separate and purify ^{233}U is an important aspect of thorium fuel cycle, and it greatly influences the economics of the fuel cycle. Separation of uranium and thorium is rendered more difficult than separation of uranium and plutonium because thorium does not display variable oxidation states. Hence, one needs to exploit the difference in the complexation behavior of thorium(IV) vis-à-vis uranium(VI) to arrive at experimental conditions where desired separation factors (S.F.) could be achieved. At present, the thorium-uranium extraction (THOREX) process utilizes tri-*n*-butylphosphate (TBP) to separate thorium and uranium from each other and from fission products [Bond 1990]. The THOREX process was originally developed in the early 1950's to recover ^{233}U from irradiated thorium targets, and that application has constituted its principal usage [Gresky 1953; Gresky 1956; Stevenson et al. 1961; Haas and Smith

1976]. However, this process has certain limitations largely due to the low solubility of $Th(NO_3)_4$. xTBP (where $x = 3$ or 4) in *n*-dodecane, low separation factor of uranium(VI) over thorium(IV) and also interference caused by the radiolytic and hydrolytic degradation products of TBP [Pathak et al. 2000]. Thus, there is a need to design and develop alternate extraction systems to TBP for the efficient separation of uranium from irradiated thorium.

Synergistic solvent extraction systems containing di-2-ethylhexylphosphoric acid (D2EHPA) and tri-*n*-octylphosphine oxide (TOPO), have often been used commercially for the recovery of uranium from wet process phosphoric acid [Musikas and Schulz 1992]. The introduction of cation selectivity into synergistic solvent extraction system is best accomplished by the use of crown ethers that form both stable in-cavity complexes with the target cation and have adequate functionalisation to impart organophilicity [Bond et al. 2000]. When these two criteria are met, the crown ether is both an effective ligand and an effective extractant/synergist. The former criterion requires some understanding of the coordination chemistry and particularly, knowledge of the solution speciation of the cation and the extractants. However, remarkably few studies of synergistic extraction have probed the cation coordination environment [Mathur and Choppin 1993; Bond et al. 2000; Kannan et al. 2001].

This thesis aims to generate the knowledge base, especially, to understand the interaction of crown ethers or neutral organophosphorus extractants with heterocyclic β-diketonate complexes of thorium(IV) and uranium(VI), with a view to achieve better selectivity.

Solvent extraction: general

It is well known that separation processes based on ion exchange technique yield high purity compounds. However, these processes are time consuming and inherently expensive. Methods based on solvent extraction emerged as a novel and unique technique for the separation of metal ions because of its simplicity, versatility and ready adaptability to scaling up of the process. Solvent extraction highlights the usefulness of phase distribution and is based on the principle that a solute can distribute itself in a certain ratio between two immiscible solvents. In this method, a solute distributes itself between an aqueous and organic phases. According to Gibbs phase rule,

$$P + V = C + 2 \qquad (1)$$

where P is the number of phases, V the variance or degrees of freedom and C the number of components. The distribution of a solute between two immiscible solvents is univariant at constant temperature and pressure. That is, if we choose the concentration of the solute in one phase, its concentration in the other phase is fixed.

The distribution law, stated by Berthelot and Jungfleisch, states that at a particular temperature for a solute 'X' distributing between two immiscible solvents 1 and 2, at equilibrium, the ratio of concentration of the solute in the two phases is a constant, provided the nature of the species is the same in both the phases.

$$D = [X]_1 / [X]_2 \qquad (2)$$

The constant, D, is known as the distribution or extraction coefficient. The chemical potential of the solute is the same in each phase at equilibrium, provided temperature and pressure are constant, i.e.,

$$\mu_1 = \mu_2 \tag{3}$$

where the subscripts 1 and 2 refer to the respective solvent phases. Substituting suitable expressions of μ,

$$\mu_1^o + RT \ln m_1 + RT \ln \gamma_1 = \mu_2^o + RT \ln m_2 + RT \ln \gamma_2. \tag{4}$$

where μ^o represents the chemical potential of the solute in a hypothetical ideal 1 molal solution, m, the solute concentration in molality and γ, the molal activity coefficient. The molal distribution coefficient,

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} e^{-(\mu_2{}^o - \mu_1{}^o)/RT} \tag{5}$$

For a system in which the two solvents are completely immiscible under all circumstances the exponential term is a constant, K, so that

$$D = \frac{m_2}{m_1} = \frac{\gamma_1}{\gamma_2} K \tag{6}$$

Thus, D depends on the activity coefficients of the solute in each of the phases. When the activity coefficients approach unity, i.e., at low concentrations, D becomes constant. The distribution coefficient is related to the percentage extraction, E, by the equation

$$E = \frac{100D}{D + \frac{V_{aq}}{V_{org}}} \tag{7}$$

where V_{aq} and V_{org} are the volumes of the aqueous and organic phases, respectively. The separation factor, S.F., is given by

$$\text{S.F.} = D_1 / D_2 \tag{8}$$

where D_1 and D_2 are the distribution coefficients for elements 1 and 2, respectively.

Synergistic solvent extraction

The phenomenon in which two extractants taken together extract a metal ion species with much higher efficiency as compared to the normal additive effect of these extractants is called 'synergism'. The converse of this effect is called 'antagonism'.

An increase in the hydrophobic character of the extracted metal complex is observed in the synergistic extraction of mixed complexes. Three different mechanisms are postulated [Choppin and Morgenstern 2000]. The first one involves the opening of one or more of the chelate rings and occupation by the adduct molecule(s) of the vacated metal coordination site(s). In the second mechanism, the metal ion is not coordinately saturated by the ligand and hence, it retains residual water in the coordination sphere, which can be replaced by the adduct molecules. The third mechanism involves an expansion of the coordination sphere of the metal ion to allow bonding of the adduct molecules.

Measure of synergism

The synergistic coefficient (S.C.) may be described by

$$\text{S.C.} = \log \frac{D_{1,2}}{D_1 + D_2}$$

where D_1, D_2 and $D_{1,2}$ are the distribution coefficients of a metal ion with two extractants taken separately and with the mixture of the two extractants, respectively. When S.C. > 0, the extraction is synergistic. The cases where S.C. < 0 involve an antagonistic effect.

Chapter 2

Review of Literature

Synergistic solvent extraction of thorium(IV) and uranium(VI): Literature review

Synergism acquired its name only in 1958 when a group of researchers from Oak Ridge National Laboratory, U.S. investigated the extraction of uranium(VI) by combinations of organophosphorus extracting agents [Blake et al. 1958]. Since the original report of synergism, many mixed extractants have been studied to take advantage of this effect, especially in the nuclear field. The addition of tri-*n*-butylphosphate (TBP) or tributylphosphine oxide (TBPO) to uranium(VI)-thenoyltrifluoroacetone (HTTA) system increases the extraction efficiency by several orders of magnitude ($5x10^3$ and $1.6x10^4$) compared with HTTA alone [Irving 1967]. Synergistic extraction systems have also been used commercially for the recovery of uranium from phosphoric acid leach liquors using mixtures of D2EHPA and TOPO [Musikas and Schulz 1992].

The review of literature reveals that the synergistic extraction of thorium(IV) and uranium(VI) utilizes three well known classes of chelating reagents, namely, 1,3-β-diketones (thenoyltrifluoroacetone and acetylacetone type), 1-phenyl-3-methyl-4-acyl-5-pyrazolones and 3-phenyl-4-acyl-5-isoxazolones, in the presence of various neutral oxo-donors. The synergistic solvent extraction of thorium(IV) and uranium(VI) with various β-diketones in the presence of neutral oxo-donors has been well studied, and these data are covered in review articles on 'Synergistic Solvent Extraction' [Ramakrishna and Patil 1984; Bond et al. 2000].

1,3-β-Diketones + Oxo-donors

The thermodynamic, ^{1}H NMR and hydration data indicate that the interactions of crown ethers (CEs) with HTTA complexes of f-element cations is a multi-faceted problem [Mathur and Choppin 1993]. The extraction of f-elements by mixtures of CEs and HTTA involves a variety of geometric, enthalpic and entropic effects. The CEs do exhibit synergistic behavior but the fit of the cation and crown cavity size does not seem to be a significant factor in these HTTA complexes. There is evidence that the metal ions may interact with only a few of the potential donor oxygens and steric effects are probably significant in establishing this number.

The partitioning of uranium(VI) by mixtures of 1,3-β-diketones and various CEs has been investigated, but the extraction systems are not yet well characterized [Godbole et al. 1986; Ensor et al. 1988; Thakur et al. 1998]. Macrocyclic rings of 12, 15, 18 or 24 members, including the common cyclohexyl or benzo derivatives, were shown to synergize uranium(VI) extraction into benzene [Godbole et al. 1986;

Mathur and Choppin 1993]. Based on the synergism observed for macrocyclics containing 12 and 15 members, it appears that the cavity size is not an important factor in the synergism of uranium(VI) extraction by these CEs [Godbole et al. 1986; Mathur and Choppin 1993]. For synergistic extraction using 18-crown-6 (18C6) and its derivatives, in-cavity complexation of uranium(VI) is possible, because direct insertion of uranyl cation into 18 membered macrocyclic polyethers has been observed in the solid state [Navaza et al. 1984; Deshayes et al. 1994]. The solid state structural study of $[UO_2(TTA)_2H_2O]_2$(benzo-15-crown-5) shows that the benzo-15-crown-5 (B15C5) forms a 'secondary sphere coördination' compound with $[UO_2(TTA)_2H_2O]$ and is hydrogen bonded to the water molecule [Kannan et al. 2001]. However, the dibenzo-18-crown-6 (DB18C6) forms a 'third sphere coordination' compound with $[UO_2(TTA)_2H_2O]$.

Many studies have been reported on the synergistic extraction of thorium(IV) and uranium(VI) with various 1,3-β-diketones (HTTA, acetylacetone = AA, dibenzoylmethane = DBzM, benzoyltrifluoracetone = BTFA, hexafluoroacetyl acetone = HFAA in the presence of neutral organophosphorus and organosulphur extractants (TBP, TOPO, triphenylphosphine oxide = TPhPO, dialkyl and aryl sulphoxides) and these data are well documented [Ramakrishna and Patil 1984].

The synergistic extraction of uranyl ion from dilute nitric acid medium employing HTTA/1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) in toluene and their mixture with several structurally modified monoamides viz. di-2-ethylhexylacetamide (D2EHAA), di-2-

ethylhexylpropanamide (D2EHPrA), di-2-ethylhexylisobutyramide (D2EHiBA), di-2-ethylhexylpivalamide (D2EHPvA) has been investigated. The nature of the extracted species for the binary and ternary extraction systems were reported as UO_2A_2 and $UO_2A_2.B$, respectively, where A = TTA or PMBP and B = D2EHAA, D2EHPrA, D2EHiBA or D2EHPvA. A linear correlation was observed between the basicity of the amide and the corresponding adduct formation constants [Bhattacharya et al. 2003].

Investigations on the extraction behavior of thorium(IV) and uranim(VI) from perchlorate solutions with mixtures of HTTA and diamides like N,N′-dimethyl-N,N′-dihexyl-3-oxapentanediamide (DMDHOPDA), N,N′-dihexyl-3-thiopentanediamide (DHTPDA) and N,N′-dihexyl-3-oxapentanediamide (DHOPDA) indicated the extracted complexes as $Th(TTA)_3(A)(X)$ and $UO_2(TTA)_2(A)$, where A = diamide and X = perchlorate [Sasaki and Choppin 1996].

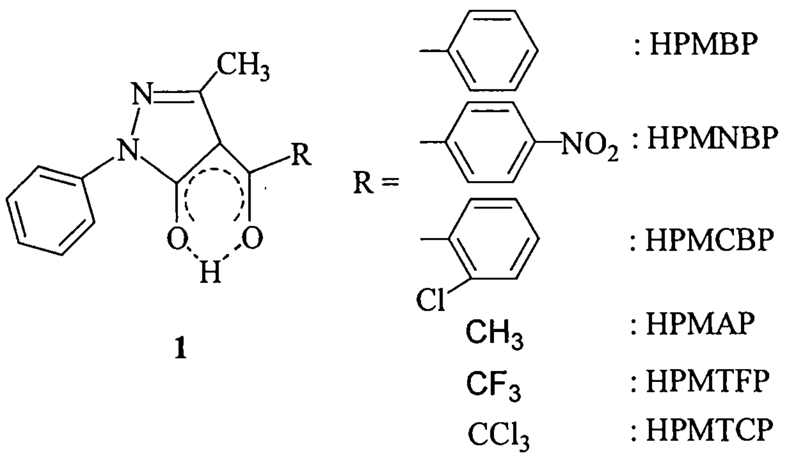
The extraction behavior of uranium(VI) from nitrate solutions by mixtures of HDBzM and oxo-donors (S) such as TOPO, TPhPO or tri-phenylarsine oxide (TPAsO) in chloroform has been studied and reported the nature of the extracted complexes as $UO_2(DBzM)_2.S$ or $UO_2(DBzM)_2.2S$. The synergistic extraction efficiency with various neutral donors follows the order TPAsO > TOPO > TPhPO [Thakur et al. 1999].

Synergistic extraction studies of uranium(VI) from nitric acid solutions with HTTA in the presence of mono- (diphenyl sulphoxide = DPSO, TBP, TOPO) and bi-functional neutral donors (di-hexyl-di-ethyl carbamoylmethyl phosphonate = DHDECMP and octyl(phenyl)-

N,N′-diisobutyl-carbamoylmethylphosphine oxide = CMPO) into benzene have been investigated and noticed a linear correlation between the organic phase adduct formation constant (log K_S) and basicity of the neutral oxo-donor (log K_H) [Pai et al. 2000; Pai et al. 2002].

4-Acyl-5-pyrazolones + Oxo-donors

Another exotic class of β-diketones, first synthesized at the turn of the nineteenth century, is represented by 4-acyl-5-pyrazolones, which possess a pyrazole fused to the chelating ring. The pyrazolone ring, having electronegativity similar to trifluoromethyl anion; greatly influences the properties of these ligands and of their corresponding metal complexes. The extraction behavior of thorium(IV) and uranium(VI) from perchlorate solutions with various 1-phenyl-3-methyl-4-acyl-5-pyrazolones (**1**) (acyl = benzoyl, acetyl, chloroacetyl, trichloroacetyl, trifluoroacetyl = HX) in chloroform has been investigated and reported the extracted complexes as ThX_4 and UO_2X_2 [Bacher and Keller 1973].



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The synergistic extraction of thorium(IV) and uranium(VI) from perchlorate media into toluene solutions of 12-crown-4 (12C4), 15-crown-5 (15C5), 18C6, dicyclohexano-18-crown-6 (DC18C6) or DB18C6 and HPMBP did not show correlation between the cationic radii and the crown ether cavity size nor did the values follow a simple order of ether basicity [Yonezawa and Choppin 1989]. The synergistic constants for the 12C4, 15C5 and 18-membered macrocyclic complexes generally decrease with decreasing effective charge of the actinide cation: that is, Th(IV) > $U(VI)O_2^{2+}$. The crown ether basicity, steric effects and the number of ether oxygens bound to the cation are the combined factors which seemingly determine the pattern of $M(PMBP)_n$-CE interaction.

Investigations on the synergistic extraction of uranyl ion with 4-acyl-5-pyrazolones such as HPMTFP, HPMAP or HPMBP in combination with DC18C6 has been carried out at various temperatures [Mundra et al.1987]. The results indicated that the equilibrium constants of the organic phase addition reaction are almost constant for the above systems. Thermodynamic data for the chelate extraction with HPMTFP evaluated by the temperature coefficient method indicates that a hydrated chelate is extracted into the organic phase. Also, the organic phase addition reaction with DC18C6 is stabilized by exothermic enthalpy change, the entropy change counteracting in all the three cases.

Synergistic extraction of uranium(VI) with HPMBP and aliphatic sulphoxides of varying basicities, *viz.* diisoamyl (DIASO), di-*n*-hexyl (DHSO), di-*n*-septyl (DSSO), di-*n*-octyl (DOSO), di-*n*-nonyl

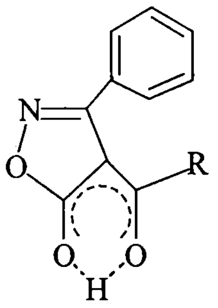
(DNSO) or di-*n*-decyl (DDSO) sulphoxides has been investigated [Pai and Subramanian 1987]. The organic phase equilibrium constant has been found to increase with the basicity of sulphoxides upto DOSO beyond which there is a gradual decreasing trend which has been attributed to the effect of possible steric hindrance (spatial) involved in the bonding of the higher sulphoxides (> 8 carbon atoms) with $UO_2(PMBP)_2$-chelate.

The extraction behavior of uranium(VI) from aqueous acidic solutions with various 4-acylpyrazolones such as HPMBP, HPMAP, 1-phenyl-3-methyl-4-(2-chlorobenzoyl)-5-pyrazolone (HPMCBP), 1-phenyl-3-methyl-4-(p-nitrobenzoyl)-5-pyrazolone (HPMNBP) and 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP) in the presence and absence of neutral oxo-donors like TBP, DOSO, TOPO and DPSO has been studied and reported the extracted species as $UO_2A_2.B$ (HA = chelating agent, B = neutral oxo-donor). The results showed that the addition of neutral organophosphorus extractant to the metal-pyrazolonate system significantly enhances the extraction efficiency of uranium(VI). The extraction efficiency of these chelating agents increase in the order PMCBP > PMNBP > PMTFP = PMBP > PMAP and the synergistic extraction power of oxo-donors follows the order TOPO > DOSO > DPSO > TBP [Pai and Subramanian 1985; Jiajun et al. 1991].

The studies on the synergistic extraction of thorium(IV) from dilute nitric acid and perchloric acid solutions with HPMBP in the presence and absence of TOPO indicates the extracted complexes of the type $Th(X)(PMBP)_3.(HPMBP)$ and $Th(X)(PMBP)_3.TOPO$ for binary and ternary extraction systems, respectively (X = NO_3^- / ClO_4^-) [Mohapatra et al. 1999].

4-Acyl-5-isoxazolones + Oxo-donors

4-Acyl-5-isoxazolones (**2**) are a class of fascinating chelating extractants capable of extracting metal ions from strong acid solutions due to its lower pK_a values (pK_a of 3-phenyl-4-benzoyl-5-isoxazolone, HPBI = 1.23) as compared to conventional β-diketones such as HTTA (pK_a = 6.25). The strong acidity of 4-acyl-5-isoxazolones could be partly attributed to the heterocyclic π-electron conjugation system, which contains both electronegative nitrogen and oxygen. The presence of phenyl group imparts the desired partitioning behavior of the ligand. As a consequence, stronger adducts of metal-isoxazolonates with neutral oxo-donors are formed leading to significantly larger enhancement in metal extraction.



R = C_6H_5 : HPBI
CH_3 : HPAI

2

Among 4-acyl-3-phenyl-5-isoxazolones, HPBI has been widely employed for the extraction of thorium(IV) and uranium(VI) from nitrate solutions [Jyothi and Rao 1990; Manchanda et al. 1996; Sahu et al. 2000; Banerjee et al. 2003] and reported the extracted complexes as

$Th(PBI)_4$ and $UO_2(PBI)_2$. The addition of a CE, DC18C6, B18C6, DB18C6 or B15C5 to the Th-HPBI or U-HPBI chelate system enhances the extraction efficiency and also improves the selectivity between thorium(IV) and uranium(VI) when extracted from nitric acid solutions, especially in the presence of B15C5 or DB18C6 [Sahu et al. 2000]. The high extraction efficiency of thorium(IV) with HPBI in the presence of B15C5 has been explained on the basis of 'size-fitting effect' of thorium(IV) in the cavity of B15C5. On the other hand, the sharp decrease in the complexation of uranium(VI) from DC18C6 to B18C6 and to DB18C6 has been attributed to the increase in steric effects and decrease in basicity of these crown ethers.

Investigations on the synergistic extraction of thorium(IV) and uranium(VI) from nitric acid solutions with HPBI in the presence of neutral organophosphorus extractants such as TOPO or TBP into xylene revealed the extracted complexes as $Th(PBI)_4.TBP$, $UO_2(PBI)_2.TBP$ and $Th(PBI)_4.2TOPO$, $UO_2(PBI)_2.TOPO$ [Thakur et al. 1996; Mansingh et al. 1996; Mohapatra et al. 1997]. The extraction efficiency of the metal ions increases linearly with the basicity of these neutral organophosphorus extractants.

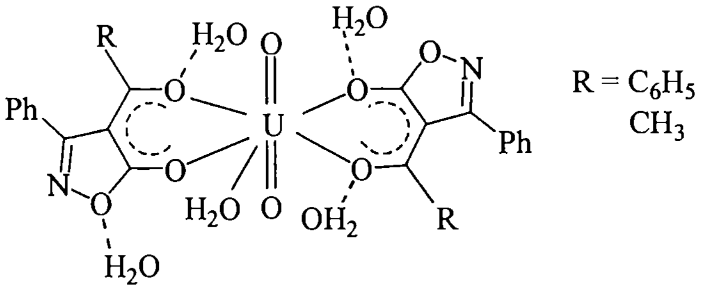
The synergistic extraction behavior of uranium(VI) from dilute nitric acid solutions using HPBI or HPAI (HA) and several amides with varying degree of branching such as D2EHAA, D2EHPrA, D2EHiBA, D2EHPvA as neutral donors into toluene medium has been investigated. It has been found that the two-phase binary extraction occurs via the simultaneous release of two protons from HPBI or HPAI and four water molecules from the inner co-ordination sphere of the uranyl ion which is represented as [Banerjee et al. 2003; Bhattacharya. et al. 2004].

$$UO_2^{2+}(H_2O)_{x\,aq} + 2\,HA_{org} \underset{}{\overset{K_{ex}}{\rightleftharpoons}} UO_2A_2(H_2O)_{x-4\,org} + 2\,H^+_{aq} + 4\,H_2O$$

An inverse linear relation between log K_{ex} and pK_a values of various β-diketones (HPBI, HPAI, HTTA and HPMBP) has been noticed which deviated for HPBI and HPAI and this has been attributed to steric factors. The synergistic extraction equilibrium of uranium(VI) with HPAI in the presence of various amides (B) has been reported as

$$UO_2^{2+}(H_2O)_{x\,aq} + 2\,HA_{org} + n\,B_{org} \overset{K}{\rightleftharpoons} UO_2A_2 \cdot nB_{org} + 2\,H^+_{aq} + 4\,H_2O$$

The synergistic equilibrium constants (K) were found to vary linearly with the basicity of the amides (D2EHAA > D2EHPrA > D2EHiBA > D2EHPvA), where as the adduct formation constant follows an inverse dependence on the basicity of the neutral donors. The role of steric factors in the co-ordination of the amides to the uranyl-isoxazolonates and the adduct formation in the case of ternary complexes was explained on the basis of molecular modeling. The proposed structure (**3**) of the uranyl isoxazolonate stabilized by both inner and outer sphere of hydration has been reported as

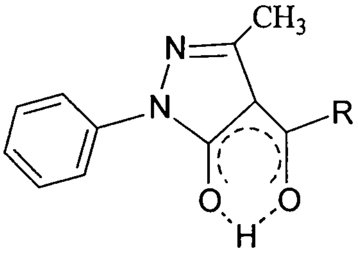


3

Chapter 3

Para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones as chelating agents for the synergistic extraction of thorium(IV) and uranium(VI) in the presence of various crown ethers

The review of literature presented in the earlier chapter concludes that various 1-phenyl-3-methyl-4-acyl-5-pyrazolones (**1**) have been extensively used for the extraction of thorium(IV) and uranium(VI) from acidic solutions due to their lower pK_a values (2.56 – 4.02) as compared to conventional β-diketones, such as acetylacetone (pK_a = 9.0) and thenoyltrifluoroacetone (pK_a = 6.25) [Bacher and Keller 1973; Jia-Jun et al. 1991; Bond et al. 2000]. The nature of the substituent in the fourth position of the pyrazolone ring causes significant variations in the electronic, steric and solubility parameters of the ligand, thereby affecting complexation and extraction of metal ions.

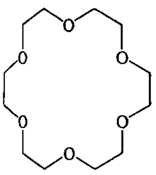


R = CH_3 : HPMAP
CF_3 : HPMTFP
C_6H_5 : HPMBP

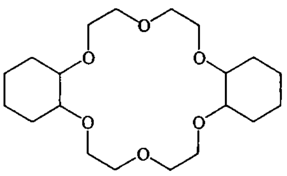
1

As compared to 4-acyl-5-pyrazolones, to our knowledge, no attempts have been made to study the para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones for the extraction of actinides. The electron withdrawing substituents like fluorine have been often introduced in the 1,3-β-diketones to enhance the acidity of the ligand, so that metal ions can be extracted from strong acidic solutions. These factors prompted us to synthesize para-substituted 4-aroyl derivatives of 1-phenyl-3-methyl-5-pyrazolones, namely, 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone (HPMFBP) and 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (HPMTP), by introducing both electron withdrawing (-F) and electron donating ($-CH_3$) groups and study their effects on the extraction behavior of thorium(IV) and uranium(VI).

Synergistic extraction systems offer unique benefits in cation separations, and it can be argued that such systems hold the best promise for large-scale application of crown ethers in separation science. Significant fundamental and developmental research is still required, however, only with well-planned and carefully executed research will the full potential of size-selective synergism be realized. The synergistic extraction of thorium(IV) and uranium(VI) with HTTA or HPMBP in the presence of crown ethers has been well studied, and these data are covered in a recent review on incorporating size selectivity with crown ethers into synergistic solvent extraction systems [Bond et al. 2000]. The most versatile class of ion-specific extractants is arguably the crown ethers, in which the macrocyclic cavity size, chelate ring size, macrocycle rigidity, and the number and type of donor atoms may be tuned to provide a high degree of metal ion selectivity [Pedersen 1967; Hiraoka 1982; Lindoy 1989]. This stimulated us to investigate new synergistic systems involving crown ethers (**2**) as synergists and para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolone as chelating agent with the goal of elucidating the nature of the complexes extracted into the organic phase and the selectivity among these metal ions.



18C6



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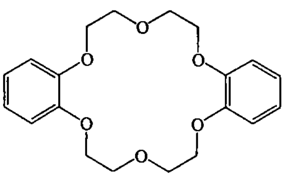

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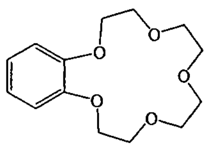


B15C5

EXPERIMENTAL

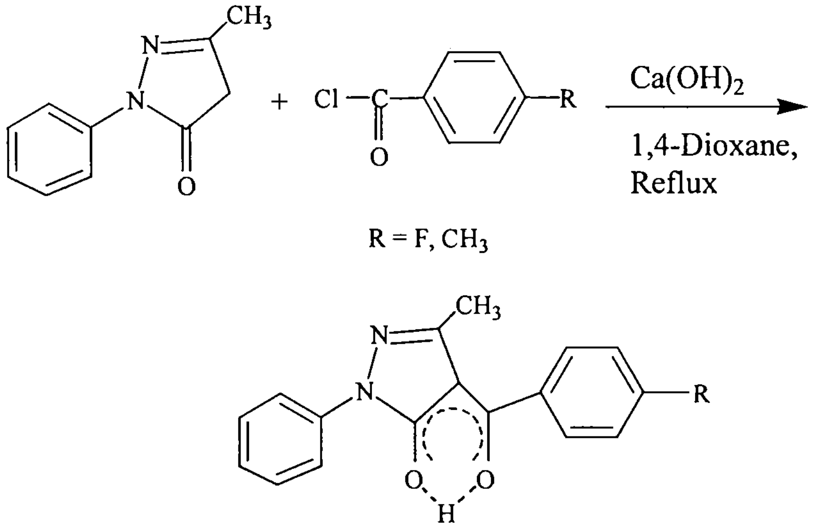
Chemicals

HPMBP ($\geq$ 99% purity) and Arsenazo-III obtained from Fluka Chemika, Germany were used in the present study. The acid chlorides (para-toluoyl chloride: 98% purity; 4-fluorobenzoyl chloride: 98% purity) and crown ethers (*cis*-dicyclohexano-18-crown-6: 98% purity; benzo-15-crown-5: 98% purity; dibenzo-18-crown-6: 98% purity; 18-crown-6: 99% purity) were purchased from Aldrich Chemical Company, U.S.A. $Th(NO_3)_4{\cdot}6H_2O$ and $UO_2(NO_3)_2{\cdot}6H_2O$ used in the present work were obtained from Loba-Chemie, India. Chloroform of analytical reagent quality supplied by Merck, India was used as a diluent in the present study. All other chemicals used were of analytical reagent grade.

Stock solutions of thorium(IV) and uranium(VI) were prepared by dissolving appropriate amounts of $Th(NO_3)_4{\cdot}6H_2O$ and $UO_2(NO_3)_2{\cdot}6H_2O$ in distilled water and standardized by complexometric titration with EDTA [Vogel 1996]. The initial metal ion concentration was maintained at 1×10^{-4} mol/dm^3 for thorium(IV) and 5×10^{-4} mol/dm^3 for uranium(VI) for all extraction studies. Ionic strength was maintained at 1.0 mol/dm^3 using sodium nitrate. All organic phase solutions were prepared by dissolving weighed amounts of HPMBP, HPMFBP, HPMTP or CE in chloroform and diluting to the required volume. Arsenazo-III solution was prepared by dissolving 250 mg of the reagent in 250 dm^3 of distilled water.

Syntheses of para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones

The para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones, HPMFBP and HPMTP were synthesized from 1-phenyl-3-methyl-5-pyrazolone and the corresponding acid chloride by the Jensen's method [Jensen 1959] (**Scheme 3.1**).



Scheme 3.1

1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone

The synthesized 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone was identified by elemental analyses, IR and ^{1}H NMR spectral data. HPMFBP: m.p. 132°-133°C. Elemental analysis: Calc. for $C_{17}H_{13}N_2O_2F$: C 68.92, H 4.39, N 9.46%. Found: C 69.06, H 4.26, N 9.48%.^{1}H NMR ($CDCl_3$) data δ (ppm): 7.17-7.87 (m, 9H, phenyl); 2.12 (s, 3H, CH_3 of the pyrazole ring). IR (KBr) data (ν cm^{-1}): 2800, 1620 (C=O), 1590, 1500, 1356, 1214, 752. In the ^{1}H NMR spectrum of HPMFBP (Fig. 3.1), no peak corresponding to the enolic -OH has been observed. However, the absence of a peak at δ 3.4 ppm, corresponding to the methyne proton at the fourth position of the pyrazolone ring, confirms the existence of HPMFBP in the enolic form.

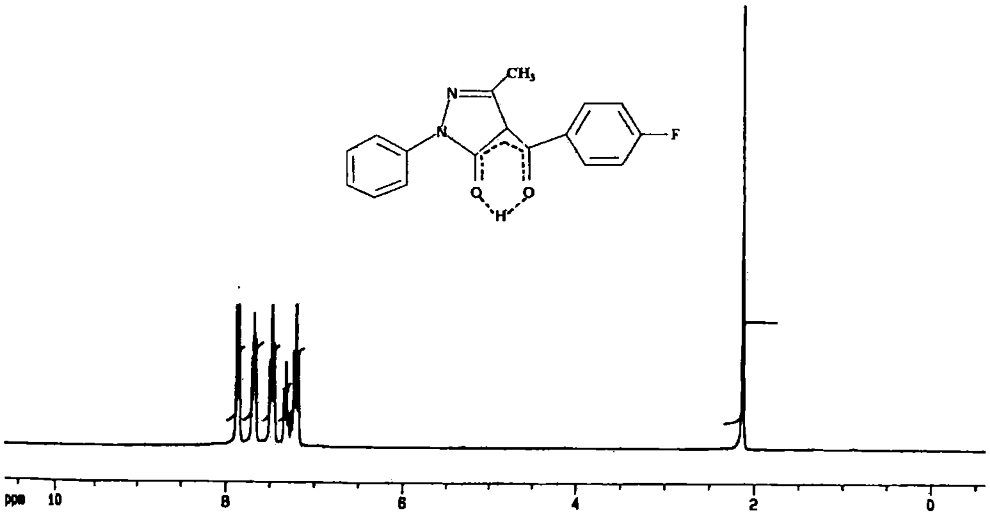


Figure 3.1. ^{1}H NMR spectrum of HPMFBP.

1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone

The synthesized 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone was identified by elemental analyses, IR and ^{1}H NMR spectral data. HPMTP: m.p. 105°-106°C. Elemental analysis: Calc. for $C_{18}H_{16}N_2O_2$: C 73.97, H 5.48, N 9.59%. Found: C 74.64, H 5.66, N 9.57%. ^{1}H NMR ($CDCl_3$) data δ (ppm): 7.2-7.98 (m, 9H, phenyl); 2.14 (s, 3H, CH_3 of pyrazole ring); 2.45 (s, 3H, CH_3 of the aromatic ring). IR (KBr) data (ν cm^{-1}): 1600 (C=O), 1537, 753. In the ^{1}H NMR spectrum of HPMTP (Fig. 3.2), no peak corresponding to the enolic -OH has been observed. However, the absence of a peak at δ 3.4 ppm, corresponding to the methyne proton at the fourth position of the pyrazolone ring, confirms the existence of HPMTP in the enolic form.

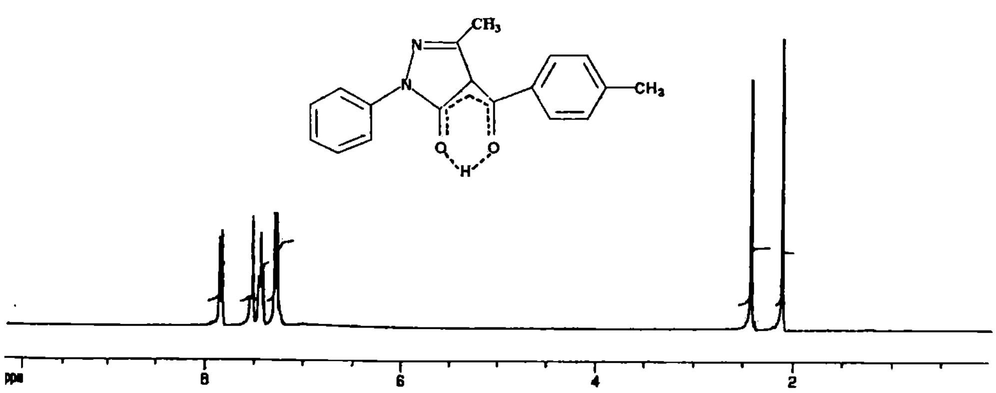


Figure 3.2. ^{1}H NMR spectrum of HPMTP.

Apparatus

A Hitachi 220 (Japan) double-beam microprocessor based spectrophotometer was used for measuring absorbances. An Orion 720A (USA) Ion Analyzer was used for the pH measurements. The Nicolet Impact 400D IR (USA) spectrophotometer using potassium bromide pellet was employed to obtain the IR spectral data. C, H and N analyses were performed with a Perkin Elmer Series 2 Elemental Analyzer 2400. The Bruker (USA) 300 MHz DPX FT-NMR spectrometer was used to obtain the ^{1}H NMR spectra of the extractants dissolved in $CDCl_3$. All the computer programs were written in FORTRAN 77 and executed on a Pentium PC (HCL, India). Semi-empirical PM3 molecular orbital calculations [Stewart 1989] were carried out using Titan Version 1 from Wave function, Inc. CA.

Solvent extraction and analytical procedure

Distribution ratios were determined by shaking equal volumes of the aqueous and the organic phases for 60 min in a glass-stoppered vial with the help of a mechanical shaker at 303 ± 1K. Preliminary experiments showed that the extraction equilibrium was attained within 30 min for both thorium(IV) and uranium(VI). The solutions were then allowed to settle, the phases separated and assayed spectrophotometrically. Both thorium(IV) and uranium(VI) in the aqueous phase were determined spectrophotometrically as their arsenazo III complexes in HCl solution at 660 and 656 nm, respectively [Snell 1978]. The absorbances of the complexes were measured within 5 min of mixing. The metal concentrations in the aqueous phase were computed from the respective calibration graphs. The concentration of the metal ion in the organic phase was then obtained by a material balance. These concentrations were used to calculate the distribution ratio, *D*. All the experiments were performed in duplicate and the general agreement with distribution ratio values obtained was within ± 5%.

Distribution of para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones

Equal volumes of aqueous (1.0 mol/dm^3 sodium nitrate and 0.01 mol/dm^3 sodium acetate as buffering component adjusted to desired pH) and organic phases (5 x 10^{-4} mol/dm^3 of HPMFBP/HPMTP/HPMBP in cyclohexane) were equilibrated for 60 min at 303 ± 1K. After centrifugation, the pH of the aqueous phase was measured and taken as the equilibrium value. The ligand concentration in the organic phase was then measured spectrophotometrically at 340 nm. The ligand concentration in the organic phase was computed from the respective calibration graph. The concentration of the ligand in the aqueous phase was then obtained by material balance. These concentrations were used to calculate the distribution ratio, D_{HX}, of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones.

Preparation of metal complexes

The metal complexes were prepared by the following procedure: Stoichiometric amounts of thorium nitrate or uranyl nitrate were added to a well-stirred solution of HPMFBP or HPMTP in methanol, and the mixture was stirred for 60 min. To this mixture, CE dissolved in methanol was added, and the resultant mixture was refluxed for 4h in order to ensure completion of the reaction. The methanol was evaporated off, and the precipitates formed were filtered, washed with methanol, and dried in a desiccator over fused $CaCl_2$. The complexes were characterized by IR, elemental analyses, and ^1H NMR spectral data. Metal ions in the complexes were determined by the following method: A certain quantity of complex was decomposed by heating in a small amount of HNO_3 solution and excess acid was evaporated. The residue was diluted with distilled water and thorium(IV) and uranium(VI) were determined spectrophotometrically as their Arsenazo-III complexes. The solutes studied were $Th(PMFBP)_4$, $UO_2(PMFBP)_2$, $Th(PMTP)_4$, $UO_2(PMTP)_2$, $Th(PMFBP)_4 \cdot B15C5$ and $UO_2(PMFBP)_2 \cdot DC18C6$.

RESULTS AND DISCUSSION

Distribution of ligands

In a quantitative treatment for the distribution of the ligand, (HX), the acid dissociation constant, K_a, and the partition constant, P_{HX}, are defined as

$$K_a = \frac{[H^+]_{aq}[X^-]_{aq}}{[HX]_{aq}} \qquad (1)$$

$$P_{HX} = \frac{[HX]_{org}}{[HX]_{aq}} \qquad (2)$$

where $[HX]_{aq}$ and $[X^-]_{aq}$ are the concentrations of the neutral and anionic species of the ligand in the aqueous phase, and the subscript 'org' denotes the species in the organic phase. Thus, the distribution ratio of the ligand, D_{HX}, can be written as,

$$D_{HX} = \frac{[HX]_{org}}{([HX]_{aq} + [X^-]_{aq})}$$

$$\text{or } D_{HX} = \frac{P_{HX}}{(1 + K_a[H^+]^{-1}_{aq})} \qquad (3)$$

when $[H^+]$ is much greater than K_a, D_{HX} equals P_{HX}, while log D_{HX} is given by log P_{HX} + pK_a – pH when $[H^+]$ is much less than K_a. The distribution behavior of HPMFBP between the cyclohexane and aqueous phase as a function of pH is given in Fig. 3.3. The distribution curve exhibits an asymptote, log P_{HX}, in a low pH region, and to a straight line with a slope of –1, i.e., the theoretical line (Eq.(3)) in a high pH region. The pK_a and log P_{HX} of HPMFBP were calculated treating the distribution curve by the nonlinear least-square method on the basis of Eq.(3) and are given in Table 3.1. The distribution behavior of HPMBP and HPMTP were determined in a similar manner and the pK_a and log P_{HX} values are given in Table 3.1. The low pK_a value of HPMFBP observed can be explained on the basis of the electron withdrawing nature of para-substituted fluorine in the benzoyl moiety of 4-aroyl-5-pyrazolone. Further, it is also clear from Table 3.1 that log P_{HX} value increases as the 4-aroyl group becomes bulkier.

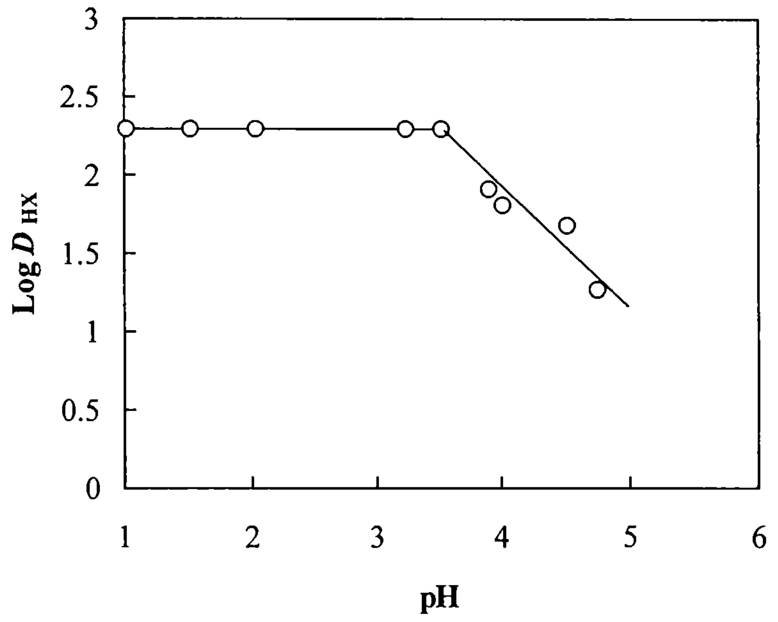


Figure 3.3. Distribution of HPMFBP between cyclohexane and water as a function of pH.

Extraction of thorium(IV) and uranium(VI) with various 1-phenyl-3-methyl-4-aroyl-5-pyrazolones

The effect of HPMFBP, HPMBP and HPMTP concentrations on the extraction of thorium(IV) and uranium(VI) from 1.0 mol/dm^3 sodium nitrate solutions has been studied by keeping the metal (1 x 10^{-4} mol/dm^3 thorium(IV); 5 x 10^{-4} mol/dm^3 uranium(VI)) and nitric acid concentrations (0.1 mol/dm^3) constant. The results are shown in Figs. 3.4 and 3.5. It is clear from the results that the extraction of both thorium(IV) and uranium(VI) increases with increase in concentrations of 1-phenyl-3-methyl-4-aroyl-5-pyrazolones (HX). The relevant log-log plots gave slopes of 4.0 $\pm$ 0.1 and 2 $\pm$ 0.05 for thorium(IV) and uranium(VI), respectively, indicating the involvement of four and two molecules of para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolone in the extracted complexes of these metal ions. The

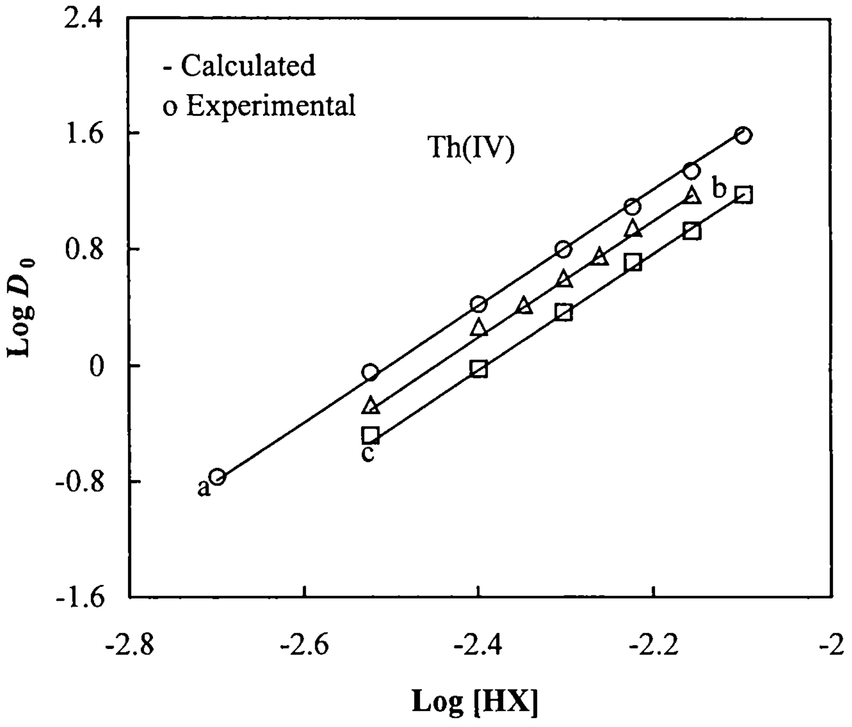


Figure 3.4. Effect of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone (HX) concentration on the extraction of thorium(IV). Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 1.0). Slope of the line (a) HPMFBP = 4.0 ± 0.1 (b) HPMBP = 4.0 ± 0.1 (c) HPMTP = 4.0 ± 0.1.

extraction of thorium(IV) and uranium(VI) with various para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones (0.005 mol/dm^3 for thorium(IV) and 0.1 mol/dm^3 for uranium(VI)) in chloroform as a function of hydrogen ion ? concentration (0.05 – 0.2 mol/dm^3 for both thorium(IV) and uranium(VI)) at constant nitrate ion (1 mol/dm^3) and metal ion (1 x 10^{-4} mol/dm^3 thorium(IV); 5 x 10^{-4} mol/dm^3 uranium(VI)) concentrations has been studied using HNO_3

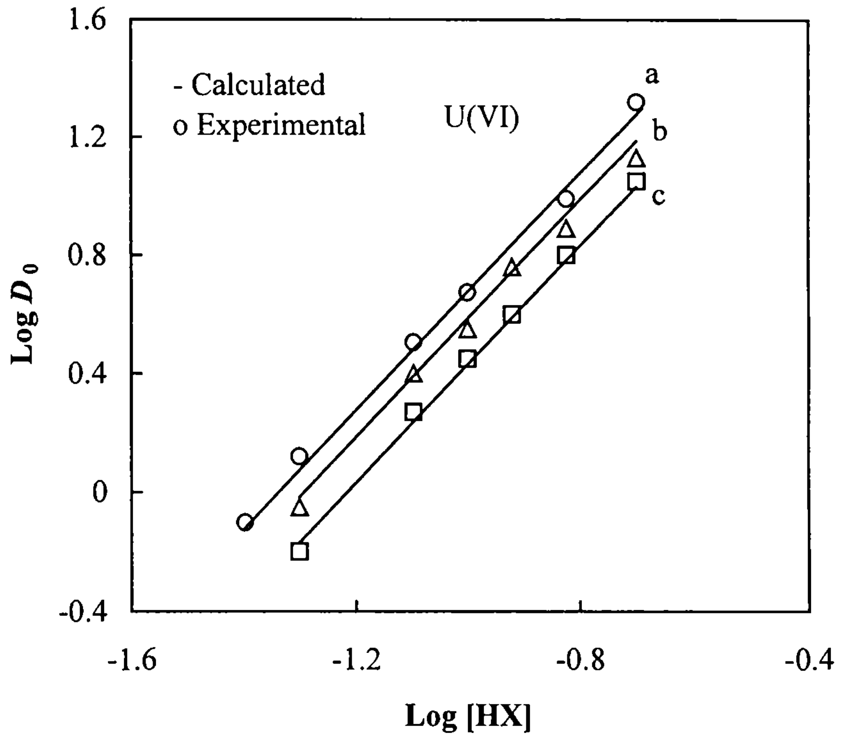


Figure 3.5. Effect of 1-phenyl-3-methyl-4-aroyl-5-pyrazolone (HX) concentration on the extraction of uranium(VI). Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 1.0). Slope of the line (a) HPMFBP = 2.0 ± 0.05 (b) HPMBP = 2.0 ± 0.05 (c) HPMTP = 2.0 ± 0.05.

+ $NaNO_3$ mixtures. In both cases, the extraction behavior shows an inverse dependence on the acidity. The log-log plots for the hydrogen ion variation for thorium(IV) (Fig. 3.6) and uranium(VI) (Fig. 3.7) gave slopes of –4.0 ± 0.1 and -2.0 ± 0.05, respectively, confirming the formation of simple metal chelates, ThX_4 and UO_2X_2 (X = PMFBP or PMBP or PMTP). Similar simple metal chelates have been observed by many investigators in the extraction of thorium(IV) and uranium(VI) with 1-phenyl-3-methyl-4-acyl-5-pyrazolones

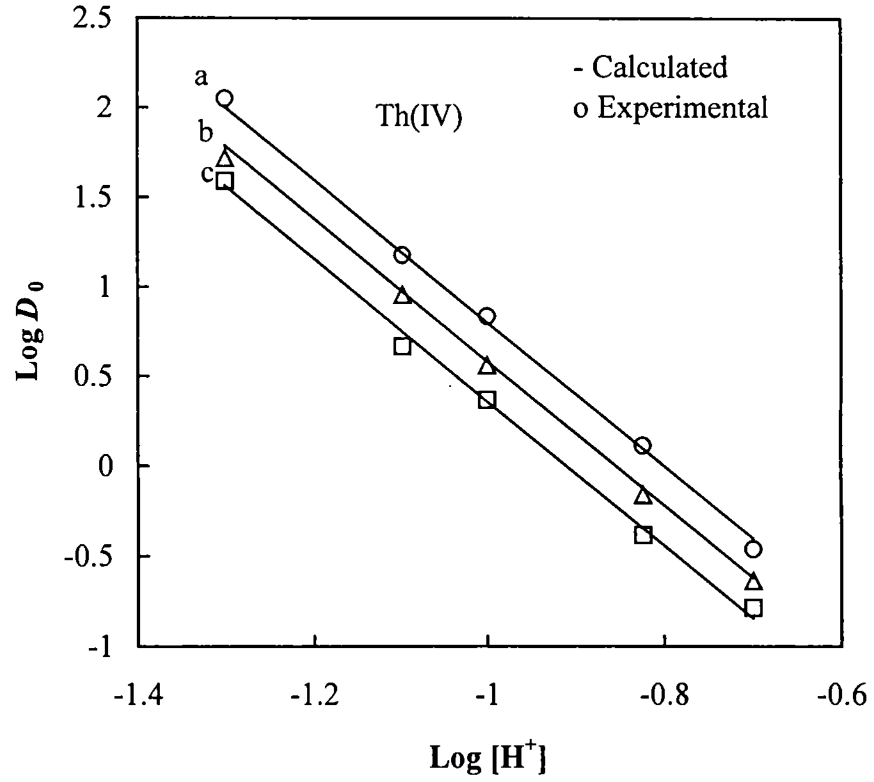


Figure 3.6. Effect of hydrogen ion concentration on the extraction of thorium(IV). Aqueous phase = 1.0 mol/dm^3 NaNO$_3$; [HPMFBP] = [HPMBP] = [HPMTP] = 0.005 mol/dm^3. Slope of the line (a) HPMFBP = -4.0 ± 0.1 (b) HPMBP = -4.0 ± 0.1 (c) HPMTP = -4.0 ± 0.05.

[Bacher and Keller 1973; Pai et al. 2000; Pai et al. 2002; Bhattacharya et al. 2003] and HTTA [Bhattacharya et al. 2003].

Based on the preceding studies, the extraction equilibria of thorium(IV) and uranium(VI) with chelating extractants, HX (= HPMFBP or HPMBP or HPMTP) alone from nitric acid solutions may be represented as

$$\mathrm{Th}^{4+}_{aq} + 4(\mathrm{HX})_{org} \xrightleftharpoons{K_{ex,0}} \mathrm{ThX}_{4\,org} + 4\mathrm{H}^{+}_{aq} \qquad (4)$$

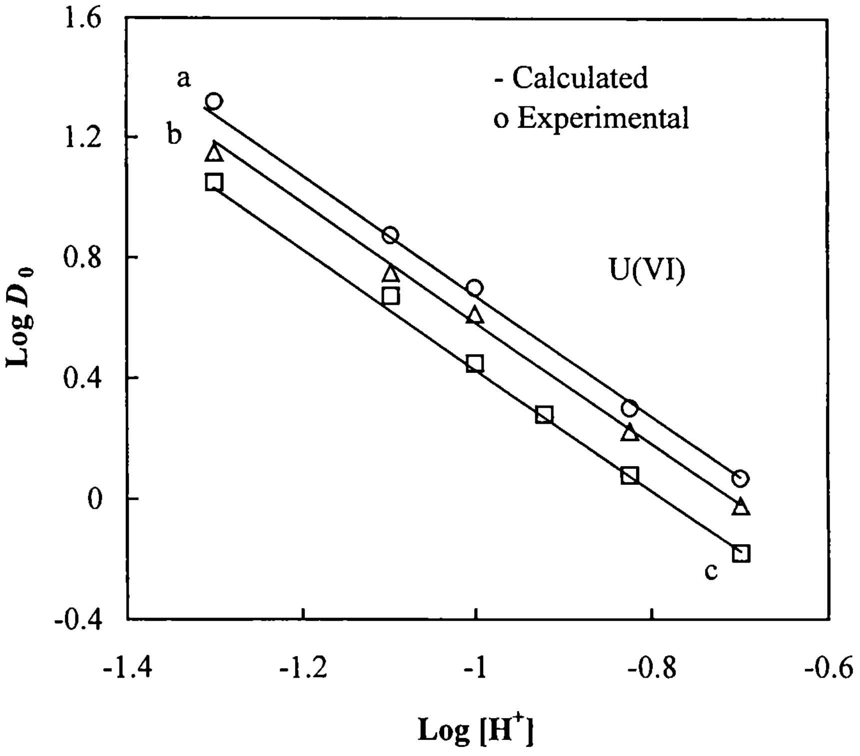


Figure 3.7. Effect of hydrogen ion concentration on the extraction of uranium(VI). Aqueous phase = 1.0 mol/dm^3 $NaNO_3$; [HPMFBP] = [HPMBP]= [HPMTP] = 0.1 mol/dm^3. Slope of the line (a) HPMFBP = -2.0 ± 0.1 (b) HPMBP = -2.0 ± 0.05 (c) HPMTP = -2.0 ± 0.05.

$$UO^{2+}_{2\,aq} + 2(HX)_{org} \xrightleftharpoons{K_{ex,0}} UO_2X_{2\,org} + 2H^+_{aq} \qquad (5)$$

where $K_{ex,0}$ denotes the equilibrium constant. As it is clear from Table 3.1 that the partition coefficients of various para-substituted 4-aroyl-5-pyrazolones are found to be very high, the concentration of pyrazolonate anion in the aqueous phase can be neglected. The thorium ion in the aqueous phase forms a variety of complexes in the presence of nitrate ions.

$$Th^{4+}_{aq} + i\,NO^-_{3\,aq} \xrightleftharpoons{\beta_i} Th\,(NO_3)^{(4-i)^+}_{i\,aq} \qquad (6)$$

where $i = 0$, 1 and 2. Then the total thorium metal ion (Th_T) concentration can be expressed as

$$Th_{T,aq} = [Th^{4+}]_{aq} + [Th(NO_3)^{3+}]_{aq} + [Th(NO_3)_2^{2+}]_{aq}$$

$$= [Th^{4+}]_{aq}\{1 + \beta_1[NO_3^-]_{aq} + \beta_2[NO_3^-]^2_{aq}\} \qquad (7)$$

The distribution ratio, D_0, of thorium(IV) is given by

$$D_0 = \frac{[ThX_4]_{org}}{[Th^{4+}]_{aq}\{1+\beta_1[NO_3^-]_{aq}+\beta_2[NO_3^-]^2_{aq}\}} \qquad (8)$$

where β_i is the stability constant of thorium(IV) with nitrate ion in the aqueous phase. The values of stability constants ($\log \beta_1 = 0.1$; $\log \beta_2 = 0.8$) were taken from the literature [Oliver and Davis 1972]. Then the distribution ratio, D_0, of thorium(IV) can be written from the Eqs. (4) and (8) as

$$D_0 = \frac{K_{ex,0}[HX]^4_{org}}{[H^+]^4_{aq}\{1+\beta_1[NO_3^-]_{aq}+\beta_2[NO_3^-]^2_{aq}\}} \qquad (9)$$

Similarly, the D_0 of uranium(VI) can be written as

$$D_0 = \frac{K_{ex,0}[HX]^2_{org}}{[H^+]^2_{aq}\{1+\beta_1[NO_3^-]_{aq}\}} \qquad (10)$$

The log stability constant for uranium(VI) ($\log \beta_1 = -0.3$) with nitrate ion was taken from the literature [Kotrly and Sucha 1985]. The equilibrium constants ($K_{ex,0}$) for the above extracted complexes were determined by nonlinear regression analysis using the following procedure:

1. A value of $K_{ex,0}$ is assumed.
2. Values of D under the given conditions are calculated from Eqs. (9) and (10) and compared with the experimental values.
3. The value of equilibrium constant which leads to a minimum root mean square fractional error, y, where

$$y=\sqrt{\frac{1}{N}\sum_{i=1}^{N}\left\{\frac{Dcal,i - Dexp,i}{Dexp,i}\right\}^2} \qquad (11)$$

for all the experimental data is taken as the equilibrium constant for the system under consideration. The equilibrium constant (Table 3.1) thus calculated refer only to the concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions.

In order to evaluate the influence of acidity of the various para-substituted 4-aroyl-5-pyrazolones on the extraction behavior of thorium(IV) and uranium(VI), the correlation between log $K_{ex,0}$ and pK_a value was investigated. Fig. 3.8 shows a linear correlation between log $K_{ex,0}$ and pK_a for both metal ions. This means that there is no obvious steric effect due to the para-substituents in the chelate formation reaction. Further, as can be seen from Fig. 3.8, log $K_{ex,0}$ value increases as pK_a value decreases.

Table 3.1. Log equilibrium constants (log $K_{ex,0}$) for the extraction of thorium(IV) and uranium(VI) with various para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones.

Extractants	pK_a	Log P_{HX}	O--O distance (Å)	Log $K_{ex,0}$	
				Th(IV)	U(VI)
HPMFBP	3.52	2.29	2.67	6.94 ± 0.04	0.85 ± 0.03
HPMBP	3.92	2.33	2.67	6.72 ± 0.04	0.76 ± 0.04
HPMTP	4.02	2.88	2.67	6.50 ± 0.04	0.60 ± 0.04

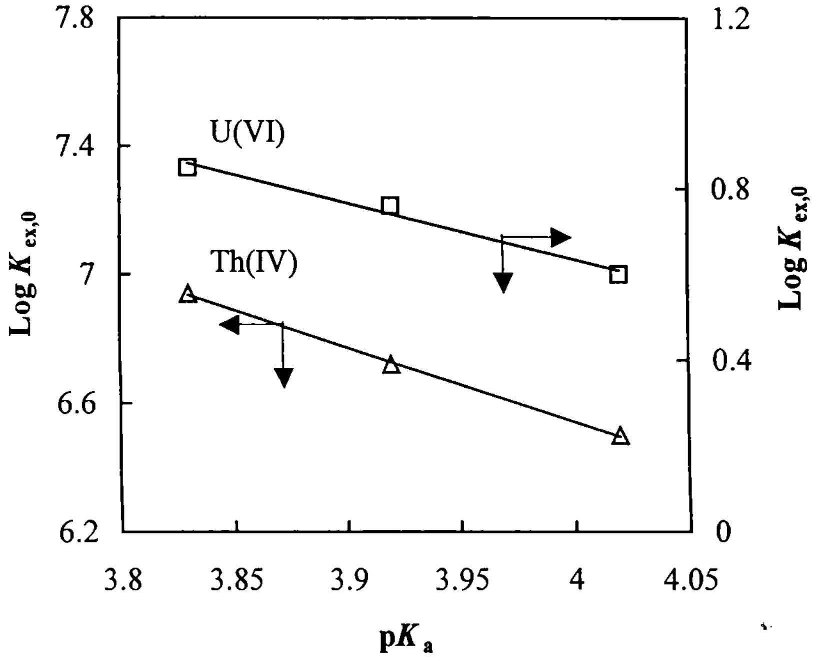


Figure 3.8. Plots of log $K_{ex,0}$ *vs* pK_a for the extraction of thorium(IV) and uranium(VI) with various para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones.

Recently, the O---O distance has been identified as one of the most significant factors that governs the selectivity in the complexation of β-diketones with metal ions [Umetani et al. 2000]. Hence in the present study the O---O distances in para-substituted 4-aroyl-5-pyrazolones have been determined by semi-empirical PM3 molecular orbital calculations [Stewart 1989] taking into account the hydrogen bond and are given in Table 3.1. The ball-and-stick representation based on the PM3/H optimized structures of HPMFBP, HPMBP and HPMTP are given in Fig. 3.9. The O---O distance found from the PM3 model for HPMBP (2.67 Å) is in good agreement with the earlier reports (2.65 Å), calculated by MNDO/H calculation method [Umetani et al. 2000]. It can be concluded from the O---O distance values that

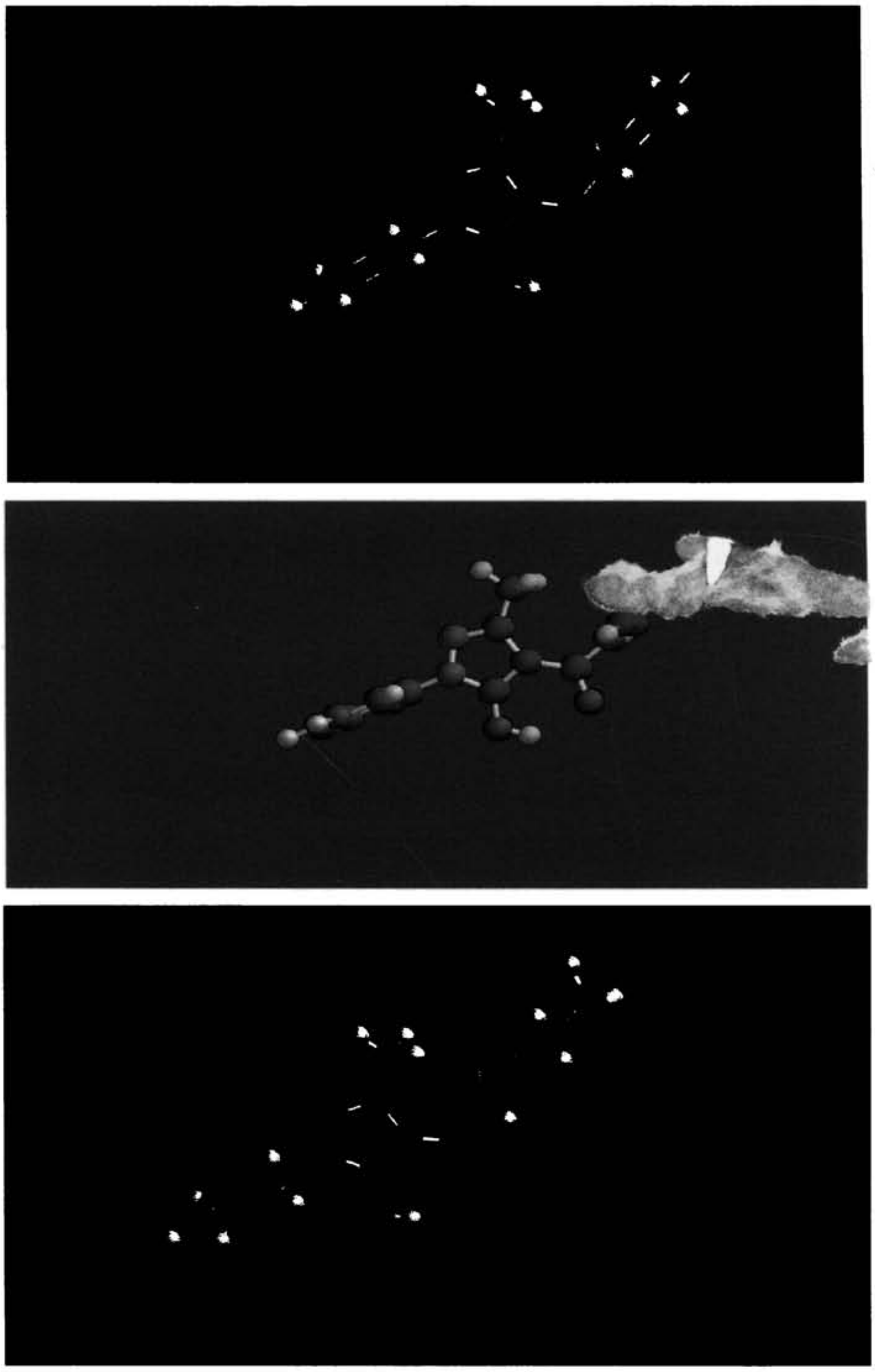


Figure 3.9. Ball-and-stick representation based on the PM3/H optimized structures of HPMFBP, HPMBP and HPMTP, respectively.

the para-substitution in 1-phenyl-3-methyl-4-aroyl-5-pyrazolones ultimately does not induce any steric repulsion between the 3-methyl group and the 4-aroyl group, thereby narrowing the O---O distance (i.e., bite size). However, it is clear from the present study that the log $K_{ex,0}$ values for both thorium(IV) and uranium(VI) with various para-substituted 4-aroyl-5-pyrazolones varies in accordance with the nature of the substituent, electron withdrawing (-F) or electron donating ($-CH_3$) group, on the benzoyl moiety of the HPMBP.

Solid complexes of thorium(IV) and uranium(VI) with 4-aroyl-5-pyrazolones and their characterization

Solid complexes of thorium(IV) and uranium(VI) with HPMFBP/HPMTP were characterized by elemental analyses, IR and ^{1}H NMR spectroscopic techniques.

Elemental analyses of binary complexes

The analytical data presented in Table 3.2 show that thorium(IV) and uranium(VI) reacted with HPMFBP/HPMTP, in the metal : ligand mole ratio of 1 : 4 and 1 : 2, respectively.

IR spectra of binary complexes

Figs. 3.10 and 3.11 show the IR spectra of thorium(IV) and uranium(VI) with HPMFBP and HPMTP, respectively. The IR spectra of the complexes of the metal ions show a broad absorption in the region 3000 - 3500 cm^{-1}, indicating the presence of extensive H-bonding between the N-atoms of the heterocyclic ring and the –OH group of H_2O, as observed in the transition metal complexes of 4-acylpyrazolonates [Marchetti 2001].

Table 3.2. Elemental analyses of the binary complexes.

Complex	% C Found	% H Found	%N Found	% M Found
$Th(PMFBP)_4 \cdot 2H_2O$	56.03 (56.35)	3.32 (3.59)	8.35 (7.73)	16.36 (16.02)
$UO_2(PMFBP)_2 \cdot H_2O$	46.06 (46.47)	2.61 (2.96)	6.37 (6.38)	26.64 (27.11)
$Th(PMTP)_4 \cdot 2H_2O$	59.92 (60.34)	4.01 (4.47)	8.12 (7.82)	16.54 (16.20)
$UO_2(PMTP)_2 \cdot H_2O$	49.71 (49.66)	3.61 (3.68)	6.63 (6.44)	27.59 (27.36)

Figures in parentheses indicate calculated values.

The presence of water molecules have also been observed in the 1-phenyl-3-methyl-4-acyl-5-pyrazolonato complexes of uranium(VI) [Mundra et al. 1987; Okafor et al. 1990]. The broad band due to intramolecular O-H---O stretching vibration, which is observed in the free ligands, in the range 2300 - 3000 cm^{-1} has disappeared in the complexes. In the 1500 – 1650 cm^{-1} region some strong bands due to ν (C=O), ν (C=N) and ν (C=C) of the aromatic rings have been observed in the spectra of the complexes, where the carbonyl band (1620 cm^{-1} in HPMFBP and 1600 cm^{-1} in HPMTP) shifted to lower frequency (1603 cm^{-1} in both Th-HPMFBP and U-HPMFBP, 1578 cm^{-1} in Th-HPMTP and 1570

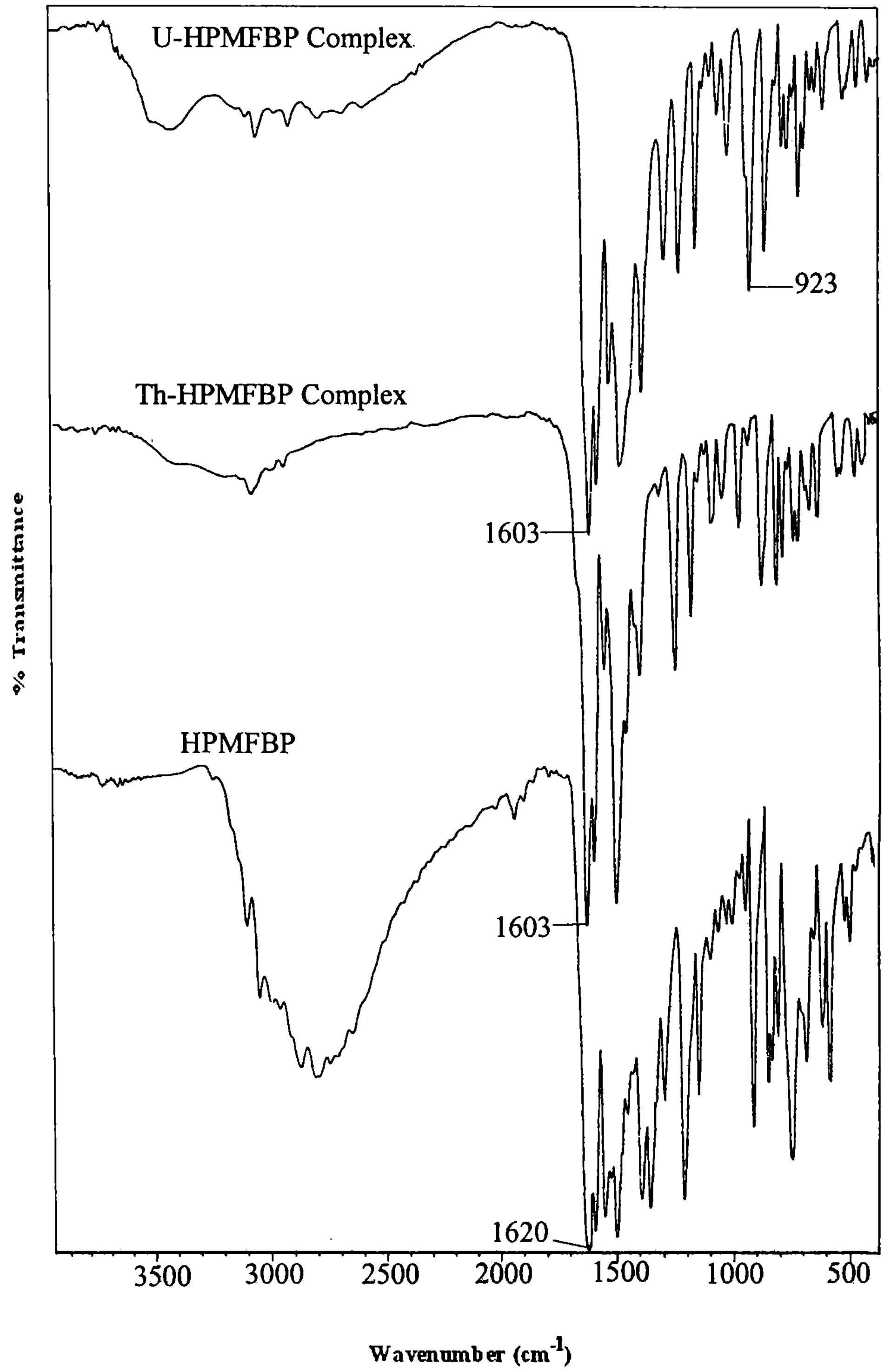


Figure 3.10. IR spectra of HPMFBP ligand, Th-HPMFBP complex and U-HPMFBP complex.

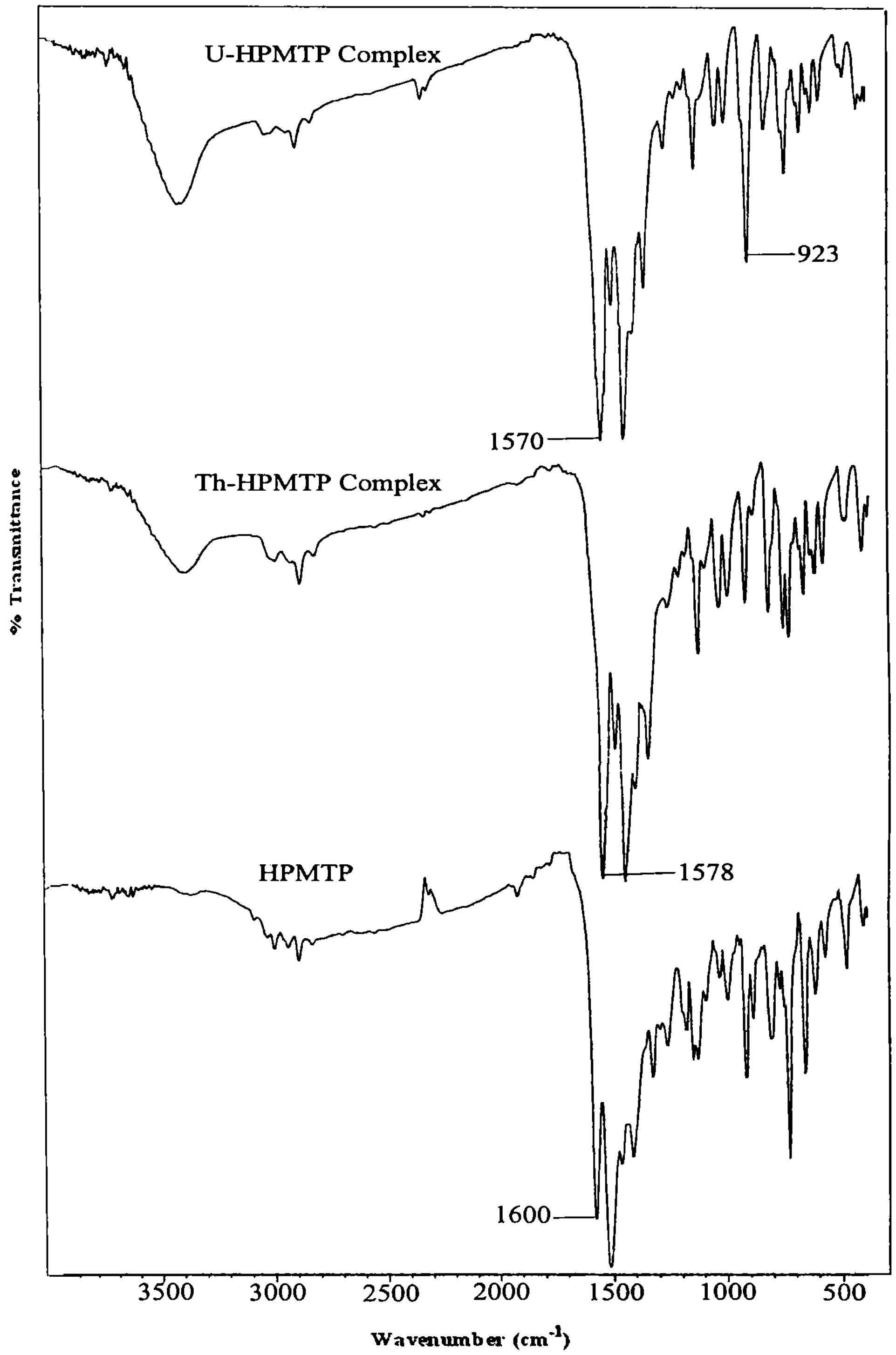


Figure 3.11. IR spectra of HPMTP ligand, Th-HPMTP complex and U-HPMTP complex.

cm^{-1} in U- HPMTP complexes) upon coordination with metal ion. Further, a strong absorption band occurring around 923 cm^{-1} (U-HPMFBP and U-HPMTP complexes) may be assigned to *v* (O=U=O) of uranyl ion [Sahu et al. 2000; Kannan et al. 2004]. These features are in accordance with deprotonation of para-substituted 4-aroyl-5-pyrazolones and coordination to the thorium(IV) or uranium(VI) through carbonyl oxygen atom.

^{1}H NMR spectra of binary complexes

The ^{1}H NMR spectral data of the binary complexes (Figs. 3.12 and 3.13; Table 3.3) shows all the expected resonances for 4-aroyl-5-pyrazolonates and the free ligands, the integration of the signals being in accordance with the formulae proposed. The signal of 3-CH_3 group has been

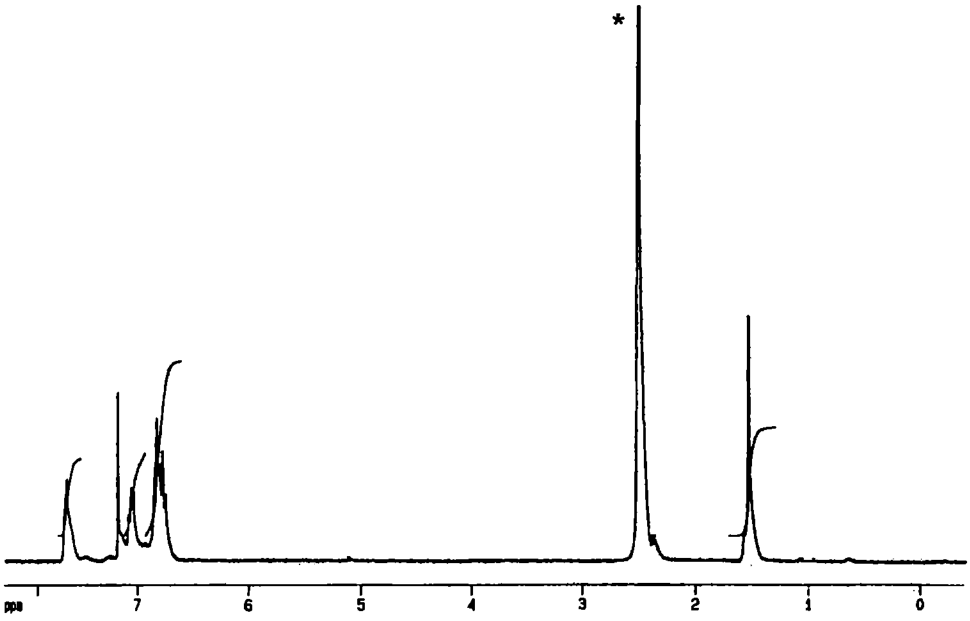


Figure 3.12. ^{1}H NMR spectrum of Th-HPMFBP complex.* denote the DMSO peak.

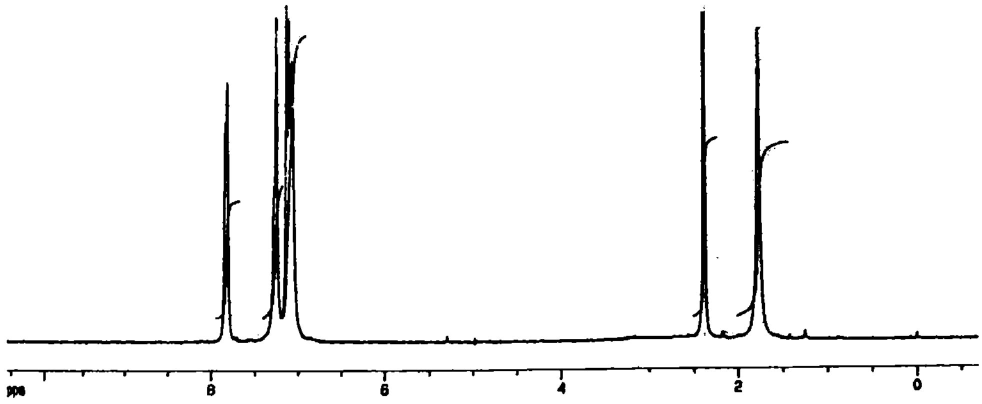


Figure 3.13. ^1H NMR spectrum of Th-HPMTP complex.

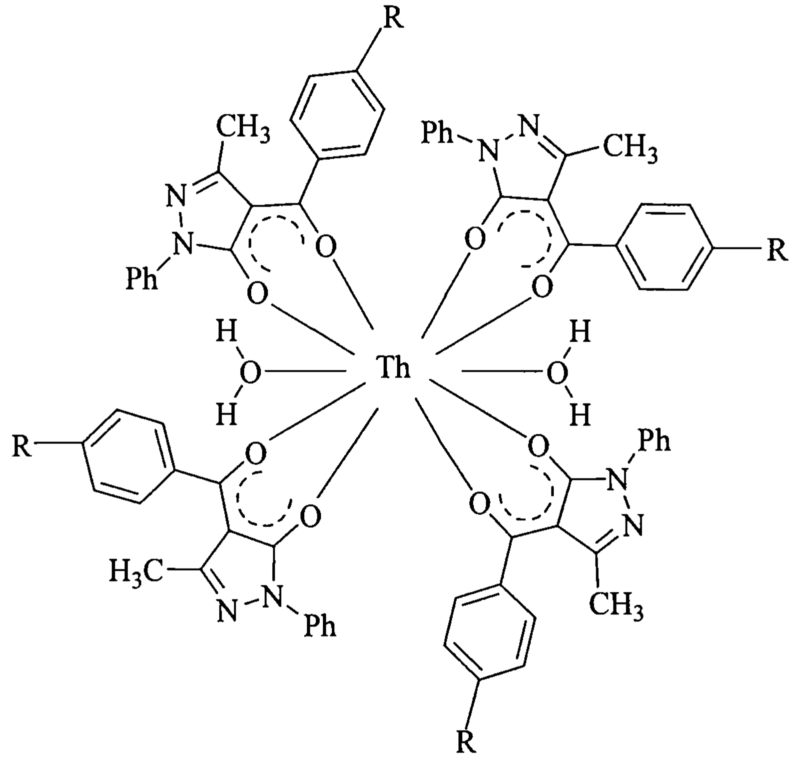
Table 3.3. ^1H NMR spectral data for free ligands and binary complexes.

Compound	Phenyl protons (ppm)	CH_3 protons (ppm)	
		Pyrazole ring	Aromatic ring
HPMFBP	7.17 - 7.88 (m)	2.12 (s)	-
HPMTP	7.20 - 7.98 (m)	2.14 (s)	2.45 (s)
Th-HPMFBP	6.75 - 7.69 (m)	1.54 (s)	-
U-HPMFBP	7.19 - 8.20 (m)	1.93 (s)	-
Th-HPMTP	7.09 - 7.83 (m)	1.79 (s)	2.39 (s)
U-HPMTP	7.28 - 8.32 (m)	2.09 (s)	2.41 (s)

always found shifted to higher field upon coordination with metal ion in all the binary complexes. The upfield shifts observed were larger for thorium than in uranium complexes. On the other hand, downfield field shift of the phenyl protons has been observed in all uranium-pyrazolonate complexes. In the case of thorium complexes, the phenyl protons have been found shifted to higher field upon complexation.

Fig. 3.14 gives the proposed structures of thorium(IV) and uranium(VI) with various para-substituted 4-aroyl-5-pyrazolones, on the basis of elemental analyses, IR and ^1H NMR spectral data. The uranyl ion is surrounded by two molecules of para-substituted 4-aroyl-5-pyrazolones and one water molecule to give a coordination number of seven and pentagonal bipyramidal geometry, as observed in uranium-HTTA [Kannan et al. 2001] and uranium-HPMBP/HPMAP complexes [Okafor et al. 1990]. In the case of Th-HPMFBP/HPMTP complex, Th^{4+} is surrounded by four para-substituted 4-aroyl-5-pyrazolone molecules and two water molecules, arranged in a capped cubic array, to give a coordination number of 10, as observed in Th-HTTA [Mathur and Choppin 1993] and thorium nitrate-triphenylphosphine oxide complexes [Shriver and Atkins 1999].

Table 3.4 gives the separation factors between thorium(IV) and uranium(VI) at various concentrations of para-substituted 4-aroyl-5-pyrazolones. It is clear from the table that the selectivity between thorium(IV) and uranium(VI) increases with increasing concentrations of para-substituted 4-aroyl-5-pyrazolones at constant acidity. Further, these separation factors are found to be significantly higher than that of TBP system (S.F. = D_U/D_{Th} = 17 at 1 mol/ dm^3 HNO_3 [Pathak et al. 1999]), which is commercially used in the Nuclear Industry. In view of the better extraction efficiency and selectivity observed, HPMFBP was chosen for further experimentation, especially to study the synergistic extraction in presence of various crown ethers.



R = F, CH_3

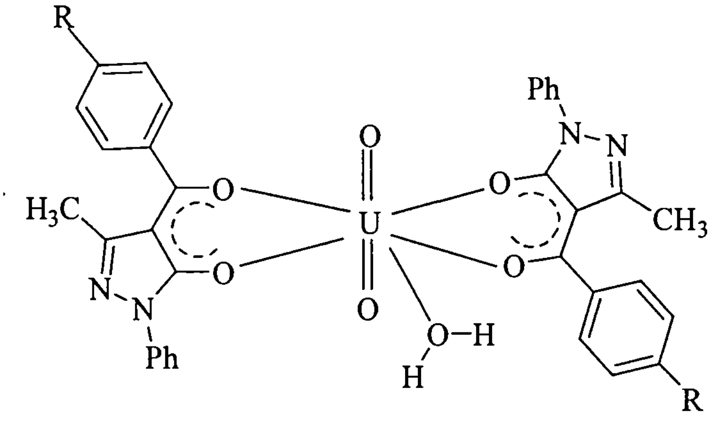


Figure 3.14. Proposed structures of thorium(IV) and uranium(VI) with para-substituted 4-aroyl-5-pyrazolones.

Table 3.4. Separation factors (S.F.) between thorium(IV) and uranium(VI) with various 4-aroyl-5-pyrazolones (HX) at 1.0 mol/dm^3 NaNO$_3$ of pH =1.0.

[HX] mol/dm^3	S.F. (D_{Th} / D_{U})		
	HPMFBP	HPMBP	HPMTP
0.008	1.38 x 10^3	1.02 x 10^3	8.79 x 10^2
0.01	2.15 x 10^3	1.60 x 10^3	1.36 x 10^3
0.02	8.51 x 10^3	6.38 x 10^3	5.46 x 10^3
0.04	3.42 x 10^4	2.56 x 10^4	2.18 x 10^4
0.05	5.35 x 10^4	3.99 x 10^4	3.40 x 10^4

Extraction of thorium(IV) and uranium(VI) with mixtures of HPMFBP and crown ethers

The synergistic extraction equilibrium of thorium(IV) with a chelating agent, HPMFBP (HX) and crown ether (CE) can be expressed as

$$\mathrm{Th}^{4+}_{\mathrm{aq}} + 4(\mathrm{HX})_{\mathrm{org}} + n\,\mathrm{CE}_{\mathrm{org}} \xrightleftharpoons{K} \mathrm{ThX_4}.n\mathrm{CE}_{\mathrm{org}} + 4\mathrm{H}^{+}_{\mathrm{aq}} \qquad (12)$$

where n = 0 or 1. The synergistic equilibrium constant, K, is given by the expression

$$K = \frac{[\mathrm{ThX_4}.n\,\mathrm{CE}]_{\mathrm{org}}\,[\mathrm{H}^+]^4_{\mathrm{aq}}}{[\mathrm{Th}^{4+}]_{\mathrm{aq}}[\mathrm{HX}]^4_{\mathrm{org}}[\mathrm{CE}]^n_{\mathrm{org}}} \qquad (13)$$

The distribution ratio, D, of the synergistic extraction system is given by Eq. (14)

$$D = \frac{[\mathrm{ThX_4}]_{\mathrm{org}} + [\mathrm{ThX_4.CE}]_{\mathrm{org}}}{[\mathrm{Th}^{4+}]_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}} + \beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\}} \qquad (14)$$

From Eqs. (9), (13) and (14)

$$K = \frac{(D-D_0)[\mathrm{H}^+]^4_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}} + \beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\}}{[\mathrm{HX}]^4_{\mathrm{org}}[\mathrm{CE}]_{\mathrm{org}}} \qquad (15)$$

where $[\mathrm{CE}]_{\mathrm{org}} = \dfrac{[\mathrm{CE}]_{\mathrm{initial}}}{(1+\frac{1}{K_{\mathrm{D}}})}$.

Taking logarithms for Eq. (15),

$$\mathrm{Log}\,K = \log(D - D_0) - 4\log[\mathrm{HX}]_{\mathrm{org}} - \log[\mathrm{CE}]_{\mathrm{org}} + 4\log[\mathrm{H^+}]_{\mathrm{aq}} + \log\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}+\beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\} \quad (16)$$

The organic phase adduct formation reaction is represented as

$$\mathrm{ThX_4}_{\,\mathrm{org}} + n\mathrm{CE}_{\mathrm{org}} \xrightleftharpoons{K_{CE}} \mathrm{ThX_4}.n\mathrm{CE}_{\mathrm{org}} \quad (17)$$

where K_{CE} is the organic phase adduct formation constant and is given as

$$K_{\mathrm{CE}} = \frac{[\mathrm{ThX_4}.n\mathrm{CE}]_{\mathrm{org}}}{[\mathrm{ThX_4}]_{\mathrm{org}}[\mathrm{CE}]_{\mathrm{org}}} \quad (18)$$

From Eqs. (4), (12), (17) and (18)

$$K_{\mathrm{CE}} = \frac{K}{K_{\mathrm{ex,0}}} \quad (19)$$

For a synergistic extraction system employing a neutral donor, CE, the extraction equilibrium of uranium(VI) with a chelating agent may be represented as

$$\mathrm{UO}^{2+}_{2\,\mathrm{aq}} + 2(\mathrm{HX})_{\mathrm{org}} + n\,\mathrm{CE}_{\mathrm{org}} \xrightleftharpoons{K} \mathrm{UO_2X_2}.n\mathrm{CE}_{\mathrm{org}} + 2\mathrm{H}^+_{\mathrm{aq}} \quad (20)$$

where n = 0 or 1. Then the distribution ratio, D, of the synergistic extraction system for uranium(VI) is given by

$$\mathrm{D} = \frac{[\mathrm{UO_2X_2}]_{\mathrm{org}} + [\mathrm{UO_2X_2.CE}]_{\mathrm{org}}}{[\mathrm{UO_2^{2+}}]_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}\}} \quad (21)$$

From Eqs. (10), (20) and (21)

$$K = \frac{(D-D_0)[\mathrm{H^+}]^2_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}\}}{[\mathrm{HX}]^2_{\mathrm{org}}[\mathrm{CE}]_{\mathrm{org}}} \quad (22)$$

The organic phase adduct formation reaction is represented as

$$UO_2X_{2\,org} + nCE_{org} \xrightleftharpoons{K_{CE}} UO_2X_2.nCE_{org} \qquad (23)$$

where K_{CE}, the organic phase adduct formation constant is given by

$$K_{CE} = \frac{K}{K_{ex,0}} \qquad (24)$$

The equilibrium concentration of 18C6 was calculated using the partition coefficient (log $K_{D,18C6}$ = 0.8) taken from the literature [Mohapatra and Manchanda 1991]. Since the partition coefficients of DC18C6, DB18C6 and B15C5 (log $K_{D,DC18C6}$ = 3.52; log $K_{D,DB18C6}$ = 3.9; log $K_{D,B15C5}$ = 2.5 [Hasegawa et al. 1984]) are known to be quite large, no correction is necessary for the partitioning of these CEs into the aqueous phase. It has been reported that the interaction between the chelating agent and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the oxo-donor [Sekine et al. 1983]. Hence it is assumed that there is negligible interaction between HPMFBP and CEs in chloroform.

For confirming the above extraction equilibria, the extraction of thorium(IV) and uranium(VI) from 1.0 mol/dm^3 sodium nitrate solutions (pH = 1.0) with mixtures of HPMFBP (0.002 – 0.007 mol/dm^3 for thorium(IV) and 0.02 – 0.1 mol/dm^3 for uranium(VI)), and 18C6 (0.04 – 0.1 mol/dm^3 for thorium(IV) and 0.16 – 0.3 mol/dm^3 for uranium(VI)), DC18C6 (0.05 – 0.12 mol/dm^3 for thorium(IV) and 0.08 – 0.2 mol/dm^3 for uranium(VI)), DB18C6 (0.06 – 0.15 mol/dm^3 for thorium(IV) and 0.2 – 0.35 mol/dm^3 for uranium(VI)) or B15C5 (0.008 – 0.1 mol/dm^3 for thorium(IV) and 0.1 – 0.3 mol/dm^3 for uranium(VI)) into chloroform was studied. It was found that the extraction of these metal ions into chloroform with CE alone was negligible under the present experimental conditions. However, with mixtures of HPMFBP and CEs, a considerable synergistic enhancement (Synergistic enhancement factor = $D/D_{\mathrm{HPMFBP}} + D_{\mathrm{CE}}$, where D = distribution ratio with HPMFBP + CE, D_{HPMFBP} = distribution ratio with HPMFBP alone, and D_{CE} = distribution ratio with CE alone) in the extraction of these metal ions was observed (Table 3.5).

Table 3.5. Synergistic enhancement factors of thorium(IV) and uranium(VI) with HPMFBP in presence of crown ethers.

Extraction system	Synergistic enhancement factors	
	Th(IV)	U(VI)
HPMFBP + 18C6	4	10
HPMFBP + DC18C6	3	5
HPMFBP + DB18C6	2	2
HPMFBP + B15C5	28	4

Th(IV): 0.004 mol/dm^3 HPMFBP + 0.1 mol/dm^3 CE
U(VI): 0.05 mol/dm^3 HPMFBP + 0.2 mol/dm^3 CE

It is clear from the plots (Figs. 3.15 and 3.16) of log (D - D_0) *vs*. log [HPMFBP] that at constant CE (0.1 mol/dm^3 for thorium(IV) and 0.2 mol/dm^3 for uranium(VI)) and nitric acid concentrations (0.1 mol/dm^3), only four HPMFBP moieties in the case of thorium(IV) and two HPMFBP moieties in the case of uranium(VI) are involved in the synergistic species extracted into the organic phase. The plots (Figs. 3.17 and 3.18) of log (D - D_0) *vs*. log [CE] at constant HPMFBP concentration (0.004 mol/dm^3 for thorium(IV) and 0.05 mol/dm^3 for uranium(VI)) gave slopes of unity for both metal ions, indicating the participation of only one CE molecule in the synergistic extracted species.

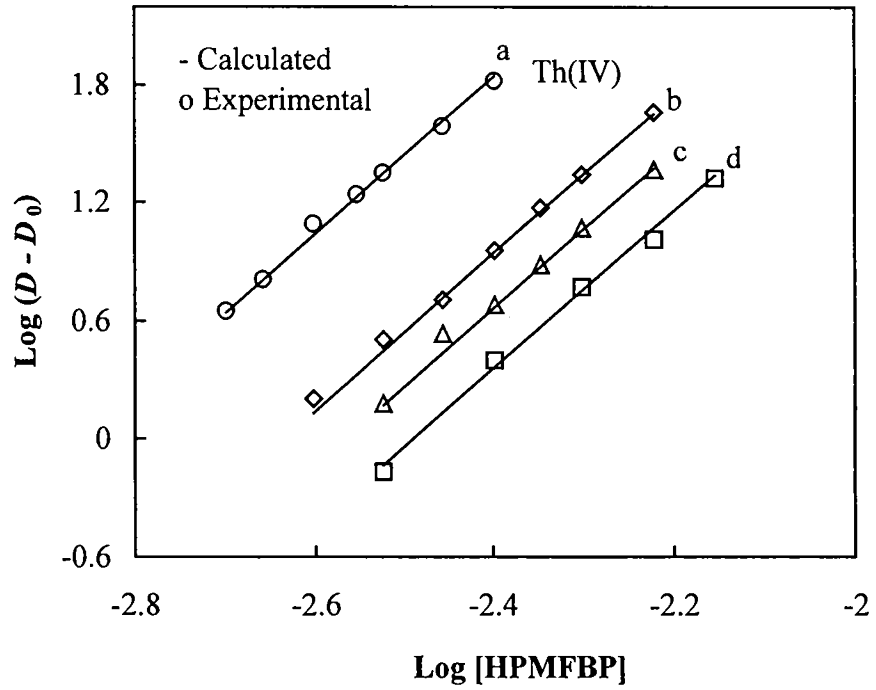


Figure 3.15. Effect of HPMFBP concentration on the extraction of thorium(IV) at constant CE (0.1 mol/dm^3) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 1.0). Slope of the line (a) B15C5 = 4.0 ± 0.2 (b) 18C6 = 4.0 ± 0.2 (c) DC18C6 = 4.0 ± 0.2 (d) DB18C6 = 4.0 ± 0.05.

These results, in conjunction with the slopes of –4.0 ± 0.1 and –2.0 ± 0.05 observed for thorium(IV) and uranium(VI), respectively, with hydrogen ion (0.08 - 0.35 mol/dm^3) variation (Figs. 3.19 and 3.20) at constant HPMFBP + CE (0.004 mol/dm^3 HPMFBP + 0.1 mol/dm^3 CE for thorium(IV) and 0.05 mol/dm^3 HPMFBP + 0.2 mol/dm^3 CE for uranium(VI)), indicate the extraction of the complexes, $Th(PMFBP)_4{\cdot}CE$ and $UO_2(PMFBP)_2{\cdot}CE$. Similar synergistic complexes, $Th(PMBP)_4{\cdot}CE$ and $UO_2(PMBP)_2{\cdot}CE$, have been observed for the extraction of thorium(IV) and uranium(VI) from perchlorate solutions with HPMBP in the presence of various CEs [Yonezawa and

Choppin 1989]. Synergistic complexes of the same type, $UO_2X_2{\cdot}DC18C6$, have also been reported for the extraction of uranium(VI) from nitrate solutions using various 4-acyl-5-pyrazolones (HX = HPMTFP; HPMAP; HPMBP) in the presence of DC18C6 [Mundra et al. 1987]. The synergistic equilibrium constants (*K*) of the above extracted complexes for these metal ions were deduced by nonlinear regression analysis and are given in Table 3.6. The adduct formation constants, K_{CE}, for the organic phase synergistic reaction of Th-HPMFBP-chelate or U-HPMFBP-chelate with various CEs were also calculated and are given in Table 3.6.

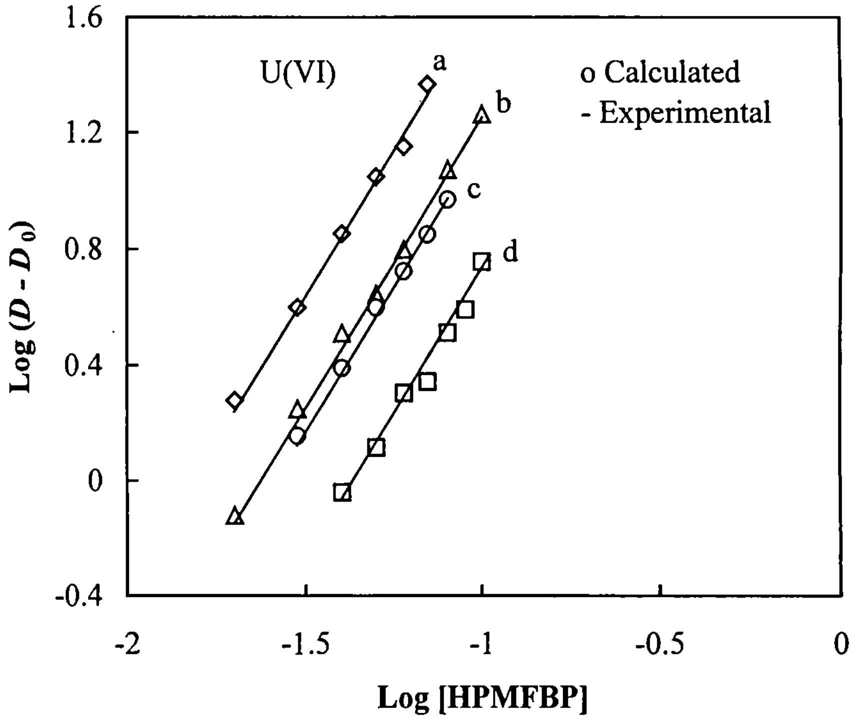


Figure 3.16. Effect of HPMFBP concentration on the extraction of uranium(VI) at constant CE (0.2 mol/dm^3) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 1.0). Slope of the line (a) 18C6 = 2.0 $\pm$ 0.05 (b) DC18C6 = 2.0 $\pm$ 0.05 (c) B15C5= 2.0 $\pm$ 0.1 (d) DB18C6 = 2.0 $\pm$ 0.1.

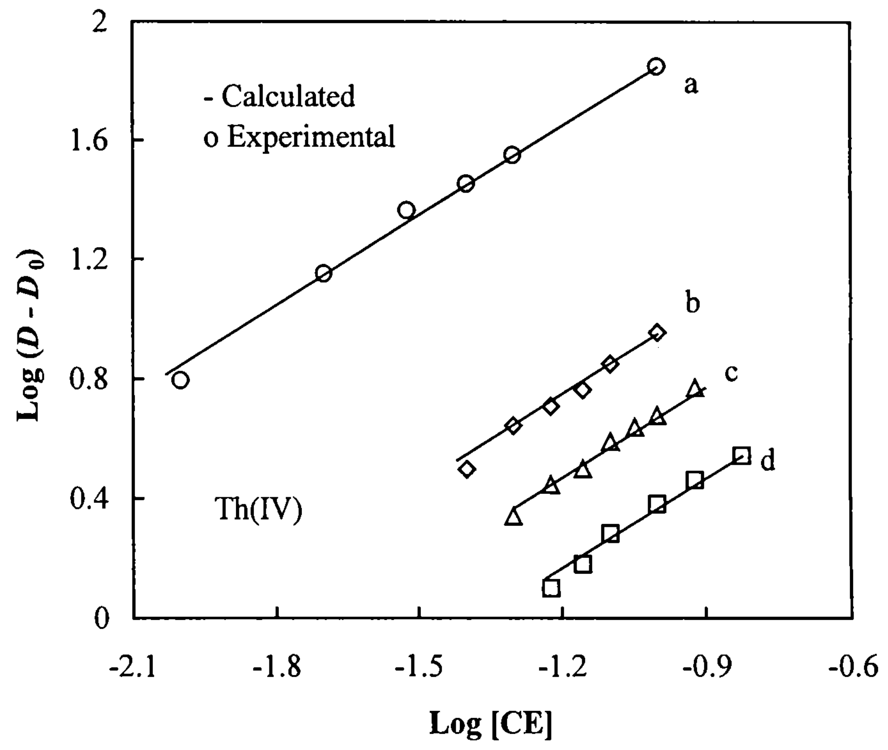


Figure 3.17. Effect of CE concentration on the extraction of thorium(IV) at constant HPMFBP (0.004 mol/dm^3) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 1.0). Slope of the line (a) B15C5 = 1.0 ± 0.05 (b) 18C6 = 1.0 ± 0.1 (c) DC18C6 = 1.0 ± 0.1 (d) DB18C6 = 1.0 ± 0.1.

The sharp decrease in complexation for both thorium(IV) and uranium(VI) from 18C6 to DC18C6 to DB18C6 mostly reflects increasing steric effects and decreasing basicity. This seems reasonable, since extensive thermodynamic studies on cation-CE complexation have shown that the cation binding ability of the CE containing benzo groups is lower than that for the parent CE, and have demonstrated that the diminished complex stability is due

Table 3.6. Two phase synergistic equilibrium constants (*K*) and organic phase adduct formation constants (K_{CE}) of thorium(IV) and uranium(VI) with HPMFBP-CE-Chloroform system.

CE	Log *K*		Log K_{CE}	
	Th(IV)	U(VI)	Th(IV)	U(VI)
18C6	8.47 ± 0.04	2.50 ± 0.04	1.53 ± 0.04	1.65 ± 0.04
DC18C6	8.19 ± 0.04	2.12 ± 0.04	1.25 ± 0.04	1.27 ± 0.04
DB18C6	7.89 ± 0.04	1.61 ± 0.05	0.95 ± 0.04	0.76 ± 0.05
B15C5	9.37 ± 0.05	2.04 ± 0.04	2.43 ± 0.05	1.19 ± 0.04

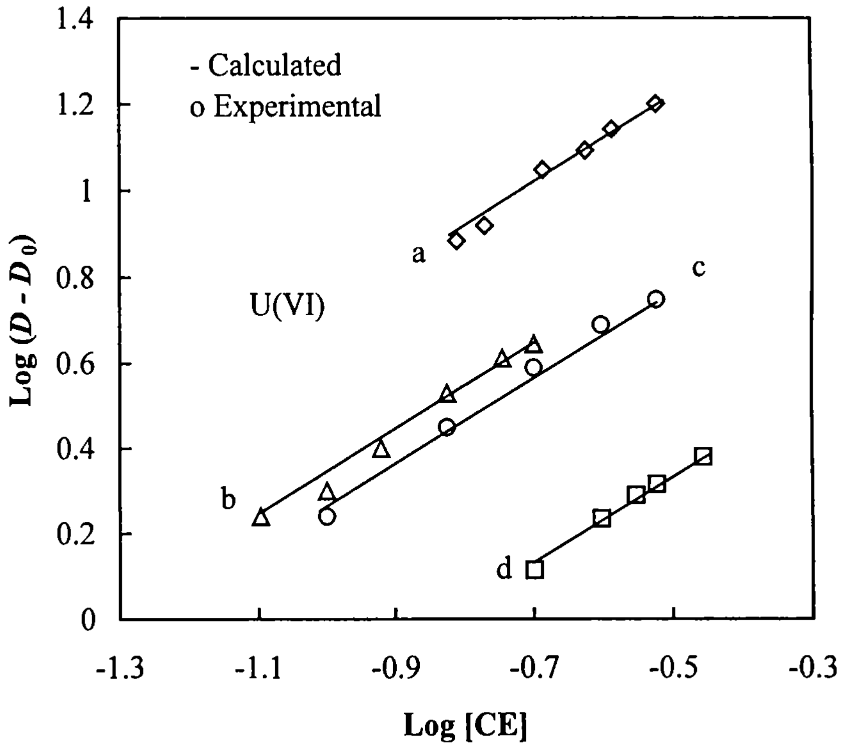


Figure 3.18. Effect of CE concentration on the extraction of uranium(VI) at constant HPMFBP (0.05 mol/dm^3) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 1.0). Slope of the line (a) 18C6 = 1.0 ± 0.1 (b) DC18C6 = 1.0 ± 0.1 (c) B15C5 = 1.0 ± 0.1 (d) DB18C6 = 1.0 ± 0.1.

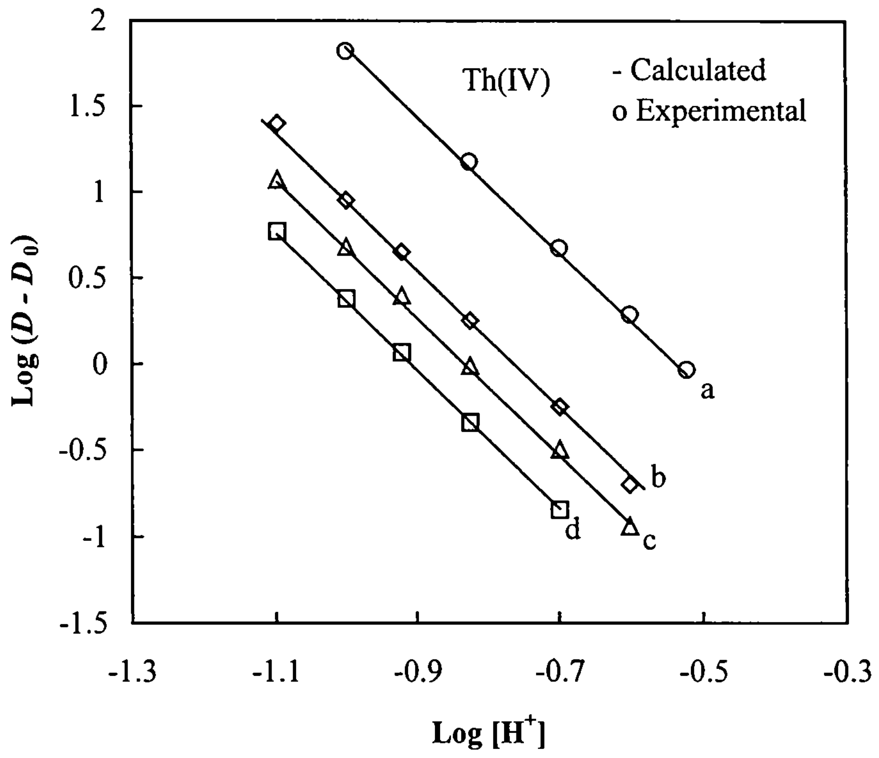


Figure 3.19. Effect of hydrogen ion concentration on the extraction of thorium(IV) at constant HPMFBP (0.004 mol/dm^3) + CE (0.1 mol/dm^3) concentration. Slope of the line (a) B15C5 = -4.0 ± 0.1 (b) 18C6 = -4.0 ± 0.2 (c) DC18C6 = -4.0 ± 0.05 (d) DB18C6 = -4.0 ± 0.1.

to the decreased electron density of donor oxygens produced by the electron withdrawing aromatic ring [Liu et al. 2000]. The cyclohexano group has a less dramatic effect on the stability of the complex and cation selectivity [Izatt et al. 1985]. The high adduct formation constant value (log K_{CE} = 2.43) for Th(PMFBP)$_4$·B15C5 is likely to be associated with a good fit of Th^{4+} (ionic diameter = 0.20 nm [Yonezawa and Choppin 1989]) in the cavity of B15C5 (cavity size = 0.17 – 0.22 nm [Mathur and Khopkar 1988]). A similar trend was observed for the extraction of thorium(IV) with mixtures of HPBI and B15C5 [Sahu et al. 2000]. In the case of uranium(VI) (ionic diameter = 0.15

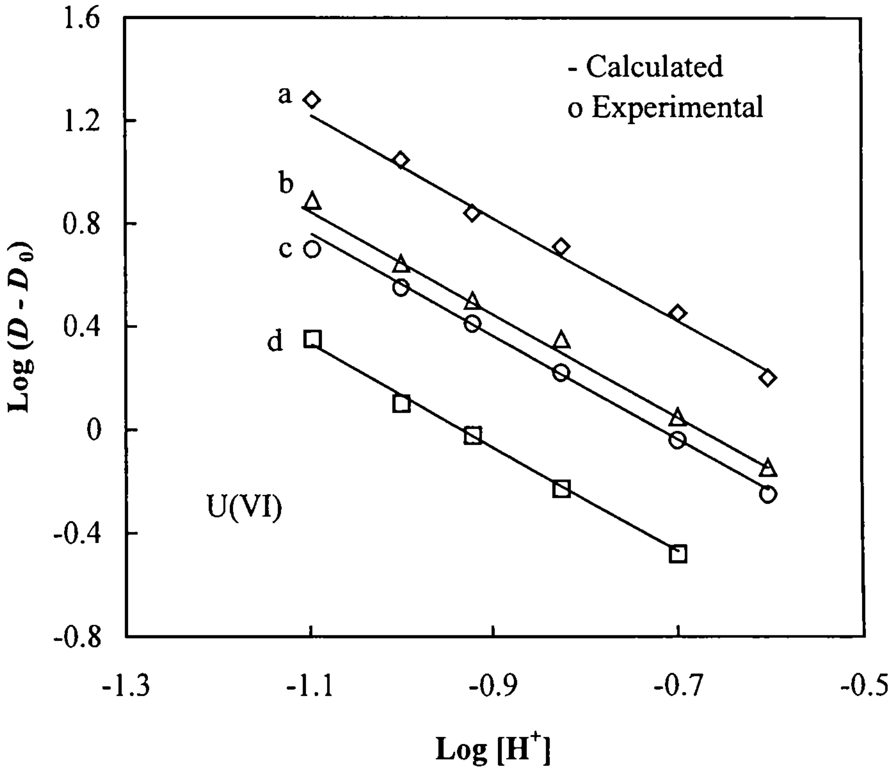


Figure 3.20. Effect of hydrogen ion concentration on the extraction of uranium(VI) at constant HPMFBP (0.05 mol/dm^3) + CE (0.2 mol/dm^3) concentration. Slope of the line (a) 18C6 = -2.0 ± 0.1 (b) DC18C6 = -2.0 ± 0.05 (c) B15C5 = -2.0 ± 0.1 (d) DB18C6 = -2.0 ± 0.05.

nm for U in uranyl ion [Yonezawa and Choppin 1989]) the adduct formation constant values increases regularly to 18C6 (cavity size = 0.26–0.32 nm [Pedersen 1970]) and it appears that the compatibility of the cation and crown cavity size is not the determining factor in the synergistic complexes of uranyl ion. The adduct formation constant follows the order 18C6 > DC18C6 > B15C5 > DB18C6. The unusual behavior observed in the present investigations may be attributed to a variety of geometric (cavity size and steric repulsion between extractants), enthalpic (donor basicity) and entropic (cation dehydration) effects involved in the extraction of f-elements with CEs in the presence of HPMFBP. A better understanding of the interactions of CEs with metal-chelate systems requires more detailed investigations of the solution structures of these complexes.

Solid complexes of thorium(IV) and uranium(VI) with mixtures of HPMFBP and CEs and their characterization

Elemental analyses of ternary complexes

The analytical data presented in Table 3.7 show that thorium(IV) and uranium(VI) reacted with HPMFBP and crown ether in the metal : ligand : crown ether mole ratio of 1 : 4 : 1 and 1 : 2 : 1, respectively.

Table 3.7. Elemental analyses of ternary complexes.

Complex	% C Found	% H Found	%N Found	% M Found
$Th(PMFBP)_4 \cdot B15C5 \cdot H_2O$	58.27 (57.95)	4.56 (4.12)	6.29 (6.60)	13.46 (13.66)
$UO_2(PMFBP)_2 \cdot DC18C6 \cdot H_2O$	51.48 (51.84)	5.15 (4.96)	4.35 (4.48)	19.32 (19.04)

Figures in parentheses indicate calculated values.

IR Spectra of ternary complexes

The IR spectra of the ternary complexes of the metal ions (Fig. 3.21) show a broad absorption in the region 3000 - 3500 cm^{-1}, indicating the presence of extensive H-bonding between the N-atoms of the heterocyclic ring and the –OH group of H_2O. In the ternary complexes the carbonyl stretching

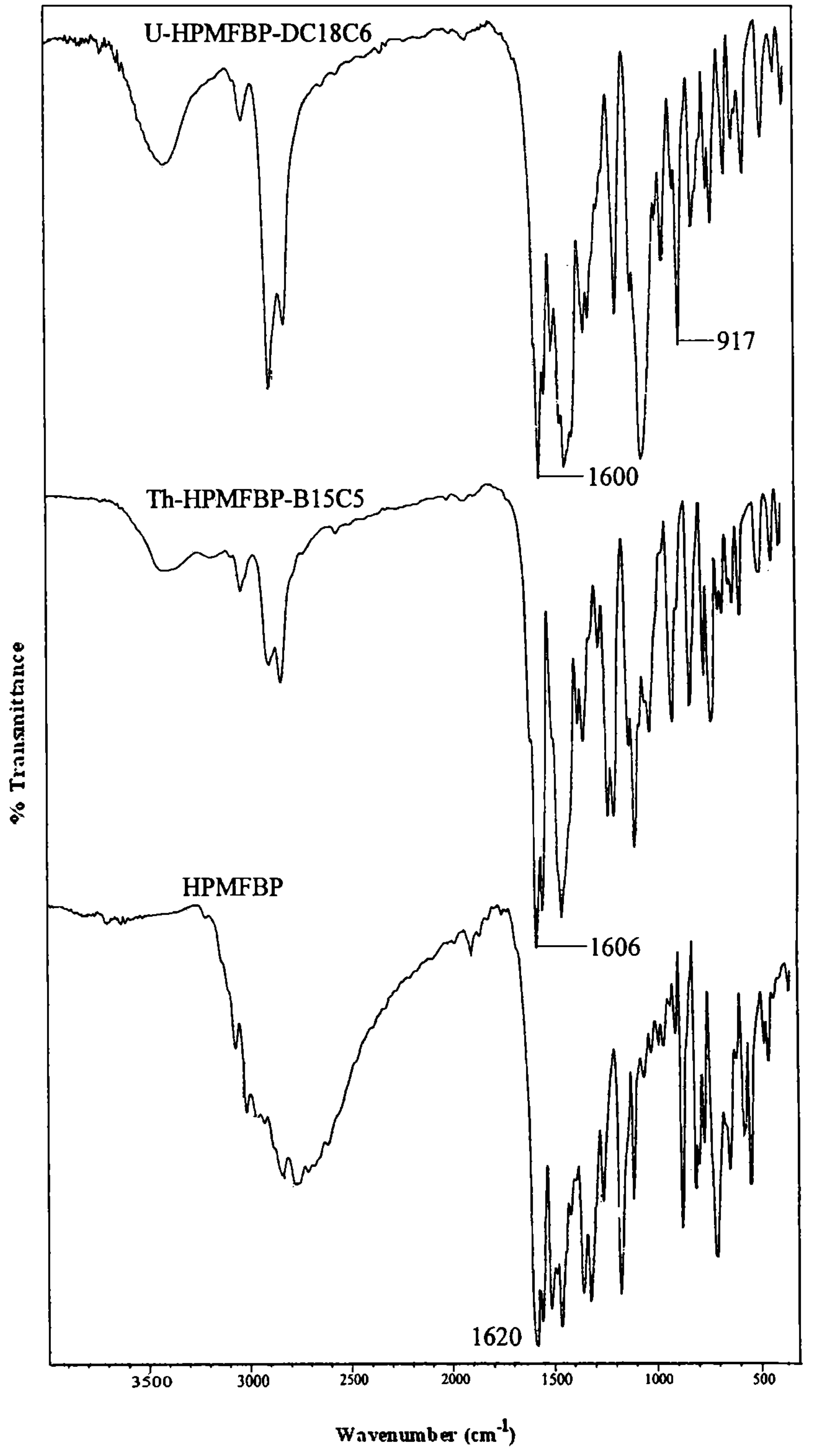


Figure 3.21. IR spectra of HPMFBP ligand, Th-HPMFBP-B15C5 complex and U-HPMFBP-DC18C6 complex.

frequency of HPMFBP has shifted from 1620 to 1606 cm^{-1} and 1600 cm^{-1} in Th-HPMFBP-B15C5 and U-HPMFBP-DC18C6, respectively, upon coordination with metal ion. This suggests that the carbonyl group in HPMFBP is involved in the complex formation with the metal ion. Further, the strong absorption band occurring around 917 cm^{-1} in U-HPMFBP-DC18C6 complex may be assigned to ν (O=U=O) of uranyl ion [Sahu et al. 2000; Kannan et al. 2004]. In the Th-HPMFBP-B15C5 ternary complex, the bands at 1129 - 1255 cm^{-1} assigned to ν (C–O) of polyether became noticeably weaker as compared to free B15C5, which suggests the involvement of oxygen of the CE in the adduct formation. The C-O-C stretching vibration at 1096 cm^{-1} in free DC18C6 appeared with less intensity in U-HPMFBP-DC18C6 complex suggesting the involvement of oxygen of the CE in the complex formation.

^{1}H NMR spectra of ternary complexes

The ^{1}H NMR spectral data of the ternary complexes (Table 3.8) show all expected resonances for 4-aroyl-5-pyrazolonates and other donor ligands, the integration of the signals being in accordance with the formulae proposed (the spectra of the ternary complexes were taken in DMSO-d_6-$CDCl_3$ medium). The signal of 3-CH_3 group and the phenyl group of HPMFBP has been shifted to higher field upon coordination with metal ion in Th-HPMFBP-B15C5 complex. On the other hand, the downfield shift of the methyl and phenyl protons of HPMFBP has been observed in the uranium ternary complex. In the Th-HPMFBP-B15C5 complex (Fig. 3.22), the methylene protons of B15C5 appears as a multiplet with upfield shift, indicating nonuniform interactions of the ethereal oxygens with the metal ion. The CH_2

protons of cyclohexyl and methylene protons of DC18C6 were observed as a multiplet with downfield shift in the U-HPMFBP-DC18C6 complex (Fig. 3.23), indicating nonuniform interactions of ethereal oxygens.

Table 3.8. ^1H NMR spectral data for the free ligands and ternary complexes.

Compound	Phenyl protons (ppm)	CH_3 protons of Pyrazole ring (ppm)	CH_2 protons of CE (ppm)
HPMFBP	7.17 - 7.88 (m)	2.12 (s)	-
B15C5	6.89 (d)	-	3.76 (s), 3.9 - 3.93 (t), 4.12 - 4.16 (t)
DC18C6	-	-	3.67 (s), 1.5^a (m)
Th-HPMFBP-B15C5	6.87 - 7.88 (m), 6.84^b	1.69 (s)	3.70 (s), 3.84 -3.87 (t), 4.07 - 4.09 (t)
U-HPMFBP-DC18C6	6.97 - 8.23 (m)	2.35 (s)	3.11 - 3.57 (m), 1.03 - 2.06 $(m)^a$

a: - cyclohexyl -CH_2 protons ; b: phenyl protons of B15C5.

From the FT-IR spectra and elemental analyses of the $Th(PMFBP)_4{\cdot}H_2O{\cdot}B15C5$ and $UO_2(PMFBP)_2{\cdot}H_2O{\cdot}DC18C6$ complexes, it is clear that crown ethers are not able to replace water molecules in the binary complexes of $Th(PMFBP)_4{\cdot}2H_2O$ and $UO_2(PMFBP)_2{\cdot}H_2O$. Similar hydrated complexes have also been observed earlier in the extraction of $Th(TTA)_4{\cdot}H_2O{\cdot}18C6$ [Mathur and Choppin 1993] and $[UO_2(TTA)_2{\cdot}H_2O]_2(B15C5)$ [Kannan et al. 2001].

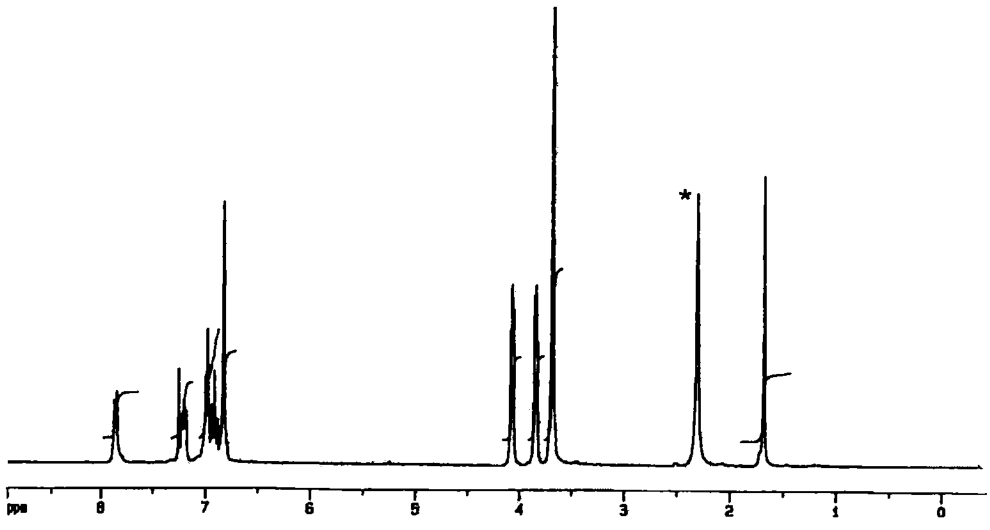


Figure 3.22. ^{1}H NMR spectrum of Th-HPMFBP-B15C5 complex. * denote the DMSO peak.

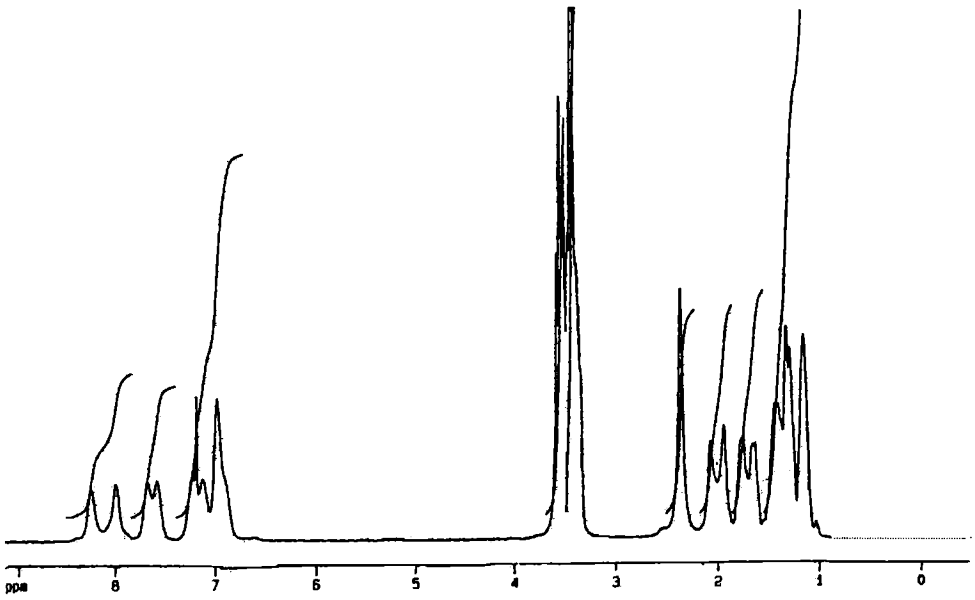


Figure 3.23. ^{1}H NMR spectrum of U-HPMFBP-DC18C6 complex.

Since the maximum coordination number for these metal ions is 6 to 10, this hydration strongly suggests that the oxygens of the crown ethers are not all equally bound to the metal ion. Further, crown ethers may form a secondary coordination sphere with $UO_2(PMFBP)_2{\cdot}H_2O$ and hydrogen bonded to the water molecule, as reported elsewhere in the molecular structure of $[UO_2(TTA)_2{\cdot}H_2O]_2{\cdot}$B15C5 with the aid of X-ray single crystal data [Kannan et al. 2001]. A coordination number of 10 (eight oxygens from HTTA + one oxygen from the residual water molecule + one oxygen from 18C6) has been reported in the $Th(TTA)_4{\cdot}H_2O{\cdot}$18C6 complex [Mathur and Choppin 1993]. There is evidence that the metal ions may interact with only a few of the potential donor oxygens and steric effects are probably significant in establishing this number [Mathur and Choppin 1993]. The weakness of the metal-crown ether interactions is reflected in residual hydration of the extracted complexes. What is clear about the extraction of these metal ions by mixtures of crown ethers and HPMFBP is that crown ether basicity, steric effects, cation dehydration and the number of ether oxygens bound to the cation are the combined factors which seemingly determine the pattern of metal-chelate and crown ether interactions.

The separation factors (S.F.) between thorium(IV) and uranium(VI), defined as the ratio of respective distribution ratios, with HPMFBP (0.01 mol/dm^3) and HPMFBP + CE (0.1 mol/dm^3) systems at 0.1 mol/dm^3 nitric acid solutions have been calculated. It is interesting to note that the addition of B15C5 significantly improves the S.F. value (2.36 x 10^4) between thorium(IV) and uranium(VI) as compared with HPMFBP (2.15 x 10^3) alone. This can be explained on the basis of the 'size-fitting effect' of the Th^{4+} with B15C5. The addition of DB18C6 to the HPMFBP system moderately enhances the S.F.

(2.58 x 10^3) value and this can be interpreted in terms of steric factors of DB18C6. On the other hand, the addition of DC18C6 (S.F. = 2.08 x 10^3) or 18C6 (S.F. = 1.74 x 10^3) to the metal-chelate system decreases the selectivity between the metal ions.

Chapter 4

Enhanced extraction of thorium(IV) and uranium(VI) with 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone in the presence of various neutral organophosphorus extractants

Studies on the solvent extraction of metal ions with 4-acyl-5-pyrazolones [Bacher and Keller 1973; Umetani et al. 2000; Bhattacharya et al. 2003], which are structurally analogous to β-diketones, derived from 5-membered heterocyclic compounds, revealed that improved extraction with strongly acidic extractants is usually accompanied by poor selectivity. These ligands are found to have longer distances (Table 4.1) between the two donating oxygens, as compared to the conventional β-diketones (HTTA), according to the estimation by molecular orbital calculations [Umetani et al. 2000].

Table 4.1. O---O distances of various β-diketones determined by semi-empirical molecular orbital MNDO/H calculations [Umetani et al. 2000].

β-diketone	O---O distance (Bite size) Å
HPMBP	2.65
HPMTFP	2.66
HPMAP	2.60
HTTA	2.50

The O---O distance between the two donating oxygens of the free molecule of an enolizable β-diketone is a key factor for its coordination to a metal ion and has been recognized as one of the most significant factor that governs the selectivity in the extraction of metal ions [Le et al. 1997]. Our previous investigations (Chapter 3) conclude that the para-substitution by an electron withdrawing (-F) or electron donating (-CH_3) group on the benzoyl moiety of HPMBP was unable to narrow the distance between the two donating oxygens. Hence, if the structure of the β-diketone could suitably be modified by introducing a bulky group at suitable position to create a steric effect, this distance could intentionally be controlled, and consequently the extractability and / or the selectivity could be improved. This has prompted us to synthesize 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone (HPMPP) by introducing a bulky group (pivaloyl) at the fourth position of the 1-phenyl-3-methyl-5-pyrazolone, with a view to create a steric repulsion between the 3-methyl group and the 4-acyl group to narrow the O---O distance, which may enhance the selectivity between thorium(IV) and uranium(VI). This chapter incorporates the results of the investigations carried out on the extraction of thorium(IV) and uranium(VI) with HPMPP in the presence and absence of various mono- (TBP and TOPO) and bi-functional (CMPO) organophosphorus extractants (Fig. 4.1).

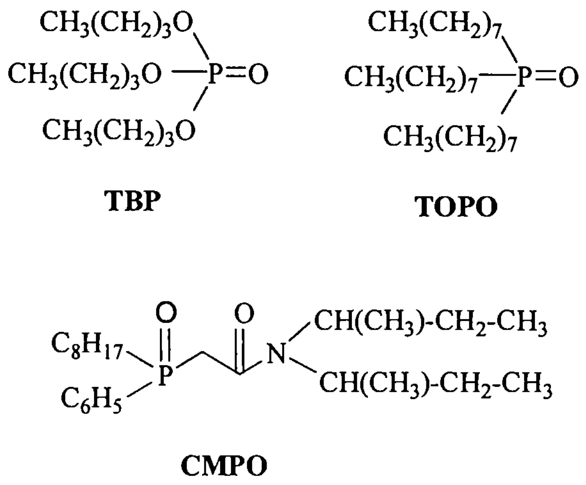


Figure 4.1. Structures of various mono- and bi-functional organophosphorus extractants.

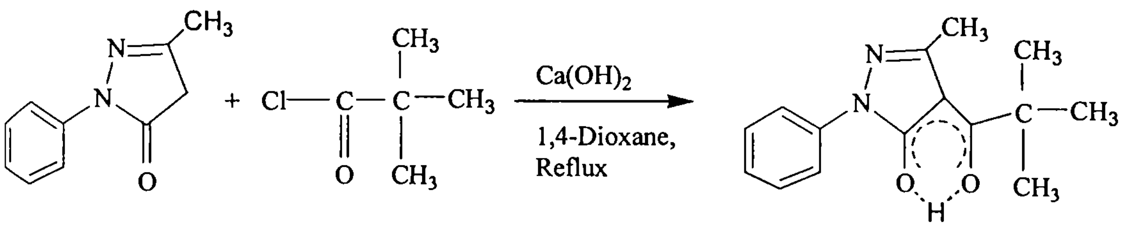
EXPERIMENTAL

Chemicals

1-Phenyl-3-methyl-5-pyrazolone, pivaloyl chloride, TBP and TOPO were obtained from Aldrich Chemical Company. CMPO was synthesized and purified by standard procedures in our laboratory [Mathur et al. 1992; Gatrone et al. 1987]. The methodology adopted for the preparation of stock solutions of metal ions is the same as described in the earlier chapter.

Synthesis of 1-phenyl-3-methyl-4-pivaloyl-5-pyrazolone

1-Phenyl-3-methyl-4-pivaloyl-5-pyrazolone was synthesized by the acylation of 1-phenyl-3-methyl-5-pyrazolone with pivaloyl chloride by the Jensen's method [Jensen 1959] (Scheme 4.1).



Scheme 4.1

The purity of the compound was established by elemental analyzes, IR and ^1H NMR spectral data. HPMPP: m.p. 93–94°C. Elemental analyses: Calc. for $C_{15}H_{18}N_2O_2$: C 69.74, H 7.02, N 10.84%. Found: C 69.65, H 6.82, N 10.96%. ^1H NMR ($CDCl_3$) δ (ppm): 1.4 (s, 9H, pivaloyl CH_3), 2.64 (s, 3H, CH_3 of the ring), 7.28-7.32 (t, 1H, Ar-p-H), 7.44-7.48 (t, 2H, Ar-m-H), 7.84-7.86 (d, 2H, Ar-o-H). IR data, ν (cm^{-1}): 3118, 2820, 1646 (C=O), 1620, 1545, 1500, 1387, 1328, 1116, 957, 844, 738, 692. In the ^1H NMR spectrum of HPMPP (Fig. 4.2) no peak corresponding to the enolic-OH has been observed. However, the absence of a peak at δ 3.4 ppm, corresponding to the methyne proton at the fourth position of the pyrazolone ring, confirms the existence of HPMPP in the enolic form.

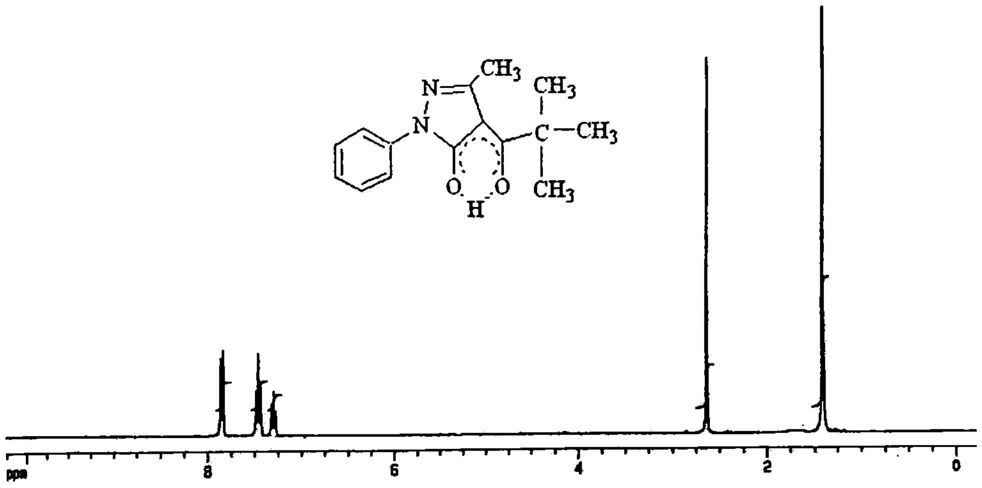


Figure 4.2. ^1H NMR spectrum of HPMPP.

Apparatus

^{31}P NMR spectra of the synergistic complexes (in $CDCl_3$ and 85% H_3PO_4 as an external standard) were recorded using a Bruker 121.47 MHz NMR spectrometer. All other instruments used were the same as described in Chapter 3.

Solvent extraction procedure

Solvent extraction and analytical procedures followed were the same as described in Chapter 3. Preliminary experiments showed that the extraction equilibrium was attained within 60 min for both thorium(IV) and uranium(VI).

Preparation of metal complexes

The metal complexes were prepared by the following procedure: Stoichiometric amounts of thorium nitrate or uranyl nitrate were added to a well stirred solution of HPMPP in methanol and the mixture was stirred for 1h. To this mixture, neutral organophosphorus extractant (TBP, CMPO or TOPO) dissolved in methanol was added and the resultant mixture was refluxed for 4h in order to ensure completion of the reaction. The methanol was evaporated off and the resulted complexes were characterized by FT-IR and ^{31}P NMR spectral data. The solutes studied were $Th(PMPP)_4$, $UO_2(PMPP)_2$, $Th(PMPP)_4 \cdot TOPO$, $UO_2(PMPP)_2 \cdot TOPO$, $Th(PMPP)_4 \cdot CMPO$, $UO_2(PMPP)_2 \cdot CMPO$, $Th(PMPP)_4 \cdot TBP$ and $UO_2(PMPP)_2 \cdot TBP$.

RESULTS AND DISCUSSION

Extraction of thorium(IV) and uranium(VI) with HPMPP alone

The extraction behavior of thorium(IV) (1×10^{-4} mol/dm^3) and uranium(VI) (5×10^{-4} mol/dm^3) from 1.0 mol/dm^3 sodium nitrate solutions with HPMPP alone into chloroform as a function of the extractant (0.005-0.02 mol/dm^3 for thorium(IV) and 0.10-0.40 mol/dm^3 for uranium(VI)) and hydrogen ion (0.005-0.02 mol/dm^3) concentrations, respectively, has been investigated. The relevant log-log plots (Figs. 4.3 and 4.4) gave straight lines with slopes of 4.0 ± 0.05 and 2.0 ± 0.05 for thorium(IV) and uranium(VI) with HPMPP variation and slopes of –4.0 ± 0.1 and –2.0 ± 0.1 with hydrogen ion variation, respectively, indicating the extraction of simple metal-chelates,

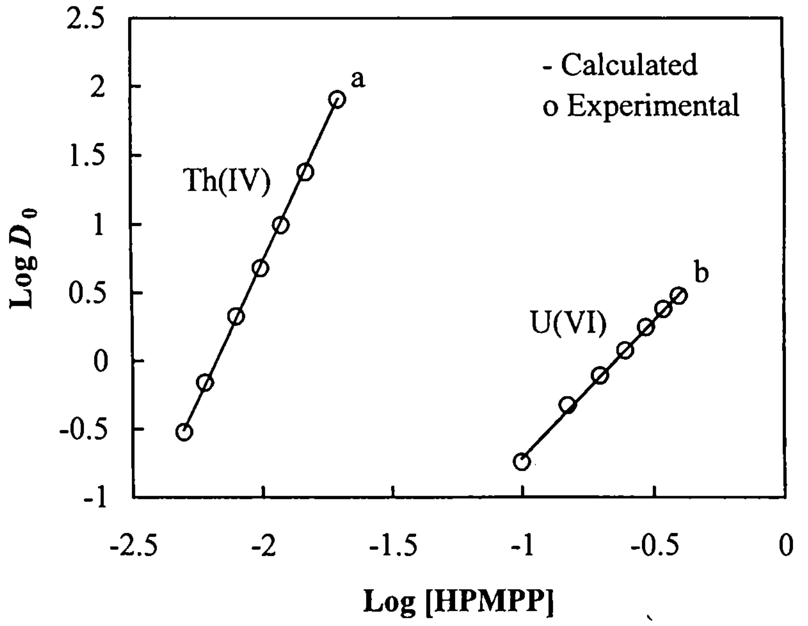


Figure. 4.3. Effect of HPMPP concentration on the extraction of thorium(IV) and uranium(VI). Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 2.0). Slope of the line (a) thorium(IV) = 4.0 ± 0.05 (b) uranium(VI) = 2.0 ± 0.05.

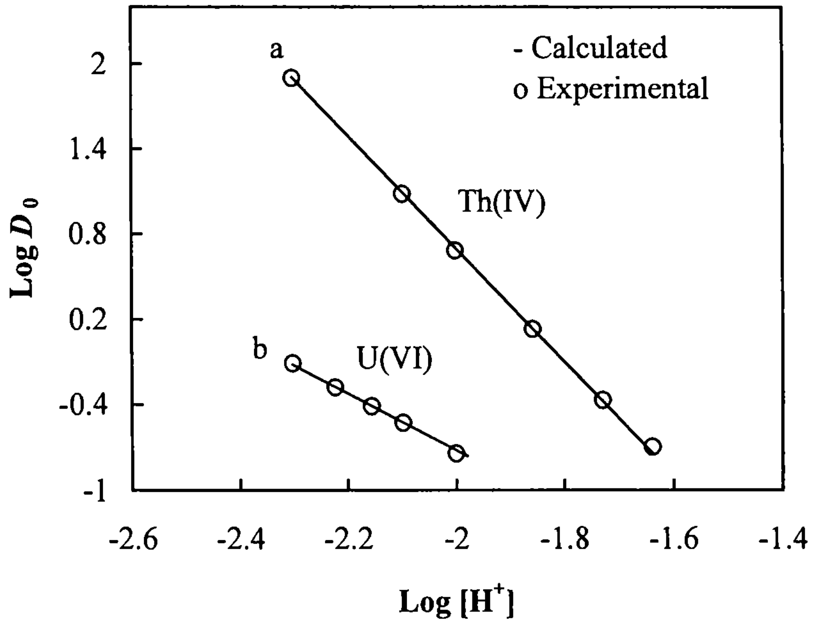


Figure. 4.4. Effect of hydrogen ion concentration on the extraction of thorium(IV) and uranium(VI). HPMPP = 0.01 mol/dm^3 for thorium(IV) and 0.10 mol/dm^3 for uranium(VI). Slope of the line (a) thorium(IV) = -4.0 ± 0.1 (b) uranium(VI) = -2.0 ± 0.1.

$Th(PMPP)_4$ and $UO_2(PMPP)_2$. Similar metal chelates have also been reported for the extraction of thorium(IV) and uranium(VI) with various 1-phenyl-3-methyl-4-acyl-5-pyrazolones (acyl = benzoyl, acetyl, chloroacetyl, trichloroacetyl, trifluoroacetyl) [Bacher and Keller 1973].

Based on the preceding studies, the extraction equilibrium of thorium(IV) and uranium(VI) with a chelating extractant, HPMPP, alonc may be expressed as

$$\mathrm{Th}^{4+}_{\mathrm{aq}} + 4\,(\mathrm{HPMPP})_{\mathrm{org}} \overset{K_{\mathrm{ex},0}}{\rightleftharpoons} \mathrm{Th(PMPP)}_{4\,\mathrm{org}} + 4\,\mathrm{H}^{+}_{\mathrm{aq}} \tag{1}$$

$$\mathrm{UO}^{2+}_{2\,\mathrm{aq}} + 2\,(\mathrm{HPMPP})_{\mathrm{org}} \overset{K_{\mathrm{ex},0}}{\rightleftharpoons} \mathrm{UO_2(PMPP)}_{2\,\mathrm{org}} + 2\,\mathrm{H}^{+}_{\mathrm{aq}} \tag{2}$$

where $K_{ex,0}$ denotes the equilibrium constant. Since the partition coefficient of HPMPP was found to be very high (log P_{HA} for HPMPP = 2.64 [Umetani et al. 2000]) the concentration of pyrazolonate anion in the aqueous phase can be neglected. The distribution ratio, D_0, of thorium(IV) is given by

$$D_0 = \frac{[\mathrm{Th(PMPP)_4}]_{org}}{[\mathrm{Th^{4+}}]_{aq}\{1+\beta_1[\mathrm{NO_3^-}]_{aq}+\beta_2[\mathrm{NO_3^-}]_{aq}^2\}} \qquad (3)$$

where β_i is the stability constant of thorium(IV) with nitrate ion in the aqueous phase. The values of the log stability constants (log β_1 = 0.1; log β_2 = 0.8) were taken from the literature [Oliver and Davis 1972]. Then the D_0 of thorium(IV) can be written from Eqs. (1) and (3) as

$$D_0 = \frac{K_{ex,0}[\mathrm{HPMPP}]_{org}^4}{[\mathrm{H^+}]_{aq}^4\{1+\beta_1[\mathrm{NO_3^-}]_{aq}+\beta_2[\mathrm{NO_3^-}]_{aq}^2\}} \qquad (4)$$

Similarly, the D_0 of uranium(VI) can be written as

$$D_0 = \frac{K_{ex,0}[\mathrm{HPMPP}]_{org}^2}{[\mathrm{H^+}]_{aq}^2\{1+\beta_1[\mathrm{NO_3^-}]_{aq}\}} \qquad (5)$$

The log stability constant for uranium(VI) (log β_1 = -0.3) with nitrate ion was taken from the literature [Kotrly and Sucha 1985].

The $K_{ex,0}$ of the above extracted complexes were determined by nonlinear regression analysis as described in chapter 3 and are given in Table 4.2. The $K_{ex,0}$ thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. Comparing the equilibrium constants of HPMPP, HPMAP and HPMBP with their pK_a values for the extraction of early actinides, it can be concluded that the equilibrium constant value increases as the pK_a value decreases (Table 4.2).

Table 4.2. Equilibrium constants for the extraction of thorium(IV) and uranium(VI) with various 1-phenyl-3-methyl-4-acyl-5-pyrazolones.

Extractants	pK_a	Log $K_{ex,0}$	
		Th(IV)	U(VI)
HPMPP	4.26	1.63 ± 0. 02	-2.55 ± 0.02
HPMAP	3.94	-	0.02 ± 0.04**
HPMBP	3.92	6.72 ± 0.04*	0.76 ± 0.04*

* [Meera and Reddy 2004] ** [Bacher and Keller 1973]

IR Spectra of binary complexes

Fig. 4.5 shows the IR spectra of the complexes of thorium(IV) and uranium(VI) with HPMPP. The broad absorption in the region 3000 - 3500 cm^{-1}, indicates the presence of extensive H-bonding between the N-atoms of the heterocyclic ring and the –OH group of H_2O, as observed in the transition metal complexes of 4-acylpyrazolonates [Marchetti 2001]. The presence of water of hydration has been well documented in the 1-phenyl-3-methyl-4-acyl-5-pyrazolonato complexes of uranium(VI) [Okafor et al. 1990]. The stretching frequency of the C=O group in the free ligand of HPMPP has been shifted from 1646 cm^{-1} to 1600 cm^{-1} in $Th(PMPP)_4$ and $UO_2(PMPP)_2$ complexes, which suggests that the carbonyl group is involved in chelation process with the metal ion. The other strong absorption band occurring around 924 cm^{-1} in $UO_2(PMPP)_2$, may be assigned to ν (O=U=O) of UO_2^{2+} [Kannan and Venugopal 1995; Kannan et al. 2002].

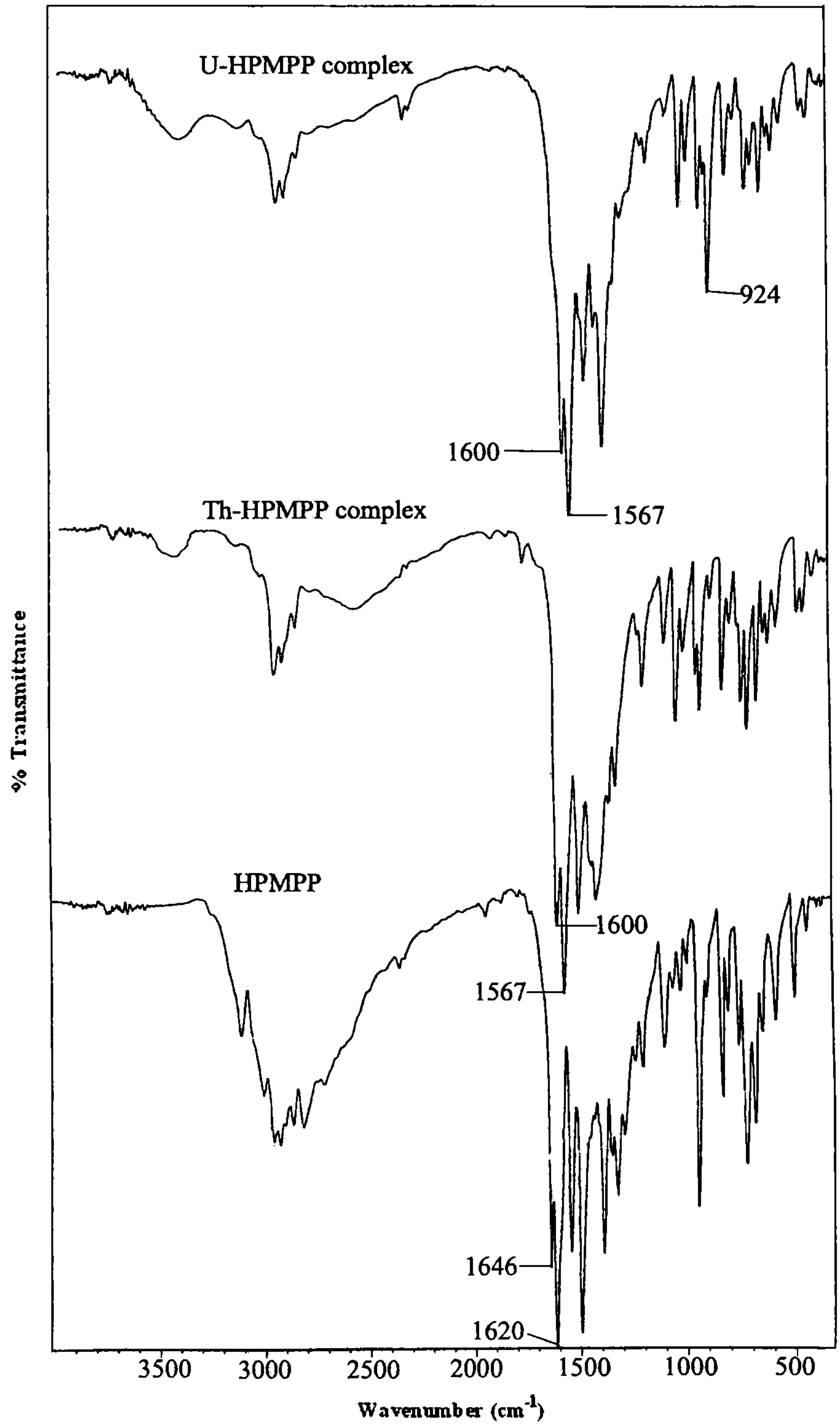


Figure 4.5. IR spectra of HPMPP ligand, Th-HPMPP and U-HPMPP complexes.

It is clear from Table 4.3 that the selectivity between thorium(IV) and uranium(VI) increases with increase in the concentration of HPMPP. In order to correlate the selectivity between these metal ions with the O---O distance (bite size) of 4-acyl-5-pyrazolones, in the present study, the O---O distance in HPMPP has been determined by semi-empirical PM3/H molecular orbital calculations [Stewart 1989] taking into account the hydrogen bond. A ball-and-stick representation based on the PM3/H optimized structure is shown in Fig. 4.6. The selectivity observed between thorium(IV) and uranium(VI) with HPMPP (S.F. = 2.8 x 10^3 at 0.01 mol/dm^3) has been found to be higher than para-substituted 4-aroyl-5-pyrazolones (S.F. = 2.15 x 10^3 at 0.01 mol/dm^3 HPMFBP; S.F. = 1.60 x 10^3 at 0.01 mol/dm^3 HPMBP, bite size = 2.67 Å). This improvement could be attributed to the narrowed distances between the two donating oxygens (bite size = 2.6 Å for HPMPP), which is caused by the steric repulsion between the 3-methyl and bulky 4-pivaloyl group. Further, the selectivity observed between thorium(IV) and uranium(VI) in the present system with HPMPP is found to be significantly higher than that of TBP (S.F. = D_U/D_{Th} = 17), which has been widely employed in the THOREX process for the separation of uranium(VI) from thorium(IV) [Pathak et al. 1999].

Table 4.3. Separation factors (S.F.) between thorium(IV) and uranium(VI) with HPMPP.

[HPMPP], mol/dm^3	S.F. (D_{Th}/D_U)
0.01	2.8 x 10^3
0.02	1.0 x 10^4
0.10	2.8 x 10^5

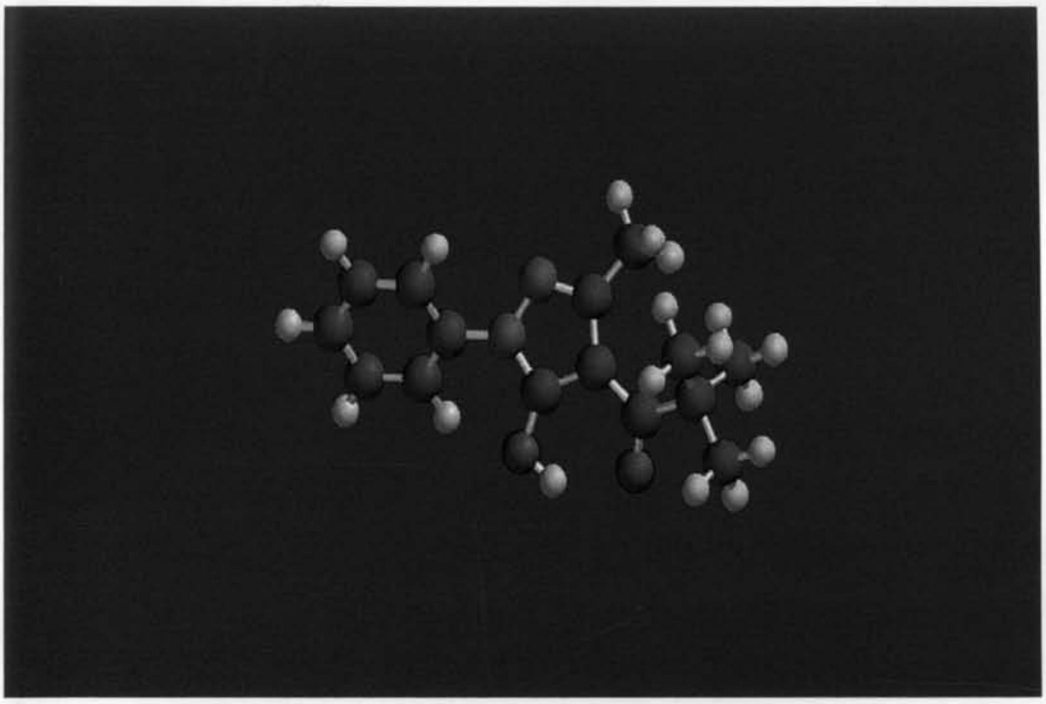


Figure 4.6. Ball-and-stick representation based on PM3/H optimized structure of HPMPP.

Extraction of thorium(IV) and uranium(VI) with mixtures of HPMPP and neutral organophosphorus extractants

The synergistic extraction equilibrium of thorium(IV) with HPMPP in presence of a neutral organophosphorus extractant (S) such as TBP, CMPO or TOPO may be expressed as

$$\mathrm{Th}^{4+}_{\mathrm{aq}} + 4(\mathrm{HPMPP})_{\mathrm{org}} + n\,\mathrm{S}_{\mathrm{org}} \xrightleftharpoons{K} \mathrm{Th(PMPP)}_4.n\,\mathrm{S}_{\mathrm{org}} + 4\mathrm{H}^{+}_{\mathrm{aq}} \quad (6)$$

The overall extraction constant, *K*, is given as

$$K = \frac{[\mathrm{Th(PMPP)}_4.n\,\mathrm{S}]_{\mathrm{org}}\,[\mathrm{H}^+]^4_{\mathrm{aq}}}{[\mathrm{Th}^{4+}]_{\mathrm{aq}}\,[\mathrm{HPMPP}]^4_{\mathrm{org}}\,[\mathrm{S}]^n_{\mathrm{org}}} \quad (7)$$

where $n = 0$ or 1. The distribution ratio, *D*, of the synergistic extraction system is given by Eq. (8)

$$D = \frac{[\mathrm{Th(PMPP)_4}]_{\mathrm{org}} + [\mathrm{Th(PMPP)_4.S}]_{\mathrm{org}}}{[\mathrm{Th}^{4+}]_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}} + \beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\}} \qquad (8)$$

From Eqs. (3), (7) and (8)

$$K = \frac{(D - D_0)[\mathrm{H}^+]^4_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}} + \beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\}}{[\mathrm{HPMPP}]^4_{\mathrm{org}}[\mathrm{S}]_{\mathrm{org}}} \qquad (9)$$

Taking logarithms,

$$\begin{aligned}\mathrm{Log}\, K &= \log (D - D_0) - 4 \log [\mathrm{HPMPP}]_{\mathrm{org}} - \log [\mathrm{S}]_{\mathrm{org}} + 4 \log [\mathrm{H}^+]_{\mathrm{aq}} \\ &\quad + \log \{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}+\beta_2 [\mathrm{NO_3^-}]^2_{\mathrm{aq}}\} \qquad (10)\end{aligned}$$

It has been reported that the interaction between a β-diketone and a neutral oxo-donor in chloroform are, in general, weaker when the solvent solute interactions are stronger [Sekine et al. 1983]. Hence in the present study, it has been assumed that there is negligible interaction between HPMPP and neutral organophosphorus extractants in chloroform. The organic phase adduct formation reaction is represented as

$$\mathrm{Th(PMPP)_4}_{\,\mathrm{org}} + \mathrm{S}_{\mathrm{org}} \xrightleftharpoons{K_{\mathrm{S}}} \mathrm{Th(PMPP)_4.S}_{\,\mathrm{org}} \qquad (11)$$

where K_{S} is the organic phase adduct formation constant and is given as

$$K_{\mathrm{S}} = \frac{[\mathrm{Th(PMPP)_4.S}]_{\mathrm{org}}}{[\mathrm{Th(PMPP)_4}]_{\mathrm{org}}[\mathrm{S}]_{\mathrm{org}}} \qquad (12)$$

From Eqs. (1), (6), (11) and (12)

$$K_{\mathrm{S}} = \frac{K}{K_{\mathrm{ex,0}}} \qquad (13)$$

Similarly, the synergistic extraction equilibrium of uranium(VI) with HPMPP in the presence of a neutral organophosphorus extractant may be represented as

$$\mathrm{UO}^{2+}_{2\,\mathrm{aq}} + 2(\mathrm{HPMPP})_{\mathrm{org}} + n\, \mathrm{S}_{\mathrm{org}} \xrightleftharpoons{K} \mathrm{UO_2(PMPP)_2}.n\mathrm{S}_{\mathrm{org}} + 2\mathrm{H}^+_{\mathrm{aq}} \qquad (14)$$

where $n = 0$ or 1. Then the D of the synergistic extraction system for uranium(VI) is given by

$$D = \frac{[UO_2(PMPP)_2]_{org} + [UO_2(PMPP)_2.S]_{org}}{[UO_2^{2+}]_{aq}\{1+\beta_1[NO_3^-]_{aq}\}} \qquad (15)$$

From Eqs.(5), (14) and (15)

$$K = \frac{(D - D_0)[H^+]_{aq}^2\{1+\beta_1[NO_3^-]_{aq}\}}{[HPMPP]_{org}^2[S]_{org}} \qquad (16)$$

The organic phase adduct formation reaction is represented as

$$UO_2(PMPP)_{2\,org} + S_{org} \xrightleftharpoons{K_S} UO_2(PMPP)_2.S_{org} \qquad (17)$$

where K_S, the organic phase adduct formation constant is given by

$$K_S = \frac{K}{K_{ex,0}} \qquad (18)$$

To confirm the above extraction equilibria, the extraction behavior of thorium(IV) and uranium(VI) from 1.0 mol/dm^3 sodium nitrate solutions (pH = 2.0) with mixtures of HPMPP (0.005 - 0.01 mol/dm^3 for thorium(IV) and 0.05 - 0.20 mol/dm^3 for uranium(VI)) and TOPO (0.001 - 0.005 mol/dm^3 for thorium(IV) and 0.001 - 0.005 mol/dm^3 for uranium(VI)) or CMPO (0.005 - 0.02 mol/dm^3 for thorium(IV) and 0.004 - 0.01 mol/dm^3 for uranium(VI)) or TBP (0.20 - 0.50 mol/dm^3 for thorium(IV) and 0.10 - 0.30 mol/dm^3 for uranium(VI)) in chloroform has been studied. It was found that the addition of a neutral organophosphorus extractant to the metal-chelate system significantly enhances the extraction efficiency of these metal ions as compared to that of HPMPP or neutral organophosphorus extractant. The synergistic enhancement factors (Synergistic enhancement factor = $D/(D_{HPMPP} + D_S)$, where D = distribution ratio with HPMPP + S; D_{HPMPP} = distribution ratio with HPMPP alone and D_S = distribution ratio with S alone) with mixtures of HPMPP and various neutral organophosphorus extractants for thorium(IV) and uranium(VI) increases with increasing neutral organophosphorus extractant concentration (Tables 4.4 and 4.5).

Table 4.4. Synergistic enhancement factors for thorium(IV) with HPMPP (0.005 mol/dm^3) in the presence of various neutral organophosphorus extractants.

Neutral donor	Concentration, mol/dm^3	Synergistic enhancement factor
TOPO	1×10^{-3}	5
	2×10^{-3}	8
	4×10^{-3}	15
	5×10^{-3}	19
CMPO	6×10^{-3}	8
	8×10^{-3}	10
	1×10^{-2}	13
	2×10^{-2}	24
TBP	2×10^{-1}	7
	3×10^{-1}	9
	4×10^{-1}	12
	5×10^{-1}	15

It is clear from the plots (Figs. 4.7 and 4.8) of log (D – D_0) *vs.* log [HPMPP] that at constant neutral organophosphorus extractant concentration (TOPO = 0.001 mol/dm^3; CMPO = 0.005 mol/dm^3; TBP = 0.20 mol/dm^3) only four HPMPP molecules in the case of thorium(IV) and two HPMPP molecules in the case of uranium(VI) are involved in the synergistic complexes extracted into the organic phase. Figs. 4.9 and 4.10 give results on the effect of neutral organophosphorus extractant concentration on the extraction of thorium(IV) and uranium(VI), respectively, at constant HPMPP concentration (0.005 mol/dm^3 for thorium(IV) and 0.1 mol/dm^3 for uranium(VI)) when extracted from 1.0 mol/dm^3 sodium nitrate solutions (pH = 2.0). The plots gave a slope of unity for all systems, indicating the participation of one neutral organophosphorus extractant molecule in the synergistic extracted complexes.

Table 4.5. Synergistic enhancement factors for uranium(VI) with HPMPP (0.1 mol/dm^3) in the presence of various neutral organophosphorus extractants.

Neutral donor	Concentration, mol/dm^3	Synergistic enhancement factor
TOPO	2×10^{-3}	24
	3×10^{-3}	35
	4×10^{-3}	46
	5×10^{-3}	58
CMPO	4×10^{-3}	24
	6×10^{-3}	35
	8×10^{-3}	46
	1×10^{-2}	58
TBP	1×10^{-1}	13
	2×10^{-1}	24
	2.5×10^{-1}	30
	3×10^{-1}	36

These in conjunction with the slopes of –4.0 ± 0.05 and –2.0 ± 0.05 observed for thorium(IV) and uranium(VI) (Figs. 4.11 and 4.12), respectively, with hydrogen ion variation (0.005 - 0.02 mol/dm^3) at constant HPMPP + S, indicate the extraction of the complexes, $Th(PMPP)_4 \cdot S$ and $UO_2(PMPP)_2 \cdot S$. Similar synergistic extracted complexes, $Th(PMBP)_4 \cdot TOPO$ and $UO_2(PMBP)_2.S$ (S = TOPO, TBP or DPSO), have been observed for the extraction of thorium(IV) and uranium(VI) from nitrate solutions with HPMBP in the presence of various neutral oxo-donors [Pai and Subramanian 1985; Mohapatra et al. 1999]. Similar species have also been observed in the extraction of these metal ions with HTTA in presence of neutral organophosphorus extractants [Caceci et al. 1985].

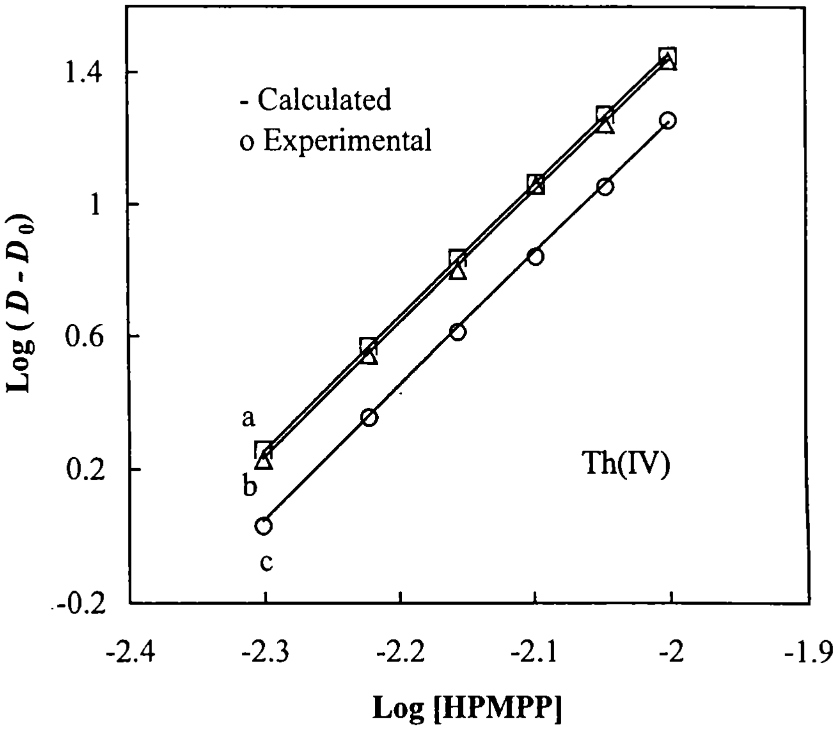


Figure. 4.7. Effect of HPMPP concentration on the extraction of thorium(IV) at constant neutral organophosphorus extractant (S) concentration. Aqueous phase = 1.0 mol/dm^3 NaNO$_3$ (pH = 2.0). TOPO = 0.001 mol/dm^3; CMPO = 0.005 mol/dm^3; TBP = 0.20 mol/dm^3. Slope of the line (a) CMPO = 4.0 ± 0.05 (b) TBP = 4.0 ± 0.05 (c) TOPO = 4.0 ± 0.05.

The equilibrium constants of the synergistic extracted complexes (K) were deduced by nonlinear regression analysis and are given in Table 4.6 along with the K_H (where K_H is the equilibrium constant for the HNO$_3$ uptake by S expressed as: $H^+_{aq} + NO^-_{3\,aq} + S_{org} \xrightleftharpoons{K_H} HNO_3 \cdot S_{org}$) values of various neutral organophosphorus extractants. It can be clearly seen from the

Table 4.6 that the log *K* for both the metal ions increases in the order TBP < CMPO < TOPO, which is also the order of the K_H values [Sahu et al. 2000] of neutral organophosphorus extractants.

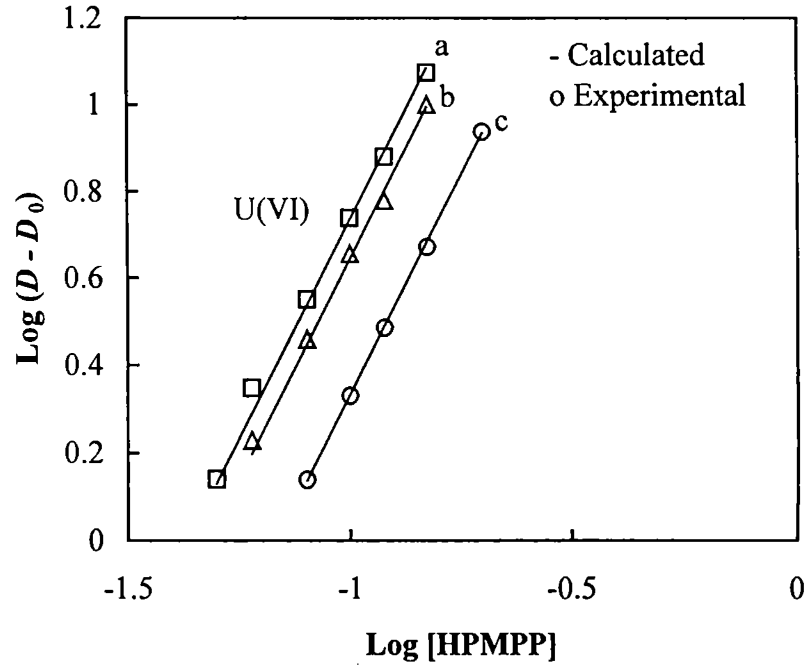


Figure. 4.8. Effect of HPMPP concentration on the extraction of uranium(VI) at constant neutral organophosphorus extractant (S) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 2.0). TOPO = 0.001 mol/dm^3; CMPO = 0.005 mol/dm^3; TBP = 0.20 mol/dm^3. Slope of the line (a) CMPO = 2.0 ± 0.1 (b) TBP = 2.0 ± 0.1 (c) TOPO = 2.0 ± 0.05.

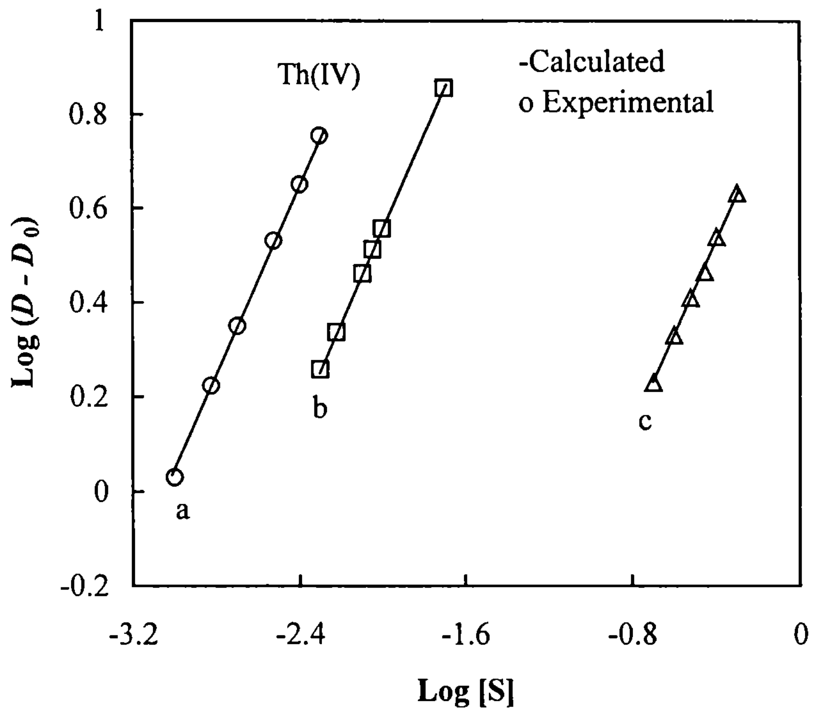


Figure. 4.9. Effect of neutral organophosphorus extractant (S) concentration on the extraction of thorium(IV) at constant HPMPP (0.005 mol/dm^3) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 2.0). Slope of the line (a) TOPO =1.0 ± 0.05 (b) CMPO = 1.0 ± 0.05 (c) TBP = 1.0 ± 0.05.

Table 4.6. Two phase synergistic equilibrium constants (K) and organic phase adduct formation constant (K_S) of thorium(IV) and uranium(VI) with HPMPP-S-Chloroform systems.

S	K_H	Log K		Log K_S	
		Th(IV)	U(VI)	Th(IV)	U(VI)
TOPO	8.9	5.18 ± 0.03	1.51 ± 0.04	3.55 ± 0.03	4.05 ± 0.03
CMPO	2.9	4.69 ± 0.03	1.21 ± 0.03	3.06 ± 0.03	3.75 ± 0.03
TBP	0.2	3.07 ± 0.03	-0.48 ± 0.02	1.45 ± 0.03	2.06 ± 0.03

K_H = nitric acid uptake constant of neutral organophosphorus extractant.

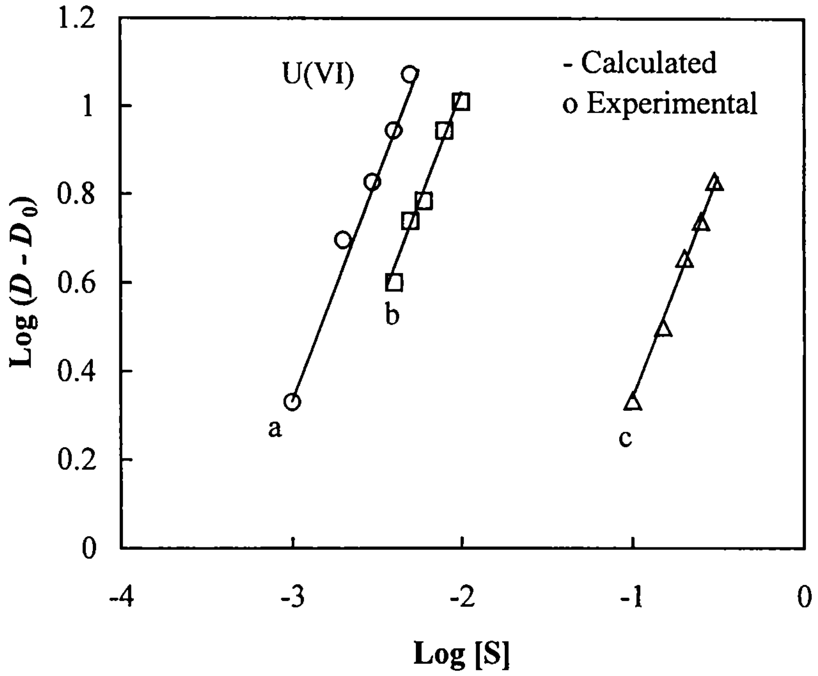


Figure. 4.10. Effect of neutral organophosphorus extractant (S) concentration on the extraction of uranium(VI) at constant HPMPP (0.10 mol/dm^3) concentration. Aqueous phase = 1.0 mol/dm^3 $NaNO_3$ (pH = 2.0). Slope of the line (a) TOPO = 1.0 $\pm$ 0.05 (b) CMPO = 1.0 $\pm$ 0.05 (c) TBP = 1.0 $\pm$ 0.05.

The adduct formation constants, K_S, for the organic phase synergistic reaction of Th-HPMPP chelate or U-HPMPP chelate with various neutral organophosphorus extractants were calculated and are given in Table 4.6. The sharp decrease in the complexation of thorium(IV) and uranium(VI) from TOPO to TBP, mostly reflects in the decrease in the basicity of the phosphoryl oxygen of the neutral organophosphorus extractant. By comparing the log K_S values (Table 4.7) for the extraction of uranium(VI) with β-diketones in presence of neutral organophosphorus extractants, it can be concluded that stable adduct formation reaction is usually brought out by strong acidic extractants.

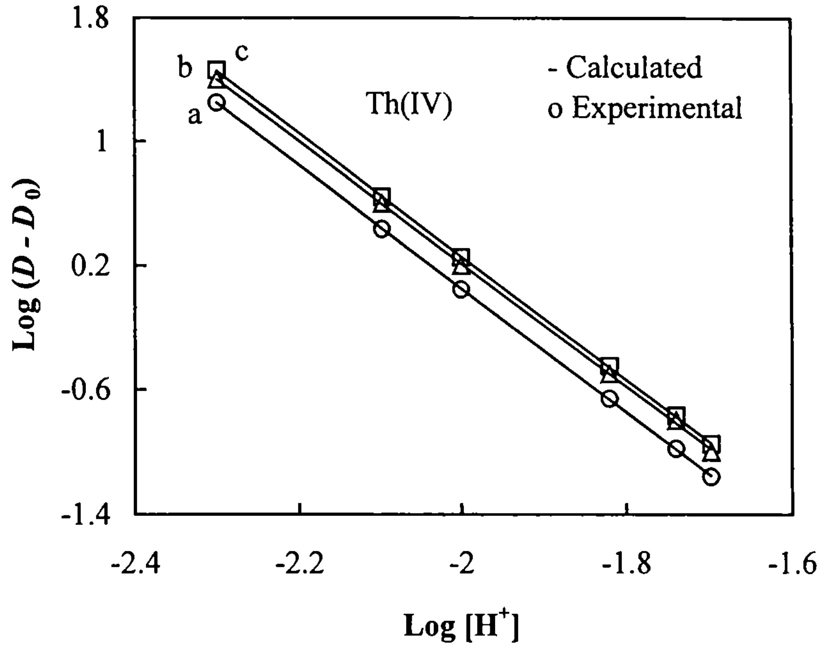


Figure 4.11. Effect of hydrogen ion concentration on the extraction of thorium(IV) at constant HPMPP (0.005 mol/dm^3) + S (TOPO = 0.001 mol/dm^3; CMPO = 0.005 mol/dm^3; TBP = 0.2 mol/dm^3) concentration. Slope of the line (a) TOPO = -4.0 ± 0.05 (b) TBP = -4.0 ± 0.05 (c) CMPO = -4.0 ± 0.05.

Table 4.7. Organic phase adduct formation constants of uranium(VI) with various heterocyclic 1,3-β-diketones in presence of neutral organophosphorus extractants.

Neutral donor	Log K_S		
	HPMPP (pK_a = 4.26)	HPMBP (pK_a = 3.92)	HPBI (pK_a = 1.23)
TOPO	4.05	6.45[(a)]	8.70[(b)]
TBP	2.06	4.28[(a)]	5.12[(b)]
CMPO	3.75	5.03[(c)]	-

(a) [Pai and Subramanian 1985] (b) [Mansingh et al. 1996] (c) [Pai et al. 2000].

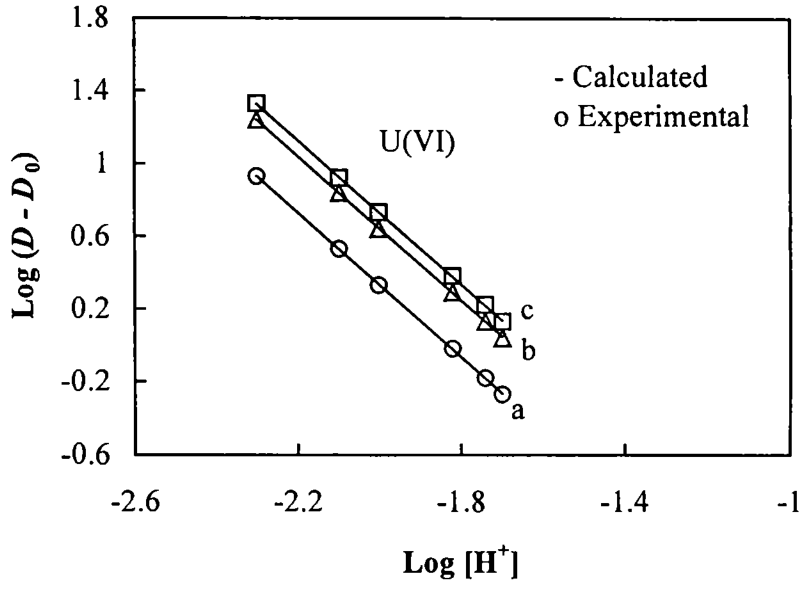


Figure 4.12. Effect of hydrogen ion concentration on the extraction of uranium(VI) at constant HPMPP (0.1 mol/dm^3) + S (TOPO = 0.001 mol/dm^3; CMPO = 0.005 mol/dm^3; TBP = 0.2 mol/dm^3) concentration. Slope of the line (a) TOPO = -2.0 ± 0.05 (b) TBP = -2.0 ± 0.05 (c) CMPO = -2.0 ± 0.05.

Correlation of ^{31}P NMR chemical shifts of neutral organophosphorus extractants with the synergistic equilibrium constants

The ^{31}P NMR spectral data may help to study the influence of neutral organophosphorus extractant in the synergistic extraction systems, as there exists a strong correlation between the electron density on 'O' of P=O group in neutral organophosphorus extractant molecules [Ionova et al. 2001]. Fig. 4.13 shows that the log *K* (synergistic equilibrium constant) value of thorium(IV) and uranium(VI) increases linearly with increase in δ (^{31}P) NMR chemical shift of the neutral O-bearing organophosphorus extractant (TBP < CMPO < TOPO). Thus, the donor ability of the phosphoryl oxygen, which is correlated with the δ (^{31}P) NMR chemical shift (i.e., a high electron density on the oxygen atom induces a low electron density on the phosphorus atom and thus a high value of the δ (^{31}P) NMR chemical shift) is the key parameter for the increase in the extraction efficiency of thorium(IV) and uranium(VI) with HPMPP in the presence of neutral organophosphorus extractant. Further, the linear correlation between log *K* and δ (^{31}P) NMR chemical shift of neutral organophosphorus extractants support the fact that bi-functional CMPO behave as mono-functional extractant in the present system, as is also evident from the FT-IR spectral data.

The ^{31}P NMR spectra of the complexes show that the phosphorus atom of the phosphoryl group is deshielded relative to the free ligands (δ_{PO} for free ligand of CMPO = 38 ppm; TOPO = 48.5 ppm; TBP = -1.0 ppm), indicating that the ligand is coordinating through oxygen of the P=O group to the metal ion in all the synergistic complexes.

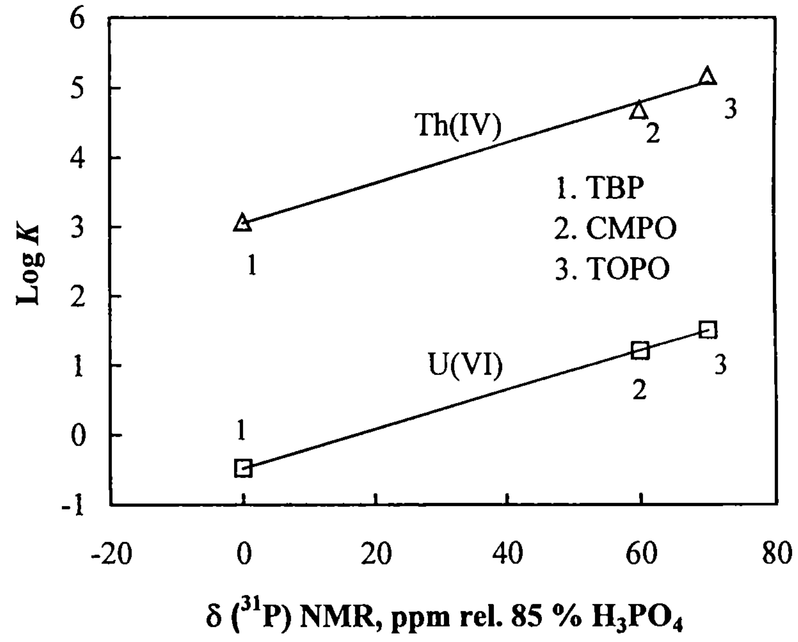


Fig. 4.13. Variation of Log *K* of thorium(IV) and uranium(VI) with δ (^{31}P) NMR chemical shift values of neutral organophosphorus extractants.

IR Spectra of ternary complexes

In the IR spectra of the ternary complexes (Figs. 4.14 - 4.16), the stretching frequency of the C=O group in the free ligand, HPMPP, has been shifted from 1646 cm^{-1} to lower frequency in the $Th(PMPP)_4{\cdot}TOPO$, $UO_2(PMPP)_2{\cdot}TOPO$, $Th(PMPP)_4{\cdot}CMPO$, $UO_2(PMPP)_2{\cdot}CMPO$, $Th(PMPP)_4{\cdot}TBP$ and $UO_2(PMPP)_2{\cdot}TBP$ complexes, upon coordination with metal ion. The other strong absorption band occurring around 924 cm^{-1} in $UO_2(PMPP)_2{\cdot}TOPO$, $UO_2(PMPP)_2{\cdot}CMPO$ and 930 cm^{-1} in $UO_2(PMPP)_2{\cdot}TBP$ may be assigned to ν (O=U=O) of UO_2^{2+} [Kannan and Venugopal 1995; Sahu et al. 2000]. Further, in the ternary complexes of $Th(PMPP)_4{\cdot}S$ and $UO_2(PMPP)_2{\cdot}S$, the P=O stretching frequency of neutral organophosphorus extractant (1143 cm^{-1} in TOPO; 1268 cm^{-1} in CMPO; 1280 cm^{-1} in TBP) has been shifted to lower frequency indicating the involvement of phosphoryl oxygen in the coordination of these metal ions. On the other hand, in the complexes of $Th(PMPP)_4{\cdot}CMPO$ and $UO_2(PMPP)_2{\cdot}CMPO$, the P=O stretching frequency has shifted from 1268 to 1216 cm^{-1} and at the same time C=O stretching frequency (1633 cm^{-1}) has not been altered. This indicates that CMPO act as a mono-functional extractant through the participation of phosphoryl oxygen in the adduct formation with the metal ion and not the carbonyl oxygen. A similar type of behavior has been noticed in the extraction of uranium(VI) with HPMBP and HTTA in the presence of CMPO [Pai et al. 2000; Pai et al. 2002]. The disappearance of the absorption band in the region 3000-3500 cm^{-1}, due to water of hydration, indicates the absence of water molecules in the coordination sphere of the ternary metal complexes.

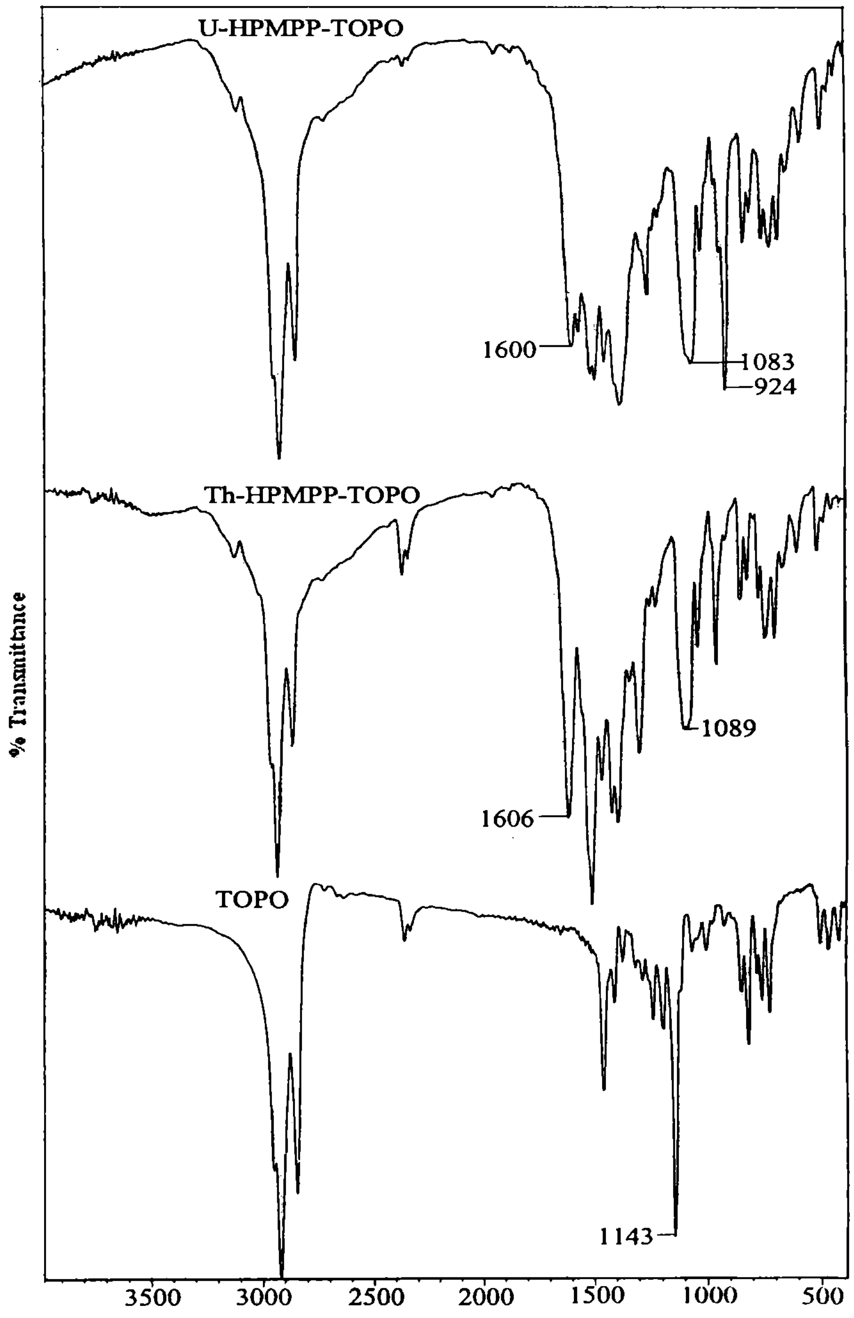


Figure 4.14. IR spectra of TOPO neutral oxo-donor, Th-HPMPP-TOPO and U-HPMPP-TOPO complexes.

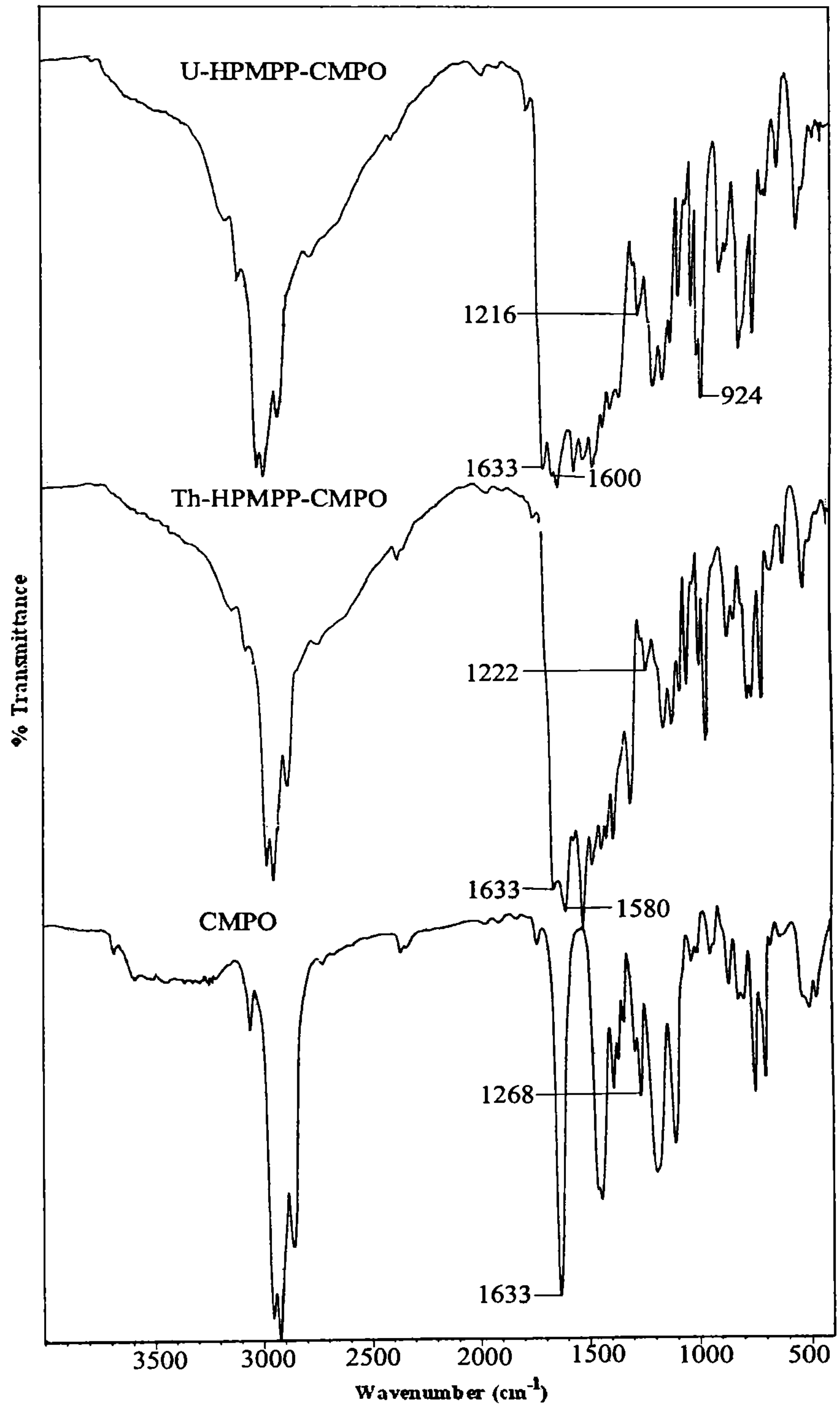


Figure 4.15. IR spectra of CMPO neutral oxo-donor, Th-HPMPP-CMPO and U-HPMPP-CMPO complexes.

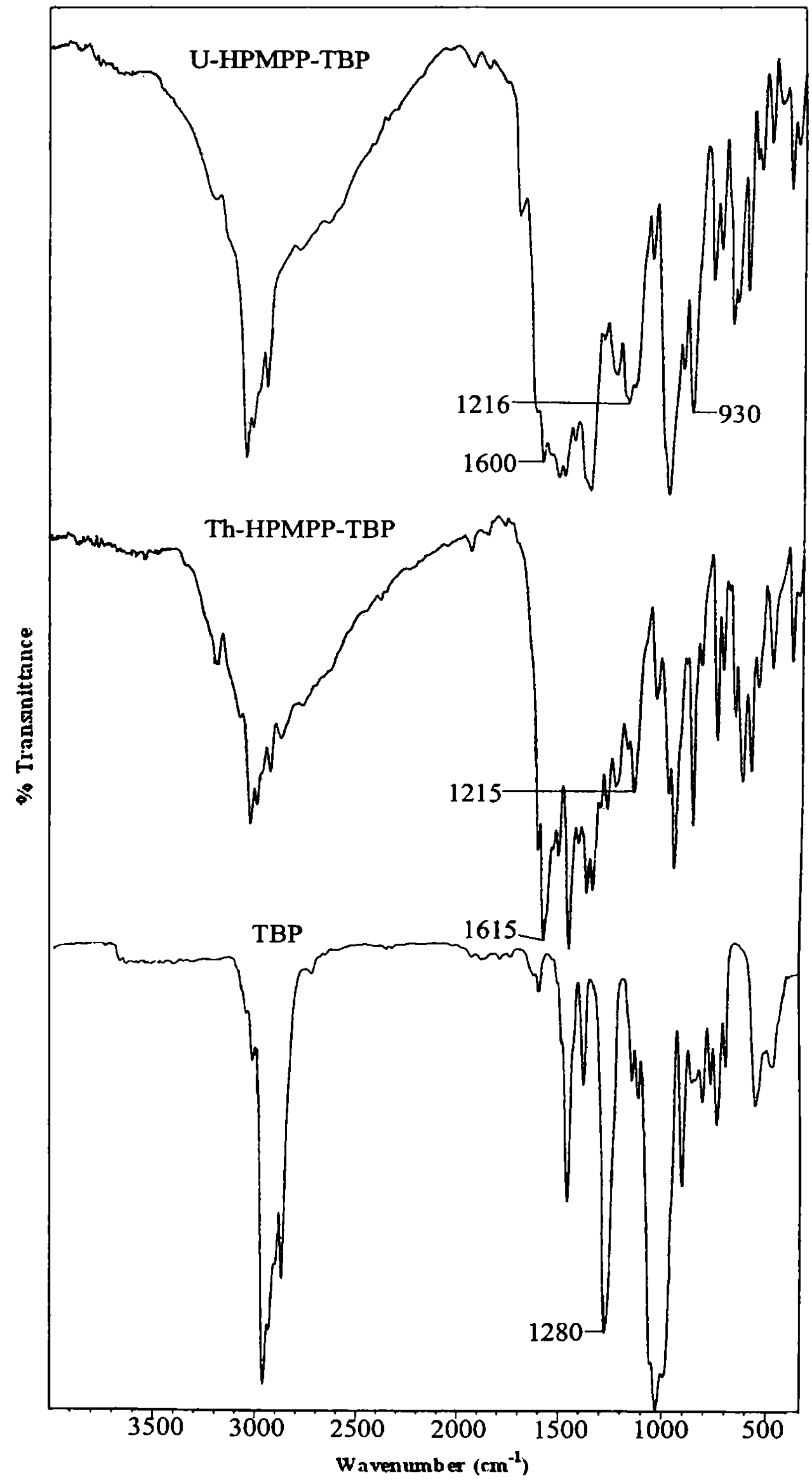


Figure 4.16. IR spectra of TBP neutral oxo-donor, Th-HPMPP-TBP and U-HPMPP-TBP complexes.

It can be concluded from the IR spectral data that the neutral organophosphorus extractant forms an adduct with the metal-chelate by replacing water molecules that are present in the primary coordination sphere of the simple metal-chelate.

From the extraction and FT-IR and ^{31}P NMR spectral data, the proposed structures of thorium(IV) and uranium(VI) with HPMPP in the presence of TBP are given in Fig. 4.17. Th^{4+} is surrounded by nine oxygen atoms (eight oxygens from four HPMPP + one oxygen from organophosphorus extractant) in a tricapped trigonal prismatic geometry [Kettle 1975]. On the other hand, in the $UO_2(PMPP)_2 \cdot S$ (where S = TOPO/CMPO/TBP), uranyl ion is surrounded by five oxygen atoms (four oxygens from two HPMPP + one oxygen from organophosphorus extractant) in a pentagonal bipyramidal geometry, as reported in the uranium dibenzoyl methanate-triphenylphosphine oxide [Alagar et al. 2003].

Table 4.8 gives the separation factors (S.F.) between thorium(IV), and uranium(VI), defined as the ratio of the respective distribution ratios, with HPMPP and with mixtures of HPMPP and neutral organophosphorus extractant systems when extracted from 1.0 mol/dm^3 sodium nitrate solutions of pH = 2.0. It is clear from the table that the addition of neutral organophosphorus extractant clearly diminishes the selectivity among these metal ions even though it enhances the extraction efficiency.

Table 4.8. Separation factors (S.F.) between thorium(IV) and uranium(VI) with HPMPP (0.01 mol/dm^3) and mixtures of HPMPP and neutral organophosphorus extractants (TOPO = 0.001 mol/dm^3; CMPO = 0.005 mol/dm^3; TBP = 0.2 mol/dm^3).

Extractant system	S. F. D_{Th}/D_U
HPMPP	2.8 x 10^3
HPMPP + TOPO	1.14 x 10^3
HPMPP + CMPO	6.70 x 10^2
HPMPP + TBP	8.0 x 10^2

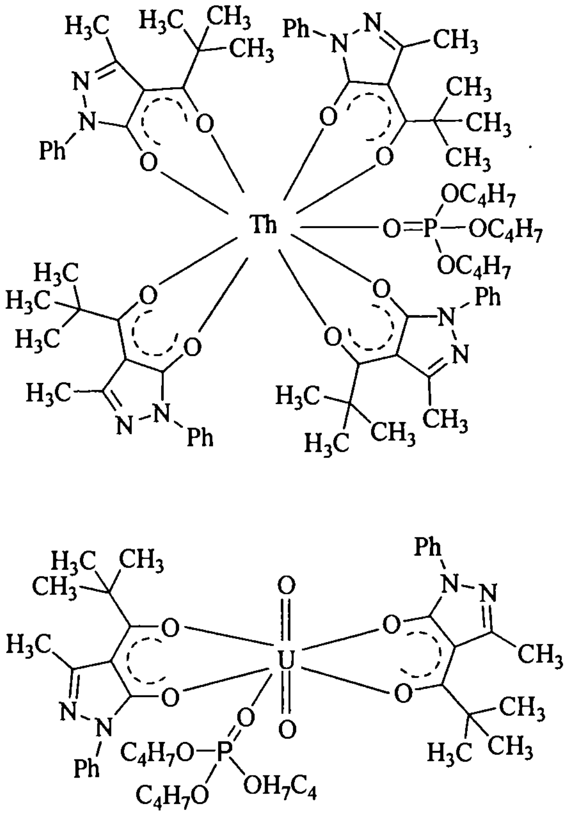
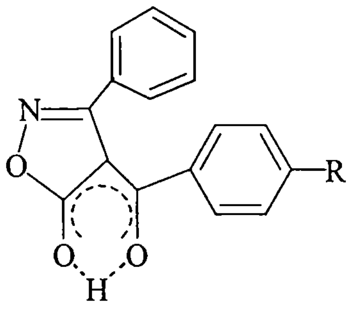


Figure 4.17. Proposed structures of thorium(IV) and uranium(VI) with HPMPP in the presence of TBP.

<u>*Chapter 5*</u>

Para-substituted 3-phenyl-4-aroyl-5-isoxazolones as chelating agents for the synergistic extraction of thorium(IV) and uranium(VI) in the presence of various crown ethers

effects on the extraction behavior of thorium(IV) and uranium(VI) from nitric acid solutions.



R = H : HPBI
F : HFBPI
CH_3 : HTPI

1

The synergistic extraction of thorium(IV) and uranium(VI) with 4-acyl-3-phenyl-5-isoxazolones in the presence of various neutral organophosphorus extractants [Mansingh et al. 1996; Thakur et al. 1996; Mohapatra et al. 1997] and amides [Banerjee et al. 2003; Bhattacharya et al. 2004] have been widely investigated. Recently from our laboratory, high selectivity has been reported between thorium(IV) and uranium(VI) with HPBI in the presence of B15C5 and has been attributed to the crown ether size compatibility with Th^{4+} [Sahu et al. 2000]. The introduction of cation selectivity into synergistic solvent extraction is best accomplished by the use of crown ethers that form both stable in-cavity complexes with the target cation and have adequate functionalisation to impart organophilicity [Bond et al. 2000]. Hence in the present study, the synergistic extraction of thorium(IV) and uranium(VI) with HFBPI in the presence and absence of various crown ethers, benzo-15-crown-5 (B15C5), dicyclohexano-18-crown-6 (DC18C6) and dibenzo-18-crown-6 (DB18C6) has been investigated with a view to improve the selectivity between these actinides.

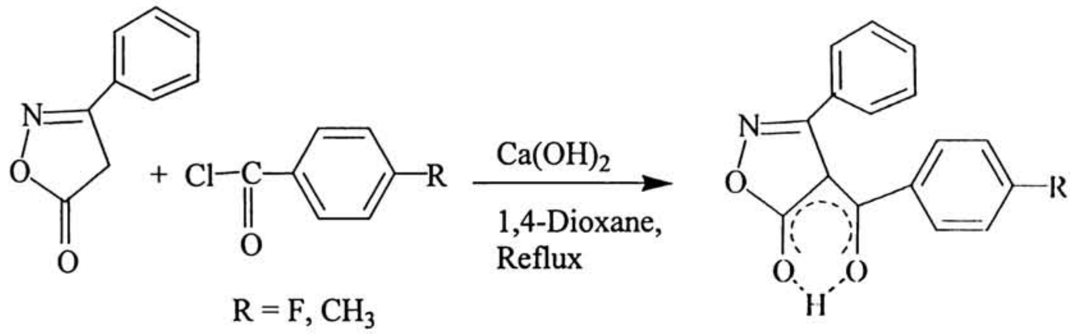
EXPERIMENTAL

Chemicals

3-Phenyl-5-isoxazolone and corresponding acid chlorides were obtained from Aldrich Chemical Company. All other chemicals used were the same as in Chapter 3.

Syntheses of various para-substituted 3-phenyl-4-aroyl-5-isoxazolones

The para-substituted 3-phenyl-4-aroyl-5-isoxazolones, HFBPI and HTPI were synthesized from 3-phenyl-5-isoxazolone and the corresponding acid chloride following the method described elsewhere [Korte and Storiko 1961] (Scheme 5.1).



Scheme 5.1

3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone

The synthesized 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone was identified by elemental analyses, IR and ^{1}H NMR spectral data. HFBPI: m.p. 148^{0}C. Elemental analyses: Calc. for $C_{16}H_{10}NO_3F$: C 67.84, H 3.53, N 4.95 %. Found: C 67.70, H 3.92, N 4.95 %. ^{1}H NMR ($CDCl_3$) data δ (ppm): 6.80-7.39 (m, 9H,phenyl); IR (KBr) data (ν cm $^{-1}$): 3429, 1706 (C = O), 1619, 1480. In the ^{1}H NMR spectrum of HFPBI (Fig. 5.1), no peak corresponding to the enolic –OH has been observed. However, the absence of a peak at δ 3.8 ppm corresponding to the methyne proton, at the fourth position of the isoxazolone ring, confirms the existence of HFBPI in the enolic form.

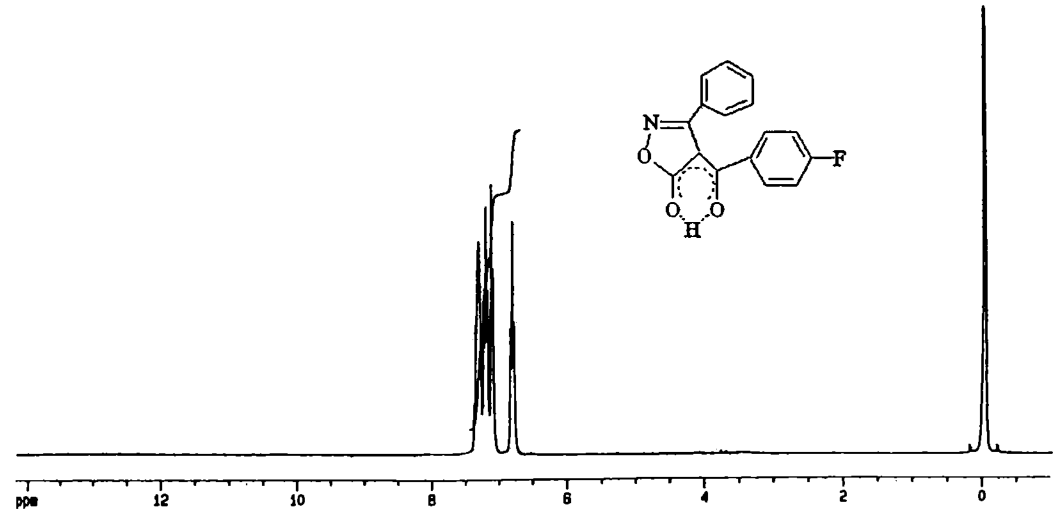


Figure 5.1. ^{1}H NMR spectrum of HFBPI.

3-phenyl-4-(4-toluoyl)-5-isoxazolone

The synthesized 3-phenyl-4-(4-toluoyl)-5-isoxazolone was identified by elemental analyses, IR and ^{1}H NMR spectral data. HTPI: m.p. 144^{0}C; ^{1}H NMR ($CDCl_3$) data δ (ppm): 6.92 – 7.34 (m, 9H, phenyl), 2.32 (s, 3H, CH_3 of the aromatic ring); IR (KBr) data (ν cm $^{-1}$): 2600, 1706 (C=O), 1626, 1593; Elemental analyses: Calc. for $C_{17}H_{13}NO_3$: C 73.12, H 4.66, N 5.02%. Found: C 73.48, H 4.38, N 5.31%. In the ^{1}H NMR spectrum of HTPI (Fig. 5.2), no peak corresponding to the enolic-OH has been observed. However, the absence of a peak at δ 3.8 ppm corresponding to the methyne proton, at the fourth position of the isoxazolone ring, confirms the existence of HTPI in the enolic form.

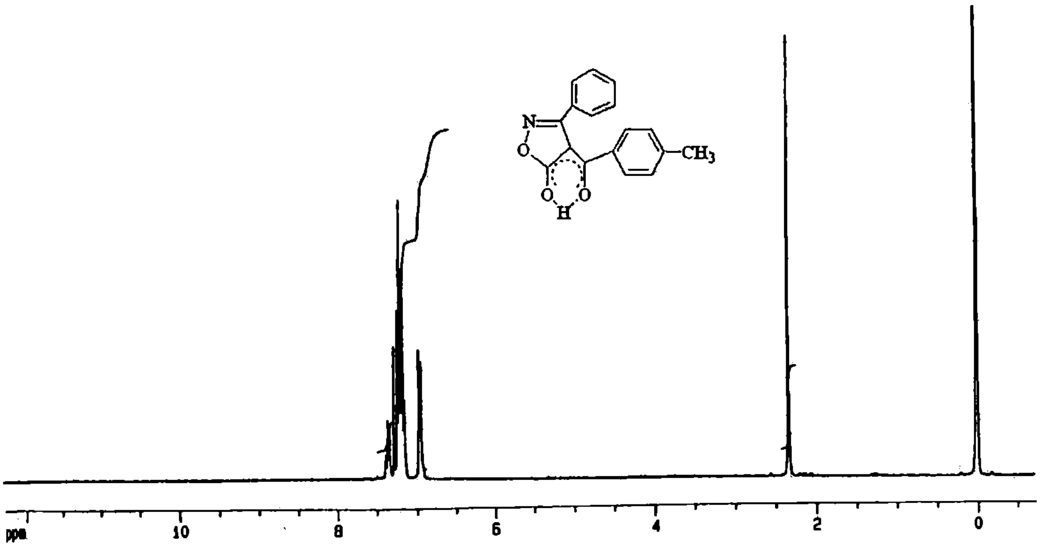


Figure 5.2. ^{1}H NMR spectrum of HTPI.

Solvent extraction and analytical procedure

The solvent extraction and analytical procedures followed in this chapter are the same as described in Chapter 3. Preliminary experiments showed that the extraction equilibrium was attained within 30 min for thorium(IV) and 60 min for uranium(VI).

Preparation of metal complexes

The metal-3-phenyl-4-aroyl-5-isoxazolone complexes were prepared by the procedures as described in Chapter 3. The complexes were characterized by elemental analyses, IR and ^{1}H NMR spectral data. The solutes studied were $Th(FBPI)_4$, $Th(TPI)_4$, $Th(FBPI)_4{\cdot}B15C5$, $UO_2(FBPI)_2$, $UO_2(TPI)_2$, $UO_2(FBPI)_2{\cdot}B15C5$.

RESULTS AND DISCUSSION

Extraction of thorium(IV) and uranium(VI) with HFBPI or HTPI

The extraction of thorium(IV) and uranium(VI) with HFBPI or HTPI (HX) alone in chloroform as a function of the extractant concentration from 1.0 mol/dm^3 sodium nitrate solutions at constant metal (1 x 10^{-4} mol/dm^3 for both thorium(IV) and uranium(VI)) and nitric acid (0.5 mol/dm^3) concentrations has been investigated and the results are depicted in Fig. 5.3. Plots (Fig. 5.3) of log D_0 *vs.* log [HX] have slopes of 4.0 $\pm$ 0.05 for thorium(IV) and 2.0 $\pm$ 0.1 for uranium(VI), indicating the extraction of complexes Th(FBPI)$_4$, Th(TPI)$_4$, UO$_2$(FBPI)$_2$ and UO$_2$(TPI)$_2$. These in conjunction with the slopes of –4.0 $\pm$ 0.05 and –2.0 $\pm$ 0.1 observed for thorium(IV) and uranium(VI), respectively, with hydrogen ion variation (Figs. 5.4 and 5.5) at constant HFBPI/HTPI (0.005 mol/dm^3 for thorium(IV) and 0.05 mol/dm^3 for uranium(VI)) concentration, confirm the extraction of simple metal-chelates.

Based on the above results, the extraction equilibria of thorium(IV) and uranium(VI) with chelating extractants HX (= HFBPI or HTPI) alone may be expressed as

$$\mathrm{Th}^{4+}_{aq} + 4(\mathrm{HX})_{org} \xrightleftharpoons{K_{ex,0}} \mathrm{ThX}_{4\,org} + 4\mathrm{H}^{+}_{aq} \qquad (1)$$

$$\mathrm{UO}^{2+}_{2\,aq} + 2(\mathrm{HX})_{org} \xrightleftharpoons{K_{ex,\,0}} \mathrm{UO_2X_2}_{\,org} + 2\mathrm{H}^{+}_{aq} \qquad (2)$$

where $K_{ex,0}$ denotes the equilibrium constant. Since the partition coefficients of para-substituted 3-phenyl-4-aroyl-5-isoxazolones were found to be very high (log K_D for HFBPI = 2.8; for HTPI = 2.78 [Odashima et al. 1995]), the concentration of isoxazolonate anion in the aqueous phase can be neglected.

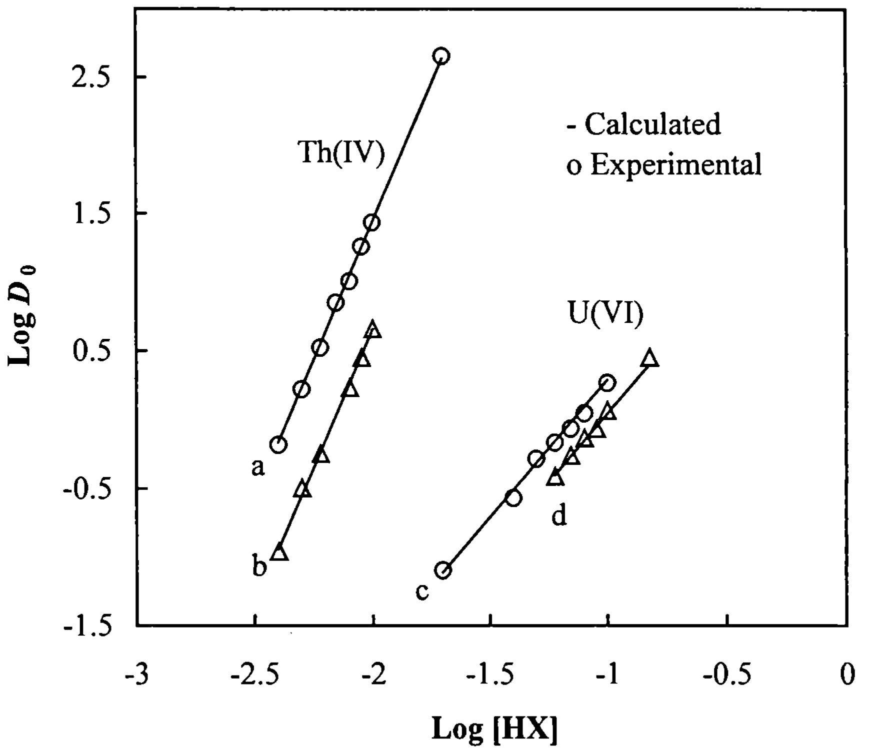


Figure 5.3. Effect of 3-phenyl-4-aroyl-5-isoxazolone (HX) concentration on the extraction of thorium(IV) and uranium(VI). Aqueous phase = 0.5 mol/dm^3 + 0.5 mol/dm^3 NaNO$_3$. Slope of the line (a) HFBPI = 4.0 ± 0.05 (b) HTPI = 4.0 ± 0.05 (c) HFBPI = 2.0 ± 0.1 (d) HTPI = 2.0 ± 0.1.

The distribution ratio, D_0, of thorium(IV) is given by

$$D_0 = \frac{[\mathrm{ThX_4}]_{\mathrm{org}}}{[\mathrm{Th^{4+}}]_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}+\beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\}} \qquad (3)$$

where β_i is the complex formation constant of thorium(IV) with nitrate ions in the aqueous phase. The values of stability constants (log β_1 = 0.1; log β_2 = 0.8) were taken from the literature [Oliver and Davis 1972]. Then the distribution ratio, D_0, of thorium(IV) can be written from Eqs. (1) and (3) as

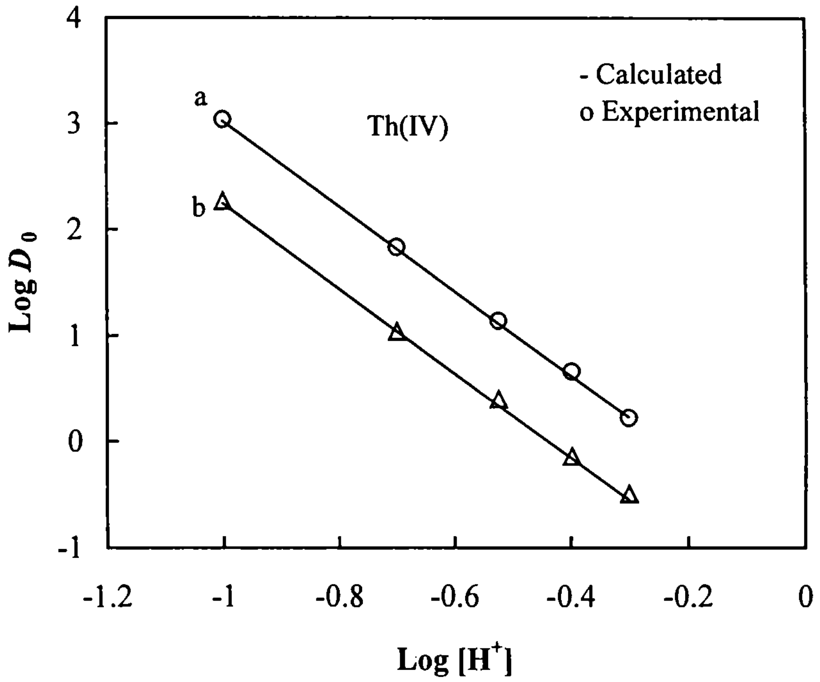


Figure 5.4. Effect of hydrogen ion concentration on the extraction of thorium(IV). Aqueous phase = 1.0 mol/dm^3 NaNO$_3$; [HFBI] = [HTPI] = 0.005 mol/dm^3. Slope of the line (a) HFBPI = - 4.0 ± 0.05 (b) HTPI = - 4.0 ± 0.05.

$$D_0 = \frac{K_{ex,0}[HX]^4_{org}}{[H^+]^4_{aq}\{1+\beta_1[NO_3^-]_{aq}+\beta_2[NO_3^-]^2_{aq}\}} \qquad (4)$$

Similarly, the distribution ratio, D_0, for uranium(VI) can be written as

$$D_0 = \frac{K_{ex,0}[HX]^2_{aq}}{[H^+]^2_{aq}(1+\beta_1[NO_3^-]_{aq})} \qquad (5)$$

The stability constant for uranium(VI) (log β_1 = -0.3) with nitrate ion was taken from the literature [Kotrly and Sucha 1985].

The formation of the above simple metal chelates were further confirmed by analyzing the equilibrium data (presented in the Figs. 5.3 - 5.5) using Eq. (4) for thorium(IV) and Eq. (5) for uranium(VI). The equilibrium constants for the above complexes were determined by nonlinear regression

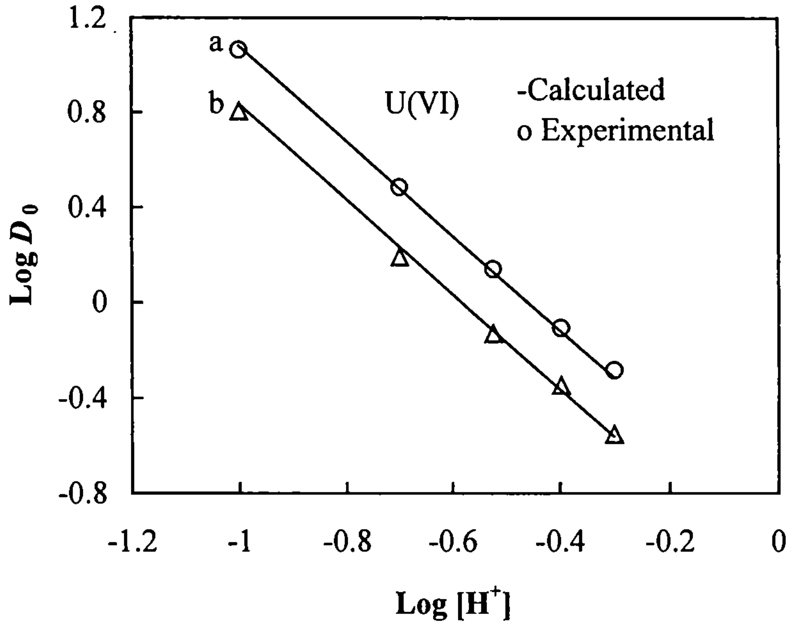


Figure 5.5. Effect of hydrogen ion concentration on the extraction of uranium(VI). Aqueous phase = 0.5mol/dm^3 HNO_3 + 0.5 mol/dm^3 $NaNO_3$; [HFBPI] = [HTPI] = 0.05 mol/dm^3. Slope of the line (a) HFBPI = -2.0 ± 0.1 (b) HTPI = -2.0 ± 0.1.

analysis as described in Chapter 3. The equilibrium constants thus calculated refer only to concentration quotients, calculated on the assumption that the activity coefficients of the species involved do not change significantly under the present experimental conditions. It is clear from Table 5.1 that the log equilibrium constant value of thorium(IV) with HFBPI is about 7-fold higher than that of uranium(VI). A similar behavior has been observed in the extraction of thorium(IV) and uranium(VI) with HPBI [Sahu et al. 2000] from nitric acid solutions. A linear correlation between log $K_{ex,0}$ values of various heterocyclic β-diketones for the extraction of thorium(IV) and uranium(VI) with their pK_a values is shown in Fig. 5.6. It is clear from the figure that the log equilibrium constant value decreases as the pK_a value increases.

Table 5.1. Log equilibrium constants (log $K_{ex,0}$) for the extraction of thorium(IV) and uranium(VI) with various heterocyclic β-diketones.

Extractant	pK_a	Log $K_{ex,0}$	
		Th(IV)	U(VI)
HFBPI	0.65[a]	9.16 ± 0.02	1.86 ± 0.03
HTPI	1.48[a]	8.38 ± 0.03	1.61 ± 0.02
HPBI	1.23[b]	8.71 ± 0.03[c]	1.67 ± 0.03[c]
HPMBP	3.92	6.72 ± 0.04[d]	0.76 ± 0.04[d]

a [Odashima et al.1995] b [Le et al. 1993] c [Sahu et al.2000] d [Meera and Reddy 2004].

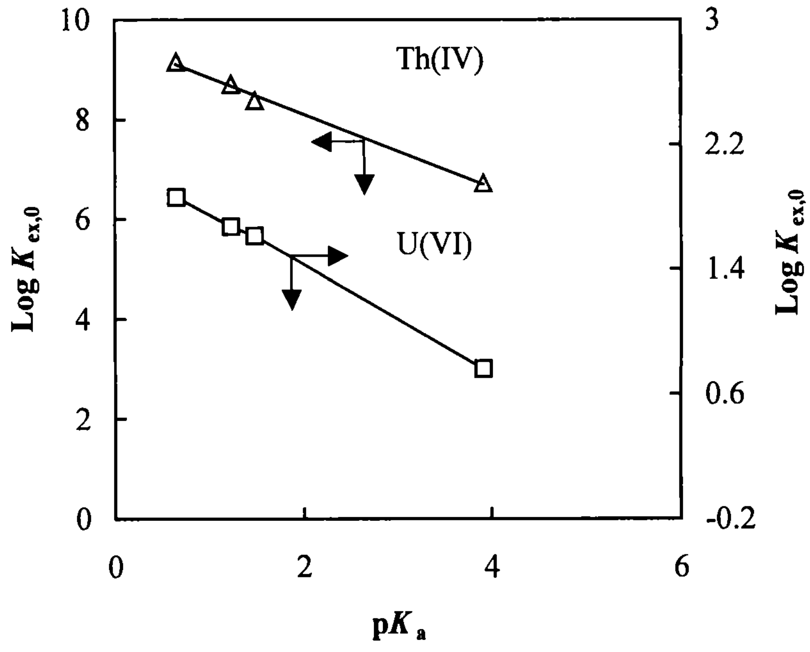


Figure 5.6. Plots of log $K_{ex,0}$ vs pK_a for the extraction of thorium(IV) and uranium(VI) with various heterocyclic β-diketones.

The strong acidity of 4-aroyl-5-isoxazolones could be partly attributed to the heterocyclic π-electron conjugation system, which contains electronegative nitrogen and oxygen. The O---O distance between two donating oxygen atoms of the various derivatives of 4-aroyl-5-isoxazolones should be significant with respect to the stability of the intramolecular hydrogen bonding and the formation of metal complexes. Hence, the O---O distances of various para-substituted 4-aroyl-5-isoxazolones were determined by semi-empirical PM3/H molecular orbital calculations [Stewart 1989] taking into account the hydrogen bond. A ball-and-stick representation based on PM3/H optimized structures of HFBPI, HPBI and HTPI are given in Fig. 5.7. It is clear from the above results that the para-substitution in 3-phenyl-4-benzoyl-5-isoxazolone do not narrow the O---O distances (O---O distance of HPBI = 2.83 Å; HFBPI = 2.83 Å; HTPI = 2.83 Å) between the two donating oxygen atoms. The larger O---O distances observed in para-substituted 4-aroyl-5-isoxazolones would decrease the stability of the intramolecular hydrogen bonding, resulting in great enhancement of acidity. However, it is clear from the present study that the log $K_{ex,0}$ values for both thorium(IV) and uranium(VI) varies in accordance with the nature of the substituent, electron withdrawing (-F) or electron donating ($-CH_3$) group, on the benzoyl moiety of the HPBI system. It is also evident from the results that the extraction efficiency of these metal ions with various para-substituted derivatives of 3-phenyl-4-benzoyl-5-isoxazolones varies in accordance with their pK_a values.

Solid complexes of thorium(IV) and uranium(VI) with para-substituted 3-phenyl-4-aroyl-5-isoxazolones and their characterization

Solid complexes of thorium(IV) and uranium(VI) with HFBPI/HTPI were characterized by elemental analyses, IR and ^{1}H NMR techniques.

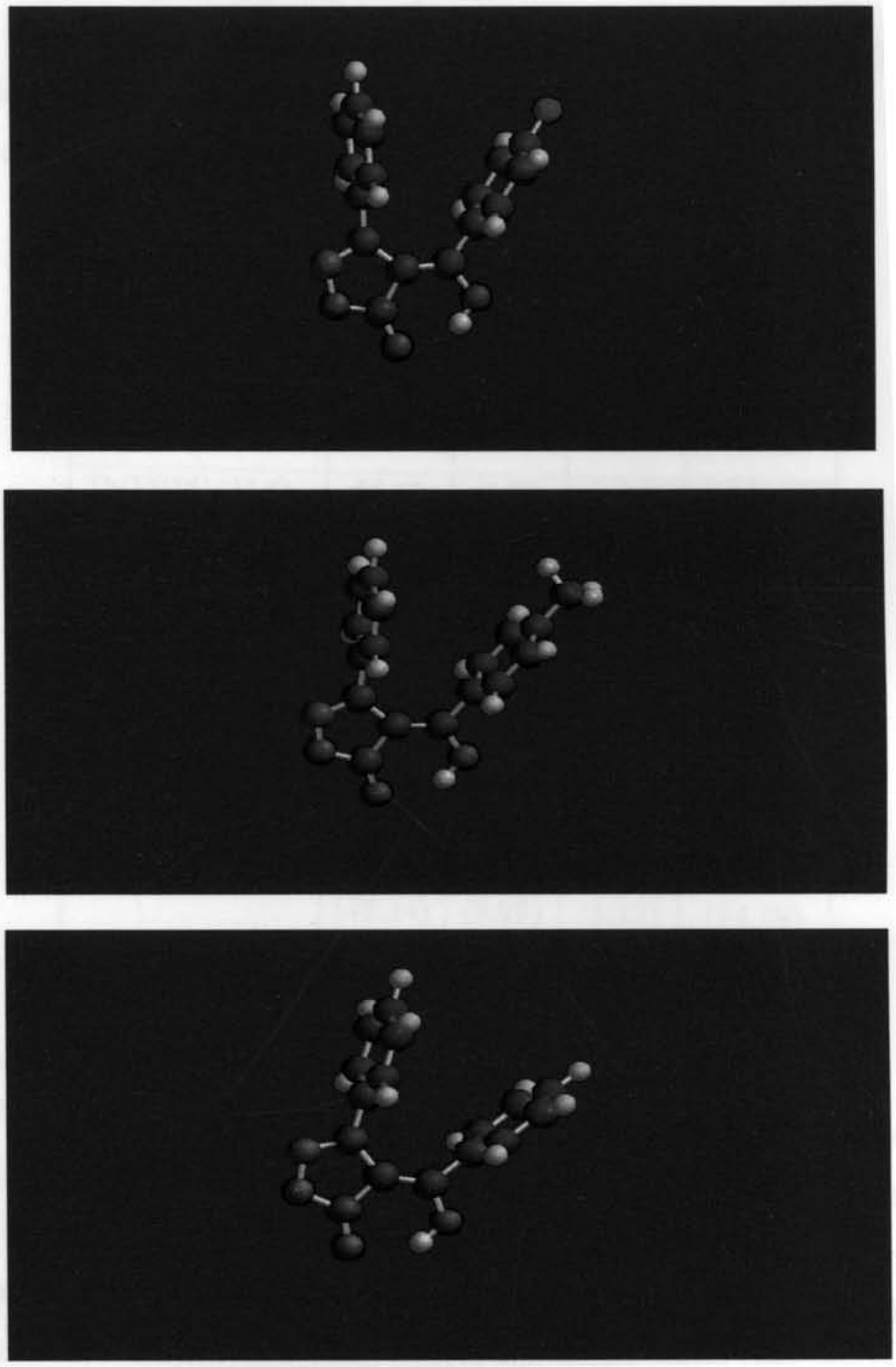


Figure 5.7. Ball-and-stick representation based on PM3/H optimized structures of HFBPI, HTPI and HPBI, respectively.

Elemental analyses of binary complexes

The analytical data presented in Table 5.2 show that thorium(IV) and uranium(VI) reacted with HFBPI and HTPI, in the metal : ligand mole ratio of 1 : 4 and 1 : 2, respectively.

Table 5.2. Elemental analyses of the binary complexes.

Complex	% C Found	% H Found	%N Found	% M Found
$Th(FBPI)_4.H_2O$	56.62 (55.73)	2.77 (2.76)	4.08 (4.06)	16.93 (16.84)
$UO_2(FBPI)_2.H_2O$	46.22 (45.07)	2.52 (2.35)	3.61 (3.29)	28.26 (27.93)
$Th(TPI)_4.H_2O$	60.55 (59.91)	3.71 (3.67)	4.15 (4.11)	16.97 (17.03)
$UO_2(TPI)_2.H_2O$	48.99 (48.34)	3.24 (3.08)	3.22 (3.32)	28.65 (28.20)

Figures in parentheses indicate calculated values.

IR spectra of binary complexes

Figs. 5.8 and 5.9 show the IR spectra of the complexes of thorium(IV) and uranium(VI) with HFBPI and HTPI, respectively along with free ligands. In the spectra of the complexes, the broad absorption in the region 3000-3500 cm^{-1}, indicate the presence of water of hydration, as observed in actinide metal complexes of 4-aroylpyrazolonates [Meera and Reddy 2004]. The presence of inner and outer sphere of hydration in uranyl isoxazolonate has been well documented [Mohapatra et al. 1997; Banerjee et al. 2003].

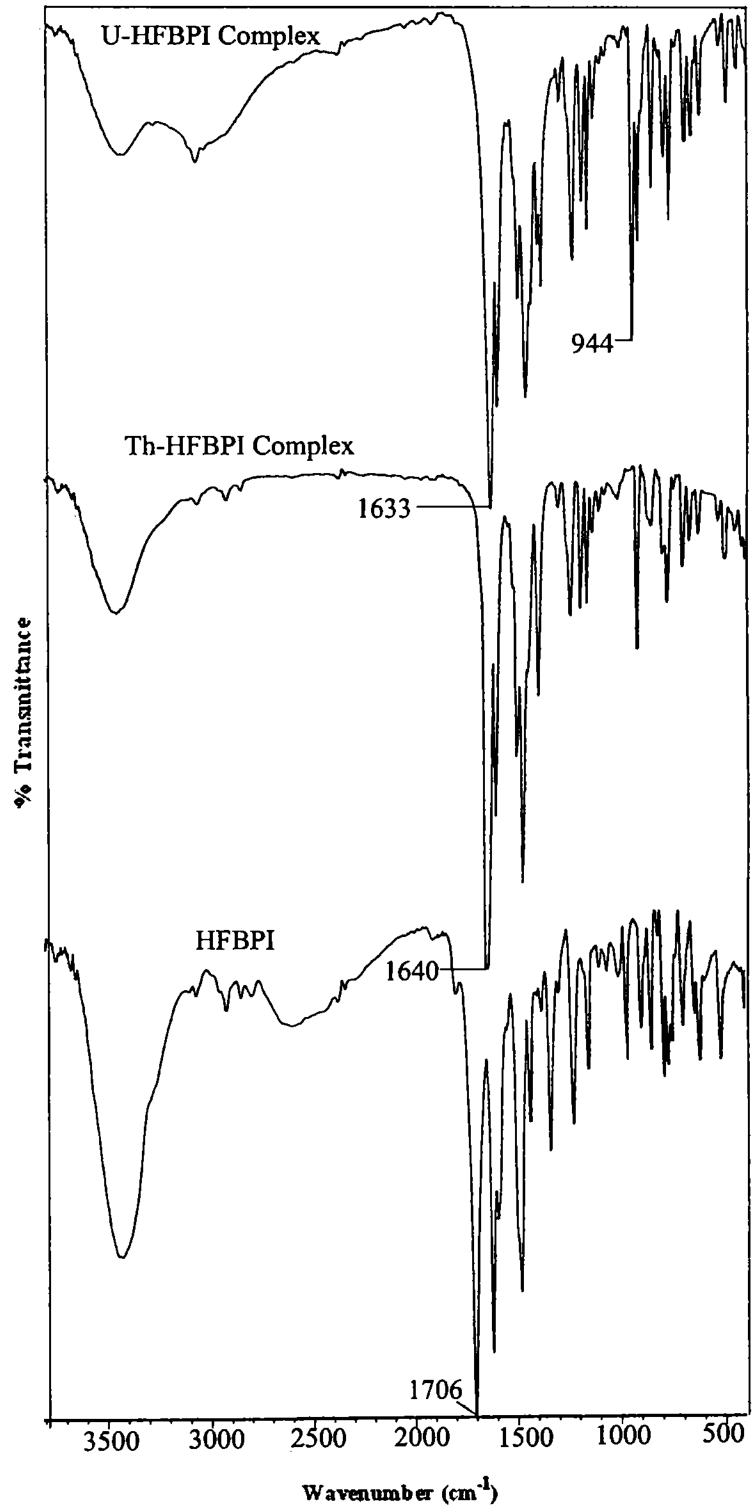


Figure 5.8. IR spectra of HFBPI ligand, Th-HFBPI and U-HFBPI complexes.

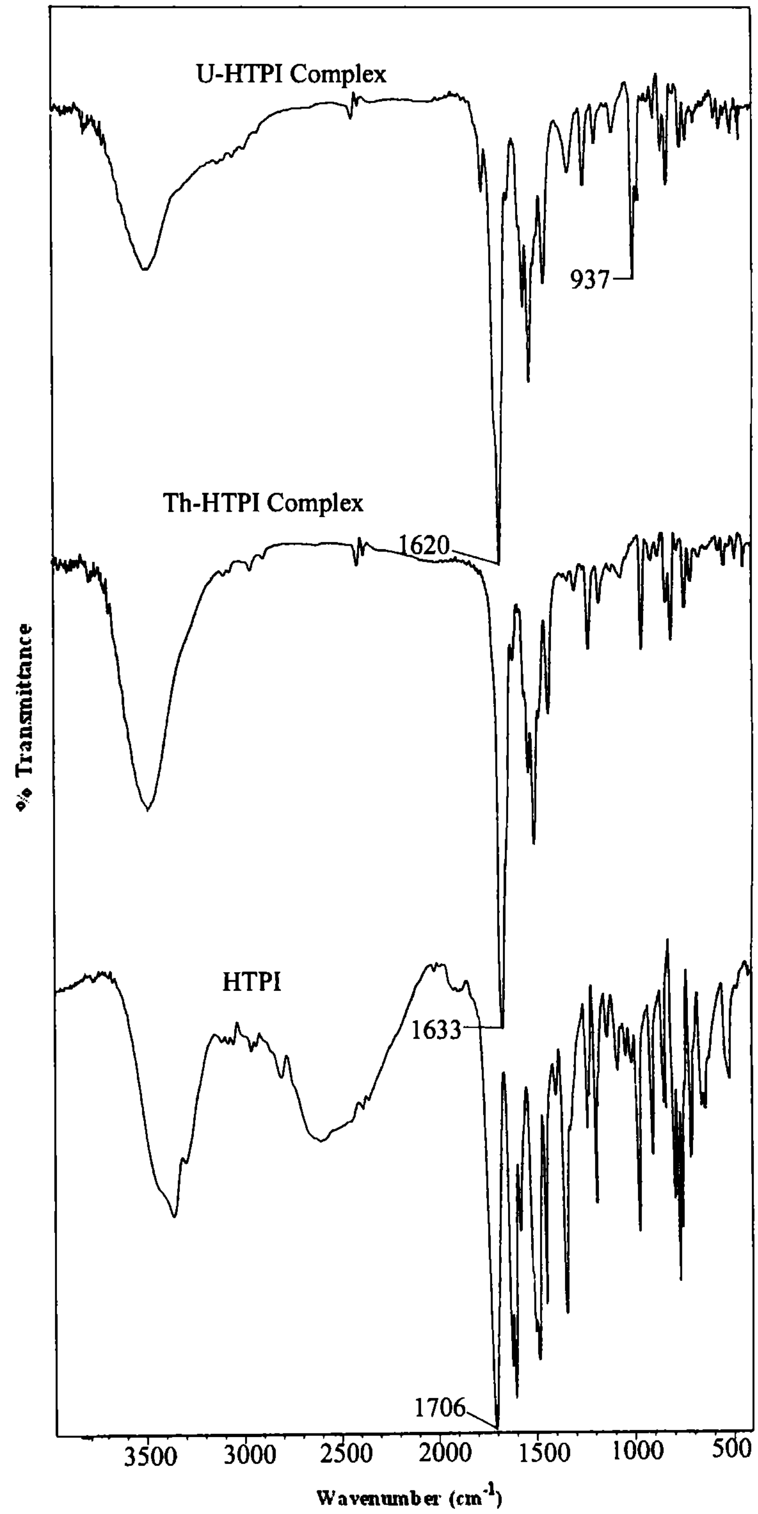


Figure 5.9. IR spectra of HTPI ligand, Th-HTPI and U-HTPI complexes.

The intense broad band centered around 2600 cm^{-1}, which is assigned to the ν (O-H) in the spectrum of the ligands, is absent in the spectra of the complexes, indicating the enolization of the O-H group and the involvement of oxygen of the hydroxyl group in chelation. The stretching frequency of the C=O group has been shifted from 1706cm^{-1} in the free ligand to lower frequency (1640 in $Th(FBPI)_4$, 1633 in $Th(TPI)_4$ and $UO_2(FBPI)_2$, 1620 cm^{-1} in $UO_2(TPI)_2$) in the complexes, which suggests that the carbonyl group is involved in complexation. The other strong absorption occurring around 937-944 cm^{-1} may be assigned to ν(O=U=O) of UO_2^{2+} [Kannan et al. 2002].

^1H NMR spectra of binary complexes

The ^1H NMR spectral data of the binary complexes (Table 5.3) shows all the expected resonances for 4-aroyl-5-isoxazolonates and the free ligands, the integration of the signals being in accordance with the formulae proposed. The downfield shift of the phenyl protons has been observed in both thorium(IV) and uranium(VI) complexes of HFBPI and HTPI. The signal of CH_3 protons of methyl group in HTPI has also been shifted downfield upon coordination with metal ion in all the binary complexes. The downfield shifts observed were larger for thorium than in uranium complexes.

From the elemental analyses, FT-IR and ^1H NMR spectral data, the proposed structures of thorium(IV) and uranium(VI) with HFBPI and HTPI is given in Fig. 5.10. The uranyl ion is surrounded by two molecules of HFBPI/HTPI and one water molecule to give a coordination number of seven and pentagonal bipyramidal geometry, as observed in uranium-HTTA and uranium-HPMBP/HPMAP complexes [Okafor et al. 1990; Kannan et al. 2001]. In the case of Th-HFBPI/HTPI complex, Th^{4+} is surrounded by four

HFBPI/HTPI molecules and one water molecule, to give a coordination number of 9.

Table 5.3. ^1H NMR spectral data for free ligands and binary complexes.

Compound	Phenyl protons	Methyl protons
HFBPI	6.80–7.39 (m)	–
HTPI	6.92–7.34 (m)	2.32 (s)
Th-FBPI	7.01–7.46 (m)	–
U-FBPI	6.89–7.71 (m)	–
Th-TPI	6.75–7.91 (m)	2.68 (s)
U-TPI	6.98–7.70(m)	2.52 (s)

It is clear from the results (Fig. 5.3) that the selectivity between thorium(IV) and uranium(VI) increases with increase in the concentration of HFBPI at constant nitric acid concentration (Separation Factor, S.F. = 5.4 x 10^3 at 0.02 mol/dm^3 HFBPI; S.F. = 2.2 x 10^4 at 0.04 mol/dm^3 HFBPI). Further, these S.F. values are found to be lower than that of HPMFBP (S.F. = 8.51 x 10^3 at 0.02 mol/dm^3 HPMFBP; S.F. = 3.42 x 10^4 at 0.04 mol/dm^3 HPMFBP) system [Meera and Reddy 2004]. These results suggest that the O---0 distance is one of the most important factors that governs the selectivity. The separability of thorium(IV) and uranium(VI) with ligands of shorter O---0 distance is found to be better (bite size of HPMFBP = 2.67 Å; bite size of HFBPI = 2.83 Å). In view of the better extraction efficiency and selectivity observed, HFBPI was chosen for further experimentation, especially to study the synergistic extraction in presence of crown ethers.

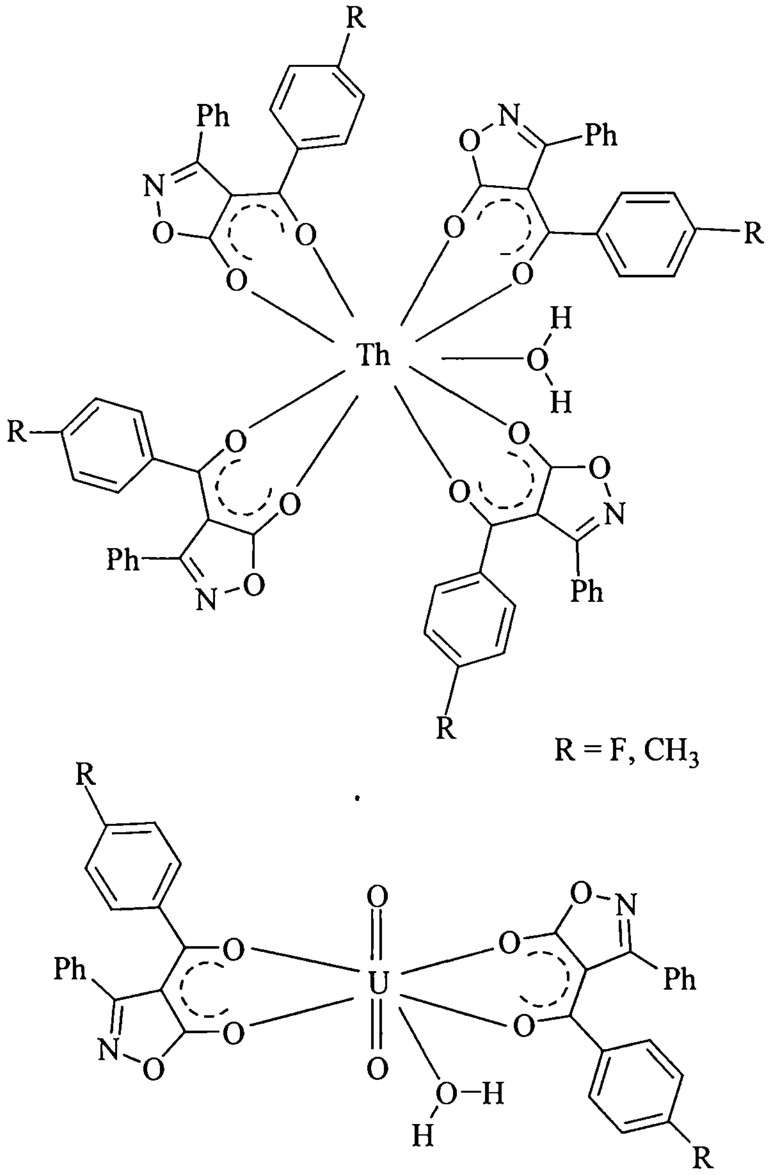


Figure 5.10. Proposed structures of thorium(IV) and uranium(VI) with HFBPI or HTPI.

Extraction of thorium(IV) and uranium(VI) with mixtures of HFBPI and crown ethers

The extraction of thorium(IV) and uranium(VI) from 0.5 mol/dm^3 nitric acid + 0.5 mol/dm^3 sodium nitrate solutions with mixtures of HFBPI (0.001-

0.008 mol/dm^3 for thorium(IV) and 0.02-0.1 mol/dm^3 for uranium(VI)) and DC18C6 (0.0004 - 0.002 mol/dm^3 for thorium(IV) and 0.002 - 0.006 mol/dm^3 for uranium(VI)), DB18C6 (0.0006 - 0.004 mol/dm^3 for thorium(IV) and 0.002 - 0.007 mol/dm^3 for uranium(VI)) or B15C5 (0.0004 - 0.002 mol/dm^3 for thorium(IV) and 0.001 - 0.006 mol/dm^3 for uranium(VI)) in chloroform has been studied. It was found that the extraction of these metal ions into chloroform with crown ether alone was negligible under these experimental conditions. However, with mixtures of HFBPI and crown ethers a considerable synergistic enhancement (Synergistic enhancement factor = $D/D_{HFBPI} + D_{CE}$, where D = distribution ratio with HFBPI + CE; D_{HFBPI}= distribution ratio with HFBPI alone and D_{CE}=distribution ratio with CE alone) in the extraction of these metal ions has been observed (Table 5.4).

Table 5.4. Synergistic enhancement factors of thorium(IV) and uranium(VI) with HFBPI in presence of crown ethers.

Extraction system	Synergistic enhancement factor	
	Th(IV)	U(VI)
HFBPI + DC18C6	3	9
HFBPI + DB18C6	2	2
HFBPI + B15C5	9	4

Th(IV): 0.005 mol/dm^3 HFBPI + 0.002mol/dm^3 CE;
U(VI): 0.1 mol/dm^3 HFBPI + 0.006mol/dm^3 CE.

It is clear from the plots (Figs. 5.11 and 5.12) of log $(D - D_0)$ *vs* log [HFBPI] that at constant CE (0.001 mol/dm^3 for thorium(IV) and 0.005 mol/dm^3 for uranium(VI) and nitric acid concentrations (0.5 mol/dm^3), only four HFBPI moieties in the case of thorium(IV) and two HFBPI moieties in

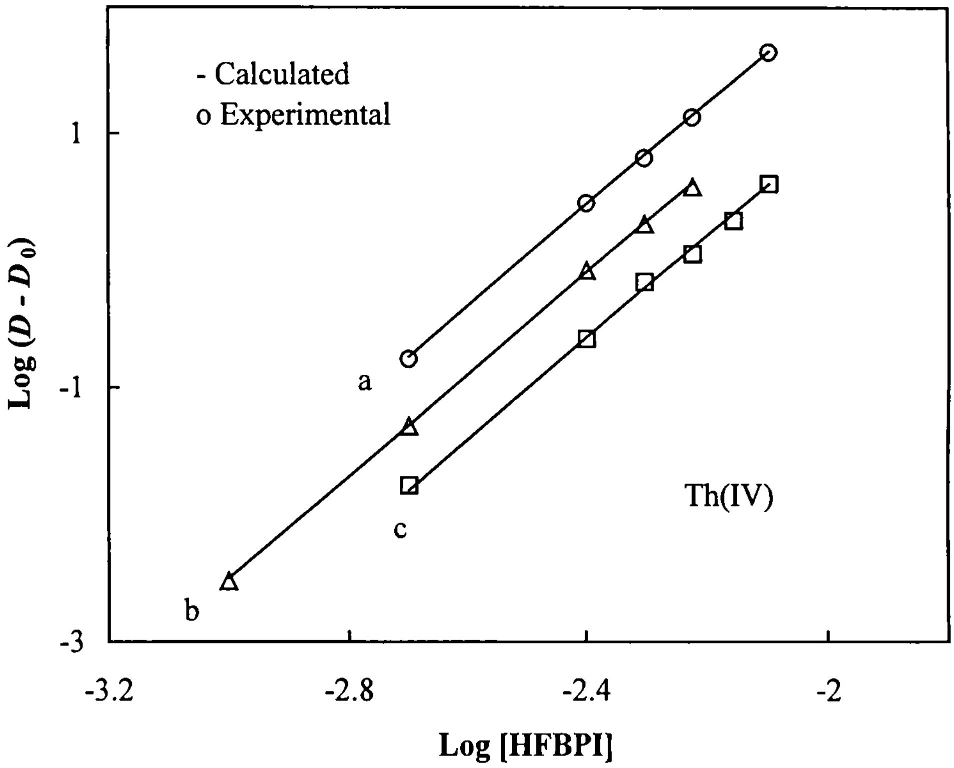


Figure 5.11. Effect of HFBPI concentration on the extraction of thorium(IV) at constant CE (0.001 mol/dm^3) concentration. Aqueous phase = 0.5 mol/dm^3 HNO_3 + 0.5 mol/dm^3 $NaNO_3$. Slope of the line (a) B15C5 = 4.0 ± 0.05 (b) DC18C6 = 4.0 ± 0.05 (c) DB18C6 = 4.0 ± 0.1.

the case of uranium(VI) are involved in the synergistic species extracted into the organic phase. The plots (Figs. 5.13 and 5.14) of log $(D - D_0)$ *vs* log [CE] at constant HFBPI concentration (0.005 mol/dm^3 for thorium(IV) and 0.1 mol/dm^3 for uranium(VI)) gave slopes of unity for both metal ions indicating the participation of only one CE molecule in the synergistic extracted species. These in conjunction with the slopes of –4.0 ± 0.05 and –2.0 ± 0.05 observed for the extraction of thorium(IV) and uranium(VI) (Figs. 5.15 and 5.16), respectively, with H^+ variation experiments at constant HFBPI + CE, indicate the nature of the extracted complexes as Th(FBPI)$_4$·CE and UO$_2$(FBPI)·CE. Similar synergistic complexes, Th(PBI)$_4$.CE and UO$_2$(PBI)$_2$.CE have been observed with HPBI in presence of various crown ethers [Sahu et al. 2000].

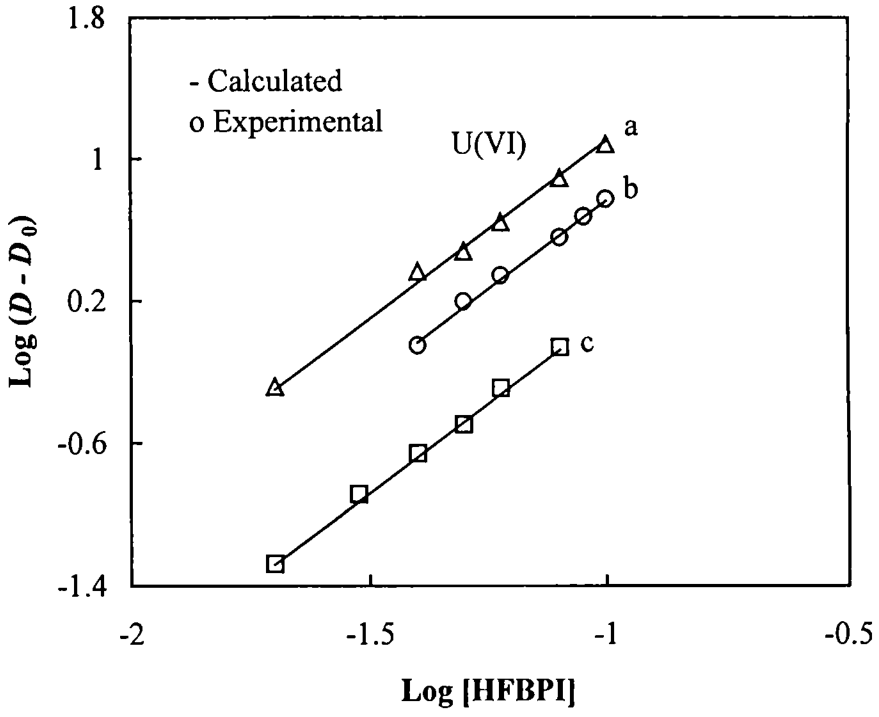


Figure 5.12. Effect of HFBPI concentration on the extraction of uranium(VI) at constant CE (0.005 mol/dm^3) concentration. Aqueous phase = 0.5 mol/dm^3 HNO$_3$ + 0.5 mol/dm^3 NaNO$_3$. Slope of the line (a) DC18C6 = 2.0 ± 0.1 (b) B15C5= 2.0 ± 0.05 (c) DB18C6 = 2.0 ± 0.05.

From the preceding studies, the synergistic extraction equilibrium of thorium(IV) with HFBPI (HX) in the presence of crown ether, CE, may be represented as

$$\mathrm{Th}^{4+}_{aq} + 4(\mathrm{HX})_{org} + n\,\mathrm{CE}_{org} \xrightleftharpoons{K} \mathrm{ThX}_4.n\mathrm{CE}_{org} + 4\mathrm{H}^{+}_{aq} \qquad (6)$$

The overall extraction constant, *K*, is given as

$$K=\frac{[\mathrm{ThX_4}.n\,\mathrm{CE}]_{\mathrm{org}}\,[\mathrm{H^+}]^4_{\mathrm{aq}}}{[\mathrm{Th^{4+}}]_{\mathrm{aq}}[\mathrm{HX}]^4_{\mathrm{org}}[\mathrm{CE}]^n_{\mathrm{org}}} \tag{7}$$

where $n = 0$ or 1. The distribution ratio, D, of the synergistic extraction system is given by Eq. (8)

$$D=\frac{[\mathrm{ThX_4}]_{\mathrm{org}}+[\mathrm{ThX_4.CE}]_{\mathrm{org}}}{[\mathrm{Th^{4+}}]_{\mathrm{aq}}\{1+\beta_1[\mathrm{NO_3^-}]_{\mathrm{aq}}+\beta_2[\mathrm{NO_3^-}]^2_{\mathrm{aq}}\}} \tag{8}$$

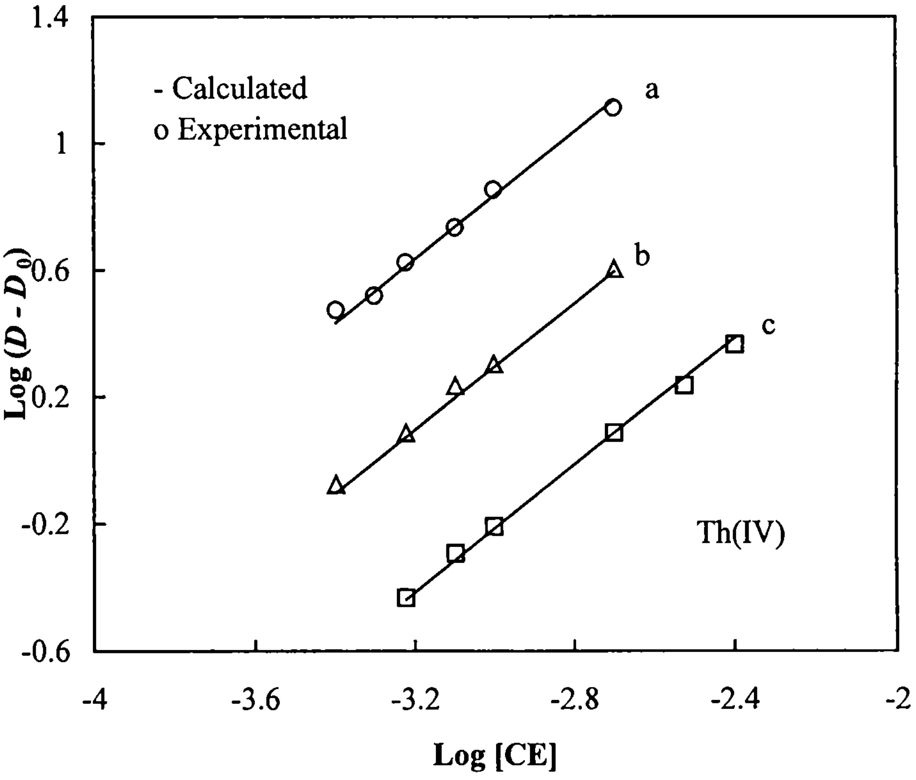


Figure 5.13. Effect of CE concentration on the extraction of thorium(IV) at constant HFBPI (0.005 mol/dm^3) concentration. Aqueous phase = 0.5 mol/dm^3 HNO_3 + 0.5 mol/dm^3 $NaNO_3$. Slope of the line (a) B15C5 = 1.0 ± 0.1 (b) DC18C6 = 1.0 ± 0.05 (c) DB18C6 = 1.0 ± 0.05.

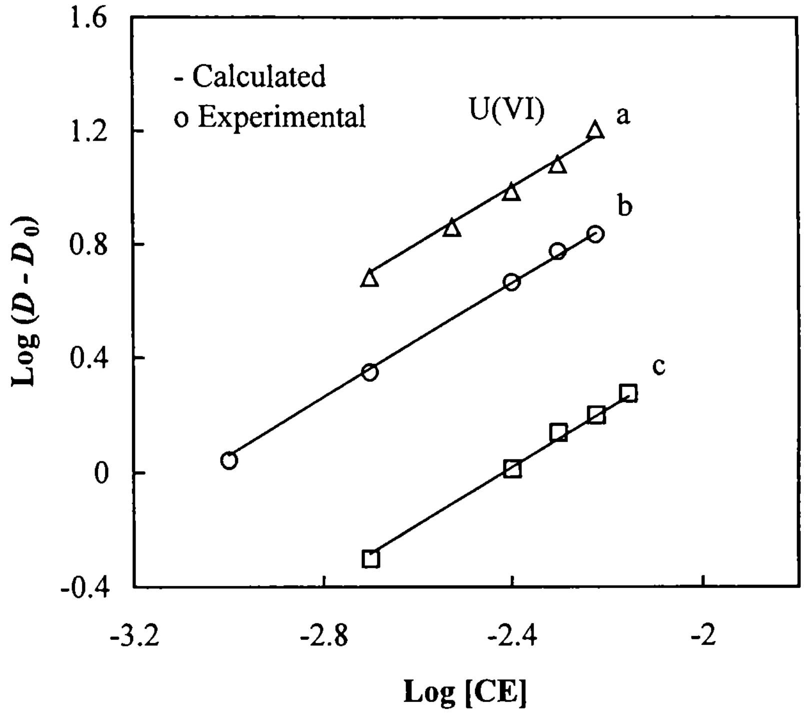


Figure 5.14. Effect of CE concentration on the extraction of uranium(VI) at constant HFBPI (0.1 mol/dm^3) concentration. Aqueous phase = 0.5 mol/dm^3 HNO_3 + 0.5 mol/dm^3 $NaNO_3$. Slope of the line (a) DC18C6 = 1.0 ± 0.1 (b) B15C5 = 1.0 ± 0.05 (c) DB18C6 = 1.0 ± 0.1.

From Eqs. (3), (7) and (8)

$$K = \frac{(D - D_0)[H^+]^4_{aq}\{1 + \beta_1[NO_3^-]_{aq} + \beta_2[NO_3^-]^2_{aq}\}}{[HX]^4_{org}[CE]_{org}} \tag{9}$$

Taking logarithms for Eq. (9),

$$\text{Log}\, K = \log (D - D_0) - 4 \log [HX]_{org} - \log [CE]_{org} + 4 \log [H^+]_{aq} + \log\{1+\beta_1[NO_3^-]_{aq}+\beta_2 [NO_3^-]^2_{aq}\} \tag{10}$$

The organic phase adduct formation reaction is represented as

$$ThX_{4\,org} + nCE_{org} \xrightarrow{K_{CE}} ThX_4.nCE_{org} \tag{11}$$

where K_{CE} is the organic phase adduct formation constant and is given as

$$K_{CE} = \frac{[ThX_4.nCE]_{org}}{[ThX_4]_{org}[CE]_{org}} \qquad (12)$$

From Eqs. (1), (6) (11) and (12)

$$K_{CE} = \frac{K}{K_{ex,0}} \qquad (13)$$

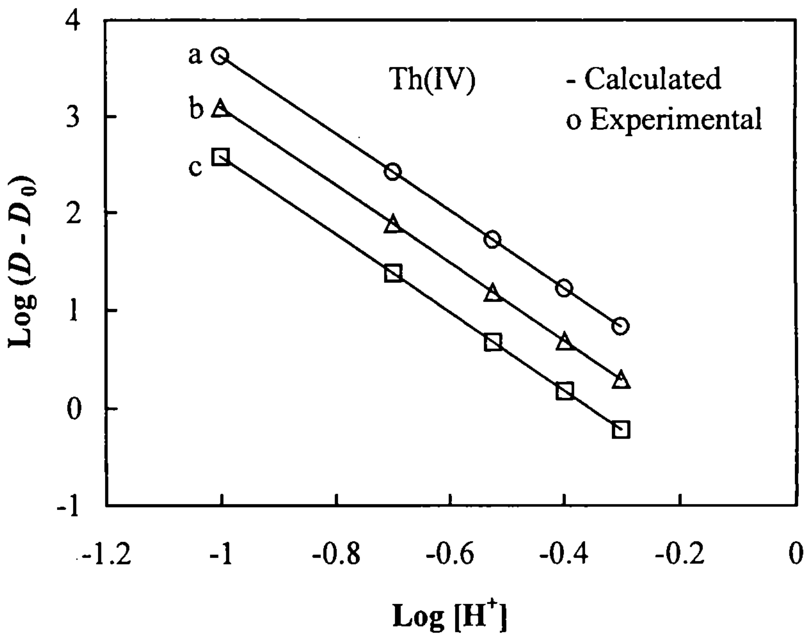


Figure 5.15. Effect of hydrogen ion concentration on the extraction of thorium(IV) at constant HFBPI (0.005 mol/dm^3) + CE (0.001 mol/dm^3) concentration. Slope of the line (a) B15C5 = -4.0 ± 0.05 (b) DC18C6 = -4.0 ± 0.05 (c) DB18C6 = -4.0 ± 0.05.

For a synergistic extraction system employing CE, the extraction equilibrium of uranium(VI) may be represented as

$$UO^{2+}_{2\,aq} + 2(HX)_{org} + n\,CE_{org} \overset{K}{\rightleftharpoons} UO_2X_2.nCE_{org} + 2H^+_{aq} \qquad (14)$$

where $n = 0$ or 1. Then the distribution ratio, D, of the synergistic extraction system for uranium(VI) is given by

$$D = \frac{[UO_2X_2]_{org} + [UO_2X_2.CE]_{org}}{[UO_2^{2+}]_{aq}\{1 + \beta_1[NO_3^-]_{aq}\}} \qquad (15)$$

From Eqs. (5), (14) and (15)

$$K = \frac{(D - D_0)[H^+]_{aq}^2\{1 + \beta_1[NO_3^-]_{aq}\}}{[HX]_{org}^2[CE]_{org}} \qquad (16)$$

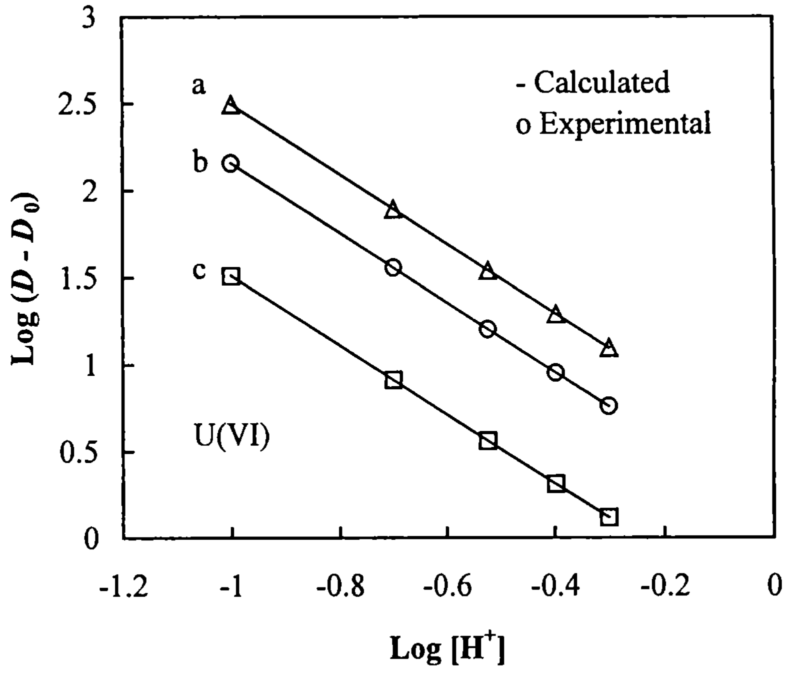


Figure 5.16. Effect of hydrogen ion concentration on the extraction of uranium(VI) at constant HFBPI (0.1 mol/dm^3) + CE (0.005 mol/dm^3) concentration. Slope of the line (a) DC18C6 = -2.0 ± 0.05 (b) B15C5 = -2.0 ± 0.05 (c) DB18C6 = -2.0 ± 0.05.

The organic phase adduct formation reaction is represented as

$$UO_2X_{2\,org} + nCE_{\,org} \overset{K_{CE}}{\rightleftharpoons} UO_2X_2.nCE_{org} \qquad (17)$$

where K_{CE}, the organic phase adduct formation constant is given by

$$K_{\mathrm{CE}} = \frac{K}{K_{\mathrm{ex,0}}} \tag{18}$$

Since the partition coefficients of CEs used (log $K_{\mathrm{(D,DC18C6)}}$ = 3.52 [Mohapatra et al. 1991], log $K_{\mathrm{(D,DB18C6)}}$ = 3.9 [Hasegawa et al. 1984], and log $K_{\mathrm{(D,B15C5)}}$ = 2.5 [Hasegawa et al. 1984]) are known to be quiet large, no correction is necessary for the partitioning of these crown ethers in the aqueous phase. It has been reported that the interaction between the chelating agent and a neutral oxo-donor in chloroform are, in general, weaker when the diluent itself has strong interaction with the oxo-donor [Sekine et al.1983]. Hence it is assumed that there is negligible interaction between HFBPI and CEs in chloroform. The above extracted complexes were further confirmed by analyzing the equilibrium data using Eq. (9) for thorium(IV) and Eq. (16) for uranium(VI). The synergistic equilibrium constants of the above extracted complexes for these metal ions were deduced by nonlinear regression analysis and are given in Table 5.5.

Table 5.5. Two phase synergistic equilibrium constants *(K)* and organic phase adduct formation constants (K_{CE}) of thorium(IV) and uranium(VI) with HFBPI-CE-Chloroform systems.

CE	Log *K*		Log K_{CE}	
	Th(IV)	U(VI)	Th(IV)	U(VI)
DC18C6	12.23 ± 0.02	4.97 ± 0.02	3.07 ± 0.02	3.11 ± 0.02
DB18C6	11.71 ± 0.03	3.99 ± 0.02	2.56 ± 0.03	2.13 ± 0.01
B15C5	12.77 ± 0.02	4.64 ± 0.01	3.6 ± 0.02	2.78 ± 0.02

The adduct formation constants, K_{CE}, for the organic phase synergistic reaction of Th-HFBPI-chelate or U-HFBPI-chelate with various crown ethers were calculated and are given in Table 5.5. The sharp decrease in the complexation for both thorium(IV) and uranium(VI) from DC18C6 to DB18C6 mostly reflect the increase in steric effects and decrease in basicity of crown ethers. A similar trend has been observed in the extraction of thorium(IV) and uranium(VI) with HPBI [Sahu et al. 2000] and HTTA [Mathur and Choppin 1993] in the presence of these crown ethers. The adduct formation constant (log $K_{\mathrm{CE}} = 3.60$) of $\mathrm{Th(FBPI)_4{\cdot}B15C5}$ is higher than that of $\mathrm{Th(PBI)_4{\cdot}B15C5}$ (log $K_{\mathrm{CE}} = 3.41$ [Sahu et al. 2000]). It is well known that stable adduct formation reaction is usually brought out by strong acidic extractants (pK_a of HFBPI = 0.65; HPBI= 1.23) as observed in the present system. The maximum in log K_{CE} for $\mathrm{Th(FBPI)_4.B15C5}$ is likely to be associated with a good fit of $\mathrm{Th^{4+}}$ (ionic diameter = 0.20 nm [Yonezawa and Choppin 1989]) in the cavity of B15C5 (cavity size = 0.17 - 0.22 nm [Mathur and Khopkar 1988]). On the other hand, in the case of uranium(VI) (ionic diameter = 0.15 nm for U in $\mathrm{UO_2^{2+}}$ [Yonezawa and Choppin 1989]) adduct formation constant values increases regularly to DC18C6 (cavity size = 0.26 - 0.32 nm [Mathur and Khopkar 1988]). It can be concluded that the relationship between the cavity size and the ionic diameter is not the determining factor in the complexation of $\mathrm{UO_2^{2+}}$. The unusual behavior observed in the present investigations may be attributed to a variety of geometric (cavity size and steric repulsion between extractants), enthalpic (donor basicity) and entropic (cation dehydration) effects involved in the extraction of f-elements with crown ethers in the presence of HFBPI. A better understanding of the origin of the selectivity displaced in the extraction of thorium(IV) will require more detailed investigations of the solution structure of the complexes.

Solid complexes of thorium(IV) and uranium(VI) with mixtures of HFBPI and CE and their characterization

Elemental analyses of ternary complexes

The analytical data presented in Table 5.6 show that thorium(IV) and uranium(VI) reacted with HFBPI and crown ether in the metal : ligand : crown ether mole ratio of 1 : 4 : 1 and 1 : 2 : 1, respectively.

Table 5.6. Elemental analyses of ternary complexes.

Complex	% C Found	% H Found	%N Found	% M Found
$Th(FBPI)_4{\cdot}B15C5{\cdot}H_2O$	57.65 (56.87)	3.38 (3.52)	3.77 (3.40)	14.14 (14.10)
$UO_2(FBPI)_2{\cdot}B15C5{\cdot}H_2O$	50.45 (49.29)	3.07 (3.57)	2.94 (2.50)	21.82 (21.25)

Figures in parentheses indicate calculated values.

IR Spectra of ternary complexes

The IR spectra of the ternary complexes of the metal ions (Fig. 5.17) show a broad absorption in the region 3000 - 3500 cm^{-1}, indicating the presence of water of hydration [Marchetti 2001]. The intense broad band centered around 2600 cm^{-1}, which is assigned to the ν (O-H) of HFBPI, is absent in the spectra of the complexes, indicating the enolization of the O-H

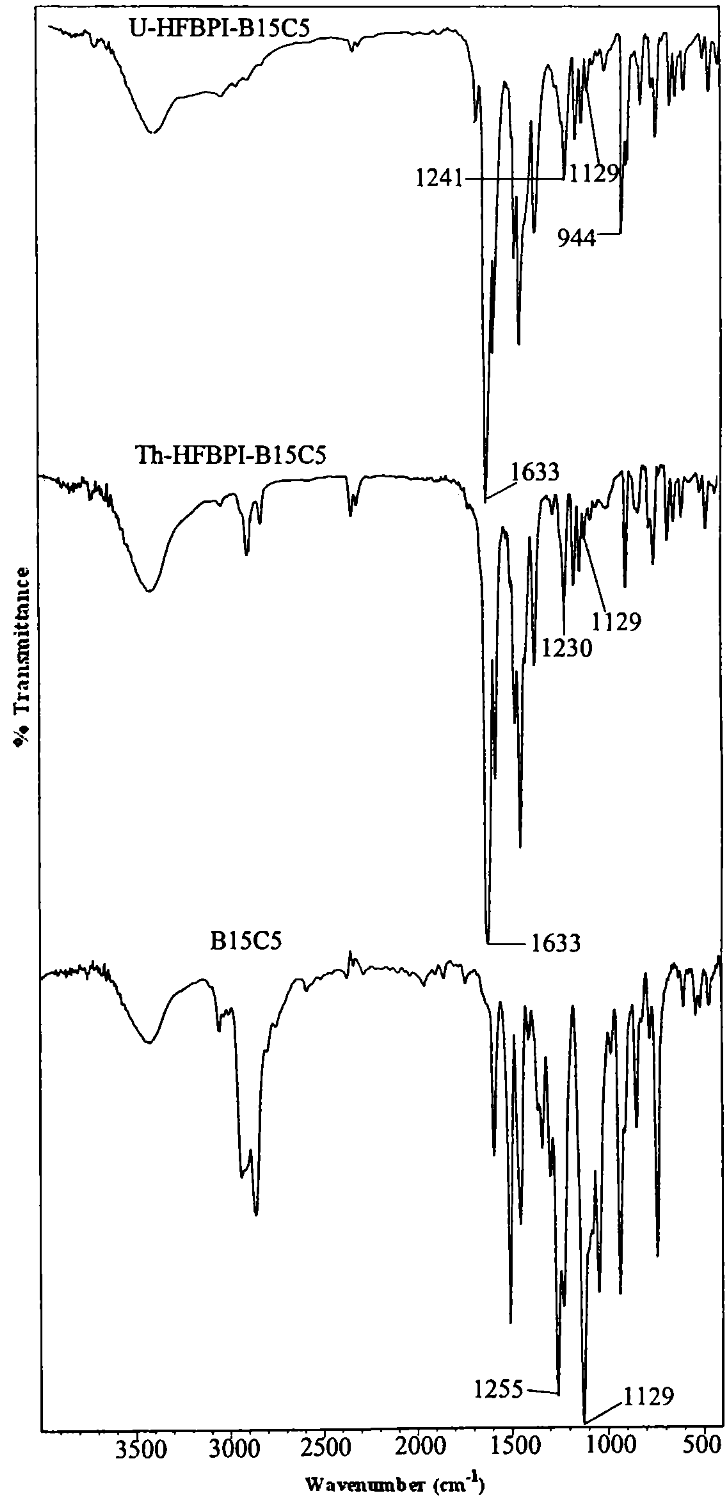


Figure 5.17. IR spectra of B15C5 ligand, Th-HFBPI-B15C5 and U-HFBPI-B15C5 complexes.

group and the involvement of oxygen of the hydroxyl group in chelation. The stretching frequency of the C=O group of HFBPI has been shifted from 1706 to 1633 cm^{-1} in both Th-FBPI-BI5C5and U-FBPI-BI5C5 complexes, which suggests that the carbonyl group is involved in chelation. The other strong absorption occurring around 937 - 944 cm^{-1} may be assigned to ν(O=U=O) of UO_2^{2+} [Sahu et al. 2000]. In the complexes of Th-FBPI-B15C5 and U-FBPI-B15C5 bands at 1129 - 1241 cm^{-1} are assigned to ν (C-O) of polyether, and became noticeably weaker as compared to free B15C5, which suggests the involvement of oxygen of the crown ether in the adduct formation.

^{1}H NMR spectra of ternary complexes

Table 5.7 shows the ^{1}H NMR chemical shifts of free HFBPI, B15C5 and its thorium and uranium complexes, the integration of the signals being in accordance with the formulae proposed. The downfield shift of the phenyl protons has been observed in both the ternary complexes. For B15C5 alone, the methylenic protons appears in the region 3.76-4.15 ppm, while the ring hydrogens are in the 6.8-6.9 ppm range. However, in the complex of $Th(FBPI)_4 \cdot B15C5$ a singlet appears at 4.69 ppm with downfield shift, indicating the uniform interaction of all ethereal oxygens of B15C5 with the Th^{4+}ion within the NMR time scale. On the other hand, in the case of $UO_2(FBPI)_2 \cdot B15C5$ two peaks were observed at 4.68 and 4.12 ppm with downfield shifts, indicating the nonuniform interaction of ethereal oxygens of B15C5 with UO_2^{2+}. Similar behavior has been observed in the ternary complex of uranium with mixtures of dibenzoylmethane and B15C5 [Thakur et al. 1998].

Table 5.7. ^1H NMR spectral data for the free ligands and ternary complexes.

Compound	Phenyl protons (ppm)	CH_2 protons of CE (ppm)
HFBPI	6.80–7.39 (m)	–
B15C5	6.89 (d)	3.76 (s), 3.90 – 3.93 (t), 4.13 – 4.15 (t)
Th-FBPI-B15C5	6.52–7.36 (m)	4.69 (s)
U-FBPI-B15C5	6.86–7.80 (m)	4.07 – 4.14 (q), 4.68 (s)

From the elemental analyses and FT-IR spectra of the $Th(FBPI)_4.H_2O.B15C5$ and $UO_2(FBPI)_2.H_2O.B15C5$ complexes, it is clear that crown ethers are not able to replace water molecules in the binary complexes of $Th(FBPI)_4.H_2O$ and $UO_2(FBPI)_2.H_2O$. Similar hydrated complexes have also been noticed earlier in the extraction of $Th(TTA)_4.H_2O.18C6$ [Mathur and Choppin 1993] and $[UO_2(TTA)_2.H_2O]_2(B15C5)$ [Kannan et al. 2001]. Since the maximum coordination number for these metal ions is 6 to 10, this hydration strongly suggests that the oxygens of the crown ethers are not all equally bound to the metal ion. Further, crown ethers may form a secondary coordination sphere with $UO_2(FBPI)_2.H_2O$ and hydrogen bonded to the water molecule, as reported elsewhere in the molecular structure of $[UO_2(TTA)_2.H_20]_2.B15C5$ with the aid of X-ray single crystal data [Kannan et al 2001]. There is evidence that the metal ion may interact with only a few of the potential donor oxygens and steric effects are probably significant in establishing this number [Mathur and Choppin 1993]. The weakness of the metal-crown ether interactions is reflected in residual hydration of the extracted complexes. What is clear about the extraction of these metal ions by mixtures of crown ethers and HFBPI is that crown ether basicity, steric effects, cation dehydration and the number of ether oxygens bound to the cation are the combined factors which seemingly determine the pattern of metal-chelate and crown ether interactions.

Table 5.8 gives the separation factors (S.F.) between thorium(IV) and uranium(VI), defined as the ratio of respective distribution ratios, with HFBPI and HFBPI + CE systems at 0.5 mol/dm^3 nitric acid + 0.5 mol/dm^3 sodium nitrate solutions.

Table 5.8. Separation factors between thorium(IV) and uranium(VI) with HFBPI (0.02 mol/dm^3) and HFBPI (0.02 mol/dm^3) + CE (0.005 mol/dm^3) systems.

Extraction system	Separation factor (S.F.) D_{Th}/D_U
HFBPI	5.4 x 10^3
HFBPI + DC18C6	5.9 x 10^3
HFBPI + DB18C6	2.3 x 10^4
HFBPI + B15C5	3.9 x 10^4

It is interesting to note that the addition of B15C5 significantly improves the S.F. values between thorium(IV) and uranium(VI) as compared with HFBPI alone. This can be explained on the basis of the 'size-fitting effect' of thorium(IV) with B15C5. The addition of DB18C6 to the HFBPI system also improves the selectivity between thorium(IV) and uranium(VI) and this can be interpreted in terms of steric factors of DBI8C6. On the other hand, the addition of DC18C6 moderately enhances the S.F. value between thorium(IV) and uranium(VI) as compared to HFBPI alone. Further the selectivity observed between thorium(IV) and uranium(VI) has been found to be significantly higher than that of TBP sytem. Thus, these mixed-ligand systems may find potential applications in the reprocessing of spent thorium based nuclear fuels and also for the recovery of thorium from mineral resources.

Chapter 6

Summary and Conclusions

The summary and conclusions of the reported work in this thesis are as follows:

1. Para-substituted 1-phenyl-3-methyl-4-aroyl-5-pyrazolones, namely, 1-phenyl-3-methyl-4-(4-fluorobenzoyl)-5-pyrazolone (HPMFBP) and 1-phenyl-3-methyl-4-(4-toluoyl)-5-pyrazolone (HPMTP) were synthesized and characterized by elemental analyses, IR and ^{1}H NMR spectral data. The synthesized ligands have been utilized for the extraction of thorium(IV) and uranium(VI) from nitric acid solutions in the presence and absence of various crown ethers. For comparison, studies also have been carried out with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP). The extraction data has been analyzed by both graphical and theoretical methods. The equilibrium constants of the extracted complexes have been deduced by nonlinear regression analysis with the aid of suitable chemically based models developed taking into account the aqueous phase complexation of the metal ions with inorganic ligands and all plausible complexes extracted into the

organic phase. In order to have a better understanding of the complexation of these metal ions with various para-substituted 4-aroyl-5-pyrazolones, the distance between the two donating oxygens of the ligands has been determined by semi-empirical PM3 molecular orbital calculations taking into account the hydrogen bond. Solid complexes of these metal ions with para-substituted 4-aroyl-5-pyrazolones and crown ethers have been isolated and characterized by elemental analyses, IR and ^{1}H NMR spectroscopic techniques to further clarify the nature of the extracted complexes. From the results of these investigations the following conclusions can be drawn:

i. The extracted complexes have been elucidated as ThX_4 and UO_2X_2 (where X = PMFBP, PMTP or PMBP) with HMPFBP/HPMTP/HPMBP alone and as $Th(PMFBP)_4.CE$ and $UO_2(PMFBP)_2.CE$ with mixtures of HPMFBP and CEs (CE = 18C6/DC18C6/DB18C6/ B15C5) for thorium(IV) and uranium(VI), respectively.

ii. The extraction efficiency of thorium(IV) and uranium(VI) with para-substituted 4-aroyl-5-pyrazolones follows the order HPMFBP > HPMBP > HPMTP. The substitution of an electron withdrawing fluorine atom (-F) in the fourth position of the benzoyl moiety in HPMBP molecule improves the extraction efficiency of these metal ions as compared with HPMBP. On the other hand, the substitution of an electron releasing methyl group (-CH_3) diminishes the extraction efficiency.

iii. The linear correlation between the log equilibrium constants of the metal ions with pK_a values of these ligands reveals that there is no obvious steric effect induced by the para-substituent in the chelate formation reaction. However, the above correlation indicates that the extraction efficiency of these metal ions with para-substituted 4-aroyl-5-pyrazolones varies in accordance with their pK_a values.

iv. The O---O distance values found by semi-empirical PM3 molecular orbital calculations for various para-substituted 4-aroyl-5-pyrazolones again clearly highlights that there is no steric effects due to para-substitution in the fourth position of the benzoyl moiety in the HPMBP molecule.

v. From the extraction, elemental analyses, FT-IR and ^{1}H NMR spectral data, it can be concluded that the Th^{4+} is surrounded by four para-substituted 4-aroyl-5-pyrazolone molecules and two water molecules, arranged in a capped cubic array to give a coordination number ten. On the other hand, the uranyl ion is surrounded by two molecules of para-substituted 4-aroyl-5-pyrazolones and one water molecule to give a coordination number seven with a pentagonal bipyramidal geometry.

vi. The separation factors (S.F. = D_{Th}/D_U = 5.35 x 10^4 with HPMFBP, S.F. = 3.99 x 10^4 with HPMBP and S.F. = 3.40 x 10^4 with HPMTP) between thorium(IV) and uranium(VI) were found to increase with increasing concentration of these ligands. Further these values are found to be significantly higher than that of TBP system (S.F. = D_U/D_{Th} = 17), which is commercially used in the Nuclear Industry.

vii. The addition of a crown ether to the metal-chelate system not only enhances the extraction efficiency but also significantly improves the selectivity between these metal ions, especially, in the presence of B15C5 (S.F. = 2.15 x 10^3 with HPMFBP alone; S.F. = 2.36 x 10^4 with HPMFBP + B15C5). Thus these mixed-ligand systems may find potential applications in the reprocessing of spent thorium based nuclear fuels and also in the separation of these metal ions from mineral resources.

viii. The complexation strength of $Th(PMFBP)_4$ chelate with various crown ethers follows the order B15C5 > 18C6 > DC18C6 > DB18C6. The high extraction efficiency of thorium(IV) with B15C5 can be explained on the basis of 'size-fitting effect'. On the other hand, the complexation strength of $UO_2(PMFBP)_2$ chelate with various crown ethers follows the order 18C6 > DC18C6 > B15C5 > DB18C6, which can be explained on the basis of crown ether basicity sequence and steric effects.

ix. The analytical data of the ternary complexes show that thorium(IV) and uranium(VI) reacted with HPMFBP and crown ether in the metal : ligand : crown ether mole ratio of 1 :4 :1 and 1 :2 : 1, respectively. From the FT-IR spectral data and elemental analyses of the ternary complexes ($Th(PMFBP)_4 \cdot H_2O \cdot B15C5$ and $UO_2(PMFBP)_2.H_2O.DC18C6$), it is clear that crown ethers are not able to replace water molecules that are present in the binary complexes.

x. The ^1H NMR spectral data indicate that the metal ion may not interact uniformly with all the potential donor oxygens of the CE.

xi. It can be concluded from these investigations that the extraction of actinides by mixtures of crown ethers and para-substituted 4-aroyl-5-pyrazolones essentially depends on the crown ether basicity, steric effects, cation dehydration and the number of ether oxygens bound to the cation and not simply due to cation-crown cavity size relationships. A better understanding of the interactions of crown ethers with metal-chelate systems require more detailed investigations of the solution structures of these complexes.

2. 1-Phenyl-3-methyl-4-pivaloyl-5-pyrazolone (HPMPP) was synthesized by introducing a bulky pivaloyl group at the fourth position of the 1-phenyl-3-methyl-5-pyrazolone, with a view to create a steric repulsion between the 3-methyl group and the 4-acyl group, which may enhance the selectivity between thorium(IV) and uranium(VI). The extraction of thorium(IV) and uranium(VI) from dilute nitric acid solutions into chloroform with HPMPP in the presence and absence of various neutral organophosphorus extractants, tri-*n*-butylphosphate (TBP), tri-*n*-octylphosphine oxide (TOPO) and octyl(phenyl)-N,N′-diisobutylcarbamoylmethylphosphine oxide (CMPO) has been investigated. In order to correlate the selectivity between thorium(IV) and uranium(VI) with the O---O distance (bite size) of 4-acyl-5-pyrazolones, the O---O distance in HPMPP has been determined by semi-empirical PM3 molecular orbital calculations, taking into account the hydrogen bond. The synergistic equilibrium constants have been correlated with the donor ability of the phosphoryl oxygen of the neutral organophosphorus extractants in terms of their ^{31}P NMR chemical shifts and nitric acid uptake constant values (K_H). Thorium(IV) and uranium(VI) complexes with HPMPP and neutral organophosphorus extractants were synthesized and characterized by IR and ^{31}P NMR spectral data to further understand the interactions of neutral organophosphorus extractants with metal-chelates. The conclusions from the above findings are as follows:

i. The results demonstrated that these metal ions are extracted into chloroform as $Th(PMPP)_4$ and $UO_2(PMPP)_2$ with HPMPP alone and as $Th(PMPP)_4 \cdot S$ and $UO_2(PMPP)_2 \cdot S$ (S = TBP, TOPO or CMPO) in the presence of neutral organophosphorus extractants.

ii. High selectivity (S.F. = 2.8×10^3) has been observed between thorium(IV) and uranium(VI) when extracted from dilute nitric acid solutions with HPMPP alone. Further, the separation factor observed between thorium(IV) and uranium(VI) is found to be significantly higher than that of para-substituted 4-aroyl-5-pyrazolones (S.F. = 2.15×10^3 with HPMFBP; S.F. = 1.60×10^3 with HPMBP and 1.36×10^3 with HPMTP). This may be due to shorter O---O distance in HPMPP (2.60 Å) than in para-substituted 4-aroyl-5-pyrazolones (2.67 Å).

iii. The addition of a neutral organophosphorus extractant to the metal-chelate system considerably enhances the extraction efficiency of these metal ions as compared to HPMPP alone.

iv. The synergistic extraction efficiency of these metal ions increases in the order TBP < CMPO < TOPO, which is also the order of the basicity (K_H) values of these neutral organophosphorus extractants.

v. The log synergistic equilibrium constant values of thorium(IV) and uranium(VI) increases linearly with increase in δ (^{31}P) NMR chemical shifts of the neutral O-bearing organophosphorus extractant (TBP < CMPO < TOPO). Further, the linear relationship also indicates that bi-functional CMPO act as a mono-functional extractant in the present system, as is also evident from the FT-IR spectral data. Thus the donor ability of the phosphoryl oxygen of the neutral organophosphorus extractant is the key parameter that controls the affinity of the synergistic extraction system.

vi. From the extraction and IR spectral data, it is clear that the neutral organophosphorus extractant forms an adduct with the metal-chelate by replacing water molecules that are present in the primary coordination sphere of the simple metal-chelate. In the $Th(PMPP)_4.S$ complex, thorium(IV) is coordinated by nine oxygen atoms in a tricapped trigonal prismatic geometry. On the other hand, in the $UO_2(PMPP)_2.S$, uranium(VI) is coordinated by seven oxygen atoms in a pentagonal bipyramidal geometry.

3. Highly acidic heterocyclic β-diketones, namely, 3-phenyl-4-(4-fluorobenzoyl)-5-isoxazolone (HFBPI) and 3-phenyl-4-(4-toluoyl)-5-isoxazolone (HTPI) were synthesized and utilized for the extraction of thorium(IV) and uranium(VI) from nitric acid solutions in the presence and absence of various crown ethers. The extraction data has also been compared with 3-phenyl-4-benzoyl-5-isoxazolone (HPBI). The equilibrium constants of the extracted complexes have been deduced by nonlinear regression analysis with the aid of suitable chemically based models developed. The equilibrium constants have been correlated with the pK_a values of these ligands. The O---O distance between the two oxygens in para-substituted 4-aroyl-5-isoxazolones has been determined by semi-empirical PM3 molecular orbital calculations and correlated with extraction efficiency and selectivity of these metal ions. The selectivity between thorium(IV) and uranium(VI) has been determined and compared with commercially available extractant, TBP. Solid complexes of thorium(IV) and uranium(VI) with para-substituted 4-aroyl-5-isoxazolones and crown ethers were isolated and characterized by various spectroscopic techniques to further clarify the nature of the extracted complexes. The conclusions from the above findings are as follows:
    i. The extraction efficiency of these metal ions with various para-substituted 4-aroyl-5-isoxazolones follows the order HFBPI > HPBI > HTPI. The substitution of an electron withdrawing fluorine atom (-F) in the fourth position of the benzoyl moiety in HPBI molecule improves the extraction

efficiency as compared with HPBI. On the other hand, the substitution of an electron donating methyl group (-CH_3) decreases the extraction efficiency.

ii. The extracted complexes from the solvent extraction data have been elucidated as ThX_4 and UO_2X_2 (X= FBPI or TPI) with HFBPI or HTPI alone and as Th(FBPI)$_4$·CE and UO_2(FBPI)$_2$·CE (CE = B15C5, DC18C6 or DB18C6) with mixtures of HFBPI and crown ethers.

iii. Comparing the equilibrium constants of various para-substituted 4-aroyl-5-isoxazolones with their pK_a values, it can be concluded that the equilibrium constant value increases as pK_a value decreases.

iv. The O---O distance values found by semi-empirical PM3 molecular orbital calculations for various para-substituted 4-aroyl-5-isoxazolones clearly highlights that the para-substitution in 3-phenyl-4-benzoyl-5-isoxazolone does not narrow the O---O distances (O---O distance of HPBI = 2.83 Å; HFBPI = 2.83 Å; HTPI = 2.83 Å) between the two donating oxygen atoms. The larger O---O distances observed in para-substituted 4-aroyl-5-isoxazolones would decrease the stability of the intramolecular hydrogen bonding, resulting in great enhancement of acidity.

v. The elemental analyses show that thorium(IV) and uranium(VI) reacted with HFBPI or HTPI in the metal : ligand mole ratio of 1 : 4 and 1 : 2, respectively.

vi. The FT-IR spectra and elemental analyses data of the complexes indicate the presence of water molecules in the coordination sphere of the metal ion. It is clear from the spectral and analytical data that uranyl ion is surrounded by two molecules of HFBPI or HTPI and one water molecule to give a coordination number seven with pentagonal bipyramidal geometry as observed in uranium-HTTA or uranium-HPMBP complexes. In the case of Th-HFBPI/HTPI complex, Th^{4+} is surrounded by four HFBPI or HTPI molecules and one water molecule to give a coordination number nine.

vii. It is clear from the results that the selectivity between thorium(IV) and uranium(VI) increases with increase in the concentration of HFBPI at constant nitric acid concentration (Separation Factor, S.F. = 5.4 x 10^3 at 0.02 mol/dm^3 HFBPI; S.F. = 2.2 x 10^4 at 0.04 mol/dm^3 HFBPI). Further, these S.F. values are found to be lower than that of HPMFBP (S.F. = 8.51 x 10^3 at 0.02 mol/dm^3 HPMFBP; S.F. = 3.42 x 10^4 at 0.04 mol/dm^3 HPMFBP) system. These results suggest that the O---O distance is one of the most important factors that governs the selectivity. The separability of thorium(IV) and uranium(VI) with ligands of shorter O---O distance is found to be better (bite size of HPMFBP = 2.67 Å; bite size of HFBPI = 2.83 Å). The S.F. values with 4-aroyl-5-isoxazolones are found to be significantly higher than that of TBP (S.F. = D_U/D_{Th} = 17), which has been employed in the Thorex process in the Nuclear Industry. Thus these 4-aroyl-5-isoxazolones, may find potential applications in the reprocessing of spent thorium based nuclear fuels and also for the recovery of thorium from mineral resources.

viii. The addition of crown ether to the metal-chelate system not only enhances the extraction efficiency but also significantly improves the selectivity of the metal ions, especially, in the presence of B15C5 (S.F. = 5.40×10^3 with HFBPI alone; S.F. = 3.90×10^4 with HFBPI + B15C5). This can be attributed to the 'size-fitting effect' of Th^{4+} with B15C5.

ix. The sharp decrease in complexation of thorium(IV) and uranium(VI) from DC18C6 to DB18C6 mostly reflects the increase in steric effects and decrease in basicity of crown ethers. The maximum value of adduct formation constant (log K_{CE}) observed for $Th(FBPI)_4.B15C5$ is likely associated with a good fit of Th^{4+} (ionic diameter = 0.20 nm) in the cavity of B15C5 (cavity size = 0.17 – 0.22 nm). On the other hand, in the case of uranium(VI) (ionic diameter = 0.15 nm for U in uranyl ion) adduct formation constant values increases regularly to DC18C6 (cavity size = 0.26 – 0.32 nm). Thus it can be concluded that the relationship between the cavity size and ionic diameter is not the determining factor in the complexation of UO_2^{2+}.

x. The stretching frequency of the C=O group of HFBPI has been shifted to lower frequency in both Th-HFBPI-B15C5 and U-HFBPI-B15C5 complexes, which suggests that carbonyl group is involved in chelation. Further the ν (C-O) of the polyether became noticeably weaker in the ternary complexes as compared to free B15C5 which indicates the involvement of oxygen of the crown ether in the adduct formation. Further, it is also clear from the IR spectral data that the crown ethers are not able to replace water molecules that are present in the coordination sphere of the metal-chelates.

xi. It is evident from the ^1H NMR spectral data of $Th(FBPI)_4 \cdot B15C5$, Th^{4+} interacts uniformly with all ethereal oxygens of B15C5. On the other hand, in the case of $UO_2(FBPI)_2 \cdot B15C5$, nonuniform interactions of ethereal oxygens of B15C5 with UO_2^{2+} has been noticed.

xii. A better understanding of the origin of the selectivity displaced in the extraction of thorium(IV) require more detailed investigations of the solution structure of Th-HFBPI-B15C5 system. Further, the study of the molecular structure of the complexes with the aid of X-ray crystallographic data may also help in understanding of the interactions of crown ethers with metal-chelate system.

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